THE VIIITH CONGRESS OF THE
INTERNATIONAL SOCIETY FOR
THEORETICAL CHEMICAL PHYSICS

BOOK OF ABSTRACTS

25-31 AUGUST 2013, BUDAPEST

Contents

Book of Abstracts

25/08 Sunday

Hall Pátria **Opening**

17:00 – 17:30 **Péter Surján, Erkki Brändas**

Congress Service Area **Welcome Reception**

19:00 –

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26/08 Monday Morning I

Hall Pátria Chair: **Ingvar Lindgren** **Congress Talk**

8:30 – 9:20 Gustavo Scuseria
Symmetry Breaking and Restoration

Hall Pátria Chair: **Jürgen Gauss** **Relativistic Effects in Molecules**

9:30 – 10:00 Stella Stopkowicz
Does Direct Perturbation Theory converge?

10:00 – 10:30 Werner Kutzelnigg
The no-photon approximation in relativistic quantum chemistry

Room Bartók Chair: **Lyudmila Slipchenko** **Biological Applications**

9:30 – 10:00 Lyudmila Slipchenko
Hybrid quantum/classical and fragmentation techniques for radicals and electronic excited states

10:00 – 10:30 Jan Halborg Jensen
Quantum Biochemistry

26/08 Monday Morning I cont’d

Room Lehár Chair: **Kresimir Rupnik** **Versatile Topics**

9:30	–	9:50	Dominika Zgid How to make Dynamical Mean Field Theory quantitative?
9:50	–	10:10	
10:10	–	10:30	Monika Musial Multireference Fock space coupled cluster method based on the RHF reference for the description of the potential energy curves

coffee break

26/08 Monday Morning II

Hall Pátria Chair: **Jürgen Gauss** **Relativistic Effects in Molecules**

11:00	–	11:30	Wenjian Liu Fundamentals of Relativistic Molecular Quantum Mechanics
11:30	–	12:00	Dieter Cremer Calculation of response properties with the normalized elimination of the small component (NESC) method
12:00	–	12:30	Lan Cheng Cost-effective approaches for relativistic electron-correlated calculations

Room Bartók Chair: **Lyudmila Slipchenko** **Biological Applications**

11:00	–	11:30	Qiang Cui QM/MM analysis of catalytic promiscuity and proton pumping in enzymes
11:30	–	11:50	Magdalena Pecul Calculations of circular dichroism and circularly polarized luminescence spectra of biologically relevant chromophors.
11:50	–	12:10	Erik Donovan Hedegård Polarizable Embedding: Multireference embedding methods and large scale applications to optical properties in proteins
12:10	–	12:30	Edina Rosta Two-Metal Ion Catalysis by Ribonuclease H

26/08 Monday Morning II cont'd

Room Lehár Chair: **Katarzyna Pernal** **Versatile Topics**

11:00	–	11:30	Petr Carsky Evaluation of exchange integrals by Fourier transform of the $1/r$ operator and its numerical quadrature
11:30	–	11:50	Ors Legeza Generalized tensor methods and entanglement measurements for electronic structure calculations
11:50	–	12:10	Feiwu Chen A new size extensive multireference perturbation theory
12:10	–	12:30	Elvira Romera Phase-space visualization of quantum phase transitions in the molecular vibron model

lunch break

26/08 Monday Afternoon I

Hall Pátria Chair: **Wenjian Liu** **Relativistic Effects in Molecules**

14:30	–	15:00	Pekka Pyykkö Aspects of accurate, relativistic quantum chemical calculations
15:00	–	15:30	Trond Saue The relativistic correlation problem
15:30	–	16:00	Ria Broer The Combined Effects of Electron Correlation and Relativity on Core Excitation Spectra
16:00	–	16:20	Artur Wodyński The influence of a presence of a heavy atom on spin-spin coupling constants between two light atoms in organometallic compounds and halogen derivatives

Room Bartók Chair: **Lyudmila Slipchenko** **Biological Applications**

14:30	–	15:00	Dennis Salahub Towards the multiscale modeling of catalysis
15:00	–	15:20	Gábor Náray-Szabó Mechanism of enzymatic phosphate ester hydrolysis: interplay of theory and experiment
15:20	–	15:40	Marc de Wergifosse Theoretical investigation of the second-order nonlinear optical response of collagen – signatures of the triple helix structure
15:40	–	16:00	Andrzej Sokalski Modeling of enzymatic organophosphate hydrolysis: towards design of new biocatalysts
16:00	–	16:20	Kresimir Rupnik Adaptive UF PPS Model Study of Structures and Reactions in Biomolecules: New Selective Bio-Molecular Probes through High Magnetic Fields

26/08 Monday Afternoon I cont'd

Room Lehár Chair: **Miroslav Urban** **Versatile Topics**

14:30 – 15:00 György Lendvay
Barrier evasion and roaming in the dynamics of elementary chemical reactions

15:00 – 15:20 Kirill Gokhberg
Decay processes mediated by long-range electron correlation

15:20 – 15:40 Jing Ma
Reactive molecular dynamics simulations of switching processes of azobenzene-based monolayer on surface

15:40 – 16:00 Kenneth Ruud
Analytic DFT calculations of anharmonic force constants

16:00 – 16:20 Roberto Cammi
Harmonic vibrational frequencies in molecules at extreme high pressure: a novel QM method

coffee break

Hall Pátria Chair: **Gustavo Scuseria** **Congress Talk**

16:50 – 17:40 Peter Pulay
Ultrafast Quantum/Molecular Mechanics Monte Carlo Simulations

26/08 Monday Evening

Aula **Poster Session I**

18:00 – 20:00

27/08 Tuesday Morning I

Room Bartók Chair: **Peter Gill** **Interpretation Models in Quantum Chemistry**

8:30 – 9:00 Peter Gill
An interpretive dance in three movements

9:00 – 9:30 Axel Becke
Two-Determinant Mixing with a Strong-Correlation Density Functional

9:30 – 9:50 Kristine Pierloot
Electronic structure of manganese(II) nitrosyl compounds: a bifocal view

9:50 – 10:10 Shmuel Zilberg
Chemical Reactions with two different elementary Transition States – Crypto Three-State System. Photo-/ Thermo-chemical aspects and VB rationalization.

10:10 – 10:30 Takao Tsuneda
A reactivity index based on orbital energies

Room Lehár Chair: **Miklos Kertesz** **Solid State Chemistry**

8:30 – 9:00 Sumit Mazumdar
Superconductivity as a problem in chemical physics

9:00 – 9:30 Claudia Draxl
From structure to opto-electronic excitations of organic-inorganic hybrid materials: State of the art and challenges

9:30 – 9:50 An Ghysels
Thermodynamics of framework breathing: free energy model for flexible porous crystals

9:50 – 10:10 Miroslav Urban
CCSD(T) calculations of confined systems: In crystal polarizabilities of anions

10:10 – 10:30 Benoît Champagne
Towards calculating and interpreting the linear and second-order nonlinear optical properties of molecular crystals

Room Brahms Chair: **Tamás Turányi** **Uncertainty Quantification**

8:30 – 9:00 Tamás Turányi
Quantification of the Uncertainty of Parameters in Chemical Kinetics

9:00 – 9:30 Michael Frenklach
UQ-Predictive Modeling of Chemical Reaction Systems

9:30 – 10:00 Judit Zádor
Uncertainties in ab initio rate coefficient calculations

10:00 – 10:30 Hai Wang
Multiscale Kinetic Knowledge Propagation – Combustion Chemistry of Small Hydrocarbons

coffee break

27/08 Tuesday Morning II

Room Bartók	Chair: **Peter Gill**	**Interpretation Models in Quantum Chemistry**
11:00 – 11:30	Weitao Yang Exchange-Correlation Energies from Paring Matrix Fluctuation and Particle-Particle-Random Phase Approximation	
11:30 – 11:50	Elfi Kraka The decisive role of hydrogen-bonds in chiral discrimination - unraveled by quantum chemical means	
11:50 – 12:10	Avital Shurki Insights on Enzyme Catalysis	
12:10 – 12:30	Jeng-Da Chai Restoration of the Derivative Discontinuity in Kohn-Sham Density Functional Theory: An Efficient Scheme for Energy Gap Correction	

Room Lehár	Chair: **Miklos Kertesz**	**Solid State Chemistry**
11:00 – 11:30	Nicola Marzari The density is not enough	
11:30 – 11:50	Kersti Hermansson Ceria chemistry at the nano-scale	
11:50 – 12:10	Karoly Nemeth Quantum-chemical Design of Improved Photoemissive Materials	
12:10 – 12:30	Mazharul M. Islam Theoretical study for lithium diffusion in $Li_2Ti_xO_y$ compounds	

Room Brahms	Chair: **Tamás Turányi**	**Uncertainty Quantification**
11:00 – 11:30	David Sheen Uncertainty Quantification and Data Discrimination in Combustion Kinetic Modeling	
11:30 – 11:50	Carsten Olm Uncertainty of the rate parameters in the wet CO combustion system	
11:50 – 12:10	Elke Goos Evaluation of the influence of thermodynamic data on the Prediction of propane and propene ignition delay times	
12:10 – 12:30	Tibor Furtenbacher Graph theory in spectroscopy and thermochemistry	

lunch break

27/08 Tuesday Afternoon I

Room Bartók Chair: **Peter Gill** **Interpretation Models in Quantum Chemistry**

14:30	–	15:00	Gernot Frenking Main Group Complexes with Unusual Donor-Acceptor Bonds
15:00	–	15:30	Andreas Savin Getting to Lewis electron pairs from quantum mechanical calculations: Maximum Probability Domains
15:30	–	15:50	Marco Nascimento Quantum Interference Provides a Unified Description of Chemical Bonding
15:50	–	16:10	Peter Karadakov Magnetic Shielding as a Source of Information about Aromaticity, Antiaromaticity and Chemical Bonding
16:10	–	16:30	Tom Ziegler Analyzing Complex Electronic Structure Calculations on Large Molecules in Simple Chemical Terms

Room Lehár Chair: **Benoît Champagne** **Solid State Chemistry**

14:30	–	15:00	Jean-Francois Halet Rings and Chains in Solid-State Chemistry. The Electron Count Matters
15:00	–	15:30	Miklos Kertesz $\pi - \pi$ stacking is different from pancake bonding: interpretations with molecular and solid state examples
15:30	–	15:50	Reinhard Maurer Towards a mechanistic understanding of photoinduced (non-)switching of metal surface adsorbed Azobenzenes.
15:50	–	16:10	Frantisek Karlicky The Reaction of Water with Iron: Surface Science by Random Phase Approximation
16:10	–	16:30	Javier Fdez. Sanz Mechanism of the Water-Gas Shift Reaction at the Metal-Oxide Interface: Insights from First Principles Calculations

27/08 Tuesday Afternoon I cont'd

Room Brahms Chair: **Judit Zádor** **Uncertainty Quantification**

14:30	–	15:00	Branko Ruscic Active Thermochemical Tables: Uncertainty Quantification in Thermochemistry
15:00	–	15:30	Markus Kraft Optimisation and Bayesian Parameter Estimation of a Kinetic Model of n-Propylbenzene Oxidation in a Shock Tube
15:30	–	15:50	Fabien Cailliez Statistical approaches to forcefield calibration and prediction uncertainty in molecular simulation
15:50	–	16:10	Tamas Varga Uncertainty quantification of the rate parameters of an ethyl iodide pyrolysis mechanism
16:10	–	16:30	Péter Jeszenszki Sensitivity analysis of state-specific multireference perturbation theory

coffee break

27/08 Tuesday Afternoon II

Room Bartók Chair: **Peter Gill** **Interpretation Models in Quantum Chemistry**

17:00	–	17:30	Jesus Ugalde Natural Orbital Functional Theory of the Molecular Electronic Structure
17:30	–	18:00	Laszlo v. Szentpaly Saving Sanderson's Principle? Order of Magnitude Improvements by Equalizing Mulliken Valence-State Electronegativities χ_{VS} Instead of DFT-Based Chemical Potentials μ
18:00	–	18:30	Istvan Mayer Extracting chemical information from molecular wave functions – some recent results
18:30	–	19:00	Paul Geerlings The linear response function as an interpretational tool: retrieving atomic shell structure, inductive and mesomeric effects, aromaticity and anti-aromaticity

Room Lehár Chair: **Benoît Champagne** **Solid State Chemistry**

17:00	–	17:30	Kazunari Yoshizawa Orbital views of molecular conductance and spintronics
17:30	–	18:00	Philip Hoggan Quantum Monte Carlo making progress with metal surfaces: CO adsorbed on Cu(100) and Pt(100)
18:00	–	18:30	Jenő Kürti Raman bands in small diameter carbon nanotubes

28/08 Wednesday Morning I

Hall Pátria Chair: **Mihály Kállay** **Electron Correlation – In Memoriam Isaiah Shavitt**

8:30 – 8:40 Mihály Kállay
Introduction

8:40 – 9:10 Poul Joergensen
The divide-expand-consolidat (DEC) coupled cluster method goes massively parallel.

9:10 – 9:40 Hans-Joachim Werner
Explicitly Correlated Multireference Electronic Structure Methods

9:40 – 10:10 Debashis Mukherjee
Unitary Group Adapted Approach to Spin-free Multi-Reference Coupled Cluster Theories: Formalisms and Applications

10:10 – 10:30 Anna Krylov
Resolution-of-Identity and Cholesky Representations of Electron-Repulsion Integrals within Coupled-Cluster and Equation-of-Motion Methods: Go One More Mile

Room Bartók Chair: **Erkki Brändas** **Fundamental Problems in Quantum Chemistry**

8:30 – 9:00 Cleanthes Nicolaides
The Fifth Age of Quantum Chemistry?

9:00 – 9:30 Moshe Shapiro
The quantum dynamics experienced by a single molecular eigenstate excited by incoherent light

9:30 – 10:00 Armin Scrinzi
Formation of doubly excited states by XUV excitation and Auger spectra in presence of strong IR fields

10:00 – 10:30 Ivana Paidarova
Extracting complex resonance energies from real calculations

Room Lehár Chair: **Miguel Castro** **Versatile Topics**

8:30 – 8:50 Elena Sheka
Graphene, Silicene and Forgotten Lessons of Surface Science

8:50 – 9:10 Evgeniy Gromov
Correlation-bound states of C_{60}^{-} anion

9:10 – 9:30 Joanna Kauczor
Complex polarization propagator: a theoretical study of molecular properties and spectra

9:30 – 9:50 Selma Engin
Probing IR-Raman rovibrationally excited HCl molecule with X-ray spectroscopies : a theoretical approach

9:50 – 10:10 Robert Góra
The Origins of Large Interaction-Induced First Hyperpolarizabilities in Hydrogen-Bonded π-Electronic Complexes

10:10 – 10:30 Irena Efremenko
Ligand effect on the electronic structure and reactivity of rhodium pincer complexes

coffee break

28/08 Wednesday Morning II

Hall Pátria Chair: **Dennis Salahub** **Electron Correlation**

11:00	–	11:30	Péter Szalay In memoriam Shi Shavitt: Application of MR-CI methods to describe the potential energy surfaces of O_3 and the dimer of O_2
11:30	–	12:00	Paul Ayers A New Mean-Field Method for Strong Correlation Using Antisymmetric Products of Nonorthogonal Geminals
12:00	–	12:30	Trygve Helgaker Molecular magnetism and density-functional theory in magnetic fields

Room Bartók Chair: **Cleanthes Nicolaides** **Fundamental Problems in Quantum Chemistry**

11:00	–	11:30	Erkki Brändas Time's Arrow Revisited
11:30	–	11:50	Peter Saalfrank Electrons in motion, or: Can we nake a Hartree-Fock state?
11:50	–	12:10	Michael Filatov Theoretical design of conical intersections in molecular motors and switches: A Density Functional Theory perspective
12:10	–	12:30	Paul Mezey Macromolecular Conformation Analysis by the LIL-ADMA Method: How to Deal With Many Atoms Moving in All Directions?

Room Lehár Chair: **W. Andrzej Sokalski** **Biological Applications**

11:00	–	11:30	Per Siegbahn Water oxidation mechanism in photosystem II
11:30	–	12:00	Alexander Nemukhin Modeling structure and spectra of fluorescent proteins
12:00	–	12:30	Oleg Prezhdo Nanoscale Carbon for DNA Sequencing and Drug Delivery

lunch break

28/08 Wednesday Afternoon

Hall Pátria Chair: **Jeppe Olsen** **Electron Correlation**

14:30	–	15:00	John Stanton How much do, and can, we “understand” about the ground state of NO_3
15:00	–	15:30	Frank Neese Recent development in pair natural orbital based local coupled cluster methods
15:30	–	16:00	Hiromi Nakai Linear-Scaling Electron-Correlation Theory for Two-Component Relativistic Hamiltonian

Room Bartók Chair: **Jiri Horacek** **Fundamental Problems in Quantum Chemistry**

14:30	–	15:00	Nimrod Moiseyev Chemistry and Physics in high-frequency strong laser fields
15:00	–	15:20	Hazel Cox The stability of Coulomb three-body systems
15:20	–	15:40	Harris Silverstone Convergence of the bipolar expansion for the Coulomb potential
15:40	–	16:00	Henryk Witek Analytical wave function of helium atom

Room Lehár Chair: **Reinhold Fink** **Versatile Topics**

14:30	–	15:00	Pedro Salvador Oxidation states from wavefunction analysis
15:00	–	15:20	Masanori Tachikawa Multi-component molecular methods for hydrogen bonded systems and positronic compounds
15:20	–	15:40	Fedor Naumkin Molecular vs atomic encapsulation of hydrogen in metal cluster-cage assemblies
15:40	–	16:00	Petra Ruth Kapralova Gaussian basis sets for complex scaling calculations

Cruising Boat “Európa” **Banquet**

19:00 –

29/08 Thursday Morning I

Room Bartók			Chair: **Hans-Joachim Werner**	**Electron Correlation**
8:30	–	9:00	Rodney Bartlett Some Considerations of Electron Correlation Introduced as a Correlation Potential	
9:00	–	9:30	Christian Ochsenfeld Linear- and sublinear-scaling Moeller-Plesset (MP2) and symmetry-adapted perturbation theory (SAPT)	
9:30	–	9:50	Karol Jankowski Unexpected features of correlation effects involving 3d-electrons	
9:50	–	10:10	Reinhold Fink Assessing ab initio methods by analyzing their wave functions	

Room Lehár			Chair: **Kersti Hermansson**	**Molecular Dynamics**
8:30	–	8:40	Kersti Hermansson Introduction	
8:40	–	9:10	Marco Masia Force Field Parameterization from a Force Matching–like Approach: Merits, Shortcomings and Future Perspectives.	
9:10	–	9:40	Bernd Ensing Ab initio molecular dynamic simulation of photoactive proteins in action	
9:40	–	10:10	Gunnar Nyman Dynamics of chemical reactions in the gas phase	
10:10	–	10:30	Andrzej Bil Modifying the Fullerene Surface Using Endohedral light guests. From Ab Initio Molecular Dynamics and Metadynamics to Quantum Chemical Topology.	

29/08 Thursday Morning I cont'd

Room Brahms			Chair: **Matthias Ernzerhof**	**Versatile Topics**
8:30	–	8:50	Toomas Tamm Conformations of Small Molecules	
8:50	–	9:10	Adel El-Azhary Conformatonal and Vibrational Analysis of 12-thiacrown-4 and 18-thiacrown-6	
9:10	–	9:30	Imre Pápai Hydrogen activation by frustrated Lewis pairs: Comparison of reactivity models	
9:30	–	9:50	Vitaly Kiselev A Novel Mechanism of Thermal Decomposition of 1,2-Diamino-1,2-Dinitroethylene (FOX-7): New Insights from High-level Quantum Chemical Calculations	
9:50	–	10:10	Jan Mitschker Interaction of water with rutile (110) – Ground and excited states	
10:10	–	10:30	Alia Tadjer Molecular Dynamics Assessment of Concentration- and Head-Size-Dependent Effects on $C_{12}E_x$ Aggregation	

coffee break

29/08 Thursday Morning II

Room Bartók			Chair: **Debashis Mukherjee**	**Electron Correlation**
11:00	–	11:30	Mark Hoffmann GVVPT2 Descriptions of Electronic Structures of Metalloid Oxides	
11:30	–	11:50	Katarzyna Pernal Electron excitation energies from reduced density matrices: extended random phase approximation and linear response theory approaches	
11:50	–	12:10	Jiri Pittner Recent Progress in Multireference Hilbert-Space Coupled Cluster Methods: Explicit Correlation, Massively Parallel Implementation, and USS Corrections	
12:10	–	12:30	Mario Piris MCPT-PNOF5: A useful method for dealing with strongly correlated systems	

29/08 Thursday Morning II cont'd

Room Lehár Chair: **Kersti Hermansson** **Molecular Dynamics**

11:00 – 11:30 Kai Nordlund
Understanding the interaction of energetic particles with fusion reactor first walls: from binary collision physics to bond conjugation chemistry
11:30 – 11:50 Przemyslaw Dopieralski
Mechanochemistry: The curious case of cyclopropane.
11:50 – 12:10 Paweł Artur Siuda
Nucleation and growth of methane clathrate hydrate crystal - molecular dynamics study
12:10 – 12:30 Maxim Tafipolski
Intermolecular Force Field Parameterization from First Principles

Room Brahms Chair: **Petr Carsky** **Versatile Topics**

11:00 – 11:30 Ágnes Vibók
Quantum control by laser-induced conical intersections
11:30 – 11:50 Yasuteru Shigeta
Free energy analyses on cluster deformations by cumulant mechanics
11:50 – 12:10 Masayoshi Nakano
Nonlinear optical properties of asymmetric diradical molecules
12:10 – 12:30 Gábor Magyarfalvi
An intrinsic measure for the reliability of calculated VCD band signatures

lunch break

29/08 Thursday Afternoon I

Room Bartók Chair: **Bogumil Jeziorski** **Electron Correlation**

14:30 – 15:00 Jeppe Olsen
Correlation Methods Using Non-Orthogonal Orbitals
15:00 – 15:30 Vitaly Rassolov
Multireference DFT based on Strongly Orthogonal Geminals
15:30 – 16:00 Piotr Piecuch
Recent progress in the active-space electron-attached and ionized equation-of-motion coupled-cluster methodologies

29/08 Thursday Afternoon I cont'd

Room Lehár Chair: **Kersti Hermansson** **Molecular Dynamics**

14:30 – 15:00 Eckhard Spohr
Molecular dynamics and reactive trajectory approaches to modeling of electrochemical reactions near the liquid/solid interface

15:00 – 15:20 Jayesh Bhatt
Molecular simulations of hydrated inorganic nanopores

15:20 – 15:40 Ben Nebgen
Theoretical investigation of the excited state proton transfer in 3-cyano-6-hydroxycoumarin

15:40 – 16:00 Kaoru Yamazaki
Selective Vibrational Mode Excitation in Nanocarbons by Tailored Intense Near-Infrared Pulses and Subsequent Intramolecular Vibrational Energy Redistributions

Room Brahms Chair: **Mark Hoffmann** **Versatile Topics**

14:30 – 15:00 Attila Bende
Quantum Theoretical Investigation to Explain the Onset of Cancer

15:00 – 15:30 Wesley Allen
Intramolecular Dispersion

15:30 – 16:00 Mikhail Basilevsky
The microscopic model for electron transfer in disordered solid matrices

coffee break

29/08 Thursday Afternoon II

Room Bartók Chair: **Péter Szalay** **Electron Correlation**

16:30 – 17:00 Jozef Noga
Expectation value coupled cluster approach using the ansatz with generalized double-substitutions cluster operator.

17:00 – 17:20 Masato Kobayashi
Geminal-based wavefunction theory and its perturbative improvement

17:20 – 17:40 Roberto Olivares-Amaya
Useful Parameters of DMRG for Everyday Quantum Chemistry Applications

17:40 – 18:00 Koji Ando
Electron Wave Packet Modeling of Chemical Bonding

29/08 Thursday Afternoon II cont'd

Room Lehár	Chair: **Kersti Hermansson**	**Molecular Dynamics**
16:30 – 17:00	Nikos Doltsinis Connecting quantum events to macroscopic phenomena: Multiscale simulation of photoresponsive materials	
17:00 – 17:20	Maciej Smiechowski Spatial decomposition and assignment of vibrational spectra: Dipolar coupling and correlated particle motion in aqueous Li^+	
17:20 – 17:40	Janos Daru Rate constants from equilibrium simulations: a new method	
17:40 – 18:00	Haibo Ma Solvent Effects on Electronic Absorption, Fluorescence and Phosphorescence of Acetone and Benzene in Water: A QM/MM Study	

29/08 Thursday Evening

Aula		**Poster Session II**
18:00 – 20:00		

30/08 Friday Morning I

Hall Pátria	Chair: **Shuhua Li**	**Fragment Approach and Electron Localization**
8:30 – 8:50	Shuhua Li Cluster-in-molecule local correlation approach	
8:50 – 9:20	So Hirata First-principles prediction of the structures, spectra, and phase diagrams of molecular crystals	
9:20 – 9:50	Martin Schuetz Local correlation methods for molecules and solids	
9:50 – 10:10	Ida-Marie Høyvik Challenges in orbital localization for orthonormal molecular orbitals	
10:10 – 10:30	Joachim Friedrich The incremental scheme for CCSD(T) and CCSD(T)(F12)	

29/08 Friday Morning I cont'd

Room Bartók			Chair: **Janos Angyan**	**London Dispersion Forces**
8:30	–	9:00	Janos Angyan State-of-the-art and perspectives in modeling of London dispersion forces	
9:00	–	9:30	Georg Jansen Dispersion interactions from intermolecular perturbation theory and random phase approximations	
9:30	–	9:50	Emmanuel Fromager Rigorous formulation of double hybrid density-functionals along the adiabatic connection	
9:50	–	10:10	Rafal Podeszwa Efficient calculations of accurate interaction energies for nano-scale systems	
10:10	–	10:30	Glenn Martyna Towards an accurate treatment of many-body dispersion and polarization for chemical accuracy via a coarse grained Gaussian Electronic Structure	

coffee break

30/08 Friday Morning II

Hall Pátria			Chair: **So Hirata**	**Fragment Approach and Electron Localization**
11:00	–	11:30	Hermann Stoll Local correlation-energy increments for solids – ground and excited states	
11:30	–	12:00	Shridhar Gadre Molecular Tailoring Approach : An Art of the Possible for ab initio	

Room Bartók			Chair: **Ágnes Nagy**	**London Dispersion Forces**
11:00	–	11:30	Bogumil Jeziorski Long-range retardation of relativistic interatomic potentials	
11:30	–	12:00	John Dobson Understanding effects beyond pairwise additivity in dispersion interactions	
12:00	–	12:30	Alexandre Tkatchenko (Un)Chemical Bonding: Surprises in Non-Covalent Interactions in Molecular Systems	

lunch break

30/08 Friday Afternoon I

Hall Pátria	Chair: **Jozef Noga**	**Versatile Topics**
14:30 – 15:00	Samantha Jenkins Concepts of Quantum Geometry from the Topological Origins of QTAIM	
15:00 – 15:30	Michael Hanrath Extending the Domain of Connectivity for MRexpT: Analysis and Results	
15:30 – 16:00	Daniel Crawford Solvation, Coupled Cluster Response Theory, and the Optical Properties of Chiral Molecules	

Room Bartók	Chair: **Dominika Zgid**	**Versatile Topics**
14:30 – 15:00	Ágnes Nagy Orbital-free density functional theory: functional derivative of the kinetic energy for spherically symmetric systems	
15:00 – 15:30	Matthias Ernzerhof New functionals through factorization of the exchange and exchange-correlation hole	
15:30 – 15:50	Miguel Castro Theoretical Study of $\text{Fe-(H}_2\text{O)}_m$, $m < 4$ and $\text{Fe}_n\text{-(C}_6\text{H}_6\text{)}_m$, $n < 7$, $m < 4$.	

coffee break

30/08 Friday Afternoon II

Hall Pátria	Chair: **Karol Jankowski**	**Versatile Topics**
16:30 – 17:00	Josef Michl Accommodation of Electronic Excitation in sigma-Bond Systems: Peralkylated Oligosilanes	
17:00 – 17:30	Pavel Hobza How accurate are „gold standard“ CCSD(T)/CBS interaction energies?	

Hall Pátria	Chair: **Peter Pulay**	**Congress Talk**
17:40 – 18:30	Ingvar Lindgren Development of Many-Body Perturbation Theory: How to combine with Quantum ElectroDynamics	

Hall Pátria		**Closing**
18:30 – 19:00		

Papers in Poster Session I

No.	Name	Title
1	Matthew Addicoat	Stochastic Structure Determination for Conformationally Flexible Clusters: CrazyLego
2	Christoph Allolio	An Ab Initio Microscope: Molecular Contributions to the Femtosecond Time-Dependent Fluorescence Shift of a Reichardt-Type Dye
3	Claudio Amovilli	Size-extensive wave functions for QMC: The J-LGVBn theory
4	Iva Angelova	Combined ab initio/semi-empirical Screening Protocol for Properties of Self-Assembled Monolayers
5	Luis Paulo Barbour Scott	Flexibility of Hunam Thioredoxin 1 and new biding sites using Normal Modes Analysis
6	Attila Bende	DNA - Protein interaction in the nucleosome system
7	Victor Bernstein	Impact induced multifragmentation of fullerene on gold: experimentally motivated molecular dynamics simulations
8	Debarati Bhattacharya	Formulation of partial triples to the electronic transition dipole moments within Fock-space multi-reference coupled cluster framework
9	Kim Bolton	Molecular-level simulations of permeation in polymer films and fibres
10	Lukas Bucinsky	Spin at the 2-component level of theory. The way in pain
11	Adem Cinarli	Theoretical DFT, FT-IR and NMR studies of 2-methoxy-6-(5-F/Cl/Br-1H-benzimidazol-2-yl)-phenols
12	Kota Daigoku	Visualization and characterization of intermolecular interaction based on the electron difference density
13	Justyna Dominikowska	Halogen-halogen interaction in light of many-body approach.
14	Matus Dubecky	Noncovalent Interactions: Quantum Monte Carlo Approaches CCSD(T) to 0.1 kcal/mol
15	Janus Eriksen	A novel framework for deriving triples and quadruples corrections to the CCSD energy
16	Olle Falklöf	Modeling of Phytochrome Absorption Spectra
17	Attila Fekete	The proteolytic reaction of papain: ONIOM-type hybrid QM/MM calculations and Poisson-Boltzmann electrostatic correction

Papers in Poster Session I cont'd

No.	Name	Title
18	Franca Maria Floris	A Polarizable Continuum Model of solvation designed for QMC: ground and excited states of solutes
19	Jerome Gomar	A combined experimental and theoretical study on the structure of genipin in solution
20	Jaroslav Granatier	The quartet-quartet crossing in Ir...benzene half-sandwich complex
21	Demet Gürbüz	Theoretical and spectral characterization of 5,6-dichloro-2-(2′,3′/2′,4′/2′,5′/3′,4′/3′,5′-dimethoxyphenyl)-1H-benzimidazoles
22	Merouani Hafida	DFT Study of the Stereo-Selectivity of Oxygenated Heterocycles from 10 to 12 Links
23	Matti Hellström	Cu on ZnO: alternating Cu charge states and accurate adsorption energy calculations upon charge transfer
24	Robert Izsak	The Equation of Motion Coupled Cluster Approach as Implemented in ORCA
25	Tomasz Janowski	Natural Correlation Orbitals in Local Laplace Transformed Triples (T) Correction
26	Hyunjun Ji	Convergence Acceleration of Relaxation-Separated Many-Body Expansion for Periodic Systems
27	Sayali Joshi	Calculation of response properties using Extended Coupled Cluster Method
28	Apostolos Kalemos	Symmetry breaking in a nutshell. The odyssey of a pseudo problem in molecular physics. The X BNB case revisited.
29	Uraiwan Kamolphop	A density functional investigation of ethylene adsorption on graphene surfaces
30	Frantisek Karlicky	Non-covalent Interactions to Graphene: Theory and Experiment
31	Małgorzata Kauch	Metal-substituted rubredoxin – theoretical prediction of the spin spin coupling constants using ZORA
32	Ali Kazemi Babhydari	Characterization of protein-ligand complexes using molecular dynamics simulations by consideration of GABAA protein as receptor and Lavender compounds as ligand
33	Maria Khrenova	Proteolysis mechanism in matrix metalloproteinases suggested by molecular modeling
34	Jaehoon Kim	A simple and accurate non-emperical doubly-hybrid density functional using quadratic approximation of adiabatic connection formula
35	Yukiumi Kita	Theoretical investigation of the binding of a positron to vibrational excited states of hydrogen cyanide molecule
36	Malte Kokoschka	Methods for the accurate description of Platinum-DNA interaction
37	Christoph Köppl	Automated optimisation of quantum chemical algorithms within an integrated tensor framework

Papers in Poster Session I cont'd

No.	Name	Title
38	Takako Kudo	Ab Initio Molecular Dynamics Simulations of H_2 Formation inside POSS Compounds
39	Antonio Largo	Theoretical studies of possible routes for the synthesis of amino acids in space
40	Tian Lu	Integrating the Laplacian of electron density in fuzzy overlap space as a measure of covalent bond order
41	Alejandro Fabián Maldonado	Relativistic and correlation effects on heavy molecules containing Sn and Pb atoms
42	Bhabani Mallik	Structure and Dynamics of ionic liquids from first principles simulations: Effects of dispersion corrected density functionals and charge density cutoff
43	Aya Matsuda	Electronic structures and hydrogen absorption properties of Pd/Pt clusters : What is the difference from bulk?
44	Yu-ichiro Matsushita	Microscopic mechanism of band-gap variations in SiC polytypes based on ab initio calculations: Roles of peculiar electron state floating in internal space
45	Petr Milko	Electronic Structure of Iron Complexes Containing Bipyridine-based PNN Pincer Ligands
46	Noriyuki Mizoguchi	Edge Effect in Finite-length Pentaheptite Nanotubes
47	Alena Moon	Solvation of tert-Butyl Alcohol in Water: An Effective Fragment Potential Study
48	Hirotoshi Mori	Electronic Band Structure Calculations on Thin Films of the $L2_1$ Full Heusler Alloys X_2YSi (X, Y = Mn, Fe, and Co): toward Spintronic Materials
49	Bastien Mussard	Analytical gradients of Random Phase Approximation correlation energies in Range-Separated-Hybrid context: theory and implementation
50	Péter Nagy	Optical activity spectra of carbon nanostructures via a novel pi-electron model
51	Szilvia Nagy	Adaptive refinement of wavelet based solutions of the Schrödinger equation by independent estimation of the fine resolution coefficients
52	Katsumi Nakagawa	Structure Optimization of Molecules Consisting of up to Period 5 Elements by Discrete Variational Xalpha Method
53	Michaela Nekardova	Quantum chemical study of binding affinity of the purine inhibitor and its bioisosteres to cyclin-dependent kinases
54	Anton Nizovtsev	Electronic rearrangements during the inversion of lead phthalocyanine
55	Nadtanet Nunthaboot	Comparison of the monomer structure of the FMN binding protein from Desulfovibrio vulgaris obtained by NMR and molecular dynamics simulation approaches
56	Miho Otsuka	Theoretical Study on Internal Alkyne/Vinylidene Isomerization on Group 8 Transition Metal Complexes

Papers in Poster Session I cont'd

No.	Name	Title
57	Ivana Paidarova	Chemistry of defects in solids
58	Balazs Pinter	Structural and Electronic Contributions to Redox-noninnocent Behavior
59	Philipp Nikolaus Pleßow	Carbon-Carbon bond activation of epoxides by a (dtbpm)Pt fragment – A theoretical study.
60	Zoltán Rolik	Towards a multireference coupled-cluster method based on a unitary transformation
61	Thanyada Rungrotmongkol	Binding mode and binding affinity prediction of inclusion complex between flavonoid and ß-cyclodextrin
62	Pradipta Kumar Samanta	Formulation of an Internally Contracted Multi-Reference Coupled-Cluster Based Linear Response Theory to Study Excited States
63	Carlos Silva	Structure- and Ligand-based Drug Design of Novel p38 Alpha MAPK Inhibitors in the Fight Against the Alzheimer's Disease.
64	Gabriella Skara	Probe molecule transformations for staining techniques in zeolites – A periodic DFT study
65	Victor Solomonik	Jahn–Teller, pseudo-Jahn–Teller, and spin-orbit coupling effects in cerium trihalide molecules
66	Elizaveta Suturina	The quantum chemical study of isotropic and anisotropic magnetic properties of molecular magnets
67	Péter Szabó	Isomerization effect on the dynamics of the H + O2 collision
68	Lóránt Szegedy	An efficient linear-scaling CCSD(T) method based on local natural orbitals
69	Luca Szegletes	Parallel Evaluation of Two-Electron Integrals using a Wavelet Approach on the Graphics Processor Unit
70	Keiko Takano	A theoretical study of the interaction between a lectin called Siglec-7 and its glycan ligand in the immune system
71	Aydin Tavman	Theoretical DFT, FT-IR and NMR studies of 2-methoxy-6-(5-H/Me/NO2-1H-benzimidazol-2-yl)-phenols
72	Zsuzsanna Tóth	Approximate lower bounds via Löwdin's bracketing function
73	Yuzuru Ujiie	Molecular dynamics study on the substrate binding free energy of Threonine Synthase
74	Nikita Vakula	Theoretical investigations of Ag/SiO_2 interface
75	Marta Wiśniewska	Potential of mean force of association of hydrophobic particles: dependence on size and temperature
76	Nurbosyn U. Zhanpeisov	Modified new carbon K4 and metal-organic framework structures: A theoretical DFT study
77	Tamás Zoboki	Linearized Coupled Cluster Corrections to Antisymmetrized Product of Strongly Orthogonal Geminals: role of dispersive interactions

Papers in Poster Session II

No.	Name	Title
1	Tomoko Akama	Real-time TDHF/TDDFT calculation with efficient time evolution
2	Zikri Altun	Modeling Spin Crossover Complexes
3	Koji Ando	Electron Transfer Pathway in Biomolecules: FMO-LCMO and Tunneling Pathway Analysis
4	Arifin	Theoretical Study of Glucose Transformation to 5-Hydroxymethylfurfural using RISM-SCF-SEDD
5	Bence Babinszki	The hydrolysis of alpha-iminocarbonyls – a quantum chemical mechanistic study
6	Carmen Barrientos	Reactivity of first-row transition metal monocations with methyl fluoride: a computational kinetic study
7	Hamid Berriche	Structure and Spectra modeling of CsRg (Rg=Ar, Xe, Kr) van der Waals Complexes
8	Edward Brothers	Limitations of reaction barrier benchmarks with fixed geometries
9		cancelled
10	Francesca Costanzo	Hydrogen dissociation on aluminum cluster interacting with carbon surfaces by first principles calculations
11	András Csehi	Theoretical investigation of molecular switch properties of several quinoline compounds
12	Botond Csontos	Dissociation of the fluorine molecule: A benchmark study
13	Jozsef Csontos	Analytic gradients for general non-iterative coupled-cluster approaches
14	Malgorzata Domagala	The substituent effect in the doubly-charged benzene
15	Faina Dubnikova	Products of quinoline thermal decomposition and theirs further reactions. Quantum chemical calculations and kinetic modeling
16	Patrick Ettenhuber	Integral direct and memory conservative CCSD algorithm
17	Felipe Fantuzzi	Revisiting the aromaticity concept: electrostatic effects are responsible for the stability of benzene towards ring distortions
18	Nicolas Fernandez	Is DFT reliable for beryllium containing systems? The example of the Be – π system interaction

Papers in Poster Session II cont'd

No.	Name	Title
19	Leon Freitag	A new look at the electronic structure of the {RuNO}^{6} moiety using density-fitting CASSCF calculations and localised orbitals
20	Werner Gyorffy	Analytical energy gradients for explicitly correlated second-order Moller-Plesset perturbation theory
21	Susanta Haldar	On the Association of the Base Pairs on the Silica Surface Based on Free Energy Biased Molecular Dynamics Simulation and Quantum Mechanical Calculations
22	Stefan Huber	Stabilization mechanisms at polar ZnO surfaces in ideal vacuum conditions: a SCC-DFTB study
23	Yasuhiro Ikabata	Local response dispersion method in periodic systems: Implementation in the package based on a plane-wave basis set
24	Rodica-Mariana Ion	CNDO/2 and Tamm-Dancoff methods for electronic structure evaluation of aluminum porphyrins involved in photodynamic therapy
25	Munendra Jain	Theoretical Study of Protein Flexibility During Molecular Docking
26	Nopporn Kaiyawet	Theoretical study on ternary complex stability and Michael addition reactivity of Thymidylate synthase/mTHF/XdUMP
27	Ilya Kaliman	Reusable software for quantum chemistry applications
28	Emile Kassab	Theoretical Study of the Dispersive Interactions Effects on the Adsorption properties of 4,4'-Bipyridine in H-ZSM-5 Zeolite
29	Michio Katouda	Development of MPI/OpenMP hybrid parallel algorithm of resolution of identity second-order Møller–Plesset perturbation calculations for massively parallel multicore supercomputers
30	Toshiaki Kawamura	Quantum-Chemical Calculations of 195Pt-NMR Chemical Shifts in Platinum(IV) Porphyrins with Axial Ligands (Cl- , Br- , I- , SCN-)
31	Andrew King	The effect of non-linear variational parameters on the energy convergence of Coulomb three-body systems
32	Steven Kirk	AIMPAC2: A next-generation QTAIM code
33	Jiri Klimes	Acceleration of basis set convergence of ACFDT-RPA and MP2 correlation energies using effective energy techniques
34	István Komáromi	The Early Phase of the Conformational Transition at Vertebrate Transglutaminases; Can We See it From Molecular Dynamics Simulations?
35	Piotr Kowalski	Predicting excitation energies from short-range density functionals combined with the long-range strongly orthogonal geminal theory
36	Justyna Kozłowska	Electric-dipole properties of spatially confined water molecule
37	Kasper Kristensen	The Divide-Expand-Consolidate MP2 scheme goes massively parallel

Papers in Poster Session II cont'd

No.	Name	Title
38	Noriyuki Kurita	Specific interactions between lactose repressor protein and DNA: classical MD and ab initio MO calculations
39	Michal Malček	Comparison between the contact and effective electron/spin densities at the IOTC quasirelativistic level of theory
40	Marco Masia	On the Excitation Energy Transfer Dependency on Pigment–Protein Interactions in the Fenna–Matthews–Olsen Complex.
41	Toru Matsui	A Density Functional Theory Based Protocol to Compute the Redox Potential for Transition Metal Complexes
42	Arthitaya Meeprasert	Classical and advanced molecular dynamics study on ligand-protein interactions targeted at HCV NS3/4A protease
43	Vladimir Mironov	Photoswitching of the kindiling fluorescent protein: a theoretical study
44	Wataru Mizukami	A second-order multi-reference perturbation method for molecular vibrations
45	Dmitry Morozov	Probing the effect of the environment on the excited state dynamics of biological chromophores by ab initio quantum chemistry.
46	Salvador Moncho Escriva	Performance of Density Functionals in Modeling the Decomposition of CH_3OH by Cu_4 Cluster
47	Yutaka Nakatsuka	Development of Relativistic Quantum Monte Carlo: Theory and parallel program
48	Sébastien Nénon	Origin of the surface-induced first hyperpolarizability in the C_{60}/SiO_2 system: a SCC-DFTB insight.
49	Yoshio Nishimoto	Theoretical and Experimental Investigations of an Aldol-type Reaction with Rh Complex
50	Kaori Noto	Fragment molecular orbital and MD calculation study: Interaction analysis of HIV-1 antibody 2G12 and glycan Ligand
51	Hiroki Otaki	Acceleration of the vibrational structure calculation with optimized vibrational coordinates
52	Takao Otsuka	Theoretical study of DNA with unnatural base pair system using order-N DFT calculations
53	Nadia Ouddai	Theoretical Investigation of Ytterbium Tri-chelates Compounds
54	Abdelhamid Ounissi	The Nature of the Metal-acetylide Interaction in the Ternary Transition Metal Acetylide Complex $C_5Me_5Ti[\eta\text{-}C_2(SnMe_3)_2]$
55	Deepa Palanisamy	Quantum Chemistry-based Docking and Scoring for Design of Protein Kinase Inhibitors
56	Marcin Palusiak	Studies on halogen bonding
57	Ewa Pastorczak	Employing ensemble variational principle to calculate electron excitation energies of molecules: a range-separated approach

Papers in Poster Session II cont'd

No.	Name	Title
58	José Juan Peña	Exactly-solvable position-dependent mass Schrödinger equation for the Thomas-Fermi and Harmonic Oscillator potentials.
59	Jiri Pittner	Fluorescence of PRODAN in Water: a Computational QM/MM MD Study
60	Malinee Promkatkaew	Photophysical Properties and Photochemistry of Substituted Cinnamates for UVB Blocking: Effect of Hydroxy, Nitro, and Fluoro Substitutions at ortho, meta, and para Positions
61	Peter Reinhardt	Dispersion-only approximation for long-range RPA correlation contributions to DFT intermolecular interaction energies
62	Julia Romanova	Vibronic and Resonance Raman Spectra of Extended Viologens Modelled by Multireference Approaches
63	Agnieszka Roztoczyńska	Two-photon absorption spectra of the spiropyran and merocyanine pair: A comparative study of solvation models
64	Lakehal Salima	Theoretical Investigation on Homoleptic Yttrium Triguanidinates:
65	Benjamin Sanchez Lengeling	A Quantum Monte Carlo and CIPSI case study: Magnetic Coupling of a meta-xylylene diradical.
66	Mitsuo Shoji	Theoretical investigation on the absorption spectrum of photosystem as a biomarker on extrasolar planets
67	Raman Singh	Reaction Energetics of the Diels-Alder Reactions: A Long-range Corrected Density Functional Theory Study
68	Jan Šmydke	Generalization of the Non-Redundant Fockian for $N > 2$ electronic systems: Application to Excited States of Be Atom
69	Victor Solomonik	Towards accurate ab initio thermochemistry and spectroscopy of lanthanide compounds: Quantifying basis set, electron correlation, and spin-orbit coupling effects in lanthanide species
70	José Surga	Atomistic Study of the Incorporation Effect of Guest Ions Mg^{2+}, Al^{3+} and Fe^{3+} in Crystalline Structure Models of Cementitious Phases Like Alite (C_3S) and Belite (C_2S)
71	Milán Szőri	Cheap HEAT protocol: CHEAT1
72	Wataru Tanaka	Theoretical research on the substrate specificity of uridine-cytidine kinase
73	Tiago Teodoro	Prolapse-Free Relativistic Adapted Gaussian Basis Sets for 87Fr up to 118Uuo
74	Carl Trindle	Computational Thermochemistry of Superbases Derived from the Cyclopropene Imine Core
75	Kosuke Usui	Theoretical investigation of the electron transfer process in water
76	Anna Vnuchenko	Determine damage depth profiling by high-energy ion channeling in Monocrystalls
77	Takeshi Yoshikawa	Acceleration of divide-and-conquer method on GPU

Abstracts of Lectures

Thursday Afternoon , Brahms

Intramolecular Dispersion

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Recently synthesized diamondoid dimers such as 1-(1-diamantyl) diamantane and 2-(1-diamantyl)[121]tetramantane exhibit the longest C–C covalent bonds ever observed, up to 1.71 Å in length [1]. Despite severe steric crowding and highly stretched central bonds, these compounds are stable even at temperatures above 200 °C. This stability has been attributed to "attractive dispersion interactions" between the coupled diamonoid units of these molecules. Such phenomena, as well as ongoing debates over the protobranching concept, highlight the need for defining and quantifying dispersion interactions *within* rather than between molecules. In the 1-(1-diamantyl) diamantane case, our formal thermochemical analysis based on massive MP2, CCSD, and CCSD(T) wave function computations with aug(H)-cc-pVDZ and aug(H)-cc-pVTZ basis sets reveals that intramolecular dispersion greatly stabilizes the central C–C bond by nearly 36 kcal mol^{-1}. In comparison, DFT methods that incorporate dispersion yield a disturbing scatter of results.

In order to place the concept of intramolecular dispersion on a firm theoretical footing that does not involved artificial partitioning into molecular fragments, we have developed a new approach for dividing electron correlation energies given by general wave function methods into long- and short-range components. By means of inverse error-function transforms, we show how the Coulomb operator within two-electron integrals can be split using *arbitrary* switching functions previously inaccessible to electronic structure theory. An optimal form of the switching function is found that allows MP2, CCSD, and CCSD(T) correlation energies to be computed as a function of a sharp cutoff distance over which electrons are allowed to interact. Preliminary results from this methodology are presented for the benzene dimer and other benchmarks that challenge common understandings but are supported by simple physical models.

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[1] Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Yu.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A. *Nature*, 477; 308–311, 2011.

Electron Wave Packet Modeling of Chemical Bonding

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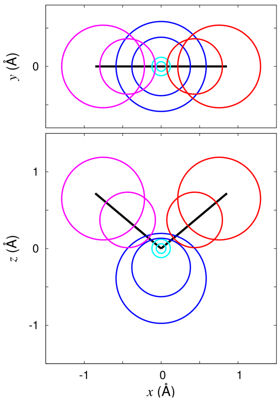
Following our recent development of nuclear wave packet (WP) molecular dynamics simulation of liquid water [1], we have been extending the method to many fermion systems [2] with aim to combine nuclear and electron WP methods in a compact and consistent manner. An essential part to this end is a proper account of the antisymmetry of fermion wave functions, for which we deploy the valence-bond (VB) theory that fits better with the localized WP picture than does the molecular orbital framework. In contrast with the conventional VB theories that employ frozen atomic orbitals (AOs) clamped on nuclear positions, our electron WPs can float and breath; namely, each electron is described by a single (minimal) spherical gaussian WP with freedom to move in space (float) and to change its width (breath). Despite its simplicity, this floating and breathing minimal electron WP with VB coupling has been found to give reasonably accurate ground state potential energy surfaces of H_2, LiH, BeH_2, CH_2 (Figure) and H_2O. Particularly interesting aspect was its capability to describe the cases in which conventional methods require nodal basis functions such as p-type AOs. This comes from the flexibility of the floating WPs to describe deformation of electron density, or polarization, in the ground state total wave functions that are generally nodeless. Roughly, the static correlation is accounted for by the floating WP and the VB coupling, while the dynamic correlation is by the breathing WP.

The method is now being extended toward electron-nuclear dynamic simulations. The WP description has a versatility to describe more complicated wave functions with quantum phase factors by invoking the coherent state path integrals with Monte Carlo sampling. Excited states will be studied by the dynamical response theory.



[1] Hyeon-Deuk, K., Ando, K. *J. Chem. Phys.* 131:064501, 2009; *ibid.* 132:164507, 2010; Ono, J., Hyeon-Deuk, K., Ando, K. *Int. J. Quant. Chem.* 113:356, 2013; Ono, J., Ando, K. *J. Chem. Phys.* 137:174503, 2012.

[2] Ando, K. *Bull. Chem. Soc. Jpn.* 82:975, 2009; *Chem. Phys. Lett.* 523:134, 2012; Hyeon-Deuk, K., Ando, K. *ibid.* 532:124, 2012.

Friday Morning I, Bartók

State-of-the-art and perspectives in modeling of London dispersion forces

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With the rapidly increasing computational power the sub-chemical level of accuracy determination of energy differences is within the reach of theoretical chemistry. This development has given a soaring rise of studies on weak intermolecular – van der Waals – forces, in particular on London dispersion interactions. The considerable importance of these universal attractive forces cannot be overestimated in chemistry, physics and biology. It has been shown on numerous examples that, in contrast to earlier ideas, London dispersion forces play an essential, sometimes decisive rôle in the understanding of the structure and energetics, not only of intermolecular complexes but also in many other situations.

The purpose of this talk is to give a broad overview of the most important wave function and density functional approximation methods, which are appropriate for a quantitative description of dispersion interactions. Different hybrid procedures have been designed to correct the failure of common density functional approximations. Special attention will be paid to the Random Phase Approximation (RPA), which gained a considerable popularity in recent years, and seems to provide a sound basis for the discussion of some conceptually interesting phenomena like different types of the non-additivity, which can be manifested in different ways.

Wednesday Morning II, Pátria

Beyond the Orbital Paradigm: A New Mean-Field Method for Strong Correlation Using Antisymmetric Products of Nonorthogonal Geminals

Paul W. Ayers[1], Peter A. Limacher[1], Paul A. Johnson[1], Stijn De Baerdemackers[2], Dimitri Van Neck[2], Patrick Bultinck[3]

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Conventional quantum chemistry methods either use a Slater determinant wavefunction directly (e.g., Hartree-Fock and Kohn-Sham density functional theory) or use this Slater determinant as the starting point for further corrections (e.g., perturbation theory and coupled cluster). A Slater determinant wavefunction is a questionable starting point, however, when the distinction between occupied and unoccupied orbitals is unclear. In these sorts of strongly correlated systems, it is important to treat the correlation between electrons explicitly. One way to do this is to approximate the wavefunction as an antisymmetric product of geminals (APG). APG wavefunctions are often excellent at capturing strong "static" correlation, but they were believed to be computationally intractable unless the geminals were chosen to be strongly orthogonal (APSG). In APSG, however, there is no correlation between different subsets of orbitals; the APSG wavefunction is therefore intermediate between the orbital picture and the geminal picture, and cannot describe some strongly correlated systems (like BCS wavefunctions, where the antisymmetrized geminal power (AGP) wavefunction is appropriate). We have recently derived, and numerically tested, several new types of APGs. The geminals in these methods are allowed to be nonorthogonal, and therefore include APSG and AGP as special cases. However, the computational scaling of these methods, which can be viewed as mean-field models for electron pairs, is Hartree-Fock-like ($O(N_{\text{basis}}^4)$). Even though these methods are very affordable and are therefore suitable for applications to large systems, they come very close (typically within 10^{-5} Hartree) of factorial-cost wavefunction-based methods like seniority-zero configuration interaction (i.e., closed-shell MCSCF). The residual dynamical correlation can be recovered using perturbation theory.

Thursday Morning I, Bartók

Some Considerations of Electron Correlation Introduced as a Correlation Potential

Rod Bartlett, Matt Strasberg, Prakash Verma, Ajith Perera

Quantum Theory Project

University of Florida

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We report on our experience in trying to describe electron correlation in terms of effective one-particle potentials. The basic idea is to add such a potential to Hartree-Fock theory to establish a kind of self-consistent approach for introducing electron correlation. Important considerations pertain to how to go from the usual Koopmans' theorem approximations for Ip's and Ea's to their exact, correlated values.

The microscopic model of electron transfer reactions in disordered solid matrices.

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Photochemistry Center, RAS, Moscow

ABSTRACT

The original model of the hopping mechanism for electronic conduction in photosensitive organic materials is considered. The electron transfer (ET) in active centers of such systems proceeds via local intra- and intermolecular modes. The active modes, as a rule, operate beyond the kinetic regimes, which are usually postulated in the existing theories of the ET. Our alternative dynamic ET model for local modes immersed in the continuum harmonic medium is formulated for both classical and quantum regimes, and accounts explicitly for the mode/medium interaction. The kinetics of the energy exchange between the local ET subsystem and the surrounding it environment determine essentially the total ET rate. The efficient computer code for rate computations is elaborated. The computations are available in the wide range of system parameters, such as the temperature, external field, the local mode frequency and the characteristics of the mode/medium interaction.

The computational algorithm is based on the technique elaborated earlier for treating H-atom transfer reactions but differs from it by several details. The most important amongst them is the idea of analytic continuation of the correlation function, representing the medium frequency spectrum, to the lower complex time half-plane. It assured the systematic and successful convergence of the rate integrals which is now extended down to a relatively low- temperature kinetic regimes. The relation of the present approach to the Marcus ET theory and to the underlying it quantum-statistical reaction rate theory (Levich-Dogonadze, 1959; Dogonadze et al and Jortner et al, 1970-1980) is discussed and illustrated by the results of computations for practically important target systems.

Tuesday Morning I, Bartók

Two-Determinant Mixing with a Strong-Correlation Density Functional

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In recent papers [A.D. Becke, J. Chem. Phys. 138, 074109 (2013) and J. Chem. Phys. 138, 161101 (2013)] a density functional for strong correlations in quantum chemistry was introduced. The functional is designed to capture molecular dissociation limits using symmetry-restricted orbitals. Here we demonstrate that the functional describes, with good accuracy, two-determinant multi-reference states. The examples of this work involve 50/50 mixing of symmetry-equivalent Slater determinants at avoided crossings. We employ exactly-computed exchange and fractional spin-orbital occupancies. The connection with dissociated systems and *single*-determinant reference states is explained.

Thursday Afternoon I, Lehár

Molecular simulations of hydrated inorganic nanopores

Jayesh S. Bhatt[1], Peter J. McDonald[1], David A. Faux[1], Serge-Henri P. Cachia[1],
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Fluid transport in porous media is of interest in fields as diverse as aquifers, oil reservoirs, cement hydration, plant-water hydraulics and human physiology. Nuclear magnetic resonance (NMR) experiments have considerably improved the understanding of the dynamics of proton-bearing fluids in porous media[1] by measuring the spin-lattice and spin-spin relaxation times, denoted as T_1 and T_2 respectively, which arise as a result of magnetic dipole coupling between diffusing spins.

In nanoscale pores, surface effects can be very prominent because, for example, paramagnetic impurities may reside in the solid surface and the transition between ‘surface’ and ‘bulk’ fluid is often blurred. Molecular simulations can play a vital role in complementing NMR experiments in terms of understanding the chemical morphology of the solid surface and the atomistic details of liquid diffusion.

We have carried out classical molecular dynamics (MD) simulations of water confined between SiO_2 and tobermorite surfaces. NMR relaxation rates are determined by taking the Fourier transform of the time-dependent dipolar spin-spin correlation function, $G^*(t)$, which captures the details of the angular and the relative translational motion of spins[2,3,4].

We have calculated the water density profile, diffusion coefficients and NMR relaxation rates as a function of slit-pore thickness in cement analogues. We find that the diffusion of water on the surface is slow, in agreement with experiments on cements, but that it may take place predominantly in one-dimensional channels rather than in two dimensions as supposed by analytical models of NMR relaxation. Surface-bulk exchange rates are estimated and interpreted in terms of these current models. The impact of aqueous calcium ions on water mobility is found to be significant and to play a critical role in the interpretation of experimental relaxation rates.

These results help us understand cement nanostructure, which is vital in creating durable and eco-friendly cements for the future.

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[2] Sholl, C.A., *J. Phys. C: Solid State Phys.* 14:447-464, 1981.
[3] Faux, D.A., Ross, D.K., Sholl, C.A., *J. Phys. C: Solid State Phys.* 19:4115-4133, 1986.
[4] Faux, D.A., McDonald, P.J., Howlett, N.C., Bhatt, J.S., Churakov, S.V., *Phys. Rev. E*, accepted.

Thursday Morning I, Lehár

Modifying the Fullerene Surface Using Endohedral light guests. From Ab Initio Molecular Dynamics and Metadynamics to Quantum Chemical Topology.

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Unlike the C_{60} molecule, C_{70} has five non-equivalent carbon atom types (commonly labelled with letters from *a* to *e*), which leads to eight non-equivalent C-C bonds. It has been shown that the *a,b*- and *c,c*- isomers are the two most stable structures on the $C_{70}O_3$ potential energy surface, which suggests that the reaction pathway toward oxide formation must proceed via the corresponding ozonide structure. We offer a mechanism for the thermally-induced dissociation of $C_{70}O_3$ that share the first two steps with the general mechanism for ozonolysis of alkenes proposed by Criegee. The calculations also reveal the likely time scale of the reaction (ab initio Molecular Dynamics), and indicate that it is the breaking of the C-C bond that triggers the whole process. [1]

Although MD study gave us a clue as for the initial steps of the ozonolysis, further steps were not accessible due to the energy barrier larger than the thermal boost. Advanced technics of the free energy surface exploration, such as a metadynamics or thermodynamical integration, allowed us to find structures relevant for the further steps of the reaction. The free energy surface has turned out to have complicated topology. [3]

New achievements in the endohedral modification of fullerenes triggered questions about influence of endohedral guests on carbon atoms reactivity and properties of fullerene derivatives. We analyzed how light endohedral guests such as noble gas atoms or small molecules (H_2, $2H_2$, CO_2, H_2O, HCl, CH_4, NH_3, BH_3) influence the thermodynamics of ozone ring-opening. The effect is isomer dependent, with the enthalpy of the reaction increasing for *a,b*-$C_{70}O_3$ and decreasing for *e,e*-$C_{70}O_3$ when doped with the heavy noble gas atoms Xe and Rn. [2] In case of light molecules we observe that at room temperature the impact of the guest is more prominent that it can be expected on the basis of the static (NEB) calculations at 0K. [3]

Quantum chemical topology provides a tool linking the concept of a chemical bond based on the Lewis theory and the quantum mechanical description of many-electron systems. We analyzed a bond evolution during the ozone ring opening on the basis of the topological features of the electron density and the electron localization function. [3]

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Wednesday Morning II, Bartók

Time's Arrow Revisited

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The field of chemical and physical processes, using principal microscopic techniques such as coupled cluster-, density matrix- and density functional methods identifiy today a fundamental branch of science at a crossroads between physics, chemistry and biology. The present consideration characterizes in more detail progress and developments that does not only define *ab initio* quantum chemistry as the most accurate emerging computational area in chemical applications [1], but also goes beyond long-established interpretations and understanding, see e.g. [2,3].

Within this broadening framework we have re-considered the 7 traditional arrows of time using precise conjugate operator representations [2]. The categorization entails original theoretical advances including non-Hermitean extensions of conventional operator representations accommodating quantum- and statistical mechanics. These developments are shown to unify various proposals of theoretical understanding including the law of self-reference. The latter unexpectedly appears as an analogy between general relativistic order and the illustrious Gödel theorem of mathematical logic, i.e. the assertion of the inherent limitations of all non-trivial axiomatic systems.

Previous considerations portraying the foundation of temporal processes and the possibility to unify the various arrows of time [2] including the prospect to tackle complex issues on the border between physics and biology [3] are extended further, establishing gravitation as the "Gödelian arrow of time". Additionally the present formulation supports the possible gravitational origin of molecular chirality and other fundamental symmetry violations.

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The Combined Effects of Electron Correlation and Relativity on Core Excitation Spectra

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Core spectroscopies can give accurate information on the electronic structure of matter, but the interpretation of the spectra is often rather complicated, especially in materials that contain open shell ions. The consequences of electron-electron interaction and in many cases also relativity influence the spectroscopic properties. For example, the relative intensities of spin-orbit split peaks in X-ray absorption spectra (XAS) can only in special cases be estimated from the statistical weights of the final states. In most cases the angular momentum couplings of the open shell valence electrons, the external crystal field and covalent effects strongly affect these branching ratios [1, 2]. Accurate first principles calculations can provide important information about these influences. It seems natural to use the 4-component relativistic formalism based on the Dirac-Fock equations to accurately calculate the spectra. This scheme is however complicated and computationally demanding. An alternative is to employ a 2-component method based on the use of the normalized elimination of the small component, combined with the restricted active space state interaction approach [3].

In this contribution we show benchmark calculations of the 4f X-ray Photo-electron Spectrum (XPS) of U^{5+} and of the 2p XPS of MnO, which show that the approach is capable of reproducing the results of the full 4-component relativistic calculations with good accuracy. Next we focus on the 2p XAS of small positively charged titanium clusters. The X-ray absorption spectra at the $L_{2;3}$ edge of size-selected clusters have been investigated experimentally by Lau and coworkers [4]. The spectrum of bulk Ti shows two broad lines, attributed to excitations from the $2p_{3/2}$ and the $2p_{1/2}$ shells. Spectra of Ti_3^+ and larger clusters have the same characteristics. The spectra of the Ti^+ and Ti_2^+ ions have however a much richer structure and the assignment of peaks nor the explanation of the branching ratios are straightforward. We have calculated the 2p XAS of these ions and, for comparison, also of a Ti atom. The computed spectra, which agree well with the experimental ones, enable us to interpret the experimental spectra in terms of many-electron and relativistic effects.

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Statistical approaches to forcefield calibration and prediction uncertainty in molecular simulation

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The great development of molecular simulation in the past decades has made it a very attractive tool for the study of condensed matter. As a matter of fact, it is now commonly used to predict thermophysical properties of fluids, both in academic studies and for industrial purposes.

The use of molecular simulation as a predictive tool requires to monitor all sources of uncertainty in the results of a simulation., among which those arising from the definition of the forcefield has long been ignored. The main reason for this is the difficulty to estimate forcefield parameters, that necessitates an extensive exploration of parameter space, incompatible until very recently with the computer time of molecular simulations.

We explored various calibration strategies and calibration models within the Bayesian framework [1] in the case of a two-parameters Lennard-Jones potential for Argon. The advantage of this system is that calibration can be done using analytical expressions. We have shown that prediction uncertainty for thermodynamical and transport properties, albeit very small, is larger than characteristic statistical simulation uncertainty [2].

For more complex systems, more parameters have to be calibrated and, in absence of analytical models, the calibration process requires to run long molecular simulations. In order to face these issues, we propose to use kriging metamodels and optimal infilling strategies to limit the number of molecular simulations to be performed during the calibration process. We have benchmarked this methodology on the water TIP4P forcefield [3].

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Monday Afternoon I, Lehár

Harmonic vibrational frequencies in molecules at extreme high pressure: a novel QM method

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ABSTRACT:
The study of molecular systems at extreme high pressure (order of GPa) is a field at the frontier of contemporary Molecular Quantum Mechanics [1]. We present here a new contribution to this field with a Quantum Chemical method (PCM-XP) [2] for the calculation of harmonic vibrational frequencies for molecular systems in dense medium at high pressures. The PCM-XP method, which is an extension on the Polarizable Continuum Model (PCM) [3] amply used for the study of the solvent effects at standard condition of pressure, is here illustrated by the case of diborane as a molecular system under high pressure. The PCM-XP vibrational frequencies (DFT level) of diborane are in a satisfactory agreement with the corresponding experimental results [4] as a function of the pressure. Moreover, the PCM-XP method gets a new light on the effect of the pressure on the vibrational frequencies, showing how this effect can be ascribed to two physically distinct influences (curvature and relaxation) on the potential energy for the motion of the nuclei of the molecular system.

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Monday Morning II, Lehár

Evaluation of exchange integrals by Fourier transform of the 1/r operator and its numerical quadrature

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This contribution deals with the use of the old idea to replace the $1/r_{12}$ operator by the Fourier transform. If numerical quadrature is applied instead of derivation of formulas for analytical calculation, we obtain

$$\int f_1(\mathbf{r_1})\frac{1}{r_{12}} f_2(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} = \frac{1}{2\pi^2}\sum_{p}^{radial}\sum_{j}^{angular}\omega_p\omega_j(f_1(\mathbf{r}_1)\exp(-\mathbf{k_{p,j}}\mathbf{r}_1)(f_2(\mathbf{r_2})\exp(\mathbf{k_{p,j}}\mathbf{r}_2),$$

where ω_p and ω_j are weights of roots of the numerical quadrature and expressions in parentheses are overlap integrals for functions *f* and plane-wave functions. The stimulus for this study arose from a need to evaluate efficiently exchange integrals of the type $(g_1(1)k_1(1)|g_2(2)k_2(2))$, where *g*'s and *k*'s, respectively, are gaussians and plane-wave functions. Evaluation of these integrals is still a bottleneck in *ab initio* calculations on electron scattering by polyatomic molecules. The objective of this contribution is to show that this way of evaluation of exchange integrals may be also beneficial for the mainstream quantum chemistry. For securing a needed accuracy of integrals the expansion of 1/r in plane-wave functions must be very large, but the formulas for overlap (*gk*) integrals and their analytical derivatives are simple and their evaluation is very fast. It will be shown that in spite of their large number considerable computer time saving may be achieved. This opens a way to treatments of electron scattering by larger molecules than it was possible so far. Possibly time saving may also be obtained in this way for the exchange energy in a pure Gaussian basis.

Friday Afternoon I, Bartók

Theoretical Study of Fe– $(H_2O)_m$, $m \leq 4$ and Fe_n–$(C_6H_6)_m$, $n \leq 7$, $m \leq 4$

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ABSTRACT

The structural, electronic, energetic and vibrational properties of transition-metal-ligand clusters which are formed by magnetic iron clusters interacting with benzene and water moieties are studied by means of density functional theory, including dispersion corrections. The obtained results for $Fe^+(H_2O)$-Ar_2 and $Fe^+(H_2O)_2Ar$, jointly with the experimental IRPD (infrared photo-dissociation spectra), provides insight on the nascent hydration for $Fe^+(H_2O)_m$ clusters in the gas phase. Solvation of one electron, localized on the iron atom, was addressed through the $Fe^-(H_2O)_6$ ions. For these clusters the B3LYP method was used. Further, using the BPW91 functional and dispersion corrections as proposed by Grimme (DFT-D2), the $Fe^+(C_6H_6)_m$, $m \leq 4$, systems were studied. It was found that the tilted-T-shape structure, appearing as the ground state for the isolated benzene dimmer, play an important role in the stabilization and growing of $Fe^+(C_6H_6)_m$. Solvent behavior for $m \geq 3$ was found. Bigger clusters were also addressed: Fe_2-$(C_6H_6)_m$, Fe_4-$(C_6H_6)_m$; $Fe_6(C_6H_6)_m$, and Fe_7-C_6H_6; on which all-electron calculations are done at the BPW91/6-311++G(2d,2p) level of theory. The obtained results allow to determinate the geometry of the ground state, GS, clusters. $Fe_6(C_6H_6)_m$ and $Fe_7(C_6H_6)$ present the so called "rice-ball" structures where the geometry of the bare cluster is preserved and the benzene molecules are bonded through 3d-π Fe—C bonding with hapticity equal to six, η^6, and equilibrium bond lengths of 2.1 to 2.2 Å. The ionization energies of the formed complexes are smaller than those of the bare Fe_n clusters confirming the existence of 3d-π bond interactions. Also the electronic affinities are smaller. The magnetic moments of these complexes are quenched strongly with respect to those of the isolated Fe_n clusters, suggesting that the magnetization play an important role in the adsorption or bonding properties of these complexes. The IR spectra was also addressed showing IR resonances near to those of bare benzene with blue shifts for the CH bending out of the plane and red shifts for the in plane C-H bending and for the in plane carbon ring distortion, implying a weakening of the bonding in the carbon ring. In some cases, some IR forbidden vibrational bands of benzene becomes active in the Fe_n-$(C_6H_6)_m$ complexes and, conversely, some become deactivated.

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Tuesday Morning II, Bartók

Restoration of the Derivative Discontinuity in Kohn-Sham Density Functional Theory: An Efficient Scheme for Energy Gap Correction

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From the perspective of perturbation theory, we propose a systematic procedure for the evaluation of the derivative discontinuity (DD) of the exchange-correlation energy functional in Kohn-Sham (KS) density functional theory, wherein the exact DD can in principle be obtained by summing up all the perturbation corrections to infinite order [1]. Truncation of the perturbation series at low order yields an efficient scheme for obtaining the approximate DD. While the zeroth-order theory yields a vanishing DD, the first-order correction to the DD can be expressed as an explicit universal functional of the ground-state density and the KS lowest unoccupied molecular orbital density, allowing the direct evaluation of the DD in the standard KS method without extra computational cost. The fundamental gap can be predicted by adding the estimated DD to the KS gap. This scheme is shown to be accurate in the prediction of the fundamental gaps for a wide variety of atoms and molecules.

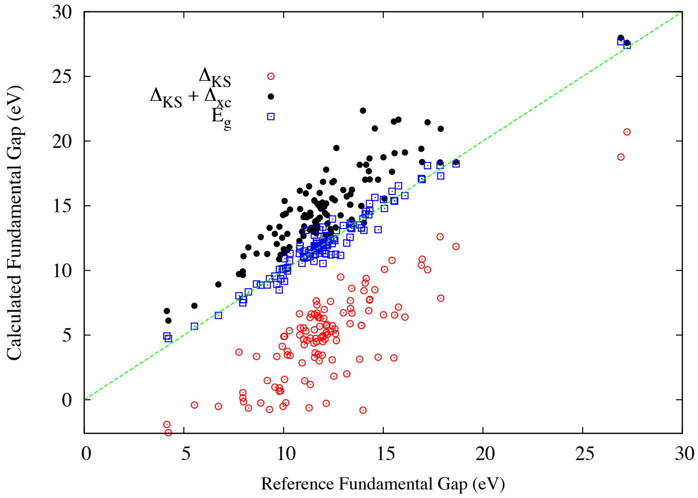

Figure: Calculated versus reference fundamental gaps for the FG115 database [2]. The fundamental gaps are calculated by three schemes (the KS gap, the KS gap + the approximate DD, the KS gap + the exact DD) using the LB94 functional [3].

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Tuesday Morning I, Lehár

Towards calculating and interpreting the linear and second-order nonlinear optical properties of molecular crystals

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In this contribution it is shown that modest calculations combining first principles evaluations of the molecular properties with electrostatic interaction schemes to account for crystal environment are reliable for predicting and interpreting the experimentally-measured electric linear and second-order nonlinear optical susceptibilities within the experimental error bars. This is illustrated by considering two molecular crystals, namely: 2-methyl-4-nitroaniline (MNA) and 4-(N,N-dimethylamino)-3-acatamidonitrobenzene (DAN) [1]. A good agreement between theory and experiment is achieved providing the electric field effects originating from the electric dipoles of the surrounding molecules are accounted for. On the other hand, the intermolecular interactions determine the geometry and thus the linear and nonlinear optical responses. This study also highlights i) the key role of the geometry on the $\chi^{(1)}$ and $\chi^{(2)}$ responses, ii) the impact of the crystal environment on the geometries, iii) the role of electron correlation on the linear and nonlinear responses of the molecular crystals, iv) the good performance of the MP2 method to evaluate static properties, in combination with B3LYP to describe the frequency dispersion effects. A second illustration deals with the two anil crystals, [N-(4-hydroxy)-salicylidene-amino-4-(methylbenzoate) and N-(3,5-di-tert-butylsalicy- lidene)-4-aminopyridine, which can switch between a enol (E) and a keto (K) form [2].

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A new size extensive multireference perturbation theory

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Abstract: A new multireference perturbation series is derived based on the Reighley-Schrödinger perturbation theory. It is orbitally invariant. Its computational cost is comparable to the single reference Møller–Plesset perturbation theory. It is demonstrated numerically that the present multireference second and third order energies are size extensive by two types of super-molecules composed of H_2 and BH monomers. Spectroscopic constants of $F_2(X^1\Sigma_g^+)$, $Cl_2(X^1\Sigma_g^+)$, $C_2^-(X^2\Sigma_g^+)$, $B_2(X^3\Sigma_g^-)$ and C_2^+ $(X^4\Sigma_g^-)$ as well as the ground state energies of H_2O, NH_2 and CH_2 at three bond lengths have been calculated with the second multireference perturbation theory. The dissociation behaviors of CH_4 and HF have also been investigated. Comparisons with other approximate theoretical models as well as the experimental data have been carried out to show their relative performances.

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Monday Morning II, Pátria

Cost-effective approaches for relativistic electron-correlated calculations

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Four-component methodologies based on the no-pair Dirac-Coulomb (DC) Hamiltonian [1] offer the possibility for a rigorous treatment of relativistic effects in quantum chemistry. Unfortunately, DC-based correlation methods such as the DC coupled-cluster (CC) approaches are at least one order of magnitude more expensive than corresponding nonrelativistic schemes due to spin-symmetry breaking. Moreover, scalar-relativistic effects often dominate the relativistic corrections; spin-orbit (SO) effects are mainly responsible for level splitting and related phenomena. [3]

In this work a cost-effective scheme is presented which consists of a high-level spin-free Dirac-Coulomb (SFDC) calculation [4, 5] augmented by an approximate treatment of SO effects via perturbation theory. [6] In the latter, we treat the difference between the DC and SFDC Hamiltonian as the perturbation, and the second-order SO energy correction is computed as a second derivative of the SFDC energy at the Hartree-Fock level. The efficacy of the proposed scheme is demonstrated in benchmark calculations of energies and electrical properties for a set of diatomic molecules. We also report a first chemical application of the suggested approach to various gold-containing compounds.

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The stability of Coulomb three-body systems

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Three-body Coulomb systems are the simplest that incorporate both atomic and molecular ions and are therefore of considerable interest not only for atomic and molecular theory but also for light isotopes containing various elementary particles, such as muons and positrons.

High accuracy non-relativistic quantum chemical calculations of the energy levels and wavefunctions of three-particle systems of the form $\{m_1^{\pm}m_2^{\pm}m_3^{\mp}\}$ are calculated using a fast and efficient series solution method in a triple orthogonal Laguerre basis set [1]. The results are presented in the form of a reciprocal mass fraction ternary diagram [2], [3] and used to calculate accurate values of g, the fractional additional binding

$$g = \frac{E_0 - E_{th}}{E_{th}}$$

where E_0 is the three-body energy and E_{th} is the lowest threshold energy.

The topology of the stability and instability domains, based on the knowledge that all symmetric systems with $m_1 = m_2$ are stable against spontaneous dissociation, has been discussed and an expression for the width of the stability band formulated in terms of the binding g as a function of the reciprocal mass fraction for the uniquely charged particle [2]. Here we present a functional fit to g and use it to define a lower bound to the stability zone of three-particle Coulomb systems.

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Friday Afternoon I, Pátria

Solvation, Coupled Cluster Response Theory, and the Optical Properties of Chiral Molecules

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The optical properties of chiral molecules are among the most challenging to predict, even for state-of-the-art quantum chemical methods because of their delicate dependence on a variety of intrinsic and extrinsic factors, including electron correlation, basis set, vibrational/temperature effects, etc.[1]-[4] This task is made even more difficult by solvation, which can have a dramatic impact on even the sign of optical rotation angles or circular dichroism rotational strengths.[5] In this lecture, we will discuss the most recent efforts from our group to attack this problem, including both implicit and explicit solvent models, and the role of reduced-scaling techniques to improve the efficiency of such computations.

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Monday Morning II, Pátria

Calculation of response properties with the normalized elimination of the small component (NESC) method

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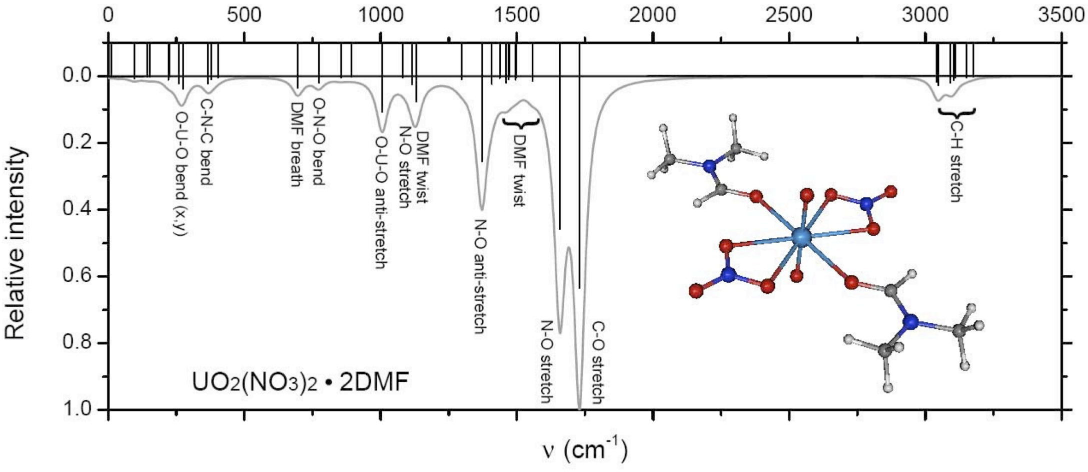
The NESC method, originally developed by Dyall and improved by Zou, Filatov and Cremer [1-5], is a first principles 2-component approach (positron components are eliminated) fully equivalent to the exact 4-component approach based on the Dirac equation. In view of the fact that NESC provides the exact 2-component relativistic description of one-electron systems, it is an ideal starting point for developing a repertoire of methods, by which routinely first and second order response properties can be calculated. Previously, we have pointed out the relationship between IORA (infinite order regular approximation) and NESC and have used this for a rapid iterative solution of the NESC equations. In this work, we present algorithm and methods for the calculation of molecular geometries, dipole moments, hyperfine structure constants, vibrational frequencies, force constants, electric polarizabilities, infrared intensities, and other response properties. We also discuss the impact of spin-orbit coupling on molecular properties. Applications are presented for mercury containing molecules and some other molecular systems containing transition metals, which require a relativistic treatment. A simple way is sketched how to obtain a quantitative characterization of the bond strength involving heavy atoms with strong relativistic effects.



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Monday Morning II, Bartók

QM/MM analysis of catalytic promiscuity and proton pumping in enzymes

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(Dated: June 14, 2013)

Abstract

I'll discuss the application of QM/MM methods developed in our lab to two fascinating problems in biochemistry: catalytic promiscuity and redox driven proton pumping. The first problem focuses on enzymes in the alkaline phosphatase (AP) superfamily, which exhibit remarkable catalytic promiscuity toward a broad class of phosphates and sulfates. Our QM/MM studies with a series of substrates in two members of the AP enzymes provide explicit support to the model that these enzymes are able to recognize and stabilize different types of transition states in a single active site. Analysis of the structural features of computed transition states indicates that the plastic nature of the bi-metallic site plays a minor role in accommodating multiple types of transition states, and that the high degree of solvent accessibility of the AP active site also contributes to its ability to stabilize diverse transition state structures without causing large structural distortions in the bimetallic motif. The second problem concerns proton pumping in Cytochrome c Oxidase (CcO). By judiciously combining QM/MM calculations and continuum electrostatic models, we demonstrate that a key element is the change of hydration level for the hydrophobic cavity that bridges the proton input channel, the binuclear center and the candidate proton loading site. The trigger of the hydration level change is the protonation of the candidate proton loading site, an event that calls for a novel proton transfer mechanism that involves an additional proton in the input channel. Together, the two research topics highlight the advantage of an efficient QM/MM framework based on SCC-DFTB and the diverse roles of water molecules in enzyme functions.

Thursday Afternoon II, Lehár

Rate constants from equilibrium simulations: a new method

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On the timescale of molecular simulations, reactions are rare-events. In most cases direct calculation of rate constants requires unaffordable computational costs. We have developed a theory and an algorithm to calculate rate constant from equilibrium simulations in a consistent and relatively cheap manner. The method requires the free energy profile of the reaction, implying that a suitable reaction coordinate is already identified. The ideas behind the method are to define the *Reactive Segment (RS)* within the reactant state and to recognize that the corresponding rate constant, k_{RS} can be calculated very efficiently. The phenomenological rate constant can be easily recovered by reweighing k_{RS} with the statistical weight of the selected *RS* within the full reactant state. If necessary the calculated rate constants can be used to derive activation free energies and related quantities. This can be useful to test the applicability of a kinetic model or to make contact with previous results.

Monday Afternoon I, Bartók

Theoretical investigation of the second-order nonlinear optical response of collagen – signatures of the triple helix structure

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Second-harmonic imaging microscopy (SHIM) is a high-resolution biomedical imaging technique, which has been developed to get contrast enhancement of non-centrosymmetric molecular arrangements. Campagnola and Loew [1] have reported that the first biological second harmonic generation (SHG) imaging experiment was done by I. Freund *et al.* [2] in 1986 on the collagen of rat-tail tendon. Measurement of the second-order hyperpolarizability of the collagen triple helix by Hyper-Rayleigh scattering (HRS) experiment was later performed by Deniset-Besseau *et al.* [3] who characterized the first hyperpolarizability (β) of the collagen I from rat-tail as well as of a short triple-helix model peptides $[(\text{Pro-Pro-Gly})_{10}]_3$ (PPG10). They concluded that the collagen large second-order nonlinear optical response originates from the tight alignment of a large number of small and weakly efficient harmonophores, presumably the peptide bonds, resulting in a coherent amplification of the nonlinear signal.

In this contribution we employ theoretical chemistry methods to calculate and to analyze the first hyperpolarizability of PPG10. The calculations are carried out by adopting the ONIOM method in combination with the TDHF or TDDFT method, which allows assessing the impact of electron correlation on the first hyperpolarizability. The different β tensor components are analyzed. In particular the first hyperpolarizability is decomposed into its dipolar and octupolar contributions and the depolarization ratio is calculated. This enables to unravel the origin of the β responses and to describe how the three intertwined helices participate to the total β.

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Understanding effects beyond pairwise additivity in dispersion interactions

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We categorize three distinct physical causes for the failure, under certain circumstances [1-9], of the concept of evaluating dispersion (van der Waals) energies by summing contributions from pairs of atoms. Although these causes frequently operate together, we give examples where just one of these three causes is the primary factor in non-additivity. We assess a number of theories and modeling approaches for their success in accounting for these three effects.

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Thursday Afternoon II, Lehár

Connecting quantum events to macroscopic phenomena: Multiscale simulation of photoresponsive materials

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A multiscale model for the simulation of a photoswitchable azobenzene-containing liquid crystal is presented, which links coarse-grained (CG) mesoscale simulations of the global structure to a nonadiabatic quantum-mechanical description of the local photoactive moiety via a classical atomistic model [1]. A nonadiabatic QM/MM approach has been developed [2, 3, 4] and applied to study the photoswitching of azobenzene in different environments — observing an increasing influence of the molecular surroundings going from vacuum, via an isotropic liquid, to an ordered liquid crystalline state. In the spirit of multiscale modelling, we have also developed a purely classical force field for photoswitching, based on the quantum data, that enables us to study a high density of photoisomerisation events and their impact on the liquid crystalline order. In order to gain access to mesoscopic time and length scales on which liquid crystalline phase transitions take place, coarse grained simulation models are used, with substantially fewer degrees of freedom compared to an all-atom level of resolution.

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Thursday Morning II, Lehár

Mechanochemistry
The curious case of cyclopropane

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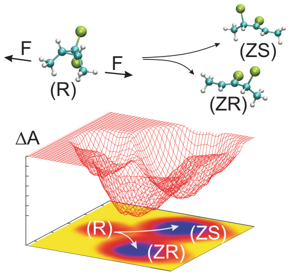
The stereochemistry of mechanochemical ring-opening reactions in cyclopropane derivatives has provided several enigmatic experimental results. [1] This issue is addressed here with advanced *ab initio* simulations - Car–Parrinello Molecular Dynamics [2, 3, 4] - of *cis*– and *trans*-1,1-dichloro-2,3-dimethylcyclopropane.

In particular, force-transformed free energy landscapes are computed via metadynamics, [5, 6] which accesses the thermodynamics of mechanochemical reactivity. Dynamical effects are probed through extensive trajectory shooting simulations. [7] It is demonstrated that forces of approximately 2 nN induce barrierless ring-opening of both cis and trans isomers, which rationalizes the lack of selectivity observed experimentally.



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Tuesday Morning I, Lehár

From structure to opto-electronic excitations of organic-inorganic hybrid materials: State of the art and challenges

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Organic-inorganic hybrid materials are most exciting in view of applications in optoelectronic applications as one can expect to find new properties, which are absent in either of the building blocks. At the same time, they represent challenges for electronic-structure theory as non-local exchange and correlation effects are crucial on all levels, from structure to electronic structure and opto-electronic excitations. Moreover, methods that turned out useful for describing one side may not be applicable for the other one, and they are likely to fail for the interfaces. I will present selected examples of hybrid interfaces to discuss which properties can be reliably computed for such materials and what is missing in our theoretical concepts to reach predictive power on a quantitative level. They will cover photoemission spectra computed by the *GW* approach as well as optical properties including excitonic effects as obtained from the Bethe-Salpeter equation of manybody perturbation theory.

Wednesday Morning I, Lehár

Ligand effect on the electronic structure and reactivity of rhodium pincer complexes

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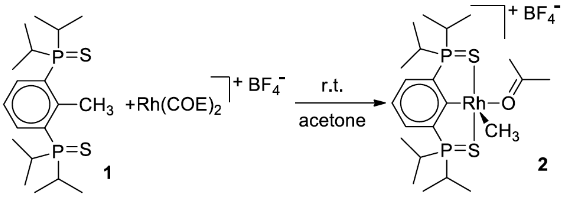
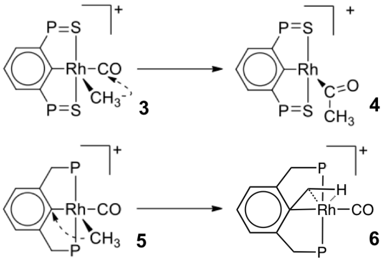
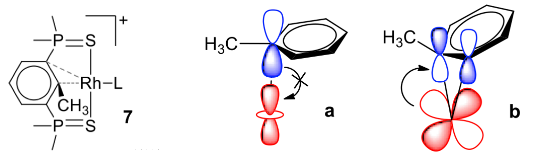


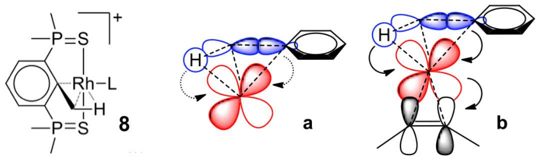
Selective activation of strong C-H and C-C bonds is one of the fundamental challenges of modern organometallic chemistry. Stable pincer frameworks provide the opportunity for mechanistic insights on such reactions. Recently synthesized Rh complexes based on SCS pincer ligands exhibited unique chemical behavior. The SCS-type ligand **1** undergoes highly selective oxidative addition of an sp^2-sp^3 C–C bond upon reaction with the Rh(I) precursor, affording the Rh(III) aryl-methyl complex **2**. Treatment of **2** with CO resulted in facile migratory insertion of CO, affording the new Rh(III) aryl-acetyl complex **4** whereas structurally similar PCP complex undergoes C–C reductive elimination to afford an η^3-arene Rh(I) species **6**.



High-level DFT study of the SCS and PCP complexes vis-à-vis their reactions in solutions demonstrated that enhanced electron density on S atom rises its electrophilicity, so that in the SCS and PCP ligands Rh-bound S and P atoms have large opposite charges. This results in different oxidation state of the Rh atom, Rh(III) in the PCP aryl-methyl complexes and Rh(V) in their SCS analogs. Excessive electron density in the SCS system determines the thermodynamic selectivity for C-C over C-H cleavage, as it is attributed to the higher electronegativity of a methyl *vs*. hydride ligand. It also gives rise to formation of two pre-cleaved intermediates: an η^2 arene complex **7** with no bonding between the metal and the methyl moiety and a novel η^3-C-C-H agostic complex **8**, the immediate precursor for both observed C-C and unobserved C-H bond cleavage.



Key interaction in an η^1-arene structure (a) and its stabilization by electron transfer to the arene ring, leading to an η^2-arene structure (b) in intermediate **7**.



Key electronic interaction in the η^3-C-C-H agostic intermediate **8** (a) and its stabilization by *cis*-2-butene through metal-to-olefin electron transfer (b).

Higher Rh oxidation state decreases Rh→CO π backdonation and weakens Rh-CO bonding in the SCS system. In contrast, stronger Rh-CO bonding in the PCP system causes enhanced CO→Rh→phenyl σ donation that weakens the Rh-C_{ipso} bond. These effects determine different direction for migration of the methyl group in the carbonyl complexes **3** and **5**.

Thursday Morning I, Brahms

CONFORMATONAL AND VIBRATIONAL ANALYSIS OF 12-THIACROWN-4 AND 18-THIACROWN-6

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We used the combined conformational and vibrational analysis to predict the structure of free 12-thiacrown-4 (12t4) and 18-thiacrown-6 (18t6). Conformational analysis was performed using the efficient CONFLEX conformational search method of cyclic molecules. The ab initio computations were done at levels as high as the MP2/6-311G** level. Conformational analysis of free 12t4 predicted that 12t4 exists in the D_4 conformation, Fig. 1.[1] Conformational analysis of free 18t6 predicted a new C_2 conformation to be the ground state conformation, Fig. 1. At the MP2/6-311G** level this new C_2 conformation is more stable by 4.67 kcal/mol than the experimentally known C_2 conformation of 18t6. The factors affecting the structure of 12t4 and 18t6 are discussed.

The vibrational spectra, IR and Raman, of 12t4 and 18t6 were measured. The vibrational spectra were calculated at the HF, B3LYP, CAM-B3LYP and MP2 levels using the 6-311G** basis set. Comparison between the calculated and experimental results is made.

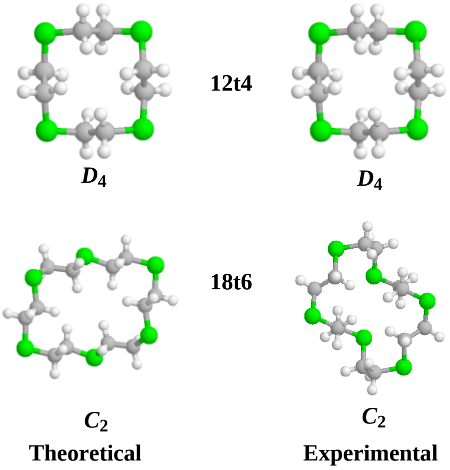

Figure 1. Structure of 12t4 and 18t6.

Keywords: Conformational analysis, vibrational analysis, thiacrown ethers.

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Wednesday Morning I, Lehár

Probing IR-Raman rovibrationally excited HCl molecule with X-ray spectroscopies : a theoretical approach

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Up to now, most of the experimental Pump-Probe devices developed to control bond dissociation routinely combine infrared frequencies (pump) and UV (probe) light frequencies. Only recent theoretical studies [1, 2] have simulated the X-ray absorption spectra of small molecules driven by strong IR pulse, the association of an IR-pump with a X-ray probe radiation being today unexplored experimentally. In the present work, we show detailed calculations of a new scheme for time control of bond dissociation. The scheme combines far-off-resonant Raman transitions [3] initiated by one chirped and one monochromatic laser pulse, with X-ray spectroscopies. The main purpose of this study is to show through a theoretical approach taking into account the rotation of the molecule, that such a pump-probe association provide a powerful tool to control dynamics of molecular dissociation through a core-binding energy analysis. An experimental scheme is then proposed, where : (1) selected vibrational states are populated by infrared (IR) laser pulses following the Raman Chirped Adiabatic Passage technique [3]; (2) the evolution of the population of the different vibrational states is tracked by following the variation of the X-ray absorption or photoelectron spectrum of the molecule. Beyond opening a unique opportunity for probing the potential surfaces of the ground, core-excited, and final molecular states [4], this technique provides a time-control of bond dissociation through modulation of core hole chemical shift with high resolution [5, 6].

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Thursday Morning I, Lehár

Ab initio molecular dynamic simulation of photoactive proteins in action

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Simulation of the mode of action of enzymatic proteins often requires advanced multiscale and rare event techniques. This presentation reviews two recent advancements: an adaptive multiscale approach that allows for hybrid quantum/forcefield (QM/MM) and atomistic/coarse-grain modeling with open boundaries [1, 2] and, secondly, a new path-metadynamics method to sample slow complex processes [3]. We apply these methods in combination with Car-Parrinello molecular dynamics and classical MD to study for example the photocycle of light sensitive proteins.

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Friday Afternoon I, Bartók

New functionals through factorization of the exchange and exchange-correlation hole

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We present approximations for the exchange and the exchange-correlation hole that share a common form; they are written as a product of two factors. In the case of the exchange hole the factors are the electron density and the exchange factor. In case of the exchange-correlation hole, the factors are the exchange hole and the correlation factor. The exchange factor as well as the correlation factor is determined such that various conditions, e.g. the normalization condition, are satisfied. The implementations as well as initial results for the holes and the exchange-correlation energies are discussed.

Mechanism of the Water-Gas Shift Reaction at the Metal-Oxide Interface: Insights from First Principles Calculations

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The traditional approach to the optimization of metal/oxide catalysts has focused on the properties of the metal and the selection of the proper oxide for its dispersion. The importance of metal–oxide interfaces has long been recognized, but the molecular determination of their properties and role is only now emerging. In this talk we focus on the water gas shift reaction, WGSR, a chemical process that allows for obtaining clean molecular hydrogen: $CO+H_2O \rightarrow CO_2+H_2$. Bulk like phases or extended surfaces of coinage metals show low catalytic activity that improves when supported on a metal-oxide. Multiple reaction mechanisms have been proposed. In the redox mechanism, CO reacts with oxygen derived from the dissociation of H_2O. In the associative process, the formation of a carbonaceous CO_xH_y intermediate must precede the production of H_2 and CO_2. The mechanism involves several steps that can take place at different sites of the catalyst: the metal, the support or the interface. Besides the dispersion effect, the role of the support is to increase the interaction with water and facilitate its dissociation. DF calculations show that supported CeO_X nanoparticles (NPs) are highly efficient in water splitting (Fig 1, left). Furthermore The M/CeO_x /TiO_2 (110) surfaces display outstanding activity for the WGS, in the sequence: Pt > Cu > Au (Fig 1, right) . Such a high catalytic activity reflects the unique properties of the mixed-metal oxide at the nanometer level. STM and DF calculations show that Ce deposition on TiO_2 (110) at low coverage gives rise to Ce_2O_3 dimers specifically aligned, indicating that the substrate imposes on the ceria NPs unusual coordination modes enhancing their chemical reactivity.

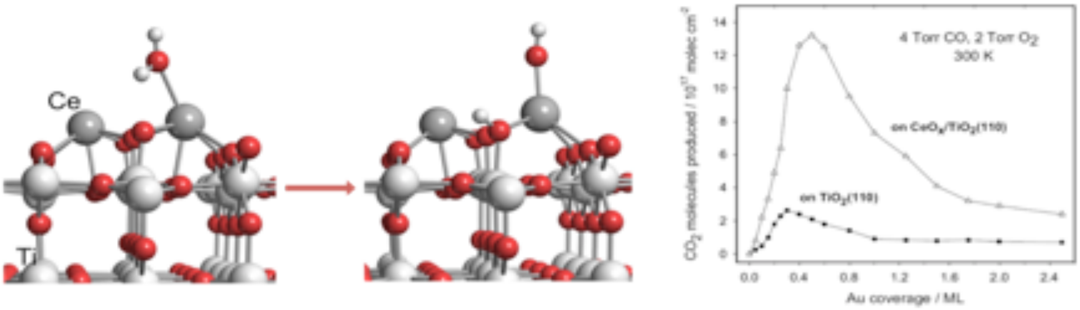

Fig. 1. Left: water dissociation on $CeO_x/TiO_2(110)$. The process is exothermic by 0.70 eV and the activation barrier is of only 0.04 eV. Right: catalytic activity of gold NPs supported on $TiO_2(110)$ and $CeO_x/TiO_2(110)$.

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Theoretical design of conical intersections in molecular motors and switches: A Density Functional Theory perspective

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It is widely recognized that conical intersections (CIs) play the dominant role for the mechanism of photochemical reactions providing very efficient funnels for radiationless relaxation processes [1]. For designing new types of photoactive molecules, such as molecular motors and switches [2], a deep understanding of the factors affecting the occurrence of CIs and the respective molecular geometries of the reactive species is needed [3]. In the present work, a computational method based on ensemble density functional theory, the spin-restricted ensemble-referenced Kohn-Sham (REKS) method [4], will be used to investigate CIs in a wide range of organic molecules and chromophores of photoactive proteins [5]. By comparing the geometries of the minimum energy CIs (MECIs) obtained with the use of various density functionals, ranging from the global hybrid functionals to the local hybrid and to the meta GGA hybrid functionals, against the reference data from the ab initio multireference (MRCI, MS-CASPT2) calculations [5], the role of the density functional for obtaining accurate MECI molecular geometries and relative energies will be investigated. The influence of the relative electronegativity of the fragments connected by the double bond undergoing photoisomerization [6] on the MECI's geometry and topography will be studied and predictions regarding the rules for designing molecular motors and switches will be drawn. These design rules will be illustrated by application to novel molecular motors with improved functionality.

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Thursday Morning I, Bartók

Assessing *ab initio* methods by analyzing their wave functions

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The quality of wave-function-based quantum-chemical approaches are assessed by comparing the obtained *wave functions* – rather than *energies* or *properties* – with reference data. This is applied to wave-functions from full configuration interaction (FCI) and coupled-cluster (CC) theory up to quadruple excitations as well as to the following first-order wave-functions of the perturbation-theory (PT) approaches: Møller-Plesset (MP)-PT, the related S2-MP-PT [1], which is a correctly spin-adapted PT incorporating spin-component-scaled MP at second order (SCS-MP2) [2], and retaining-the-excitation-degree (RE)-PT [3, 4].

It is shown that MP theory provides relatively poor first-order wave-functions. However, the MP2 energy profits from a fortuitous error compensation as the absolute contribution of the opposite-spin components to the correlation energy are underestimated while the same-spin contributions are overestimated. This trend is explained on the basis of the CI matrix-elements of the respective configurations. It is shown that the systematic error of MP2 energies increases the robustness of this method by stabilizing the opposite-spin contribution which is error-prone due to small energy denominators. We demonstrate that the SCS-MP2 parameterization of Grimme tends to correct the errors of the first-order MP wave function but overshoots. Thus, it generally underestimates the absolute value of the opposite spin contribution to the correlation energy.

CCSD and the first order RE-PT wavefunctions are rather well balanced. However, CCSD tends to underestimate the absolute value of the correlation energy which means that the doubles contributions of the CCSD wave function are consistently too small. An analysis based on the full CI matrix shows that in particular unlinked-triple excitations are systematically increasing the absolute value of the correlation energy.

In the first order RE-PT wave function this effect is partially included by neglecting exclusion principle violating terms which is a consequence of using Rayleigh-Schrödinger perturbation theory. RE-PT is the perturbation theory which provides the by far best first-order wave function. However, its total performance is not equally good as near degeneracy effects are frequently not well described. Options for improving this behavior are discussed.

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Tuesday Afternoon I, Bartók

Main Group Complexes with Unusual Donor-Acceptor Bonds

Gernot Frenking

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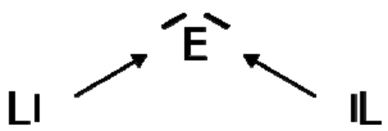
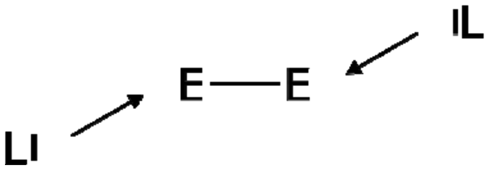
The lecture focuses on donor-acceptor complexes of main-group elements where two strong σ donor ligands bind to a single center E in L→E←L [1] or to a diatomic species E_2 in L→E_2←L. [2]



E = C, BH, N^+, Si



E = Group 13, 14, 15 atoms

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Tuesday Morning I, Brahms

UQ-Predictive Modeling of Chemical Reaction Systems

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The presentation will focus on methodology of developing chemical reaction models to attain the desired level of predictability. The knowledge gained through increasingly sophisticated experimentation and theory forms the basis for the development of models. But what makes such models truly predictive?

The theoretical dream is to build models entirely from first principles. However, even most fundamental of the present models include uncertainties. There are many sources of model uncertainties: incomplete knowledge of the physical phenomena, truncated expansions of numerical methods, numerical diffusion, and the like. One view of model predictiveness is to gain higher and higher veracity for all parts of the model and by this virtue alone acquire trust in predicted results. Even in this possibly utopian view, the question of how to judge that the model predictions are sufficiently accurate needs to be answered. Furthermore, one would like to have a direction for advancing the model predictiveness. Not all model parts and not all of their uncertainties contribute equally to the accuracy of model predictions, especially when one is interested in a specific set of conditions. The usually complex, nonlinear nature of models of physical phenomena prevents one from identifying the extent to which individual uncertainties influence model predictions without analysis.

A broad field of study and techniques related to the numerical characterization of uncertainty has been termed *uncertainty quantification* (UQ). Its main objective is the propagation of model's uncertainties to the model's prediction, and hence "uncertainty quantification" has become synonymous with "predictive modeling". We here define "predictive" to mean that the numerical result of a model is accompanied by its rigorously determined uncertainty bounds and a more *predictive* model is the one with more narrowly bounded interval. Hence, we will term such models *UQ-predictive* and the associated process *UQ-predictive modeling*.

This presentation will outline specific characteristics of chemical reaction systems and difficulties associated with development of predictive models, past and contemporary directions to predictive-model building, and the UQ framework we termed Bound-to-Bound Data Collaboration (B2B-DC). The latter is an integrating, system approach that is built on an underlying physical process and associated model, a collection of experimental observations with specified uncertainties, algebraic surrogate models (response surfaces) representing parametric dependence of the physical-model predictions of the experimental observables on the uncertain parameters, and specialized constrained-optimization algorithms. The examples will be drawn from the field of combustion chemistry, demonstrating the methodology and its capability. The presentation will outline emerging new concepts and future needs in the field of UQ-predictive modeling.

Friday Morning I, Pátria

The incremental scheme for CCSD(T) and CCSD(T)(F12)

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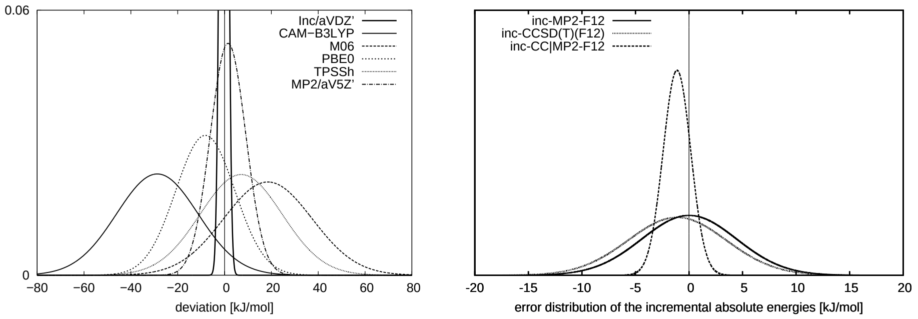
Today DFT based methods provide an optimal balance between accuracy and computational effort. However, for a highly accurate description the accuracy of DFT methods is not sufficient. If a proper basis set is applied, one can obtain the required accuracy with wave function based methods such as CCSD(T). In combination with an extrapolation to the basis set limit or explicit correlation the CCSD(T) energies have benchmark quality. The price one has to pay for the high accuracy is a huge computational effort and the standard CCSD(T) computations become quickly infeasible. Therefore it is necessary to introduce approximations to the CCSD(T) model, without significant loss of accuracy. We apply the incremental scheme [1] to exploit the local character of the electron correlation and obtain the CCSD(T) energy at reduced computational effort [2]. It was recently shown, that the errors due to the local approximations can be reduced with MP2-theory [3]. Finally we demonstrate the applicability of our approach for a CCSD(T)/aV5Z' calculation on $\mathrm{Al(H_2O)}_{25}^{3+}$ (76 atoms and 6106 AOs [4]).



a b

a: Error distributions of different state of the art quantum chemical methods with respect to a CCSD(T)/aV5Z reference for the binding energies of 45 metal solvent complexes [4]. b: Error in the absolute energies for the third order inc-CCSD(T)(F12)|MP2/cc-pVDZ-F12 method using 27 molecules [5].

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Friday Morning I, Bartók

Rigorous formulation of double hybrid density-functionals along the adiabatic connection

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We present a graphical analysis of the adiabatic connections underlying double-hybrid density-functional methods that employ second-order perturbation theory [1, 2]. Approximate adiabatic connection formulae relevant to the construction of these functionals are derived and compared directly with those calculated using accurate *ab initio* methods [3]. The discontinuous nature of the approximate adiabatic integrands is emphasized, the discontinuities occurring at interaction strengths which mark the transitions between regions that are: (i) described predominantly by second-order perturbation theory (ii) described by a mixture of density-functional and second-order perturbation theory contributions and (iii) described purely by density-functional theory. Numerical examples are presented for a selection of small molecular systems and van der Waals dimers. The impacts of commonly used approximations in each of the three sections of the adiabatic connection will be discussed along with possible routes for the development of improved double-hybrid methodologies.

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Networks in thermochemistry and spectroscopy

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Following the successes of Chemical Graph Theory (CGT), complex graphs (network) seem to gain new roles in chemistry via their ability to enhance the treatment of large databases.

The MARVEL algorithm and code we developed [1] is based on the theory of spectroscopic networks [2] and combines it with a weighted linear least-squares protocol for data inversion. MARVEL, standing for *M*easured *A*ctive *R*otational-*V*ibrational *E*nergy *L*evels, can be employed to determine experimental energy levels and their uncertainties from a database of experimentally measured and assigned transitions coming from high-resolution spectroscopy. Algorithmic improvements characterizing the second generation of the MARVEL code [3] make it possible to invert the information contained in hundreds of thousands of transitions. Some of these algorithms are explained during the talk. The most important application of MARVEL has been the determination of all the known experimental energy levels of all the major isotopologues of the water molecule.

Similar in its design to MARVEL, we also developed a thermochemical protocol and code termed NEAT [4]. Its name refers to the fact that with NEAT our aim is to move from a *N*etwork of computed reaction *E*nthalpies toward *A*tom-based *T*hermochemistry. Another aim of NEAT is to tighten the uncertainties of first-principles enthalpies of formation via forming a large number of cycles in a thermochemical network. The largest network we use contains hundreds of ab initio reaction enthalpies and results in dependable enthalpies of formation for tens of species. The NEAT enthalpies of formation are very similar to thos obtained from the ATcT approach.

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Friday Morning II, Pátria

Molecular Tailoring Approach : An Art of the Possible for *ab initio* Treatment of Large Molecules and Clusters

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The formidability of implementing large molecular calculations using these methods will be discussed. Divide-and-conquer (DC) type methods are being actively developed [1] in order to break this bottleneck of high scaling order of *ab initio* calculations of large molecules. Molecular Tailoring Approach (MTA) is one of such early attempts, which scissors the parent molecular system into subsystems (fragments) [2], the properties which are stitched back in order to estimate those for the parent system. Incorporation of the inclusion-exclusion principle into MTA allows accurate estimation of molecular properties, electronic energy, energy-gradients and Hessian.[3] The basic methodology of MTA will be summarized, along with applications to a variety of test systems. It will also highlight the versatility of this method with respect to the level of theory and basis-set. Apart from the earlier benchmarks, some newer results on geometry optimization and molecular properties of a variety of molecular clusters [5], polyaromatic hydrocarbons [6], water clusters and a protein with charged centers will be discussed. This will be followed by an account of the recently developed molecular cluster building and topography mapping algorithms, along with some examples.

Acknowledgments:
Center for Development of Advanced Computing (C-DAC), Pune and the Department of Science and Technology (DST), New Delhi.

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Tuesday Afternoon II, Bartók

The linear response function as an interpretational tool : retrieving atomic shell structure, inductive and mesometric effects, aromaticity and anti-aromaticity

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Within the context of our ongoing interest in Conceptual Density Functional Theory [1] [2] as an interpretational tool for discussing chemical reactivity we focused in recent years on the linear response function $(\partial^2 E/\delta v(\underline{r})\delta v(\underline{r}')_N$ or $(\delta\rho(\underline{r})/\delta v(r')_N$ representing the response of the system's electron density ρ at position $\underline{r}$ to a perturbation at position $(\underline{r}')$.
Recent results are reported on a judiciously chosen set of closed shell atoms, throughout the periodic table [3] reporting the most intensive study of this property hitherto. Different graphical representations of the kernel are presented and discussed, the atomic shell structure is retrieved and the polarizability values obtained started from the kernel are compared with high level calculations showing that the simple KS type ansatz for the evaluation of the kernel [4] [5] captures the trend governing α throughout the Periodic Table.
In a second part of the presentation the focus is on the use of the condensed form of the linear response function as a descriptor of aromaticity and anti-aromaticity with a series of examples varying from cyclic hydrocarbon type molecules via inorganic rings (borazine, boroxine, s-triphosphatriborin) to planar metallic systems E_4^{2-} and E_4^{2-} (E = Al, Ga) [5,6] [7].
The evolution of the linear response function along the reaction coordinate for the aromatic TS reaction between ethane and butadiene is also investigated. Combined with the earlier work on the retrieval of inductive and mesomeric effects from the condensed linear response function [8-10] this overview illustrates that this hitherto relatively unexplored second derivative in the E = E[N,v] functional Taylor expansion turns out to be of high chemical relevance.

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Thermodynamics of framework breathing: free energy model for flexible porous crystals

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The porous metal-organic framework MIL-53(Cr) may vary its cell parameters drastically while retaining its crystallinity under influence of external stimuli such as temperature and adsorption of guest molecules [1]. The hysteresis of 'framework breathing' between the large-pore and narrow-pore shapes of the material is not yet fully understood in the thermodynamic picture [2, 3, 4]. We propose a generic parametrized free energy model for the osmotic thermodynamic potential including three contributions: host free energy, guest-guest interactions, and host-guest interactions [5]. Our approach allows to determine the stable states on a two-dimensional free energy landscapes as a function of shape and adsorbed amount of guest molecules. The new model correctly reproduces the structural transitions along the experimental CO_2 and CH_4 isotherms. Assuming a first order phase transition and collective behavior, our model moreover successfully explains the adsorption versus desorption hysteresis as a consequence of the creation, stabilization, destabilization, and disappearance of a second free energy minimum. Finally we decouple the gas chemical potential μ and mechanical pressure P as two independent thermodynamic variables and predict the complete (μ, P) phase diagram for CO_2 adsorption in MIL-53(Cr).

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Tuesday Morning I, Bartók

An interpretive dance in three movements

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Amazing advances in computer hardware and quantum chemistry software have allowed researchers to generate large volumes of numbers in small amounts of time. However, this is a dangerous situation. Speakers in the "Interpretation Models" session will respond to Coulson's famous plea: "Give me insight, not numbers!"

My lecture will consist of three movements:

In the first movement, I will describe work with my student Laura McKemmish, whose PhD research has helped to explain why quantum chemical calculations in which the molecular orbitals are expanded in a Gaussian basis set, *e.g.*

$$\exp(-r) \approx \sum_{i=1}^{n} c_i \exp(-\alpha_i r^2) \tag{1}$$

exhibit surprising convergence behaviour [1].

In the second movement, I will describe work with my student Yves Bernard, whose PhD research showed that, although the Heisenberg Uncertainty Principle does not allow us to follow the path of an electron in a molecule, we can nonetheless use the posmom variable [2]

$$s = \mathbf{r} \cdot \mathbf{p} \tag{2}$$

and its quantum mechanical density $S(s)$ to learn something about the trajectories of such particles.

In the final movement, I will describe work with my colleague Pierre-François Loos, whose research on electrons moving on rings [3] shows why the Local Density Approximation (LDA)

$$E_c^{\text{LDA}}[\rho] \approx \int F(\rho(\mathbf{r}))\rho(\mathbf{r})\, d\mathbf{r} \tag{3}$$

seriously overestimates molecular correlation energies and has indicated how an improved version of the LDA can be systematically constructed.

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Monday Afternoon I, Lehár

Decay processes mediated by long-range electron correlation

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Electronically excited states of atoms and molecules embedded in an environment may efficiently decay by ionising neighbouring species in the energy or charge transfer mediated processes. Both kinds of processes become possible due to the correlation between the electrons on the excited moiety and on the surrounding species. The energy transfer driven interatomic Coulombic decay (ICD) [1] has been shown to proceed on a femtosecond timescale in a variety of weakly bonded systems (such as rare-gas or water clusters) following a localised electronic excitation in a photoionisation or Auger decay event [2, 3]. Related electron transfer mediated decay (ETMD) proceeds in a few picoseconds timescale and becomes an important relaxation pathway whenever ICD channel is unavailable [4]. In this talk we will give a short overview and discuss the importance of ICD and ETMD processes. In particular, we demonstrate that ETMD provides an efficient neutralisation pathway for the majority of the multiply charged ions produced by Auger decay in an environment [5]. As an example we show the results of an ab initio study of the $NeKr_2$ cluster following the Auger decay of 1s vacancy of Ne. The ETMD rates even at the frozen nuclei configuration can be as large as $0.130\ \text{ps}^{-1}$. We also show that nuclear dynamics may increase the rate by about an order of magnitude. The generality of the mechanism makes this neutralisation pathway important in weakly bonded environments.

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Tuesday Morning II, Brahms

Evaluation of the influence of thermodynamic data on the prediction of propane and propene ignition delay times

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The influence of thermodynamic data on prediction of auto ignition chemistry for hydrocarbons such as propane and propene has been investigated. Thermodynamic data with high sensitivity on simulation results have been evaluated thoroughly.

It was found that for example a small change in the enthalpy of formation of propene has high impact on calculated ignition delay times for different propene and propane / oxygen mixtures.

On the other hand, thermochemical data of allyl has a lower sensitivity on the prediction of ignition delay times of propene and propane than thermochemical data of propene, but its positive influence on the prediction of this technical relevant property is still important. Recently, a value of 168.6 kJ mol^{-1} ± 1.8 kJ mol^{-1}, obtained with the HEAT (High-accuracy Extrapolated Ab initio Thermochemistry) protocol, was recommended for allyl (C_3H_5) for the enthalpy of formation at 298 K [1].

The improvement of the prediction of a detailed reaction mechanism through using accurate thermochemical data, such as the Active Thermochemical Tables Results [2], the IUPAC critical evaluation of thermochemical properties of some free radicals [3] and own quantum chemical calculations with the benchmarked G3B3 composite method is shown.

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Wednesday Morning I, Lehár

The Origins of Large Interaction-Induced First Hyperpolarizabilities in Hydrogen-Bonded π-Electronic Complexes

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In this contribution we discuss the origins of interaction-induced linear and non-linear electro-optic properties of model hydrogen-bonded π-electronic complexes. In particular we report on the excess dipole moments ($\Delta\mu$), electric dipole polarizabilities ($\Delta\alpha$) and first hyperpolarizabilities ($\Delta\beta$) – focusing on the latter – of the quasi-linear dimers of urea, diformamide, 4-pyridone, 4-nitroaniline and the complex of hydrogen fluoride with nitroacetylene. The nature of intermolecular interactions as well as of the $\Delta\mu$ and $\Delta\alpha$ is very similar in all studied complexes. However, partitioning of $\Delta\beta$ into physically well defined components (cf. Góra *et al.*[1]) reveals that the origins of this effect, the magnitude of which is often comparable to that of isolated monomers, are different in each case. Interestingly, our results indicate that even though hydrogen bonding usually diminishes the non-linear response of interacting species, the first hyperpolarizability of complexes with nitro group acting as a proton acceptor is substantially increased. On the other hand, the magnitude and sign of interaction-induced first hyperpolarizability depends in some cases strongly on the intermolecular separation which could indicate potentially large vibrational contributions as well as significant sensitivity to external pressure.

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Wednesday Morning I, Lehár

Correlation-bound states of C_{60}^{-} anion

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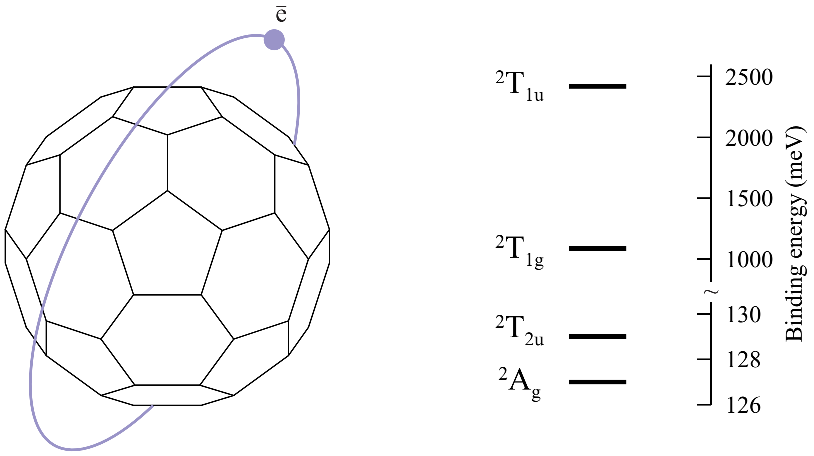
We report on large-scale *ab initio* electronic structure calculations for the *bound* electronic states of the C_{60}^{-} anion. C_{60} (buckminsterfullerene) is known to be a strong electron acceptor, able to capture one or several electrons [1]. Among the C_{60}^{-} species it is only the ground state $^2T_{1u}$ that has been thoroughly studied from both experimental and theoretical point of view [2]. It is however very little known to date about other, less bound (excited) states of C_{60}^{-}. Are there such states at all and how many are there? In fact, identifying such states in C_{60}^{-} represents a big challenge. The main obstacles here are the large number of electrons (241 valence electrons) and, what is more crucial, the necessity of a proper treatment of electron correlation effects. These effects turn out to be strong already in neutral C_{60} and ”go off scale“ in the C_{60}^{-} anion. It is in fact the electron correlation (disperse-type) effects that were found to bind the extra electron in the C_{60}^{-*} anion excited states. These states are therefore termed *correlation-bound* states.

Using the highly accurate coupled cluster (EOM-EA) method we demonstrate that C_{60}^{-} possesses at least three correlation-bound, excited electronic states. These are $^2T_{1g}$, $^2T_{2u}$ and ^2A_g in order of decreasing the electron binding energy (see the figure below). Here it is noteworthy that ^2A_g was only very recently predicted to exist (being bound) [3] whereas the $^2T_{2u}$ state has been unknown to date. In the present work we focus on characterization of the above states in terms of their binding energies as well as with regard to their electronic structure, in particular the spatial distribution of the extra electron. To this end we employ the natural bond occupation analysis based on the computed one-electron densities.



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Rings and Chains in Solid-State Chemistry. The Electron Count Matters

Jean-François Halet

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There is value in considering a solid as a molecule, a big one, but just a molecule [1]. Both molecules and solids deal with the same fundamental questions: Where are the electrons, where are the bonds? A few examples of solid-state compounds will be discussed, borrowed from the metal boron or metal boron carbon chemistries [2]. They will serve to illustrate similarities (and differences) between the bonding in molecules and solids. Parameters such as the symmetry, the electron count and the nature of the chemical elements will be analyzed with the aid of molecular and periodic density-functional theory tools to address the issues of structural arrangement and physical properties of examples containing non-metal rings and chains [3]. A comparison with molecular chemistry will be made.

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Friday Afternoon I, Pátria

Extending the Domain of Connectivity for MRexpT: Analysis and Results

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Enhancements of the multi-reference exponential ansatz (MRexpT) [1] will be presented. Based on a perturbational analysis showing new insides to the origin of the connectivity problem of MRCC two new variants of the MRexpT ansatz will be derived:

1. a Fermi vacuum invariant with extended connectivity and
2. a non-Fermi vacuum invariant, fully connected one.

Using a new connectivity test (allowing a simpler application than e.g. [2]) approaches (a) and (b) are checked to fulfill the expected connectivity properties.

Both approaches show very significant numerical improvements with respect to the original MRexpT ansatz for various model systems. For instance the non-parallelity error for BeH_2 is reduced by more than a factor of two at SDT level and more than two orders of magnitude at the SDTQ level outperforming other MRCC methods with results available for this system. Further promising examples on P4 and 2P4 (a cubic geometrical arrangement) will be given.

Variant (b) restores size-consistency also for non-localized orbitals at the price of loosing full Fermi vacuum invariance. Nevertheless, the results remain more accurate than for the SRMRCC [3] approach while symmetry breaking remains are less severe.

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Monday Morning II, Bartók

Polarizable Embedding: Multireference embedding methods and large scale applications to optical properties in proteins

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Efficient algorithms have ensured that quantum mechanical methods are rapidly moving into the areas of biology and material sciences. A major part of this development has been driven by a divide-and-conquer strategy where large scale calculations have been parted into a focused region, treated by quantum mechanics and a remaining region (the environment) treated by a force field. These hybrids (QM/MM) methods have made it possible to obtain reliable structures for fast-lived intermediates, which can provide important insight in enzyme mechanisms. Yet, the interactions between the QM system and environment can be dramatic and for accurate prediction of molecular properties, higher accuracy than provided by the MM force field can be required. Notably most force field methods neglect the mutual polarization between environment and quantum mechanical regions.

Within the recent years our group has, with focus on molecular properties, developed an embedding scheme[1] using potentials derived from first-principles calculations for the environment. This strategy builds upon a multipole expansion of each site in the environment, adding also atom-centered polarizabilities on top. Most recently, this embedding scheme was extended to MCSCF methods[2], including also the sr-DFT MCSCF hybrid method which allows dynamical and static correlation to be included simultaneously[3]. Here we present the new implementation, and emphasize the formal equality between the explicit polarizable embedding method and implicit continuum methods such as PCM. The effect of including dynamical correlation by the sr-DFT MCSCF hybrid scheme is discussed using small models and biological model complexes as examples. Furthermore, recent results for solvated systems and also for proteins with chromophores of significant multireference character is presented.

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Wednesday Morning II, Pátria

Molecular magnetism and density-functional theory in magnetic fields

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We have undertaken a quantum-mechanical study of molecules in finite magnetic fields, using a recently developed computer code London for the calculation of many-electron molecules with wave-function theory [1] and more recently with Kohn–Sham density-functional theory (DFT). These two approaches to electronic-structure theory are connected by an implementation of the Lieb variation principle [2,3], allowing us to study the exchange–correlation functional of DFT at different levels of ab initio theory.

Our calculations on molecules in strong magnetic fields have revealed and highlighted many interesting phenomena such as the transition to diamagnetism of paramagnetic molecules at a critical field strength [4]. Perhaps most interestingly, antibonding molecular orbitals are stabilized in the field, leading to strongly bound triplet H_2 and singlet He_2 molecules [5] and helium clusters [6] at about 10^5 Tesla.

The application of DFT to magnetic fields requires modifications of the standard theory, by introducing a field- or current-dependence in the exchange–correlation functional. However, essentially all applications of Kohn–Sham theory to study magnetic phenomena ignore these modifications—yielding, for example, NMR shielding constants that are unreliable [7]. We discuss here some aspects of DFT in magnetic fields, including the Hohenberg–Kohn theorem and the choice of variables in DFT [8]. Kohn–Sham calculations with different parameterizations of the Vignale–Rasolt–Geldart (VRG) functional in finite magnetic fields are presented. The results demonstrate that this functional form does not provide improvements in practical calculations and highlight the need for the development of new current-dependent approximations.

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Thursday Morning I, Lehár

Introduction

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Tuesday Morning II, Lehár

Ceria chemistry at the nano-scale

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Reducible oxide are particularly challenging to describe using theoretical chemistry/physics methods because they easily toggle between different oxidation states, so that both the electronic structure and the geometric structure are important. We are currently developing a *multi-scale approach* to unravel the chemistry of ceria (CeO_2 and CeO_{2-x}), going from DFT=> DFTB (tight-bindning DFT) => Force-field simulations (ReaxFF reactive force-field).

Our current application is ceria nanoparticles and the oxygen chemistry on them. The chemical composition, shape and structure of small metal-oxide nanoparticles (NPs) can be strongly affected by their surrounding environments. In a recent study [1], we demonstrated how reduced ceria nanoparticles could be stabilized in an oxidative environment through the adsorption of many O_2 molecules. Rather than being re-oxidized to form a CeO_2 nanoparticle, such reduced particles become supercharged with O_2^- species leading to a dramatically enhanced oxygen storage capacity.

In the current work, we study the chemical composition, shape and structure of ceria nanoparticles in reducing, oxidative and humid environments. We search for the global minimum structures using a force-field based evolutionary algorithm. From the initial screening, candidate structures are further geometry-optimized using density functional calculations and the effect of the environment is introduced through standard thermodynamic relations. Based on our calculations, we predict that small stoichiometric ceria nanoparticles will have a very limited stability range in both oxidative and humid environments. Instead, as illustrated in **Fig. 1**, the reduced ceria nanoclusters are stabilized through the adsorption of oxygen molecules in the form of superoxo species and water in the form of hydroxo species.

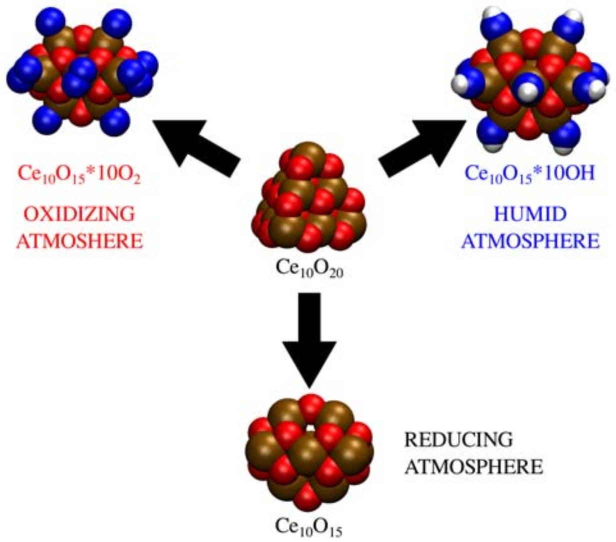

Fig. 1 Our calculations predict that stoichiometric clusters have limited stability and readily transform into reduced clusters in oxidizing, humid and reducing atmospheres. This is exemplified in this figure for the $Ce_{10}O_{20}$ (stoichiometric) and $Ce_{10}O_{15}$ (reduced) clusters.

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Friday Morning I, Pátria

First-principles prediction of the structures, spectra, and phase diagrams of molecular crystals

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An *ab initio* computational prediction of the crystal structures and complete phase diagrams has long been a dream of chemists, physicists, and materials scientists. I present a general computational method that enables routine MP2 or CCSD calculations of the energies, enthalpies, or free energies of periodic and nonperiodic molecular crystals under high pressures and intermediate temperatures.

I will discuss application of this method, which is based on the embedded fragmentation, to the electronic and (anharmonic) vibrational structures of three-dimensional solid hydrogen fluoride, solid carbon dioxide, and proton-disordered ice Ich as well as proton-ordered ice VIII. I will address the crystal structures of these solids, their pressure dependence, their phase diagram and solid-solid phase transition, the assignments of infrared and Raman bands and their crystal-field splitting, the phonon dispersion and density of states as well as the interpretation of inelastic neutron scattering, and the pressure dependence of Fermi doublets in solid carbon dioxide as a spectroscopic geo-barometer.

Friday Afternoon II, Pátria

How accurate are „gold standard“ CCSD(T)/CBS interaction energies?

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The CCSD(T) method stands out among various coupled-cluster (CC) approximations as the “golden standard” in computational chemistry and is widely and successfully used in the realm of covalent and noncovalent interactions. The CCSD(T) method provides reliable interaction energies, but their surprising accuracy is believed to arise partially from the error compensation. The convergence of the CC expansion has been investigated up to fully iterative pentuple excitations (CCSDTQP); for the smallest 8 electron complexes the full CI calculations have further been performed. We conclude that the convergence of interaction energy for the complexes studied is reached already at CCSDTQ or CCSDT(Q) levels. When even higher accuracy is required, then the non-iterative CCSDTQ(P) method is recommended.

Thursday Morning II, Bartók

GVVPT2 Descriptions of Electronic Structures of Metalloid Oxides

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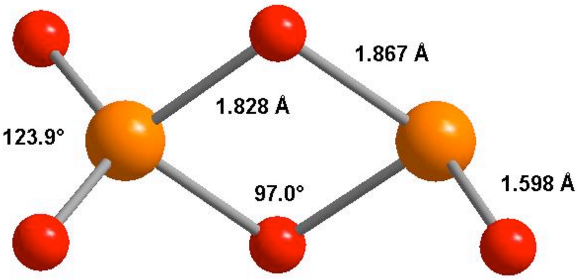

The second-order Generalized van Vleck variant of multireference perturbation theory (GVVPT2) for the description of molecular electronic structure [1] has been shown to be versatile and robust. Recently, the method has been used to elucidate the ground and low-lying electronic structures of metalloid oxides (e.g., Se_nO_m [2], As_nO_m, Sb_nO_m, where n=1,2 and m=1–5) and dimers of first and second row transition metals (e.g., Cr_2 [3], Mo_2). Such molecules have proven elusive for many methods of electronic structure theory primarily because of the subtle interplay of short-range (i.e., dynamic) and long-range (i.e., nondynamic or static) electron correlation.

GVVPT2 is capable of describing complicated molecular electronic structures because of two complementary features. First, GVVPT2 uses an intermediate Hamiltonian structure to separate energetically perturbing functions from zero-order descriptions of the functions of interest. Second, a nonlinear resolvent

$$X_{qp} = \frac{\tanh\left(\tilde{H}_q^{(0)}(p) - E_p^{(0)}\right)}{E_p^{(0)} - \tilde{H}_q^{(0)}(p)} H_{qp},$$

where $\tilde{H}_q^{(0)}(p) = \frac{1}{2}\left(H_q^{(0)}(p) + E_p^{(0)}\right) + \frac{1}{2}\sqrt{\left(H_q^{(0)}(p) - E_p^{(0)}\right)^2 + 4\sum_{q'\in m}\left(H_{q'p}\right)^2}$ is an effective zero-order energy of perturbing state q for primary (or reference) function p, avoids remaining intruder states. As a consequence, potential energy surfaces are rigorously continuous. Because the current implementation supports incomplete model spaces and utilizes a GUGA formulation for evaluation of Hamiltonian matrix elements [4], molecules that were not previously accessible on the basis of computational resources can now be addressed.

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Tuesday Afternoon II, Lehár

Quantum Monte Carlo making progress with metal surfaces: CO adsorbed on Cu(100) and Pt(100)

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For periodic solids, Quantum Monte Carlo (QMC) simulations must overcome a restriction on the size of wave functions due to 'unflolding' the k-point grid in the First Brillouin Zone. This multiplies the content by the number of k-points and rapidly the wave functions get too large for supercalculator memory. It is necessary to use this hardware, and even with shared memory, in practice, the k-point grid is limited to about 2 2 2, which is generally too small to converge values of physical properties.

The phenomenon is known as finite size effect. It can be corrected by fitting to DFT calculations but is non negligible. It is particularly large for delocalised systems like metals.

In this work, it is shown that between single k-point wave functions and those with 4 k-points, a factor of at least 25 is gained in the finite size effect for Cu(100) and Pt(100). It is also shown that the effect is little influenced by the presence of adsorbed CO. This leads us to be optimistic for cancelation of the associated errors during adsorbtion and even heterogeneous catalysis.

Nevertheless, an ad hoc fitting to DFT work is also used.

Previous work, [1] gives a 3-body correlation ansatz applied to the copper catalyst.
Some of the present results are detailed in [2].

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Friday Morning I, Pátria

Challenges in orbital localization for orthonormal molecular orbitals

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Local orthonormal occupied and virtual Hartree–Fock (HF) orbitals are of interest in the area of local correlation methods, where the goal is to use a local description to express local physical effects. Until recently, local virtual HF orbitals could not be obtained due to inadequacies of the optimization algorithms used. It has been shown that by using a trust-region algorithm for the optimization of localization functions, both local occupied and local virtual HF orbitals may be obtained. Different localization schemes, e.g., Pipek–Mezey, Boys and powers of the second (PSM) and fourth (PFM) moments give orbitals with different characteristics in terms of the spatial locality of the bulk and tails of the orbitals. In particular, PSM minimization targets to reduce the bulk extent of the orbitals, while PFM minimization targets to reduce the thickness of the orbital tails. The effects of bulk and tail locality are explored from a local correlation method point of view. The orthogonality requirement for the molecular orbitals imposes a constraint on the locality through the orbital tails. The locality analysis is therefore extended to explore the non-orthogonal atomic orbitals and projected atomic orbitals, and orthogonalized atomic orbitals.

Tuesday Morning II, Lehár

Theoretical study for lithium diffusion in $Li_2Ti_xO_y$ compounds

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Abstract

The structural properties, energetics and mobility of Li^+ in lithium containing titanates (Li_2TiO_3 and $Li_2Ti_3O_7$) are investigated theoretically with periodic quantum-chemical methods. The calculated electric field gradient (EFG) of β-Li_2TiO_3 reveals that there are three inequivalent Li sites (Li(1), Li(2) and Li(3)) and two inequivalent Ti sites (Ti(1) and Ti(2)). A honeycomb structure of LiTi2 is formed by the sharing of Ti ions and Li(3) ions. The rest of the lithium ions ((Li(1) and Li(2)) form pure lithium layers in between the $LiTi_2$ layers. The calculated Li vacancy formation energy shows that vacancy formation at the Li(3) sites is easier than those in Li(1) and Li(2) sites. Competing pathways for Li diffusion in β-Li_2TiO_3 are investigated using the climbing-image Nudged-Elastic-Band (cNEB) approach. Li^+ ions can migrate either along the crystallographic *c* direction or within the crystallographic *ab* plane. Our calculated activation energy (E_A) in the *ab* plane ranges between 0.53 and 0.78 eV, whereas E_A along the *c* direction is 0.54 eV which are in the range of experimental E_A value (0.47 to 0.80 eV) for β-Li_2TiO_3.

The structure obtained according to the XRD analysis shows that the unit cell of $Li_2Ti_3O_7$ contains 4 formula units of $Li_3Ti_1O_2$ with Li:Ti:O stoichiometric ratio 3:1:2. However, in $Li_2Ti_3O_7$, the real stoichiometry of Li:Ti:O is 2:3:7. In the present study, the structure elucidation with correct stoichiometric ratio is performed for the first time. The relative stability of various considered models is evaluated on the structurally optimized structures. It is observed that the stability varied between 0–8 eV for all the considered structures. The most stable models are then employed for the investigation of Li^+ diffusion processes. Li^+ can migrate along the 'one dimensional channel' from one occupied tetrahedral site to another unoccupied tetrahedral site or along crystallographic *ac* plane from the occupied tetrahedral sites to the empty octahedral locations. Our calculated E_A for Li^+ diffusion in the one dimensional channel ranges from 0.67 to 0.72 eV and that in the *ac* plane ranges from 0.50 to 0.80 eV. These are in well accord with the available experiment.

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Unexpected features of correlation effects involving 3d-electrons

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Two pairs of basis set sequences that systematically converge to the complete basis set (CBS) limit have been employed in the calculations of various components of the electron correlation energies of Zn^{2+} and Zn by several state-of-the-art *ab initio* techniques [1].

The correlation energies have been determined with second-order Møller-Plesset perturbation theory (MP2) and several single-reference coupled cluster (CC) methods [CCD, CCSD, CCSD(T), CCSDT, CCSDT(Q)]. The CC results represent the most accurate post-MP2 correlation energies ever obtained for closed-shell atoms including 3d-electrons .

Our results indicate that for the systems considered, the magnitudes of the MP2 correlation energies overestimate the magnitudes of the CC values for all electrons correlated as well as of their various subsets. For the all-electron correlation energies of the Zn atom, our result confirms the finding of McCarthy and Thakkar [2] obtained by means of non-*ab initio* approaches for all heavy closed-shell atoms. We have shown that both for Zn^{2+} and Zn this overestimation is directly caused by the presence of the $3d^{10}$ electron configuration.

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Friday Morning I, Bartók

Dispersion interactions from intermolecular perturbation theory and random phase approximations

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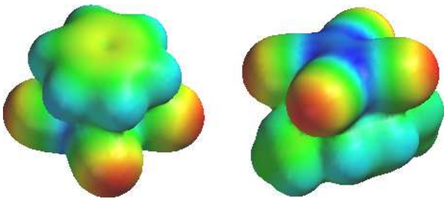
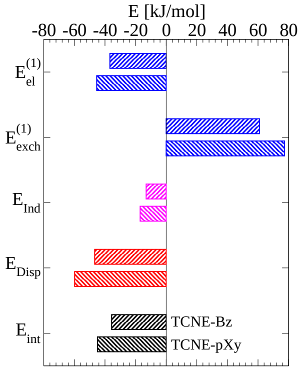
After an overview over the foundations of the DFT-SAPT approach which couples symmetry-adapted intermolecular perturbation theory (SAPT) with a description of the monomers through density functional theory (DFT) a few examples elucidating the role of dispersion interactions will be presented[1, 2, 3]. A modification of the approach avoiding the single-exchange approximation extends its application range to small intermolecular distances[4].





Furthermore, the ability of various expressions linked to the random phase approximation (RPA) to account for dispersion forces within DFT will be discussed[5, 6, 7].

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Friday Afternoon I, Pátria

Concepts of Quantum Geometry from the Topological Origins of QTAIM

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The promising early beginnings of the theoretical development of the Poincaré-Hopf relation, abandoned in the early 1980s, have inspired the recent creation of quantum topology phase-diagrams to predict new isomer topologies. Alternative uses of the Poincaré-Hopf and Euler-Poincaré relations, e.g. for molecular recognition and phase transitions in solids respectively, are discussed. The author adds their perspective [1] and demonstrates that within the quantum topology framework, new theory can be created to link with traditional chemical ideas.

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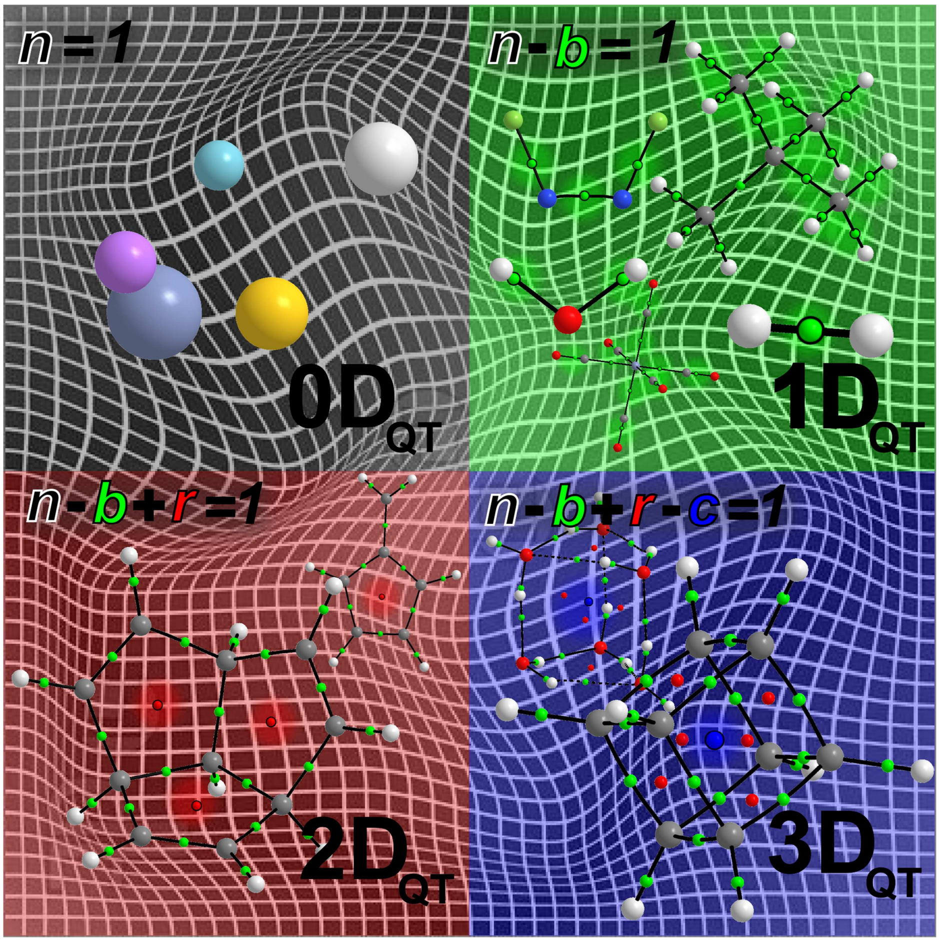

Monday Morning I, Bartók

Quantum Biochemistry

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I'll give an overview of my groups latest work in applying quantum chemistry to biochemical problems such as enzyme catalysis, enzyme design, protein-ligand binding and protein structure determination by NMR.

For a preview have a look at http://youtu.be/V45gEsJXGmI

Tuesday Afternoon I, Brahms

Sensitivity analysis of state-specific multireference perturbation theory

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Quantum chemical methods often contain certain parameters (cluster amplitudes, linear expansion coefficients, ...). A sensitivity analysis with respect to them may be interesting to monitor (or sometimes to detect) theoretical problems in the model formulated.

In this study we examine state-specific multireference perturbation theory (SS-MRPT), an electronic structure method which has been successful in describing molecules in the challenging situation of far from equilibrium. It has been observed earlier, that non-physical kinks may appear on the potential energy surface obtained by SS-MRPT while related coupled-cluster methods may face convergence difficulties.

Sensitivity analysis is used as a tool for detecting which parameter of the theory is responsible. By monitoring the singular values of sensitivity matrices, orders of magnitude increase is found in the largest value, in the vicinity of the problematic geometry point on the potential energy surface.

The ill-effect can be removed by resolving certain type of redundancy which appears in the spin-adapted version of the theory. Redundancy is eliminated by selecting a linearly independent set of spin-adapted, excited functions. By this step, non-physical kinks are elminiated. Parallel to this, sensitivities are decreased by orders of magnitude.

Friday Morning II, Bartók

Long-range retardation of relativistic interatomic potentials

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According to the Casimir-Polder theory the long-range interaction potential between spherically symmetric atoms results from the exchange of transverse virtual photons and vanishes as R^{-7} with the interatomic distance R. This damping of the nonrelativistic, London R^{-6} decay is interpreted as a result of the retardation of the propagation of electromagnetic interactions. It is known that the leading relativistic correction to the London theory derived from Dirac-Coulomb-Breit Hamiltonian behaves as R^{-4} at large R. The leading QED correction decays even slower, as R^{-3}. It will be shown how this apparently contradictory results can be reconciled and how the relativistic and QED calculations of the interatomic potential can be corrected for retardation to recover the correct R^{-7} behavior of the interatomic potential [1].

It will also be shown that for the interaction of two helium-4 atoms the Casimir-Polder retardation damping of the nonrelativistic interaction increases the dimer size by 2.0 Å relative to the nonrelativistic value of 44.6 Å. This damping is accounted for by the inclusion of the Breit interaction and the leading QED (Araki-Sucher) contributions to the potential [2]. The remaining retardation effect, of the fourth- and higher order in the fine-structure constant, is practically negligible for the bound state, but is important for the equation of state and for some thermophysical properties of gaseous helium.

As two helium-4 atoms form a dimer with significant wave function amplitudes at distances $R > 100$ Å, i.e., in the region where the retardation switches the London R^{-6} decay of the potential to the R^{-7} form, it has been assumed in the literature that this switching is responsible for the observed 2.0 Å (4.5%) increase of the bond length $\langle R \rangle$. We show that $\langle R \rangle$ is, in fact, insensitive to the potential at $R > 20$ Å and its increase is due to the Breit and Araki-Sucher corrections computed by us from expressions valid at short R, i.e., beyond the validity range of the Casimir-Polder theory [3]. Computation of these corrections seamlessly connects the Casimir-Polder theory to distances relevant for properties of long molecules.

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ABSTRACT

The divide-expand-consolidate local coupled cluster method goes massive parallel.

Poul Jørgensen, Thomas Kjærgaard, Kasper Kristensen, Ida-Marie Høyvik, Patrick Ettenhuber, Janus Juul Eriksen, Branislav Jansik, Simen Reine

It will be described how the Divide-Expand-Consolidate (DEC) strategy that previously has been applied to MP2 and CCSD can also be applied to CCSD(T) leading to a linear scaling and embarrassingly parallel algorithm. Numerical examples will be given to demonstrate the error control that may be imposed on the precision of the correlation energy through the fragment optimization threshold (FOT) parameter. This brings the DEC strategy on par with standard implementations where the parameter representing the threshold for the residual norm of the amplitude equations impose the error control on the correlation energy.

Introduction

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In this talk a short introduction is given to the recent advances in the field of ab initio electron correlation theory. In addition, the major achievements of Isaiah Shavitt, to the memory of whom this session is dedicated, are briefly reviewed.

Gaussian basis sets for complex scaling calculations

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The interest in complex scaling (CS) calculations is justified by calculations of atomic resonances – doubly excited states, atoms in strong laser fields, etc.. However, it is well known that CS calculations in conjunction with quantum chemistry methods often suffer from numerical instabilities that demonstrate itself, among others, in the emergence of complex ground state energies. In this contribution, we relate these numerical artifacts to inapropriate atomic basis sets and propose an optimization procedure for Gaussian basis sets which are resistant to the indicated problems.

First, the CS operator $\exp(-\theta\hat{x}\hat{p})$, being the foundation of the CS method, has been studied in the Wigner phase-space representation. It has been shown that this non-unitary transformation behaves similarly to the squeezing operator, rotating and amplifying Wigner quasi-probability distributions of the respective wavefunctions, where the deformation effect is mainly due to the scalar part of the respective phase-space operator, $\exp(-\sin 2\theta\, xp/\hbar)\, \exp(-\hbar \tan\theta\, \partial^2/\partial x\partial p\,/2)$ [1]. As a consequence, the basis sets for complex scaled wavefunctions generally require an increased number of basis functions to include larger momenta in the same extent of space.

Then, we have found that excited states are efficiently described by a set of virtual orbitals being defined as eigenfunctions of a non-redundant variant of the Fock operator [2]. This fact makes it possible to track many-electron wavefunctions in one-electron space and paves a natural way to an optimization of atomic basis sets based on the virtual energies. The robustness of the atomic basis sets in respect of CS is controlled by the required accuracy of the virtual energies.

The method has been applied for the atomic basis sets of helium atom. Calculations of helium doubly excited resonances illustrate the power of the method on a stability of the real and complex energies within a large interval of the CS parameter, which is incomparable with various standard basis sets [2]. Dynamical simulations of helium in strong XUV fields based on CS helium spectrum provide yet a more sensitive test to the basis sets, and still evidence a long-time independence of the calculated excitation yields on the CS parameter [3].

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Magnetic Shielding as a Source of Information about Aromaticity, Antiaromaticity and Chemical Bonding

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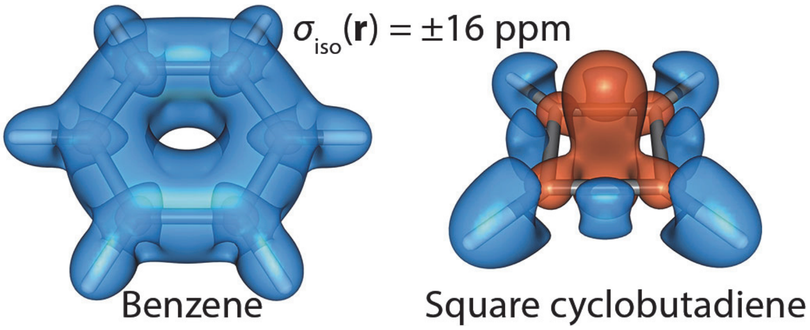
It has been demonstrated [1, 2] that that the inclusion of nondynamic electron correlation effects through an appropriate complete-active-space self-consistent field CASSCF or multi-configuration SCF (MCSCF) wavefunction is essential for a balanced analysis of the magnetic properties of cyclic conjugated hydrocarbons, including nucleus-independent shieldings (NICS), and of their ground and excited state aromaticity and antiaromaticity. In fact, detailed analyses of the changes in the isotropic shielding $\sigma_{iso}(\mathbf{r})$ within the space surrounding a molecule, calculated using CASSCF wavefunctions, rather than of discrete NICS values such as NICS(0) and NICS(1), provide significant additional insights into the differences between aromatic, and antiaromatic molecules [3].



We show that the $\sigma_{iso}(\mathbf{r})$ isosurface and contour plots are significantly more feature-rich than analogous plots depicting the total electronic density which are usually employed to analyze chemical bonding and can be used to perform meaningful comparisons of strong and weak bonds. One important advantage of the $\sigma_{iso}(\mathbf{r})$ plots is that the isotropic shielding at any point in space close to a molecule 'senses' the behaviour of the electrons in all directions originating from that point, whereas the value of the total electronic density at a point carries no information about the density distribution in its surroundings, except that inferred by the fact that it is a smooth function.

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Tuesday Afternoon I, Lehár

The Reaction of Water with Iron: Surface Science by Random Phase Approximation

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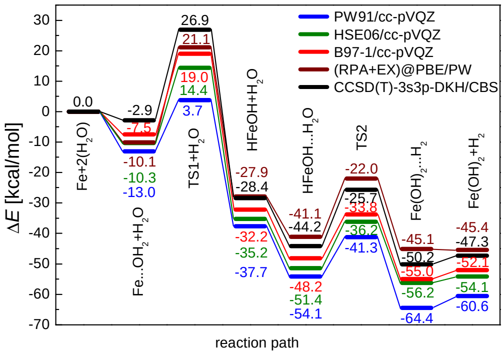
The critical processes in surface science such as adsorption, diffusion, and chemical reaction involve many-body quantum effects which reach beyond standard semilocal approximations to the exchange-correlation energy in the density functional theory (DFT). The random phase approximation (RPA) for the electron correlation energy is fully nonlocal, and in combination with the exact exchange energy represents one of the most promising methods for first-principles total energy calculations in periodic boundary conditions.

We investigate the reaction of water with zero-valent iron, which plays the key role in processes such as anaerobic corrosion and water remediation by nanoscale zero-valent iron (nZVI) particles. The reaction involves physisorption and chemisorption events in interplay with localized d-states of iron. We decipher mechanism and kinetics of the reaction of water molecule with an iron atom [1,2] and Fe(100) surface [3] and evaluate various computational methods for both models [4]. In addition, we present the reaction kinetics of nZVI nanoparticles as monitored by ^{57}Fe Mossbauer spectroscopy [5].

We show that RPA improves the description of the reaction on the Fe(100) surface with respect to gradient corrected and hybrid DFT functionals, owing to the reduction of electron self-interaction and to non-local correlation effects. The reaction of water with iron atom enables to gauge RPA against coupled-cluster theory (up to perturbative triples in complete basis set limit; CCSD(T)-3s3p-DKH/CBS). Reaction profiles demonstrate that common DFT methods significantly underestimate reaction barriers, while the reaction kinetics and thermodynamics from RPA method agree with the reference data.



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Wednesday Morning I, Lehár

Complex polarization propagator: a theoretical study of molecular properties and spectra.

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In standard response theory, absorption spectra are obtained from residues of so-called response functions and are therefore acquired by solving a generalized eigenvalue problem. In this iterative procedure only the lowest excitations are addressed, therefore the straightforward comparison between standard theory and experiment is impossible in many interesting regions of the spectrum, *e.g.* the X-ray absorption region. This problem can be solved by using the complex polarization propagator approach (CPP)[1], also known as damped (complex) response theory.

A new algorithm for solving complex response equations has recently been developed, namely: the algorithm with symmetrized trial vectors[2]. It is an iterative algorithm based on a subspace approach that combines fast convergence with a very efficient scheme of obtaining new trial vectors, where the coupling between all components are considered explicitly. Calculations of dispersion coefficients[3], one-photon absorption, electronic circular dichroism, magnetic circular dichroism[4] and near carbon K-edge X-ray absorption spectra can be performed at the Hartree-Fock, Kohn-Sham density functional theory and coupled cluster level of theory with the current implementation of the CPP solver in the DALTON program[5]. This has made it possible to perform calculations on nanoparticles[6], which were out of reach of the previous solver.

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Tuesday Afternoon I, Lehár

π–π stacking is different from pancake bonding: interpretations with molecular and solid state examples

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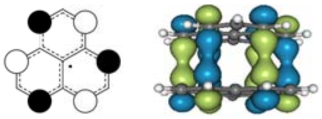
In highly conducting charge transfer salts of the TCNQ-type and in the more recent neutral radical conductors and in many other organic crystals neighboring radicals display uniquely short contacts due to the overlap of the singly occupied molecular orbitals, SOMOs. These unusual intermolecular bonds occur between (1) conjugated molecules or ions with delocalized π-electrons, and are further characterized by (2) good face to face π–π stacking overlap with (3) shorter than van der Waals (vdW) contact distances. These aggregates differ qualitatively from ordinary π–π stacking such as found between DNA base pairs that occur between closed shell systems and should therefore not be considered a type of vdW interaction.



This intermolecular interaction (termed "pancake bonding" after Mulliken-Person) has further characteristics: (4) the binding energy associated with it can be significantly larger than typical vdW interactions, (5) intermolecular orbital overlap is important and dictates preferred relative packing by maximizing SOMO-SOMO overlap, (6) there are low-lying triplet and singlet excited states. The problem is theoretically challenging because the multireference (diradicaloid) character of the ground state is coupled with significant dispersion interactions that require the inclusion of a large number of configurations. We discuss the application of wave function methods (MR-AQCC) and various density functional theory (DFT) approaches that include long-rage or dispersion terms and vdW-DFT. We explore the limits of pancake bonding: which might be the strongest/shortest pancake bond?

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Thursday Morning I, Brahms

A Novel Mechanism of Thermal Decomposition of 1,2-Diamino-1,2-Dinitroethylene (FOX-7): New Insights from High-level Quantum Chemical Calculations

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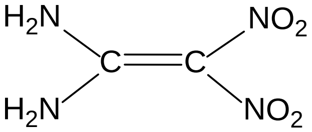
1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) is a new promising high-performance insensitive energetic compound [1-2]. Kinetics and mechanism of thermal decomposition are crucial for understanding the sensitivity and performance of this species. However, even though the thermal decomposition of DADNE under various conditions has been intensively studied experimentally, there are still some contradictory assumptions concerning the initial reactions of its thermolysis. The C-NO_2 bond dissociation reaction, nitro-nitrite and nitro-aci-nitro isomerization have been widely discussed as possible primary channels of thermal decomposition of the title compound.



DADNE

The highly accurate CCSD(T)-F12 computations revealed that *none* of these reactions dominate the thermolysis of DADNE. On the contrary, we propose the two competing primary reaction channels which have never been discussed before. The rate-limiting step of DADNE thermal decomposition is the H-transfer from the amino group to a carbon atom yielding an amino-imino derivative of dinitroethane. Only a slightly higher activation barrier was found for cyclization to oxazete-N-oxide which is prone to fast subsequent molecular decomposition.

The calculated values of effective activation energy of DADNE decomposition are in perfect agreement with the experimental data available. We also compared the decomposition mechanism of the title species with the relevant case of triaminotrinitrobenzene (TATB), another insensitive high-energy compound which is widely used in applications.

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Geminal-based wavefunction theory and its perturbative improvement

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Effective treatment of electron correlation, which is missing in mean-field Hartree–Fock (HF) calculations, has been a major topic in quantum chemistry. Electron correlation can be separated into dynamical and static effects. The static electron correlation is essentially important in calculating molecules with near-degenerate states or describing dissociation processes. The antisymmetric product of strongly-orthogonal geminals (APSG) method [1,2] is an effective theory which can account for static electron correlation. The APSG wavefunction is constructed with the two-electron wavefunction, called geminals, and it fully involves the intra-geminal two-electron correlation. To improve the APSG wavefunction by taking the inter-geminal correlation into account, we have applied the Møller–Plesset type multi-configuration perturbation theory (MP-MCPT) to the APSG wavefunction [3,4]. In this presentation, we report the geminal-based wavefunction theories that we have developed recently.

The APSG wavefunction of a closed- or open-shell system is expressed with two-electron geminals $\{\psi\}$ and one-electron natural orbitals $\{\varphi\}$ as follows:

$$\Phi_{\mathrm{APSG}} = \hat{A}\left[\psi^1(x_1,x_2)\psi^2(x_3,x_4)\cdots\psi^{N_{\mathrm{C}}/2}(x_{N_{\mathrm{C}}-1},x_{N_{\mathrm{C}}})\varphi_1(x_{N_{\mathrm{C}}+1})\cdots\varphi_1(x_{N_{\mathrm{C}}+N_{\mathrm{O}}})\right]. \qquad (1)$$

Here, $\hat{A}$ is the antisymmetrization operator, and N_{C} and N_{O} represent the numbers of closed- and open-shell electrons, respectively. We applied the MP-MCPT [3,4] to the reference function of Eq. (1). Table 1 shows the mean absolute errors of geometrical parameters of 30 open-shell diatomic molecules. The MP-MCPT method improves the results of the equilibrium distance and the dissociation energy and obtains the results as well as the other multi-reference perturbation method.

Table 1. Mean absolute errors of the equilibrium distances R_e, the harmonic vibrational frequencies f, and the dissociation energies D_0 from the results of experiments for 30 open-shell diatomic molecules (6-311G(2d,2p)) [4].

Method	R_e [pm]	f [cm^{-1}]	D_0 [eV]
UHF	2.7	180	1.95
UMP2	2.1	196	0.60
CASSCF	2.3	108	1.14
MRMP2	1.7	87	0.60
APSG	2.4	126	1.07
MP-MCPT(APSG)	1.5	166	0.65

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Tuesday Afternoon I, Brahms

Optimisation and Bayesian Parameter Estimation of a Kinetic Model of n-Propylbenzene Oxidation in a Shock Tube

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We present an optimised chemical kinetic mechanism for n-propylbenzene oxidation in a shock tube and apply a Bayesian parameter estimation technique to investigate uncertainties in model parameters and responses. The optimisation of the mechanism [1] is carried out in two stages: firstly, a quasi-random global search using a Sobol low-discrepancy sequence is conducted, followed by a local optimisation by means of a hybrid gradient-descent/Newton iteration method. The concentrations of 37 species at a variety of temperatures, pressures, and equivalence ratios are optimised against a total of 2378 experimental targets. We then apply a Bayesian methodology to study the influence of uncertainties in the experimental measurements on some of the Arrhenius parameters in the model as well as some of the predicted species concentrations. Markov Chain Monte Carlo algorithms are employed to sample from the posterior probability densities, making use of polynomial surrogates of higher order fitted to the model responses. The methodology allows analysis of the distributions of model parameters and responses, in particular their uncertainties and correlations.

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Tuesday Morning II, Bartók

The decisive role of hydrogen-bonds in chiral discrimination - unraveled by quantum chemical means

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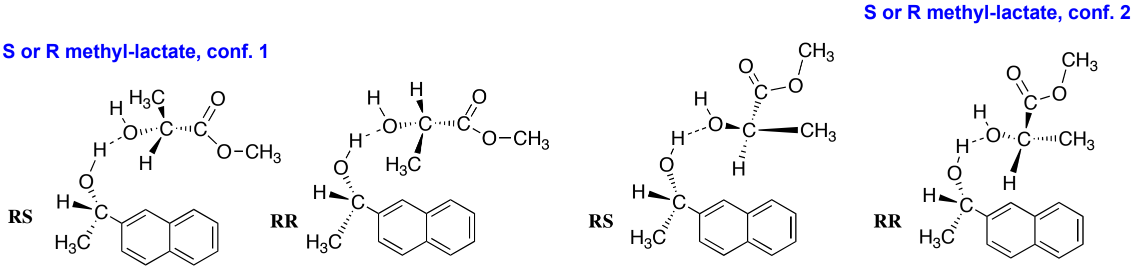
The investigation and understanding of chiral discrimination of pairs of homo- and heterochiral molecules is a challenge for both experimentalists and computational chemists. Limited success has been accomplished by analyzing molecular properties such as the chirodiastaltic energy, geometry, NMR magnetic shieldings or NMR spin-spin coupling constants. Vibrational spectroscopy is a sensitive tool for detecting H-bonding and therefore it should also distinguish H-bonding in pairs of homo- and heterochiral molecules.

The information contained in the vibrational spectra is difficult to decode, which complicates the discrimination of H-bonding in homo- and heterochiral molecules. However, the normal vibrational modes of a molecule provide all information needed to determine its local vibrational modes. The local vibrational modes, as first described by Konkoli and Cremer, lead to an accurate description of bonding, which can be exploited when distinguishing H-bonding in pairs of homo- and heterochiral molecules or to assess the role of H-bonding in chiral recognition.[1-3] Based on experimental, DFT, and CCSD(T) data, we will present an explanation for the formation of homo- and heterochiral molecules.



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Wednesday Morning I, Pátria

Resolution-of-Identity and Cholesky Representations of Electron-Repulsion Integrals within Coupled-Cluster and Equation-of-Motion Methods: Go One More Mile

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A general implementation of of resolution-of-identity (RI) and Cholesky decomposition (CD) representation of electron-repulsion integrals within coupled-cluster with single and double substitutions (CCSD) and equation-of-motion (EOM) family of methods is presented[1]. The CCSD and EOM-CCSD equations are rewritten to eliminate the storage of expensive four-index intermediates leading to significant reduction in disk storage requirements, reduced I/O penalties, and improved parallel performance. In CCSD, the number of rate-determining contractions is also reduced; however, in EOM the number of operations is increased because the transformed integrals, which are computed once in the canonical implementation, need to be reassembled at each Davidson iteration. Nevertheless, for large jobs the effect of the increased number of rate-determining contractions is surpassed by the significantly reduced memory and disk usage leading to considerable speed-up. Overall, for medium-size examples, RI/CD CCSD calculations are approximately 40% faster than the canonical implementation, whereas timings of EOM calculations are twice faster. More significant speed-ups are obtained in larger bases, i.e., more than 2-fold speedup for CCSD and almost 5-fold speed-up for EOM-EE-CCSD in cc-pVTZ. Even more considerable speedups (6-7 fold) are achieved by combining RI/CD with frozen natural orbitals approach. The numeric accuracy of RI/CD approaches is benchmarked with an emphasis on energy differences. Errors in EOM excitation, ionization, or electron-attachment energies are less than 0.001 eV with typical RI bases and with 1e-4 threshold in CD. Errors with 1e-2/1e-3 thresholds, which afford more significant computational savings, are less than 0.04 and 0.008 eV, respectively.

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Tuesday Afternoon II, Lehár

Raman bands in small diameter carbon nanotubes

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We carried out first principles calculations to obtain the phonon dispersion of single walled carbon nanotubes with small diameter. The calculations on the density functional level became possible by making use the helical symmetry of the tubes. It is very important that the Raman-spectrum of a carbon nanotube is dominated not only by Gamma-point phonons. Similarly to graphene, zone boundary phonons can be observed as well, when double resonance conditions are fulfilled. The two most important double resonant Raman bands are the disorder induced D band and its ‘overtone’, the 2D band (also known as G’ band). After briefly introducing our results for Gamma-point phonons I will concentrate on double resonance processes.

Recently an interesting band in the region of the D band was observed in bilayer graphene when the two layers were rotated with respect to each other. We have shown that similar effect may be observed in double walled carbon nanotubes with different chiralities. The effect of disorder in such cases can be replaced by interaction between the two layers. However for double walled tubes two extra constraints exist as compared to bilayer graphene.

† In memory of my PhD student Ádám Rusznyák who died tragically in May 22 2013.

Monday Morning I, Pátria

The no-photon approximation in relativistic quantum chemistry

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The construction, from quantum field theory, of a relativistic n-electron Hamiltonian in a basis representation, appropriate for quantum chemisty, is discussed. Special attention is paid to the no-photon approximation, in which the electromagnetic interaction is not quantized, and which allows a very compact approach. A Fock space theory in normal order with respect to the fermion vacuum is presented. At this level the concept of vacuum Polarization arises [1]. We are on the way to understand why the very popular Dirac-Coulomb Hamiltonian is not acceptable, and how the Brown-Ravenhall disease can be cured.

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Thursday Afternoon , Brahms

Quantum Theoretical Investigation to Explain the Onset of Cancer

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The stereostructure of DNA was established by Watson and Crick based on the X-ray investigations of Wilkins in 1953. Since that time with the refinement of the X-ray technique Richmond and Luger have given a more refined structure of DNA and the 8 nucleoproteins in the nucleosomes (particles in the cell nucleus from which the chromatins are formed) in 1997. Using this structure large scale quantum theoretical investigations have been performed using the *ab initio* HF crystal orbital method in its LCAO form. In the calculations besides the translation also the 36° rotation was simultaneously taken into account. This work was started from a single nucleotide (base with sugar and phosphate and surrounding water and Na^+ ion). The calculations were extended to periodic nucleotide stacks, stacks containing a base pair periodically repeated and in an approximate way to periodic two different nucleotide pairs. Using the obtained band structures with the help of the so-called deformation potential approximation the hole mobilities of the mentioned systems were calculated. Since, previously it was shown that chemical carcinogens and radiation hits act not only locally, but with the aid of different mechanisms in which solitons (non-linear quasi particles) play a central role, but also quite far from their original point of interaction with DNA. If a carcinogen activates in this way an oncogene through m.RNA and the occurrence of a protein (oncoprotein) at an unexpected place and time this can disturb the self-regulation of the cell. This cell then can become into another stationary state (so-called precancerous state). Since there is no contact inhibition between cancerous cells, the transition of normal cells into precancerous ones can dissipate easily and therefore a tumor can develop. The effect of a radiation hit on DNA can break one strand of the double helix. If a second hit occurs its effect can propagate with the help of the same mechanisms as in the case of carcinogens, to the site of the first hit and that causes a break of the double helix. This causes a loss of genetic information including the loss of the so-called antioncogenes. Finally, it should be mentioned that despite the large progress of the biological and chemical aspects of carcinogenesis without the understanding the physical and physico-chemical side of cancer development, it will be very difficult to find methods for its cure. This was most recently pointed out by the National Cancer Institute of NIH.

Monday Morning II, Lehár

Generalized tensor methods and entanglement measurements for electronic structure calculations

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In the past decade, we have witnessed a breakthrough in electronic structure calculations due to the density matrix renormalization group (DMRG) method invented by S. R. White [1,2] which has become in recent years a rival to the conventional multiconfiguration wave function approaches [3-5]. Inclusion of the concepts of entanglement from quantum information theory (QIT) [6,7] has paved the road for identifying highly correlated molecular orbitals leading to an efficient construction of active spaces [6,8] and for characterizing the various types of correlation effects relevant for chemical bonding [9]. Quite recently, a reformulation of DMRG in terms of so-called matrix product states (MPS) has shown that it is only one special case in a much more general set of methods: the so-called tensor network states (TNS) [10], which is expected to even outperform DMRG in the near future [11].

In this contribution, we will discuss the quantum chemistry version of the DMRG and tree-TNS algorithms and their applications to transition metal complexes [12] and polydiacetylenes [13]. In the latter case, the state of the art matrix-product-based algorithms is demonstrated by correlating 100 electrons on 100 orbitals allowing us to reproduce experimentally measured quantities with high accuracy. We identify optically dark in-gap states in the singlet and triplet sectors for the first time as seen in experiments.

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Barrier evasion and roaming in the dynamics of elementary chemical reactions

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For chemical reactions where the reactant and product domains of configuration space are separated by a barrier, the rate coefficient commonly is calculated using transition state theory (TST), an approximate statistical method. The TST rate coefficient expression is based on the properties of limited ranges of the potential energy surface (PES) of the reaction: those of the narrow region near the reactants as well as at the saddle point separating reactants from products (the energy difference of the two structures, their vibrational frequencies and rotational constants). In many chemical reactions such an approach is not satisfactory, because the details of the dynamics and the rate coefficient are determined by regions of the potential energy surface that are far from the saddle point. Such cases will be presented in the talk.

1. In reactions of vibrationally highly excited diatomic molecules, during the reactive encounters the atoms do not even approach the saddle point. Moreover, in many cases a phenomenon called roaming can be observed: after a successful reactive encounter the products first depart from each other, their flight slows down because of slight attractive forces that arise due to the high vibrational amplitude until they stop finally return from a distance as large as 5 Å, and another collision occurs that can yield new products [1].

2. On the PES of the reaction of H atoms with electronically excited O_2, there is a barrier on the reactant side of the deep potential well corresponding to electronically excited HO_2. The rate of the reaction is determined not by the chance of crossing of the SP region but by the intramolecular motion of HO_2.

3. In the photodecomposition of CH_4 the excited-state PESs are repulsive. In such cases TST is not applicable. Dynamical simulations are needed to understand the molecular mechanism of the reaction. The product distribution depends on nonadiabatic transitions between the excited PES. Near conical intersections the reacting system can be reflected back from the repulsive side of the lower cone, which leads to roaming [2].

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Development of Many-Body Perturbation Theory: How to combine with Quantum ElectroDynamics

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The basic difficulty of combining many-body perturbation theory (MBPT) with quantum electrodynamics (QED) is that the structures of the two procedures are seemingly incompatible - MBPT is based upon standard quantum mechanics with a single time, while QED is based upon relativistic covariance with individual time for each particle. In order to combine the two, one way is to sacrifice the full covariance and apply the equal-time approximation. Fortunately, it turns out that this has very small effect on problems in atomic/molecular physics and quantum chemistry.

In the first part of the lecture the standard procedures of MBPT and QED will be reviewed. Here, emphasis will be put on the so-called folded term of the Bloch equation of MBPT, which represents the remainder after the singularities, due to intermediate model-space states, are eliminated (also referred to as "model-space contribution" or "reference-state contribution"). It turns out that this plays an important role in the generalization of the procedure, needed to include QED and other energy-dependent perturbations.

In the standard procedures the effects of MBPT (primarily electron correlation) and of QED (retardation, self-energy etc) are treated independently. The second part of the lecture will deal with the possibility of treating the two effects coherently. Such a procedure has recently been developed, based upon the covariant-evolution operator (CEO) method for QED, which has a structure quite akin to that of MBPT [1, 2]. The CEO also has singularities due to intermediate model-space states, and the regular part is referred to as as the *Green's operator*, due to its analogy with the standard Green's function. This operator can be regarded as a time-dependent generalization of the wave operator of standard MBPT, and it satisfies a Bloch-type equation, quite similar to that of the MBPT counterpart. The only difference lies in the form of the folded term, which in the Green's-operator case also contains the energy derivative of the perturbation. This leads to a general *time-dependent perturbation theory* and makes it is possible to include time- or energy-dependent perturbations, such as those of QED, into the MBPT expansion in a rigorous fashion.

The combined MBPT-QED procedure is now being tested, and some numerical results for heliumlike ions will be presented.

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Cluster-in-molecule local correlation approach: Recent developments and applications

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The "Cluster-in-Molecule" (CIM) local correlation approach for post-Hartree-Fock calculations in a basis of orthogonal occupied and virtual localized molecular orbitals (LMOs) is reviewed and some recent developments and applications are shown. The main idea of the CIM approach is that significant excitation amplitudes can be approximately obtained by solving the coupled cluster (CC) (or Møller-Plesset perturbation theory (MPPT)) equations of a series of "clusters", each of which contains a subset of occupied and virtual LMOs.[1-5] Recently, we proposed two refined CIM schemes[6,7] for predicting the relative energies, in which two new strategies for building clusters are introduced. Our results show that the present CIM scheme can reproduce more than 99% of conventional correlation energies for a wide variety of systems. Furthermore, the present CIM scheme can give satisfactory descriptions for conformation energy differences of quite large systems. In general, CIM can be considered as an effective framework for extending electron structure methods to large systems.

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Fundamentals of Relativistic Molecular Quantum Mechanics

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Relativistic Molecular Quantum Mechanics (RMQM) as the union of Relativistic Quantum Chemistry (RQC) and Quantum Electrodynamics (QED) consists of three components (i.e., Hamiltonian, wave function, and property), each of which is confronted with some fundamental issues, including, e.g., 'What is the appropriate relativistic many-electron Hamiltonian?'[1,2], 'How to make explicit and/or local representations of relativistic wave functions?'[1,3,4], 'How to formulate relativistic properties?'[5], 'How to interface RQC and QED?'[1], etc. In this lecture I shall try to address these fundamental issues from both conceptual and methodological standpoints, so as to establish the `big picture' of RMQM[6].

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Thursday Morning II, Brahms

An intrinsic measure for the reliability of calculated VCD band signatures

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We present a novel measure that improves the reliability of the assignment procedure for vibrational circular dichroism (VCD) spectra. Interpretation and assignment of VCD spectra is only possible through the comparison of experimental and computed results, but agreement is rarely perfect.

The new criterion extends the useful robustness concept introduced by Nicu and Baerends [1] and enables spectroscopists to single out bands with unreliable VCD intensities. These bands, selected purely on a simple theoretical measure can be disregarded during analysis and determination of absolute configuration. [2]

We extensively use the new criterion, denoted as robustness in our studies on the conformational equilibria of flexible molecules, such as carboxylic acids and their dimers, amino acid derivatives and small peptide models.

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Thursday Afternoon II, Lehár

Solvent Effects on Electronic Absorption, Fluorescence and Phosphorescence of Acetone and Benzene in Water: A QM/MM Study

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Polar and non-polar solutes (acetone and benzene) dissolved in ambient water (AW) and supercritical water (SCW) are investigated theoretically using a sequential quantum mechanics (QM)/ molecular mechanics (MM) method.[1, 2, 3] We find both of aqueous acetone and aqueous benzene under high temperatures present three distinctive regions: low-density gas-like region, supercritical region and high-density liquid-like region. The plateau behavior of solvatochromic shift in the supercritical region is ascribed to the solvent clustering around the solute, which is a fundamental phenomenon of supercritical fluids (SCFs). The density dependence of our calculated coordination number of the first solvation shell nicely reproduces the trend of electronic absorption spectral shift and verifies the solvent clustering phenomenon of SCFs and its relationship with SCF's physicochemical properties.

Besides the electronic absorption spectral shift, we also revisit the solvent effects on the fluorescence and phosphorescence spectra of aqueous acetone.[4] It is found that such effects are very small or even negligible when compared with the large solvent effect for electronic absorption and are caused by the reduced dipole moments of acetone and accordingly much less hydrogen bonds for aqueous acetone in the electronic excited states S_1 and T_1 comparing to the ground state S_0.

In our sequential QM/MM studies, we also examine the effects of size of QM region, the choice of the density functional and the choice of the basis set as well as the sampling time length on the simulated results.[3, 4] It is revealed that the inclusion of the solvent molecules within the first solvation shell into the QM region to account for the exchange-correlation between a solute and neighboring solvent molecules is important for the highly accurate spectral shift calculations, especially vital for the non-polar solutes whose interactions with the solvents are dominated by the quantum dispersions. At the same time, sufficiently large surrounding partial charge region ($r_{cutoff} \geq 15$ Å) as well as the functional corrections to describe the long-range corrections are also essential for the study of the electronic excited states in condensed phase.

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Monday Afternoon I, Lehár

Reactive molecular dynamics simulations of switching processes of azobenzene-based monolayer on surface

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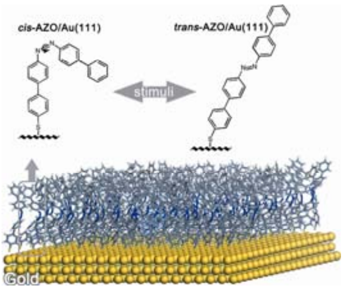
Theoretical simulation of the switching process of the self-assembled monolayer (SAM) on the metal surface is a challenge due to the complicated composition with thousands of atoms and triggering by the quantum-mechanical events. A molecular dynamics simulation with the reactive rotation potential of N=N bond[1,2] is implemented to investigate the dynamic conformational changes and packing effects on the isomerization of the terminally thiol functionalized azobiphenyls (AZOs). To distinguish the time evolutions that start from *cis* and *trans* initial configurations, respectively, two different functions are established to model the potential energy curves of *cis*-to-*trans* and *trans*-to-*cis* transitions, instead of the only one cosine function used in the conventional non-reactive force fields. In order to simulate the conformation transitions of the AZO film on surface, a random switching function, dependent on the N=N twisting angle, is constructed to consider both forward and backward *cis/trans* isomerization events and to trigger the reaction by changing the N atom types automatically. Furthermore, three azobenzene derivate self-assembled monolayers are found not only tunable with changes in wave length of ultraviolet-visible light, but also with directions of electric filed on the Au(111) surface.



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Towards an accurate treatment of many-body dispersion and polarization for chemical accuracy via a coarse grained Gaussian Electronic Structure

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Computer clock speeds are no longer increasing and increases in computational power are now limited to increases in processor number, unfamiliar territory for computational scientists who have ridden the wave of CMOS-scaling for the past 30 years. In this brave new world, gains in computational accuracy and performance will be driven by methodological development. In this lecture, a treatment of long range forces will be described to increase chemical accuracy of atomistic simulations. There are many physical systems where the non-pairwise additive nature of polarization and dispersion interactions becomes important, in particular, the complex heterogeneous systems of interest in chemistry, biology and physics. For example, the dipole moment of water changes from 1.85 Debye in the gas phase to approximately 2.6 Debye in the bulk liquid and attains intermediate values at hydrophobic interfaces due to many-body polarization. Similarly, although the bulk properties of hydrophobic fluids can be modeled using a pair potential, this underestimates the surface tension by 30% due to many-body dispersion interactions. In order to model both the full many-body polarization and dispersion interactions in atomic and molecule systems, a system of quantized Drude oscillators is introduced and a O(N) simulation method based on quantum path integrals is described using diagramatic expansions of the propagator. Applications to the phase diagram of water and water's properties at surfaces, are given.

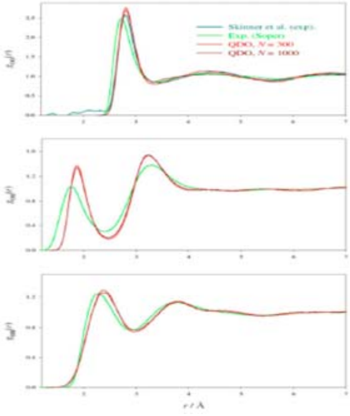

Figure 1: Comparison of the radial distribution functions of the QDO model of water to those obtained from the inversion of experimental results by Soper et al and Skinner et al.

Tuesday Morning II, Lehár

The density is not enough

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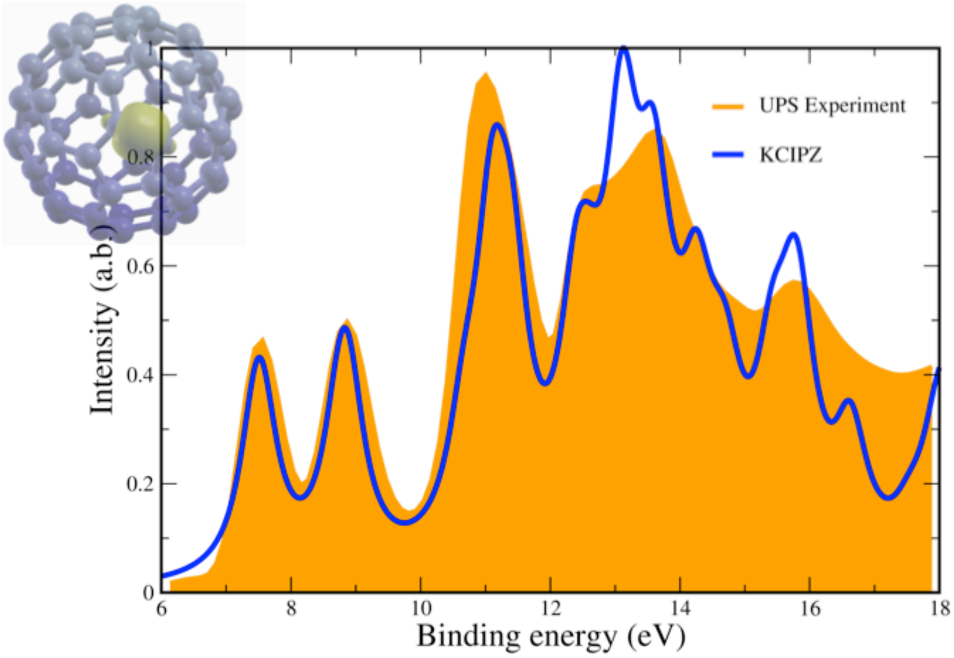
Materials' simulations based on density-functional theory (DFT) have become an extremely powerful and widely used tool for scientific discovery and technological advancement. Still, in the current approximations, they remain an imperfect tool for predicting materials' properties, with open and urgent challenges in the quest towards qualitative and quantitative accuracy.

Several of these challenges stem from the remnants of self-interaction in the electronic-structure framework, leading to qualitative failures in describing some of the fundamental processes involved e.g. in energy applications - from charge-transfer excitations to photoemission spectra to the structure and reactivity of transition-metal complexes.

I'll discuss these challenges in realistic case studies, and present a brief overview of some of our suggestions for possible solutions - including constrained DFT, DFT + onsite and intersite Hubbard terms, and Koopmans' compliant energy functionals. In particular, I'll highlight how Koopmans' compliant functionals point to a beyond-DFT formulation where both total energies and spectroscopic properties can be accounted for. Such framework will be illustrated with applications to real systems and with simplified models that can be solved exactly.

Work done in collaboration with I. Dabo (Penn State), A. Ferretti (U. of Modena), Matteo Cococcioni (EPFL), G. Borghi (EPFL), Linh Nguyen (EPFL), D. D. O' Regan (EFPL), H. J. Kulik (MIT), C. H. Park (SNU), Patrick Sit (CUHK).



Thursday Morning I, Lehár

Force Field Parameterization from a Force Matching–like Approach: Merits, Shortcomings and Future Perspectives.

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Among the various approaches used in force field development, in recent years, the *Force Matching Algorithm* and similar approaches have been extensively used [1, 2, 3, 4, 5, 6, 7]. The method is based on a least square fit of reference properties (forces, torques, energies etc.) obtained with ab initio Molecular Dynamics simulations of condensed phase systems. Its advantage with respect to conventional schemes, lies in that only physically accessible configurations are sampled, and that the number of reference data per configuration is large. The main shortcoming of the method derives from the "quality" of reference simulations might not be as good as high level quantum chemical calculations. In this talk I will show our recent findings on tayloring of the penalty function; we have found thar a proper choice of weighting functions yields force fields that faithfully reproduce most of the ab initio dynamical and statical properties. In addition, the algorithm is used to unravel the limits of most widespread functional forms for the force fields. In particular, using water as benchmark, the impact of damping dispersion forces and Coulomb interactions at short range is assessed against ab initio results. Finally, pros and cons of this approach with respect to others are discussed, with particular emphasis on future applications to heterogeneous condensed phase systems, and to coarse grained force fields.

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Tuesday Afternoon I, Lehár

Towards a mechanistic understanding of photoinduced (non-)switching of metal surface adsorbed Azobenzenes.

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Adsorption of functional molecules on metal surfaces is of specific interest to nanotechnology as it could lead to novel functionality not present in gas phase. Unfortunately, overly strong coupling with the substrate electronic degrees of freedom often quenches photo-induced reactions, such as in the case of the molecular switch azobenzene on coinage metal surfaces. Nevertheless, recent experiments revealed such a photo-induced mechanism for tetr.-*tert*-butyl functionalized azobenzene (TBA) at Au(111). It is believed that isomerization is triggered by excitation from the metal *d*-bands rather than from the adsorbate states followed by subsequent charge-transfer to the adsorbate[1]. Employing dispersion-corrected Density-Functional-Theory calculations we were able to rationalise the non-switching of azobenzene and derivatives on Ag(111) already in terms of modified groundstate energetics, which lead to an effectively destabilized metastable state[2]. In order to further investigate the detailed photo-isomerization dynamics we have established an efficient approach to low lying excited states of large adsorbate systems based on the recently proposed linear expansion Δ-Self-Consistent-Field method[3]. The method yields a topologically correct description of excited state potential energy surfaces and a qualitative account of hybridization and image charge effects. We present here excited states of adsorbed azobenzene relevant for gasphase isomerization as well as for a possible STM- or light-induced charge-resonant isomerization. Systematic mappings along important degrees of freedom for azobenzene on Ag(111) and Au(111) allow a detailed comparison with the well known gasphase case. We will also present current limitations of this approach, namely the effective treatment of hybridization and the remaining self-interaction error due to semi-local xc-treatment. The fact that some conclusions can already be drawn from the static picture encourages us to seek for a complete non-adiabatic dynamic treatment of the corresponding mechanisms.

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Extracting chemical information from molecular wave functions – some recent results

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In the lecture I am going to summarize our recent results obtained for *a posteriori* analyzing molecular wave functions in chemical terms. The topics will cover

- *Bond order index:* improved definition for correlated wave functions and calculating from results of plane wave calculations;
- *Effective atomic orbitals and effective minimal basis sets:* calculations in different theoretical frameworks;
- An improved *energy-partitioning scheme.*

Superconductivity as a problem in chemical physics.

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Superconductivity as a fundamental problem in quantum mechanics is now more than 100 years old. While the Bardeen-Cooper-Schrieffer (BCS) theory [1] gave a successful explanation of the so-called low critical temperature (low T_c) superconductivity, for more than 25 years now, since the discovery of high T_c superconductivity in the layered cuprates, it has become clear that there exists a different, and perhaps more complete theory of superconductivity that applies broadly to all systems with strong repulsive interactions between electrons. In spite of enormous collective effort by condensed matter physicists, such a theory has not been reached yet. This talk will present an approach to this problem from a perspective that has its roots in chemical physics. The condensed matter physics community recognized at the outset that the most important characteristic of correlated-electron superconductivity is that this phase is proximate to antiferromagnetism. We will begin by pointing out that there exists yet another feature that is shared by all correlated-electron superconductors, viz., superconductivity in these is limited to specific chemical stoichimetries where a particular carrier concentration is reached [2, 3, 4]. We posit that at this carrier concentration mobile electron-pairs with physical dimensions close to that in molecules occur. Superconductivity is due to the condensation of these mobile pseudomolecules, as was suggested by Schafroth a few years prior to the advent of the the BCS theory [5]. Examples will be given mostly from, but will not be limited to, carbon-based superconductors including organic charge-transfer solids, fullerides, and metal-intercalated phenacene hydrocarbons (A_3phenanthrene, A_3picene and A_3dibenzopentacene, A = K, Rb).

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Macromolecular Conformation Analysis by the LIL-ADMA Method: How to Deal With Many Atoms Moving in All Directions?

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In searching for a target conformation, such as a local energy minimum of a macromolecule, a compromise involving lower accuracy in an early, crude stage of the search, testing many conformations by some quick, but less accurate method, followed by only a few, more accurate, and more expensive computations near the crudely-located target conformation is advantageous. One such approach is a combination of the Adjustable Density Matrix Assembler (ADMA, an *ab initio* quality linear scaling method, [1-4]), and the rather quick Löwdin-Inverse-Löwdin (LIL) density matrix extrapolation method [3,5], both involving the same type of density matrices on a common AO basis, ensuring perfect compatibility.

Starting with some initial, *ab initio* quality density matrix, a quick and detailed search of the conformational space can be performed by the LIL density matrix extrapolation method, leading to a new candidate conformation to be recalculated by the more accurate, *ab initio* quality method. These steps can be repeated in an iterative fashion, combining the advantages of speed and accuracy.

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Friday Afternoon II, Pátria

Accommodation of Electronic Excitation in sigma-Bond Systems: Peralkylated Oligosilanes

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The geometrical relaxation that follows the first singlet excitation of a sigma-electron system, such as a saturated hydrocarbon or its silicon analog, an oligosilane, is likely to be more deep-seated than an analogous relaxation of a pi-electron system, because in the former case one of the very electrons that form the only bonds that hold the molecule together is being promoted to an antibonding orbital. Many though not all of these sigma electron systems fluoresce, especially at low temperatures. The Stokes shifts are often but not always extremely large, 2 - 3 eV, leaving no doubt that in many cases the relaxed excited state geometries differ very significantly from the equilibrium geometries of the ground state. We have chosen a series of peralkylated oligosilanes and asked (i) how molecular structure (linear, cyclic, or branched), size, and conformation determine the magnitude of the Stokes shift, (ii) what are the relaxed geometries in the lowest excited singlet state S_1, and (iii) what is the degree of excitation delocalization in the relaxed S_1 state. We have addressed these questions using several ab initio procedures and empirical as well as ab initio density functional methods and the results will be reported and discussed. Some of the salient results are (i) the degree of excitation delocalization is determined by conformation of the longest linear chain and is closely tied with the magnitude of the Stokes shift, (ii) unlike the ground state equilibrium geometries, in which all silicon atoms are tetrahedral, the localized S_1 geometries tend to contain one silicon atom at a trigonal bipyramidal geometry, or two adjacent silicon atoms at a geometry intermediate between tetrahedral and trigonal bipyramidal, (iii) four of the vertices in the trigonal bipyramid are occupied by the same substituents that were present in the ground state and the fifth vertex is occupied by an odd-electron-carrying hybrid orbital of intermediate valence/Rydberg nature, composed primarily of silicon 4*s* and 4*p* atomic orbitals, with an admixture of 3*d*. A similar observation of five stereoactive "valence" orbitals on a silicon atom was made for certain conformations of the radical anion of peralkylated tetrasilane and we propose that electron traps in amorphous silicon, responsible for the Staebler-Wronski effect that plagues its use in solar cells, have a similar trigonal bipyramidal structure.

Thursday Morning I, Brahms

Interaction of water with rutile (1 1 0) – Ground and excited states

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Photochemical reactions are of great interest in modern chemistry and are hard to model theoretically. Especially photo-catalytic reactions on surfaces are a great challenge. By combining quantum chemical and quantum dynamical methods, we were able to elucidate the photodesorption of small molecules from metal oxide surface from first principles.[1]

In this contribution we present first results for the water adsorption on a rutile (1 1 0) surface. This process might become very important in the near future because of the possibility to split water into oxygen and hydrogen using the energy of sun light. Thus, this reaction can open an economical and ecological relevant route to hydrogen.

Our approach is to model the H_2O/TiO_2 system by a finite cluster embedded in a field of about 4500 point charges to include long range Coulomb interaction. The cluster is of stoichiometry $Ti_9O_{18}Mg_7^{14+}$ and has successfully been used for describing the photodesorption of CO from rutile (1 1 0).[2]

Potential energy surfaces for the electronic ground state and selected electronically excited states are calculated on the CASSCF level of theory, giving the possibility to describe the bond breaking properly. The electron correlation is included by a CASPT2 treatment.

These potential energy surfaces are used for quantum dynamical calculations based on Gadzuk's jumping wave-package approach.[3, 4] Therefore, the dynamics is treated fully quantum mechanically and can include effects like tunneling or isotope substitution.

In this contribution we present first quantum chemical results for the adsorption in the electronic ground state and some preliminary results for excited states.

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Chemistry and Physics in high-frequency strong laser fields

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(Dated: May 28, 2013)

In high frequency strong laser fields the oscillating electrons in an atom behave like they are moving not in a field induced by a positive point charge of the nucleus but in a field which is smeared along the polarization direction of the light and it is peaked at +/- of the quiver length (defined as the ratio between the maximum field amplitude and the square of the laser frequency multiplied by the mass of the electron). We will show that for many electron atoms (such as sulfur and oxygen) the ground state of the laser dressed atom has a long lifetime and can be degenerated. Hence, a strong linear Stark effect rather than the usual quadratic one is obtained (new physics).

We will show that also a new chemistry is induced by the high frequency strong laser fields. For example, strong chemical bond (dissociation energy is more than 12 eV) is generated between two helium atoms with a bond length of 2 Angstroms. Similarly a strong chemical bond is created between sulfur and helium atoms which is somehow similar in its nature to the chemical bond in OH radicals.

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Thursday Evening , Aula

Performance of Density Functionals in Modeling the Decomposition of CH_3OH by Cu_4 Cluster

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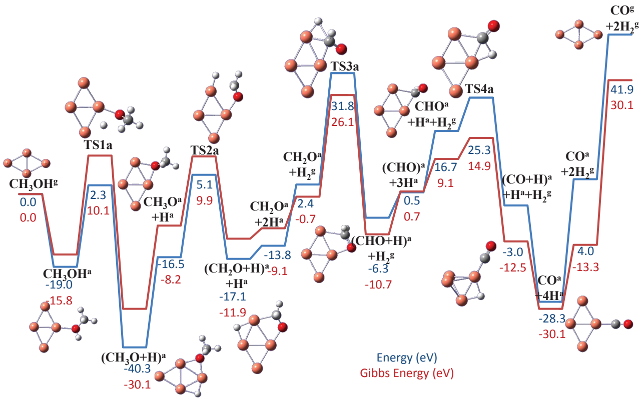
Heterogeneous catalysts are a critical part of industrial chemistry, primarily as a tool for more economically and ecologically efficient chemical processes. The activation of small abundant organic molecules such as methanol, catalyzed by metals, leads to hydrogen gas with a high atomic economy, which gives to the reaction the potential role in the development of such a promising source of energy. It is thus desirable to develop theoretical methods that can predict trends in catalytic activity and predict active catalyst for industrially important reactions. We are interested in the efficacy of DFT for modeling heterogeneous catalysis; this has to be ascertained through benchmark studies. In this study, the mechanism of the dissociation of CH_3OH by Cu_4 clusters is computed with DFT and with CCSD(T)/CBS-extrapolated. Adsorption energies of all possible decomposition products, reaction barriers for the cleavage of all possible bonds, and the reaction energies of those cleavages have been computed.We have undertaken a benchmarking study of various methods on the decomposition of methanol on small copper clusters with a wide range of DFT methods. The simulation of the reactivity of such small metal clusters is interesting both for elucidating the participation of the small clusters and also as model for the molecular-metal interactions in nanoparticles and surfaces.



Wednesday Morning I, Pátria

Unitary Group Adapted Approach to Spin-free Multi-Reference Coupled Cluster Theories: Formalisms and Applications

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In this talk, we will discuss the formulations and implementations of a suite of State-Specific (SS) and State-Universal (SU) Multi-reference Coupled Cluster (MRCC) theories, which are explicitly unitary group-adapted (UGA) and are spin-free. We will refer to all of them generically as UGA-SSMRCC and UGA-SUMRCC respectively. We will discuss briefly three distinct Ansatze for the wave operator: (a) a new multi-exponential cluster Ansatz, analogous to but different from, the one suggested by Jeziorski and Monkhorst (JM), (b) a partially contracted variant of (a), where the all-inactive double excitations are treated in an internally contracted manner, and (c) a completely internally contracted trategy (ic-MRCC). Unlike the JM Ansatz, our choice in (a) involves spin-free unitary generators for the cluster operators and we replace the traditional exponential structure for the wave-operator by a suitable normal ordered exponential. This Ansatz leads to fully spin-free finite power series structure of the 'direct term' of the MRCC equations. The UGA-SUMRCC and UGA-SSMRCC equations both follow from projection equations onto virtual functions reached from every model function. For the UGA-SUMRCC formalism, there are no redundancies for the cluster amplitudes, while the UGA-SSMRCC requires suitable sufficiency conditions to arrive at a well-defined set of equations for the cluster amplitudes. The UGA-SUMRCC and UGA-SSMRCC equations are manifestly connected and hence size-extensive. In the variant (b), the number of cluster amplitudes gets drastically reduced by internal contraction of the all-inactive cluster amplitudes for the doubles. The method (c) will be discussed to indicate the efficacy of using generalized normal ordered (GNO) representation of the cluster operators, and the manifest extensivity and orbital invariance following there from. The variants (a) and (b) will be exemplified by typical applications which will cover core ionization potentials and core-excited states. For the UGA-SSMRCC method, the effect of localization and size-consistency will also be demonstrated. Depending on the progress made, we will also present results for the method (c).

Multireference Fock space coupled cluster method based on the RHF reference for the description of the potential energy curves

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The Fock space (FS) coupled cluster (CC) method reported recently [1] is introduced to study double electron attached states. The method has a useful feature that when applied to the doubly ionized atoms or molecules it provides the full characteristics of the neutral system since the description of the neutral system is accomplished via attaching two electrons to the corresponding doubly ionized system. This way is particularly advantageous when a closed shell molecule dissociates into open shell fragments while its doubly positive cation generates the closed shell units.

A critical point of the succesful application of the FS-CC theory in molecular applications is the intermediate Hamiltonian technique. Using it we were able to compute the potential energy curves (PECs) for the series of alkali metal dimers. Moreover, the size-extensivity property of the Fock space formalism ensures the proper dissociation limit for all studied species. In all cases PECs are smooth for the entire range of interatomic distances (from the equilibrium point to the dissociation limit). Based on the calculated potential energy curves we are able to compute spectroscopic parameters of the systems studied.

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Friday Afternoon I, Bartók

Orbital-free density functional theory: functional derivative of the kinetic energy for spherically symmetric systems

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According to the Hohenberg-Kohn theorem the density can be obtained from the Euler equation. As the kinetic energy functional is unknown, density functional calculations are mainly based on the Kohn-Sham scheme. Recently, there is a growing interest in orbital-free methods. It is a huge simplification as only one equation (the Euler equation) has to be solved instead of several Kohn-Sham equations.

The talk will present an ensemble extension of the problem. This generalization allows us to solve the original Euler equation [1, 2, 3]. Ensemble non-interacting kinetic energy functional is constructed for spherically symmetric systems and the differential virial theorem is derived for the ensemble. Then a first-order differential equation is derived for the functional derivative of the ensemble non-interacting kinetic energy. A special case of the solution provides the solution of the original orbital-free problem for spherically symmetric systems.

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Linear-Scaling Electron-Correlation Theory for Two-Component Relativistic Hamiltonian

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In order to perform practical relativistic electron correlation calculations, the linear-scaling divide-and-conquer (DC)-based electron-correlation theories such as the second-order Møller–Plesset (MP2) [1] and coupled cluster theories with single and double excitations (CCSD) [2,3] as well as the Hartree-Fock (HF) [4,5] and have been combined with the local unitary transformation (LUT) scheme [6,7] at the infinite-order Douglas-Kroll-Hess (IODKH) level [8,9], which is based on the locality of relativistic effects. Numerical applications in hydrogen halide molecules, $(HX)_n$ (X = F, Cl, Br, and I) clarified that the present methods, namely DC-HF, MP2, and CCSD with the LUT-IODKH Hamiltonian, reproduce the results obtained using conventional methods with small computational costs. The combination of both LUT and DAC techniques could be the first approach that achieves overall linear-scaling with a small prefactor for relativistic electron correlation calculations (see Fig. 1) [10].

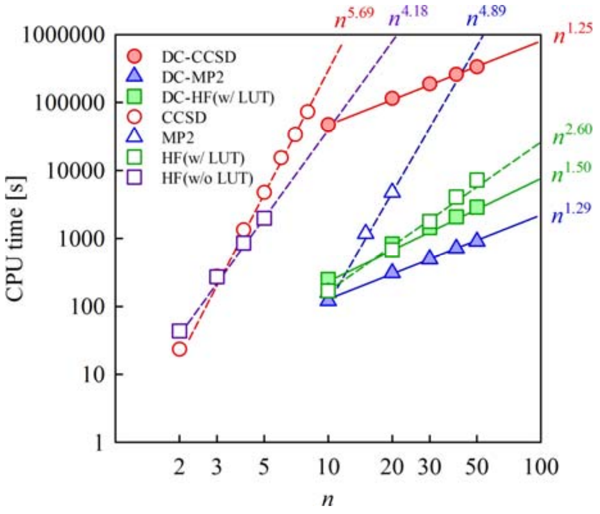

FIG. 1. System-size dependence of step CPU time in (HF)*n* (n = 2, 3, …, 50) as calculated using conventional and DAC-based HF, MP2, and CCSD methods using IODKH/IODKH Hamiltonians with (w/) and without (w/o) LUT scheme. A single core of a Hexa Core Xeon/3.33 GHz processor was used.

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Nonlinear optical properties of asymmetric diradical molecules

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Over the past few decades, a large number of experimental and theoretical investigations have been performed to explore highly active nonlinear optical (NLO) substances because of their potential applications in future photonic and optoelectronic devices. On the basis of our theoretical studies [1], a new class of open-shell singlet molecular systems has been proposed and has been found to exhibit larger NLO responses than conventional closed-shell NLO systems. Moreover, several real open-shell singlet molecular systems, e.g., polycyclic aromatic hydrocarbons (PAHs), have attracted much attention from the viewpoint of their unique open-shell singlet electronic structures, their highly effective optoelectronic responses, and their unique structure–(electronic, optical, magnetic) property relationships [2]. In this study, based on a two-site asymmetric diradical model, we newly investigate the second- and third-order NLO properties of open-shell singlet systems with asymmetric electron distributions. The asymmetric electron distribution effects on the excitation energies, excitation properties, and diradical character (a chemical index of the bond nature) are clarified theoretically and then a unified picture of the first and second hyperpolarizabilities (β and γ) (microscopic second- and third-order NLO properties, respectively) of symmetric/asymmetric diradical systems are provided as a function of several fundamental physical parameters including the diradical character. It is found that the increase of the asymmetric electron distribution causes remarkable changes in the amplitude and the sign of β and γ, and that their variations are more intensified with the increase in the diradical character. These results demonstrate that the asymmetric open-shell singlet systems with intermediate diradical characters can exhibit further enhancements of β and γ with respect to conventional asymmetric closed-shell systems and also to symmetric open-shell singlet systems with intermediate diradical characters. In addition, we present a diradical character view of the excitation energies and properties as well as of their dependences as a function of the asymmetric electron distribution, which are useful for understanding the photoresponsive properties of open-shell singlet systems and for constructing design principles of future photonic/optoelectronic materials based on open-shell singlet systems.

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Monday Afternoon I, Bartók

Mechanism of enzymatic phosphate ester hydrolysis: interplay of theory and experiment

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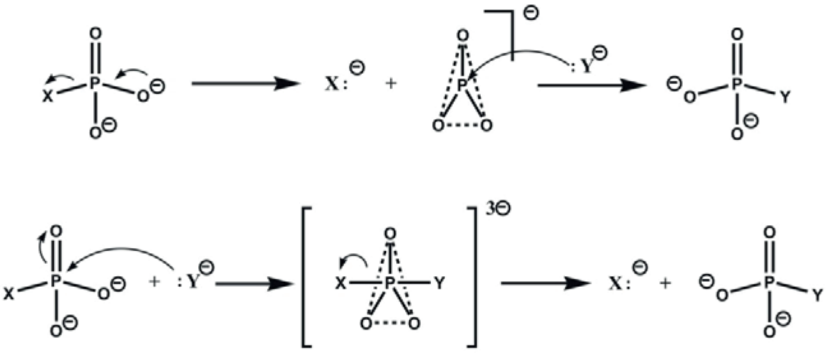
Enzymatic phosphate ester hydrolysis plays a crucial role in life processes. An especially important class is phosphorly transfer, which belongs to the most important molecular reactions in living systems. Three different types of reaction paths can be considered both for the enzymatic and non-enzymatic processes (see Figure). Dissociative (top), associative (bottom, the structure in square brackets represents an energetically locally stable intermediate), and concerted SN2-type (bottom, the structure in square brackets represents a transition state). Experimental evidence supports the concerted mechanism for the non-enzymatic hydrolysis of phosphate monoesters, while sophisticated calculations on adequate enzyme models and some X-ray diffraction studies call for the possibility of both associative and dissociative mechanisms. I will present some examples for both mechanisms and stress the importance of the effect of protein environment, especially metal ions located in the active site.



Quantum Interference Provides a Unified Description of Chemical Bonding

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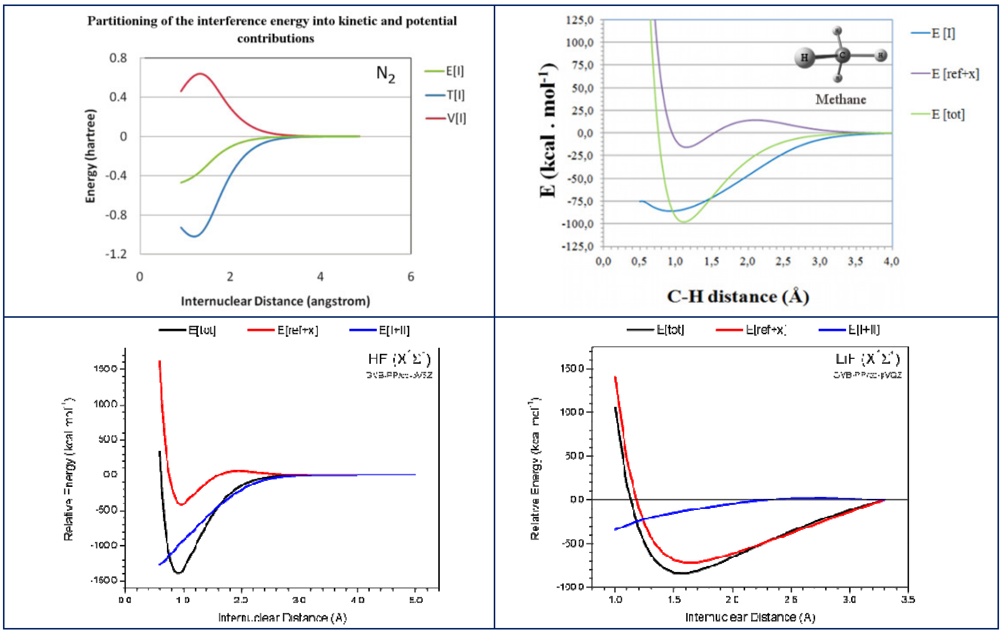
Although the chemical bond is usually considered to be a very well established concept, its origin and nature are still subject to much discussion [1-4]. It is well known that the minimum in the potential energy surface (PES) responsible for the bond in a stable system is followed by a decrease of potential energy, and a rise of kinetic energy, as required by the virial theorem. However, this analysis does not provide a model for explaining bond formation. Since total kinetic and potential energies are a direct consequence of the form of the total electronic density, the question of why the electronic density of a bonded molecule changes in such a way that results in an energy drop is unanswered by these quantities[1-4]. This can be understood through an alternative energy partitioning, derived from a density partitioning in quasi-classical and interference contributions [5-9], by recognizing that the quantum mechanical interference effect changes the electron density in a way as to reduce the energy and promote the formation of chemical bonds. The results obtained for a variety of diatomic and polyatomic molecules based on this energy partitioning attest that quantum interference plays a definite role in the formation of chemical bonds, irrespective of being classified as covalent, polar or even "ionic" [5-9]. Moreover, the developed approach provides a unique way of obtaining the total interference energy of a molecule in terms of bond contributions. Besides that, it can be shown that bond interference energies have characteristic values for a given pair of atoms in similar chemical environments [9]. In conclusion, the analysis of the chemical bond from the quantum interference perspective provides a unified description of chemical bonding (CNPq, FAPERJ).



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Molecular vs atomic encapsulation of hydrogen in metal cluster-cage assemblies

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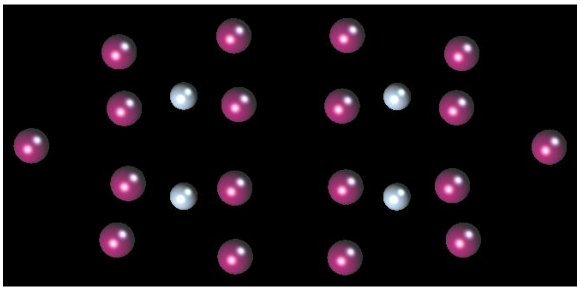
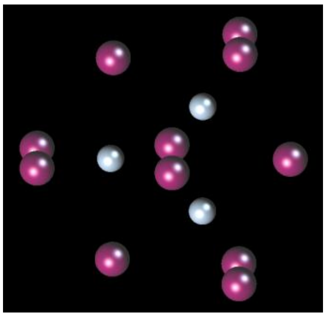
Presented are results of ab initio calculations for main-group light-metal cluster cages predicted to be able to accommodate hydrogen endohedrally, with a diatom or atom per cage for different isomers [1-3]. Such systems can also preserve their integrity when assembled into larger aggregates.

The H_2 molecules are found to dissociate due to electron-transfer from the surrounding cages which, however, confine the produced pairs of hydrogen anions electrostatically suspended inside, resulting in metastable systems. The system stabilities are characterized in terms of dissociation into hydrogen and empty cage/assembly, and of energy barriers for hydrogen exit.

Alterations of the cage structures and properties upon insertion of hydrogen are also discussed. Peculiar features concern simultaneous exit of two H atoms, relative stability of aggregates built of different isomers of monomers, specific geometry-stability relationships.

With each such hydrogen-filled cage representing a ″nanobubble″, the assemblies extrapolated to bulk material can be viewed as filled metal-nanofoams, with hydrogen storage capacity estimated as up to 10 weight-%. Furthermore, the metastability suggests low-temperature storage conditions and a relatively easy hydrogen release, unlike many alternatives schemes needing excessively high temperatures.





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Theoretical investigation of the excited state proton transfer in 3-cyano-6-hydroxycoumarin

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Photoacids are molecules that allow for local control of environmental acidity by applying a laser pulse or light source. The various applications for these molecules range across many fields, from photolithogrophy to localized drug delivery and investigations on protein folding. 3-cyano-6-hydroxycoumarin (CHCM) has been proposed as a potential super-photoacid with the ability to de-protonate on a picosecond time scale.[1] However, results from the transient absorption spectroscopy indicate that after undergoing excited state proton transfer, the molecule rapidly de-excites into the ground state of the anion becoming a conjugate base. Here we present theoretical interpretation of the experimentally observed photodynamics of CHCM. Gas-phase TD-DFT simulations of a hydrogen-bonded CHCM-water complex indicate that the bright S_1 state undergoes a conical intersection with the dark S_2 state along the proton transfer coordinate (Fig. 1). This conical intersection is a plausible mechanism of radiationless decay of the excited state population. Solvent effects are accounted for via the polarizable continuum model (PCM) and the effective fragment potential (EFP)[2] methods. The hybrid TD-DFT/EFP approach provides realistic representation of the polarizable solvent at a cost comparable to the gas phase TD-DFT computations.

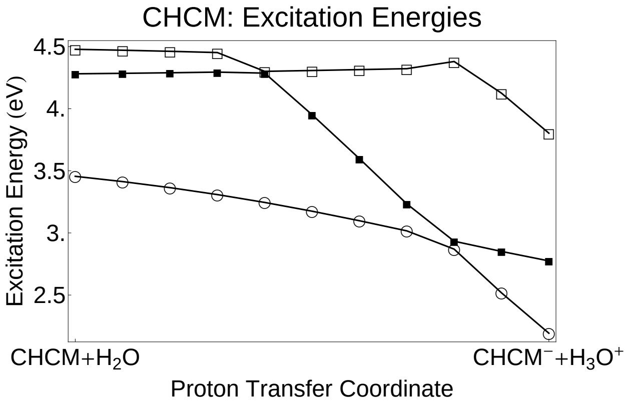

Figure 1: Three lowest electronic excited states of CHCM along the proton transfer coordinate.

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Recent development in pair natural orbital based local coupled cluster methods

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The coupled cluster method has been proven to be robust, accurate and size consistent. It hence is an ideal tool for computational chemistry. The overwhelming problem in applying coupled cluster theory in a large scale (e.g. comparable to the use of density functional theory) is its high computational cost and its unfavorable scaling with system size. Many variants of low order scaling coupled cluster methods have been proposed over the years. Our contribution to this field was to realize that highly efficient and accurate local coupled cluster methods can be based on the concept of pair natural orbitals (PNOs). The original local pair natural orbital coupled cluster method with single- and double excitations (LPNO-CCSD) has been proposed in 2009 and has since been proven to be reliable, efficient and accurate. A drawback of this method was the expansion of the PNOs in the virtual MO basis which led to some higher order scaling steps (up to O(N5)). We have now succeeded to reformulate this method in a fashion that is near linear scaling while retaining the accuracy and all the outstanding features of the original LPNO-CCSD method. The new method is termed "domain based LPNO-CCSD" (DLPNO-CCSD) and is based on the idea to expand the PNOs (which are local in nature) in projected atomic orbitals (PAOs) that belong to domains.[1] The domains are chosen to be large (typically between 10 and 20 atoms) such that an accurate expansion of the PNOs is possible. The original DLPNO-CCSD method had only three cut-off parameters. Any additional truncation in DLPNO-CCSD is based on these three cut-offs, such that the method fully retains its robust black box character. Calculations with more than 450 atoms and 8900 basis functions have been successfully carried out with this methodology. The talk will discuss this method together with other recent developments in the area.

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Tuesday Morning II, Lehár

Quantum-chemical Design of Improved Photoemissive Materials

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Improved photoemissive materials are needed for many applications, ranging from future electron and x-ray sources, such as free-electron x-ray lasers or energy-recovery linear accelerators, through night vision devices, scanners and detectors to solar cells. Several photoemissive properties need to be tailored for optimal applications. Such properties are the workfunction of the surface of the material, the quantum-efficiency (percentage photons turned into emitted electrons) and the angle of the emission cone. Furthermore, optimal devices are expected to be chemically stable under the application conditions. In a series of recent studies [1-3] we have designed improved photoemissive materials with applications-tailored properties using electronic structure calculations.

Motivated by recent results in surface catalysis, we have pointed out by electronic structure calculations that the angle of the emission cone can be tuned by the number of oxide monolayers deposited on metal surfaces [1], such as in MgO:Ag(001). The emission cone is determined by the ratio of the surface parallel and surface perpendicular momenta of the emitted electrons, and these are, in turn, determined by the extent and depth (below the Fermi-level) of the occupied portion of the surface bands in the momentum space (Brillouin-zone) of oxide-covered metals. The emission cone angle is smallest when 3 monolayers of MgO are deposited on Ag(001). Also note that the addition of a few MgO monolayers decreases the workfunction of Ag from 4.6 eV to 3.0 eV (experimentally confirmed).

In another study, we have designed [2] a chemical modification of the seasoned photoemissive material, Cs_2Te, such that the modification will preserve the exceptionally high (~20%) quantum-efficiency of Cs_2Te, while it decreases its workfunction from about 3.0 eV to ~2.4 eV. This is achieved by turning Cs_2Te into a conjugated pi-electron system through acetylation, leading to a new, designer compound of Cs_2TeC_2 in which a parallel arrangement of rod-like 1D polymers of $[TeC_2^{2n-}]_n$ is embedded in a Cs^+ matrix. Analogous compounds, such as Cs_2PdC_2 or Cs_2PtC_2 are known from the inorganic chemistry literature and we have successfully synthesized Cs_2TeC_2, as well. The lower workfunction of Cs_2TeC_2 is advantageous as it allows for using visible laser light instead of ultraviolet one (no photon loss due to wave-length down-conversion) and better pulse-shape control of the laser photons and the emitted electrons.

While searching for low-workfunction alternatives of Cs_2Te, such that preserve its high quantum-efficiency, we became aware of Cs_2Te_5, an existing phase of the Cs-Te system for which large single crystals have also been synthesized in the chemical literature. Also this material has polymeric 1D substructures embedded in Cs^+ matrix, due to polytelluride ions that form infinitely long wavy ribbons of ~4 Å diameter and are arranged parallel to each other. As low as 1.9 eV workfunction value has been calculated for the (010) surface of Cs_2Te_5 and even higher quantum efficiency than that of Cs_2Te is predicted for its illumination by visible photons.

Results from the experimental investigation of the above designer photoemissive materials will also be reviewed.

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Wednesday Morning II, Lehár

Modeling structure and spectra of fluorescent proteins

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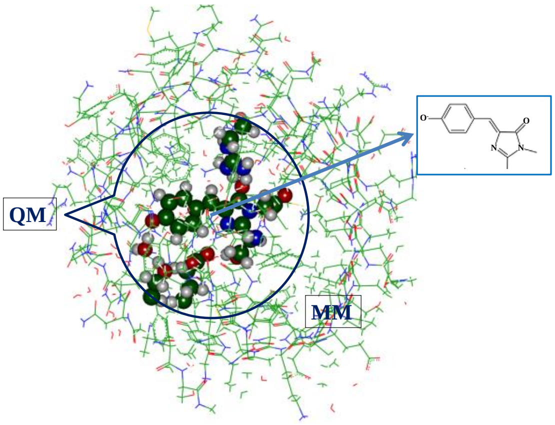
Quantum-based studies of fluorescent proteins, the important markers in live cells, are of great importance to understand the atomic details of their structure, and dynamics. Despite significant coverage this topic in the literature, plenty of details regarding properties of fluorescent proteins remain hidden, even considering the parent member of the family, the wild-type green fluorescent protein (wt-GFP). We apply quantum chemistry and quantum mechanics/molecular mechanics (QM/MM) approaches to characterize structures on the ground and excited electronic states as well as optical spectra of GFP and related proteins. Figure illustrates a model system with the chromophore molecule shown in the right-side inset.



The energy landscape along the assumed proton transfer route in wt-GFP involving the conventional A, I, and B conformational forms with different protonation states of the chromophore was computed and characterized [1]. We computationally constructed GFP variants in which the anionic chromophore is sandwiched between two tyrosine residues in a triple-decker motif [2]. We predict that excitation of the kindling fluorescent protein, the Ala143Gly variant of the natural chromoprotein asFP595, may result in fluorescence from the cationic form of the chromophore which is unusual for the members of GFP family [3]. The emission band from conformations with the *trans* cationic chromophore should be noticeably shifted to the blue side compared to the know red fluorescence from the *cis* anionic species in asFP595.

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The Fifth Age of Quantum Chemistry?

(Theory and Computation of effects of Electron Correlations as they happen!)

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Abstract of the invited talk at the 8th Conference of the International Society of Theoretical Chemical Physics, Budapest, August 25-31, 2013.

A recent publication by **Császár et al**, (2012), which discusses methods for the computation of spectroscopic effects of nuclear motion, delineated this type of modern activity in Quantum Chemistry (QC) from others, which were considered as representing "*the first three ages [of QC], principally defined by developments in electronic structure techniques*" (**Richards**, 1979). Such a categorization makes the point that the technological-experimental-theoretical progress which brought us real-time *femtosecond* spectroscopy, ushered QC (or, theoretical Chemical Physics), into a new research area, that of trying to obtain accurate potential energy surfaces in terms of which to determine the time-dependent dynamics of the motion of nuclei, viewed as classical objects.

At the very dawn of the 21st century, the first announcement of the creation of well-characterized *attosecond* (*as*) pulses (1 *as* = 10^{-18} sec) was made. Obviously, by using such pulses in pump-probe type experiments, the possibility of observing nuclear motion remains. However, now, electronic relative motion may become the object of investigation as well. One fundamental difference is that the observation of electronic relative 'motions' inside atoms and molecules cannot be rigorously described classically. The first application of single *as* pulses with spectroscopic information was reported by **Drescher et al** (2002) on the time-resolved Auger decay.

The time-resolution of such a dynamical process of electronic rearrangements had already been demonstrated theoretically-computationally by **Nicolaides and Mercouris** (1996), via the ab initio solution of the many-electron time-dependent

Schrödinger equation. Upon the first publications of the successful creation of *as* pulses, we argued and demonstrated quantitatively that, by utilizing state-specific wavefunctions, one could prepare and probe the relative 'motion' of pairs of electrons even within the same atom, (of course, the same holds for interatomic dynamics). (**Nicolaides et al** 2002, **Mercouris et al** 2004). Such problems involve the possibility of new types of spectroscopy, where excitation of *strongly correlated electronic motions* could be studied, experimentally and theoretically, within a time-dependent context, and where *the continuous spectrum and resonances within it*, play a dominant role.

The past decade has seen an increasing number of theoretical investigations of time-resolved effects of both nuclear and electronic 'motions' at the attosecond time scale. Obviously, a serious desideratum is for theory to be able to deal with systems of arbitrary electronic structures and for a variety of real-time excitation-de-excitation schemes. In that respect, the requirements of the 5th age (?) of QC are more sophisticated, formally and computationally, than those of the previous ages. In my lecture, I will provide key elements of the theoretical framework in which our work has been carried out.

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Thursday Afternoon II, Bartók

Expectation value coupled cluster approach using the ansatz with generalized double-substitutions cluster operator.

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More than a decade ago, a coupled cluster (CC) ansatz with generalized two-body cluster (GCC) operator was proposed [1, 2]

$$|\Psi\rangle = e^{\hat{\mathcal{T}}}|\Phi\rangle \tag{1}$$

with

$$\hat{\mathcal{T}} = \frac{1}{4}\sum_{p,q,r,s} \mathcal{T}^{pq}_{rs}\tilde{a}^{rs}_{pq}, \tag{2}$$

where $\mathcal{T}^{pq}_{rs}$ is an amplitude related to a replacement created by the related operator $\tilde{a}^{rs}_{pq}$ normal ordered with respect to the reference single determinant $|\Phi\rangle$ and $p,\ q,\ r,\ s$ denote arbitrary orbitals from an orthogonal one-particle basis. Generally, the constituting operators of $\hat{\mathcal{T}}$ (r.h.s. of Eq. (2)) do not mutually commute. Hence, unlike in standard CC approach, a similarity transformed hamiltonian

$$\bar{H}_N = e^{-\hat{\mathcal{T}}}H_N e^{\hat{\mathcal{T}}} \tag{3}$$

represents (at least formally) an infinite expansion. This fact disqualifies the use of $\bar{H}_N$ together with projection technique as a preferential method of determining the amplitudes of $\hat{\mathcal{T}}$. Moreover, the standard projection technique would provide a number of equations that is different from the number of parameters. Therefore, we have explored a possibility of using the ideas from the standard expectation value CC theory (XCC) that is based on the truncation of the expectation value CC expansion using an analysis stemming from the perturbation theory [3], whereas the parameters are obtained from stationarity condition for such a truncated functional. Indeed, a one to one correspondence with XCC(n) can be encountered. A feasibility of reduced scaling non-iterative corrections to standard CCSD as discussed in [4] has been investigated, too. The higher excitation non-iterative corrections from the standard CC can be exactly reproduced using the perturbation theory considerations based on the GCC ansatz. Though the scaling is formally reduced, the corrections are obtained in an iterative procedure that makes the approach less favorable. On the other hand, exact reformulation of CC with higher excitation ranks, such as with singles doubles and triples (CCSDT) is possible with such a reduced scaling with no requirement of triple-excitation amplitudes storage during the iterative procedure.

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Thursday Morning II, Lehár

Understanding the interaction of energetic particles with fusion reactor first walls: from binary collision physics to bond conjugation chemistry

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Thermonuclear fusion reactors have a very special and complicated environment for interactions between the fusion plasma and the wall materials [1]. While the central plasma is fully ionized and contains high-energy keV electrons and ions, the edge regions of the plasma that are in contact with the wall material are much cooler and contain a rich potpourri of electrons, atoms, molecules and radicals. These impact on the materials with energies ranging from a few eV to a few keV, depending on position in the reactor and plasma conditions. Understanding the ways in which these particles interact with the fusion first wall material is a crucial issue in the development of commercially viable fusion power plants, as both too high material erosion, and too high deposition of radioactive tritium to the wall materials, may be showstoppers for the reactor operation. Hence the fusion science community has long attempted to obtain an understanding of the fusion plasma-wall interactions.

The original approach used for modelling the plasma-wall conditions came from high-energy radiation physics, where solution of the classical two-body scattering integral for purely repulsive interatomic potentials is routinely used to determine the sputtering yield and penetration depths of high-energy ions. This approach has been widely used to examine fusion reactor plasma-wall interactions. However, by the late 1990's it became clear it cannot possibly explain the experimentally observed high sputtering of carbon by low kinetic energy (a few eV) incoming D ions. Around 2000, we showed using molecular dynamics and many-body reactive interatomic potentials, which describe chemical bonding, that this carbon sputtering can be understood based on a new kind of special physico-chemical endothermal sputtering reaction, "swift chemical sputtering" [2]. We later showed using both classical and quantum mechanical MD simulations that the mechanism is distinct from both binary collisions and conventional chemical reactions [3]. Most recently, we have shown that in binary plasma-facing materials such as BeC not only the nearest-neighbour bonds but also the conjugation of chemical bonds needs to be considered to properly describe fusion reactor plasma-wall interactions.

In this talk, I will overview this development of understanding from nuclear collision physics to complex bonding chemistry, and give some recent results on swift chemical sputtering of metals [4] and metal carbides [5].

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Dynamics of chemical reactions in the gas phase

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In this talk I will discuss available options for theoretical investigations of the dynamics of chemical reactions in the gas phase. This will include a comparison between standard time-dependent wave-packet and time-independent scattering calculations and also Multi Configurational Time Dependent Hartree (MCTDH) calculations [1]. I will then exemplify this by specifically showing theoretical and experimental results for the reaction between a hydrogen atom and methane forming a hydrogen molecule and a methyl radical. The focus will be on the thermal reaction rate constant [2,3].

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Linear- and sublinear-scaling Møller-Plesset (MP2) and symmetry-adapted perturbation theory (SAPT)

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Linear-scaling methods for both energy calculations at the MP2 level and the direct calculation of intermolecular interactions at the SAPT level are presented using a combination of distance-including integral estimates, linear-scaling integral contractions, and fully AO-based Laplace techniques that allow to access molecules with more than 1000 atoms [1,2]. The key feature of our linear-scaling correlation methods are distance-including two-electron integral estimates that allow to exploit the $1/R^4$ or even $1/R^6$ decay behavior of transformed integrals. Our two-electron integral estimates combine ideas of multipole-expansions and regular Schwarz bounds into so-called QQR integral estimates that are both tight and simple estimates [3] generally applicable in quantum-chemical methods. The largest system calculated so far for determining, e.g., SOS-MP2 energies is a DNA-repair complex comprising 2025 atoms and 20 371 basis functions accessible on simple workstation clusters [1]. To allow for the use of larger basis sets, we employ a combination of the resolution-of-the-identity (RI) for two-electron integrals and a Cholesky-decomposition of pseudo-density matrices within AO-based formulations (Cholesky-decomposed density MP2: CDD-MP2) [4-5]. Besides energy calculations, we present a reformulation of nuclei-selected NMR chemical shieldings at the MP2 level that opens the way to reduce the conventional MO-based $\mathcal{O}(\mathrm{M}^5)$ scaling to $\mathcal{O}(\mathrm{M}^0)$ [6].

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Thursday Afternoon II, Bartók

Useful Parameters of DMRG for Everyday Quantum Chemistry Applications

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DMRG has been utilized to probe the character of acenes, to perform FCI calculations on diatomics, including Cr_2, and a wide array of large inorganic systems. Despite its successes to treat highly-correlated chemical systems, its usage has not expanded beyond the specialized research group. Principally, the wave-function ansatz needed requires both a particular set of orbitals, as well as a specific ordering to recover the appropriate correlations. In the present contribution, we provide a set of rules to enable the widespread use of DMRG for finite chemical systems. Specifically, we provide insight on the type and shape of orbitals that are useful in different situations, the degree of dimensionality that a system can be adequately described, and the effect of orbital ordering and noise and their effects of convergence. We will present these rules based on CASCI and CASSCF calculations using polyaromatic hydrocarbons and transition metal complexes. The latter includes systems that have complicated spin states that have been to-date difficult to elucidate using both single-reference methods and (small) active spaces.

Tuesday Morning II, Brahms

Uncertainty of the rate parameters in the wet CO combustion system

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In recent years, there has been an increased interest in studying the combustion of wet CO as a promising option towards cleaner combustion technologies for power generation from coal or biogenic feedstock in IGCC-CCS plants. Predictive CFD models used in combustor design require accurate kinetic mechanisms to describe the wet CO oxidation chemistry particularly at operating conditions predominant in gas turbines.

Description of the rate parameter k inherently possesses some uncertainty as an inevitable consequence of their experimental determination method or due to assumptions made in theoretical modeling. The uncertainty of even very accurate k measurements is about 30 %, while high level theoretical calculations have an uncertainty of factor 3 [1].

The aim of this work was to improve the performance of a wet CO combustion mechanism and to reduce the uncertainty of crucial rate parameters by applying the optimization methodology of Turányi et al. [2]. Starting from a slightly modified version of the Kéromnès 2013 [3] mechanism, 32 rate coefficients (Arrhenius parameters A, n, E and 3rd body collision efficiencies) of the 11 most influential reactions were optimized based on ignition delay time data (786 shock tube data points, 166 RCM data points for hydrogen ignition, 532/444 for wet CO) and reaction rate coefficient measurements (2012 data points). The joint uncertainty domain of all optimized parameters was determined.

Multiple CHEMKIN simulations were performed to compare the newly optimized mechanism to 15 other mechanisms published between 1999 and 2013 with respect to their reproduction of the 976 wet CO ignition delay time data points, 1711 flame velocity data points and 54 concentration profile data points. The mechanism performances were characterized using a sum-of-square normalized deviation-based error function [2].

Due to a large improvement in RCM simulations, the performance of the new mechanism is 19% better in comparison to the second best mechanism. The uncertainty of the rate parameters could be reduced by 50% or more (in terms of f values).

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Thursday Afternoon I, Bartók

Correlation Methods Using Non-Orthogonal Orbitals

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ABSTRACT: Whenever a molecule contains atoms that have singly occupied orbitals with small overlap, the standard single configuration approaches become ineffective. Such orbitals occur for example during the formation and breaking of chemical bonds and at equilibrium distances for molecules containing transition metals. For such systems, the use of wave functions with non-orthogonal orbitals have great advantages: the simplest forms of these have an accuracy comparable to that of standard CASSCF wave functions using much smaller sets of parameters.

New algorithms have recently been introduced for the optimization of CI-coefficients and orbitals for wave functions with non-orthogonal orbitals. The computational complexity of these new methods is much smaller than that of previously developed methods for non-orthogonal orbitals and standard CASSCF calculations. The efficiency of the method is demonstrated by calculations on molecules with two or three transition metal atoms, thereby mimicking CASSCF calculations with upto 18 electrons in 18 orbitals. A discussion of the extension of the methods to include dynamic correlation is finally discussed.

Wednesday Morning I, Bartók

Extracting complex resonance energies from real calculations.

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Two complementary approaches are presented to demonstrate how the resonance energies and widths can be computed with a good accuracy by using standard quantum chemistry codes. The first approach is the analytic continuation in coupling constants (ACCC) method [1, 2]. The complex resonance energy is obtained from Padé approximation of the $k(\lambda) = \sqrt{E(\lambda)}$ function, where λ is the parameter of an attractive perturbation $V(\lambda)$, that may be an additional nuclear charge or a coordinate-dependent potential. Successful applications to atomic anions and negative amino acid ions will be presented.

The second approach is based on a unified formulation of the quantum theory of unstable states and of their dynamics [3]. The method has a simple and rigorous mathematical framework and is based on non-Hermitian changes of representation of the dynamics and on the analytical properties of the Fourier-Laplace transformation [4]. A hybrid computational scheme borrows from both the Hermitian stabilization methods and the non-Hermitian approaches using complex absorbing potentials. Real energies depending on a real parameter λ provided by real ab initio (or model) calculations are by the transformation $\lambda \to -\imath\,\lambda$ converted into the complex energies of the resonances, similarly as in the ACCC method. The advantages and drawbacks of the second approach will be presented on two models, spherical potential and Fano model.

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Hydrogen activation by frustrated Lewis pairs: Comparison of reactivity models

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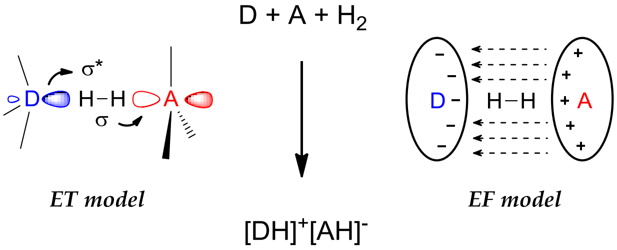
Lewis acid–base pairs with bulky substituents, the so-called frustrated Lewis pairs (FLPs), have recently shown to be reactive species towards small molecules. For instance, they can easily split dihydrogen into a proton/hydride pair and act as transition-metal-free catalysts for the hydrogenation of unsaturated compounds.

Very limited experimental information is available regarding the mechanism of these reactions; however, computational studies provided valuable mechanistic insight [1]. From these investigations, two alternative reactivity models have emerged to interpret the facile FLP-mediated heterolytic cleavage of H_2. Both models assume that the reaction takes place via reactive intermediates involving properly oriented Lewis donor (D) and acceptor (A) partners, but they differ conceptually in defining the basic interactions in the activation process. In the electron transfer (ET) model, the cleavage of H_2 is related to synergistic electron donations incorporating both active centers of the FLP and the bridging hydrogen, whereas the electric field (EF) model suggests that the heterolytic bond cleavage occurs as a result of electrostatic polarization by the strong field being present between the donor and acceptor partners (see scheme below).

In this contribution, the two models will be paralleled in terms of their abilities to account for the computed reaction characteristics as well as for the observed reactivities [2].



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Monday Morning II, Bartók

Calculations of circular dichroism and circularly polarized luminscence spectra of biologically relevant chromophors.

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Circularly polarized luminscence (CPL) measures the differential emission of left and right circularly polarized light by a chiral sample, and can therefore be regarded as the emission spectroscopic counterpart to electronic circular dichroism (CD). When the equilibrium structure of the electronically excited state differs significantly from the ground state geometry and the excited state has a lifetime long enough to allow the molecule to structurally relax, the CD and CPL bands are dissimilar, even to the extent of having opposite signs. Thus, a comparison of CPL and CD spectra allows to investigate the molecular dynamics following the electronic excitation. After the period of significant developements in the 1980s CPL spectroscopy has fallen into relative obscurity, but nowadays a renewed interest in it can be observed, boosted by the recently emerged possibility of quantum chemical calculations of the CPL spectra for chemically interesting molecules [1,2].

We have carried out calculations of CD and CPL spectra for several biologically relevant chromphores, including several variants of green fluorescen protein chromophors: blue fluorescent protein (BFP), enhanced cyan fluorescent protein, (CFP), enhanced green fluorescent protein (GFP), yellow fluorescent protein (YFP). Our main aim has been to check how the protonation and deprotonation processes, and the presence of protein environment, influence the CD and CPL spectra and therefore to investigate the potential of CPL as a structural probe of electronic excited states. The presence of environment has been modeled employing polarizable embedding density functional theory (PE-DFT) method [3], in fully polarizable QM/MM/PCM model [4].

The CPL spectrum has also been calculated for thioflavin-T. Fluorescence spectroscopy of thioflavin-T intercalated in proteins is a well-known method of investigation of protein misfolding. Thioflavin-T is achiral, but it exhibits an induced CD effect in a chiral environment (for example when intercalated in a protein) [5]. We have therefore decided to carry out quantum chemical calculations of HOMO-LUMO excited state potential energy surface of thioflavin-T in different environments and of the associated CPL spectra, in order to investigate what are the capabilities of induced CPL of thioflavin-T in protein structural studies.

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Thursday Morning II, Bartók

Electron excitation energies from reduced density matrices: extended random phase approximation and linear response theory approaches

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Reduced density matrices, RDM's, hold a promise of removing wavefunction from description of electronic systems and replacing a full N-electron Schrödinger equation by, in principle simpler, equations involving reduced density matrices only. Recently, methods that employ reduced density matrices in the description of time-dependent systems have emerged, which, accessing time-dependent 1-RDM or a frequency-dependent linear response function, allows one to obtain electronic excitation energies [1, 2]. Another possibility for obtaining excitation energies based solely on the ground state one- and two-electron reduced density matrices is offered by an approximation to the Rowe's equation of motion [3].

The approximation we have proposed involves expanding the excitation operator that enters the Rowe’s equation up to all single excitations and some double excitations (the so-called diagonal doubles), assuming a correlated vacuum, and retaining only elements of 1- and 2-RDM’s in the resulting equations [4]. The method, called Extended Random Phase Approximation 2 – ERPA2, has been applied together with the correlated RDM’s resulting from the antisymmetrized product of strongly orthogonalized geminal (APSG) theory to a number of molecules. ERPA2 that employs the APSG 1- and 2-electron density matrices provides exact singlet excitation energies for two-electron systems and highly accurate excitations for four-electron species. This can be linked to the near-satisfaction of the killer condition by the excitation operator that underlies the method. For larger systems at equilibrium geometry ERPA is comparable in accuracy to RPA. The former method, however, is capable of reproducing double excitations (that RPA misses completely) but they are usually in large error. For molecules at stretched bond geometries ERPA outperforms RPA and predicts potential energy curves of the correct shape.

It can be shown that ERPA equations with the reduced density matrices obtained by employing the strongly orthogonal germinal theory are directly related to the linear response theory equations formulated within the APSG framework. This opens an avenue to proposing a range-separation scheme and employing short-range density functionals in ERPA equations, which, in turn, leads to a significant improvement in the accuracy of the predicted excitation energies.

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Thursday Afternoon I, Bartók

Recent progress in the active-space electron-attached and ionized equation-of-motion coupled-cluster methodologies

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The active-space coupled-cluster (CC) and equation-of-motion (EOM) CC methods, in which higher-order components of the cluster and excitation operators are selected via active orbitals, represent the most straightforward way of incorporating multi-reference (MR) concepts within the CC framework [1]. At the same time, the most natural way of describing electronic structure of radicals and biradicals, and other valence systems around closed shells is provided by the electron-attached (EA) and ionized (IP) EOMCC theories, and their multiply attached and multiply ionized extensions. This talk will discuss our recent contributions to the EA/IP and active-space EOMCC methodologies, including the development of the doubly electron-attached (DEA) and doubly ionized (DIP) EOMCC theories with up to 4-particle-2-hole (4p2h) and 4-hole-2-particle (4h2p) excitations, and their inexpensive active-space variants that provide high accuracies of the full 4p2h/4h2p treatment with the CPU steps that scale as steps of CCSD times small prefactors [2]. The discussion of the key formal concepts will be augmented by the examples of benchmark calculations and selected molecular applications, including bond breaking, low-lying electronic states of radicals, and singlet-triplet and singlet-singlet gaps in biradical systems. The extension of the active-space ideas to the EA/IP, DEA/DIP, and similar EOMCC theories may bring us one step closer to a situation, where we may be able to perform accurate, straightforward, relatively inexpensive, and spin- and symmetry-adapted CC computations for some of the most typical MR problems without resorting to the complicated steps of the genuine MRCC theories.

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Tuesday Morning I, Bartók

Electronic structure of manganese(II) nitrosyl compounds: a bifocal view.

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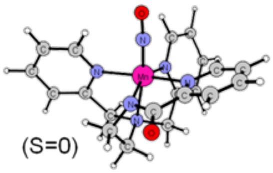
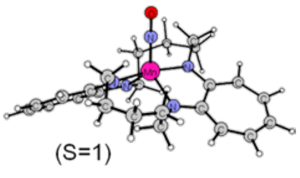
Manganese nitrosyl systems $\{MnNO\}^6$ are almost invariably diamagnetic (S=0), containing a (close to) linear Mn−N−O unit, although an intermediate (S=1) may be close-lying[1], and in exceptional cases become the ground state. Linear mononitrosyl compounds are traditionally regarded as containing nitrosyl bound to Mn^{I} as NO^{+}, although it is generally recognized that the covalent nature of the M−NO interaction precludes the assignment of a formal oxidation state to the metal and NO in nitrosyl complexes. The Enemark-Feltham notation $\{MnNO\}^6$ in fact stresses the electron delocalization in the MnNO unit, without being committed a certain formal oxidation state on either M or NO. This “noninnocent” character of the NO ligand also complicates the theoretical description of the electronic structure of metal-NO complexes, which is inherently multiconfigurational in nature.

In this work, we present a description of the electronic structure and relative energies of the ground states and the lowest excited states of a number of manganese nitrosyl systems containing an $\{MnNO\}^6$ unit in heme and non-heme environments, making use of multiconfigurational ab initio method C(R)ASPT2. Electron delocalization in the Mn-NO bond is manifested both by the strongly mixed character of the bonding and antibonding $Mn3d_{\pi}$−$NO\pi^*$ combinations and by the strong multiconfigurational character of the wave function. Such a wave function may, however, be transformed in a straightforward manner into a valence-bond-style description in terms of contributions from Mn^{II}−NO^{0}, Mn^{I}−NO^{+}, Mn^{III}−NO^{-}, by subjecting the appropriate subset of delocalized molecular orbitals in the CASSCF wave function to a (Cholesky) localization procedure. Quite strikingly, such an analysis indicates that the bonding in manganese nitrosyl systems is built from a resonance hybrid of Mn^{III}−NO^{-} and Mn^{II}−NO^{0}, with the former as the dominant resonance structure. Little or no Mn^{I}−NO^{+} character is found in any of the complexes studied.



$Mn(PaPy_3)(NO)^+$



Mn(5,5-TC)(NO)

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Thursday Morning II, Bartók

MCPT-PNOF5:
A useful method for dealing with strongly correlated systems

Mario Piris

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A series of natural orbital functionals, known in the literature as PNOFi (i=1-5), has been proposed recently [1] using a reconstruction of the two-particle reduced-density matrix (2-RDM) in terms of the one-particle RDM by ensuring necessary N-representability positivity conditions on the 2-RDM. PNOF5 [2] has proved to be the most successful. It yields a remarkable description of systems including substantial static correlation, like transition metal dimers [3], and good bond dissociation curves [4]. This functional affords a one-electron picture that agrees closely with the orbitals provided by the valence bond method and standard molecular orbital calculations [5].

It has been recently shown [6] that PNOF5 can be obtained as a particular case of the energy expression of an APSG wavefunction [7]. This result guarantees strictly the N-representability, size-extensivity and size-consistency of PNOF5. Accordingly, PNOF5 takes into account most of the non-dynamical effects, but also an important part of the dynamical electron correlation corresponding to the intrapair (intrageminal) interactions. However, no interpair (intergeminal) correlation is described by PNOF5. To correct this problem, perturbation corrections have been implemented to the generating PNOF5-wavefunction using a multiconfiguration perturbation theory size consistent at second order (SC2-MCPT) [8, 9].

In this presentation, the theory behind the MCPT-PNOF5 is outlined. Several examples ranging from van der Waals systems to covalent molecules are presented to illustrate the potential of the method. Our results are accurate values as compared to the available experimental data.

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Thursday Morning II, Bartók

Recent Progress in Multireference Hilbert-Space Coupled Cluster Methods: Explicit Correlation, Massively Parallel Implementation, and USS Corrections

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[1] J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Czech Republic
[2] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia
[3] W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, USA

The standard coupled cluster (CC) method, like other single reference methods, exhibits a poor performance when quasidegeneracies are encountered, unless high-level excitations are included. One possibility how to solve this problem is a multireference generalization of the CC method (MRCC) based on the Jeziorski-Monkhorst ansatz. This leads to Hilbert-space MRCC methods, which can be state-universal (SU MRCC), or state-specific (Brillouin-Wigner MRCC, Mukherjee's MRCC). The state-universal method suffers from the intruder state problem, while the Brillouin-Wigner method is not rigorously size-extensive, leaving the Mukherjee's MRCC (MkCC) as the most promising one from this class of methods. Although MkCC method still does not satisfy some requirements from a "wish-list" of the properties of an ideal MRCC, it represents a reasonably accurate and practicable method for small model spaces. We have thus pursued the development of explicitly correlated version of this method, at the SD level and recently also with the non-iterative triples, employing the SP ansatz and standard approximation together with the Slater (F12) correlation factor. The results confirm the significantly faster convergence with respect to the basis set limit compared to the "traditional" one.

Application of MRCC methods to realistic chemical systems requires development of parallelized implementations, which can efficiently exploit available supercomputer architectures. We present such implementations of the BWCC and MkCC methods at singles, doubles, and perturbative triples level, which offer excellent scaling up to several thousand cores.

The Universal State-Selective (USS) corrections proposed by K. Kowalski aim to improve MRCC energies towards FCI and can be applied to any type of MRCC theory based on the Jeziorski-Monkhorst Ansatz. For BWCCSD, the main effect of the USS correction is to approximately restore size-extensivity, while for MkCCSD it seems to (at least partially) take into account Hamiltonian matrix elements not present in the original MkCCSD theory due to the separate projection manifolds employed. We have recently implemented the USS correction including non-diagonal terms in the NWChem program and compare the results with the previously published approximate one, which contained only diagonal terms (USSD).

Friday Morning I, Bartók

Efficient calculations of accurate interaction energies for nano-scale systems

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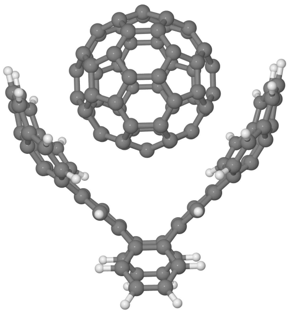
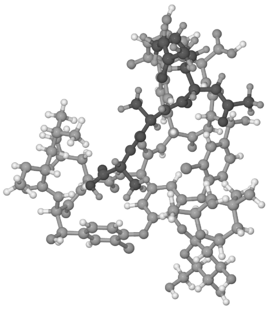
Calculations of interaction energies for nano-scale systems containing a few hundred atoms are currently beyond the reach of wave-function based *ab initio* methods. A commonly applied remedy for this problem is to use “density functional theory plus dispersion” (DFT-D) approaches but these methods are inherently limited due to the approximate character of the atom-atom type dispersion. Symmetry-adapted perturbation theory based on the DFT description of the monomers [SAPT(DFT)] provides high-quality interaction energies. Dispersion energies computed from the coupled Kohn-Sham dynamic density-density response functions used within the SAPT(DFT) method are very accurate and can solve the above-mentioned problem. We present a new highly-efficient implementation of the algorithm [1] that removes several computational barriers present in available implementations and enables calculations of dispersion energies for systems as large as 230 atoms and 5000 basis functions with modest computational resources. We applied this new code to two systems: the buckycatcher ($C_{60}H_{24}$) complex with fullerene (C_{60}) and the vancomycin ($C_{66}H_{75}Cl_2N_9O_{24}$) complex with di-acetyl-Lys-D-Ala-D-Ala ($C_{16}H_{28}N_4O_6$) bacterial wall precursor, both calculations performed with triple-zeta quality basis sets. Our implementation makes it possible to finally use *ab initio* computed dispersion energies in DFT-D schemes. We made also improvements in other interaction energy components, including the most time consuming exchange-dispersion term opening the full SAPT(DFT) capabilities to the nano-scale systems.



buckycatcher–fullerene



vancomycin–peptide

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Wednesday Morning II, Lehár

Nanoscale Carbon for DNA Sequencing and Drug Delivery

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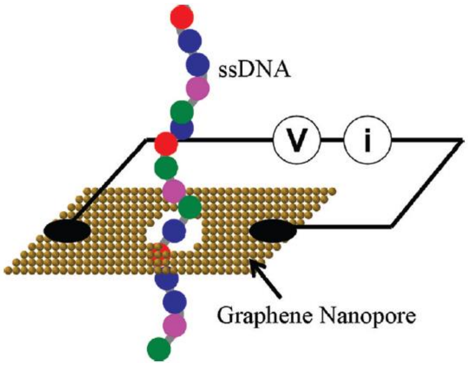
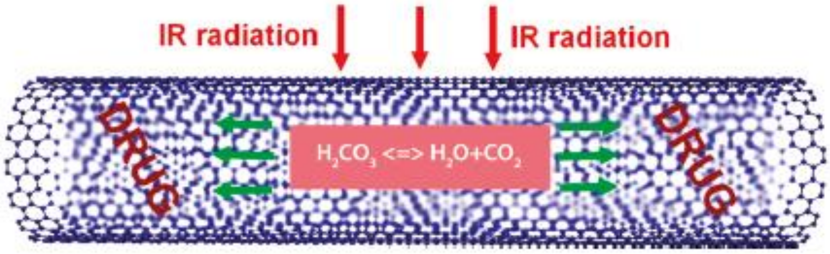
Graphene and carbon nanotubes (CNT) constitute a new class of materials exhibiting unique chemical and physical properties, and leading to new devices and applications. We will discuss our theoretical work aimed at the use of nanoscale carbon in biology and medicine.



We proposed a graphene nanopore device for detecting the base sequence of a nucleic acid [1]. Our ab initio calculations indicate that due to significant differences in the conductance spectra the proposed device has adequate sensitivity to discriminate between different nucleotides. Moreover, we show that the nucleotide conductance spectrum is affected little by its orientation inside the graphene nanopore. The proposed technique may be extremely useful for real applications in developing ultrafast, low-cost DNA sequencing methods.



We investigated the boiling process inside CNTs and showed that confinement substantially increases the boiling temperature and that a small temperature growth above the boiling point dramatically raises the inside pressure [2]. Capillary theory successfully predicts the boiling point elevation down to 2 nm, below which large deviations between the theory and atomistic simulation take place. Considering water droplets, we showed that the ordinary sequence of events with increasing temperature – boiling followed by disappearance of the liquid-vapor boundary at the critical point – is reversed inside CNTs [3]. Precise control over boiling by CNT diameter, together with the rapid growth of inside pressure above the boiling point, suggests a novel drug delivery protocol. Polar drug molecules are packaged inside CNTs [4]; the latter are delivered into living tissues and heated by laser. Solvent boiling facilitates drug release. This work was highlighted in the June 25, 2011 issue of *New Scientist* and other news media.

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Sunday Afternoon , Pátria

Ultrafast Quantum/Molecular Mechanics Monte Carlo Simulations

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A very fast and accurate quantum/molecular mechanics (QM/MM) method is presented for determining thermodynamic averages in solutions (or for active sites within a flexible environment such as in a protein). The solute is described quantum mechanically and held fixed during averaging over the MM solvent/environment configurations. Instead of repeating the quantum calculations, the response of the system to the long range electric field of the solvent is precalculated using generalized polarizabilities (GPs). The latter describe the response of the system to a spatially modulated electric field. The electric potential of the solvent is represented as a linear combination of mathematically simple (e.g., sine wave) potentials. Avoiding the recalculation of the QM wavefunction speeds up the simulations typically by 4 orders or more while retaining the full accuracy of the QM/MM calculations ([1] and Fig. 1). Unlike the usual QM/MM enzyme models, polarizability (induction) contributions of the QM system are included. This is essential to reproduce full QM/MM accurately. The Generalized Polarizability method has been implemented in a Monte Carlo program attached to the PQS suite and works with a number of water force fields. The AMBER protein force field has also been implemented. Gradient implementation is in progress.

Current applications focus in the behavior of halide ions near the air/water interface [2], the calculation of solvent effects on NMR spectra [3], and S_N2 reactions in water ([4] and Fig. 2.)

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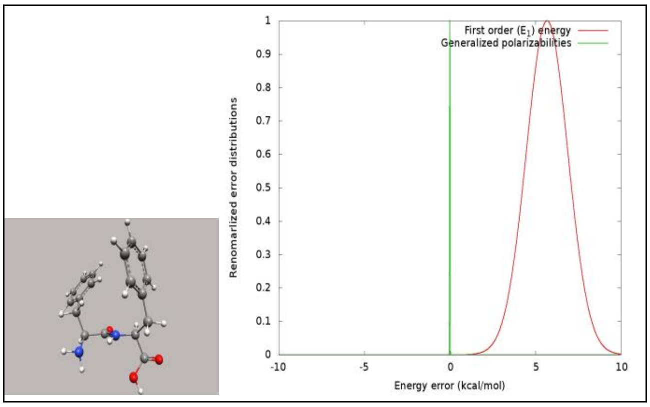

Fig. 1.

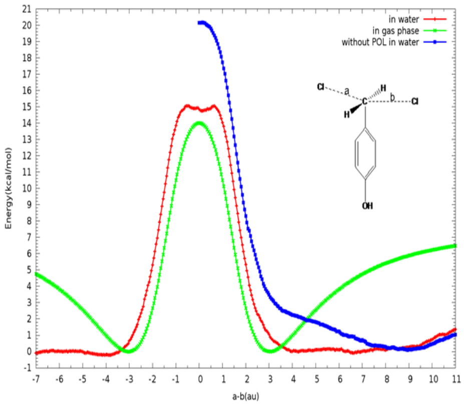

Fig. 2

Monday Afternoon I, Pátria

Aspects of accurate, relativistic quantum chemical calculations

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POB 55 (A. I. Virtasen aukio 1), 00014 Helsinki, Finland

The Dirac-Fock-Breit Hamiltonian is an excellent, but not complete, description of electronic systems. The largest missing piece is QED, that also can be independently estimated. An interesting test case are the M-C distances in the monocyanides MCN, M=Cu-Au [1]. These calculations were very recently improved [2] and the M=Au case may show preliminary evidence for QED effects.

Another case that we have pushed to the MP2 basis-set limit are the metallophilic test systems $[P(AuPH_3)_4]^+$ [3].

A task requiring as accurate calculations as possible are the determinations of nuclear quadrupole moments, eQ, from experimental quadrupole coupling constants, e^2Qq/h, and calculations of the electric field gradient, eq. The latest review is [4].

The author's latest reviews on the physical fundamentals and chemical applications of relativistic calculations are [5] and [6], respectively.

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Thursday Afternoon I, Bartók

Multireference DFT based on Strongly Orthogonal Geminals

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Abstract

Our group is among many searching for a practical multireference theory of molecular electronic structure. Electron correlation effects, which are the aim of any multireference theory, can be divided into phenomenologicaly distinct, but theoretically inseparable classes of *static* and *dynamic* correlation. Therefore it is appealing to treat each class with the tools best suited for the job, i.e. multireference (MR) wavefunctions to describe the static part, combined with the density functionals (DFT) for the dynamic part.

The strongly reference geminal model is an appealing multireference theory to use in the combined MR/DFT theory. The model is well defined, size-consistent, variational, and relatively inexpensive computationally. It has a clear physical interpretation, and is flexible enough to include essentially all static correlation. We investigate its use with correlation-only functionals. The simplest approach is to use an existing functional, re-scaled to mitigate double counting of the correlation effects already included in the geminal model. The more advanced approach is to build a functional from scratch. Both approaches are compared and contrasted by applying them to the geometries of diatomic molecules. Possible future modifications of the DFT treatment are also discussed.

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Monday Morning II, Lehár

Phase-space visualization of quantum phase transitions in the molecular vibron model

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We will present a phase-space visualization of quantum phase transition in a linear algebraic model, the vibron U(3) model. This model has been used to study the rovibrational properties in diatomic and polyatomic molecules and has turned to be very useful to study symmetry properties of quantum systems. We will show that entropic uncertainty relations give a more appropriate description of the QPT than the usual variance-based uncertainty relation in this model. We will propose a characterization of the vibron-model quantum phase transition by means of the zeros of the Husimi distribution.

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Two-Metal Ion Catalysis by Ribonuclease H

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The formation and cleavage of phosphate bonds is essential in most biological processes including nucleic acid processing. Many enzymes that catalyze phosphate hydrolysis require two bound divalent metal ions. To elucidate the poorly understood mechanism of this ubiquitous reaction we carry out hybrid quantum-classical QM/MM free energy simulations. In our calculations, we focus on the catalytic cleavage of the RNA backbone in an RNA/DNA hybrid by Bacillus halodurans Ribonuclease H (RNase H). RNase H is a prototypical member of a large family of enzymes that use two-metal ion catalysis to process nucleic acids. The active site of RNase H is almost identical across species with respect to sequence and structure, including the human enzyme and the HIV Reverse Transcriptase (HIV-RT) RNase H domain. HIV-RT is essential to viral replication, which makes it an important target in HIV drug research. In our simulations, we combine [1] Hamiltonian replica exchange with a finite-temperature string method to calculate the QM/MM free energy surface underlying the catalytic reaction. We use a histogram-free reweighting method to obtain this surface from combined multidimensional string simulations. Our method allows us to search for the optimal pathway in multiple dimensions and, therefore, to identify the detailed sequence of steps in the RNA cleavage reaction. From our calculations, coupled proton transfer reactions emerge as central factors in the catalytic RNA cleavage reaction. We also find that both Mg^{2+} ions are required for catalysis. Replacing either one of them with a Ca^{2+} ion abolishes the catalytic activity. Double Mn^{2+} or Ca^{2+} ion replacements have been characterized experimentally and our calculations agree well with measured catalytic activities. Moreover, single ion replacements, which can be performed straightforwardly in simulations, also point to the specific functional role of the metal ions in the catalytic reaction. Our new proton transfer mechanism is consistent with the kinetic effects of protein mutations and RNA backbone modifications. Moreover, the accurate transition state structure provides an ideal target for future structure-based drug design studies of new HIV-specific inhibitors.

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Adaptive UF PPS Model Study of Structures and Reactions in Biomolecules: New Selective Bio-Molecular Probes through High Magnetic Fields

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Adaptive models of ultrafast polarization phase-selective (UF-PPS) EM radiation structures and their signatures have been tested on probing dynamics and structure (imaging) of even highly coherent correlated electrons in molecules. New theoretical and experimental studies indicate their comparative advantages when applied to ultrafast events [1]. Here we demonstrate their application in bio-molecules, such as recently discovered [2] unusual cluster structures as well as unusual enzymatic, photonic and redox synthesis and electron transfers and turnovers. The models identified molecular systems that can function as specific redox agents *in vivo* and *in vitro* and indicated novel highly selective coherent channels. Of particular interest for the theoretical modeling is identification of electron and vibrational coupling. Previous models had significant difficulties when evaluating this important contribution. We discuss here results of our work and compare it to the experimental results.

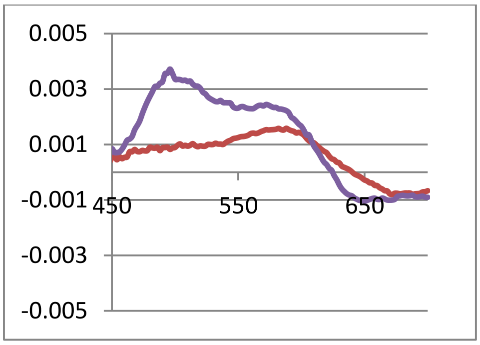

Fig 1.Temperature and magnetic field (25T) dependent PPS studies of Fe clusters in protein [3] are used to test predictions of theoretical models (x -axis is nm, y axis -PPS units).

Acknowledgement This research was carried out in part at the High Performance Computing (HPC) center at LSU and National High Magnetic Field Laboratory (NHMFL). The work was supported by UF-PPS Study Project (K Rupnik PI).

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Active Thermochemical Tables: Uncertainty Quantification in Thermochemistry

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The accepted standard for expressing uncertainties attached to thermochemical values, such as enthalpies of formation, bond dissociation energies, etc., which is followed by virtually all thermochemical tabulations (such as CODATA, Gurvich et al., JANAF, etc.), is to provide the best estimate of a 95% confidence interval [1]. This is in contrast to the ubiquitous mean absolute deviation (MAD), which is frequently used in benchmarking electronic structure computational approaches, and which leads to an underestimate of the recommended thermochemical uncertainty by a factor of 2-3.

Active Thermochemical Tables (ATcT) [2] have garnered wide recognition for delivering benchmarks of unprecedented accuracy, and were successfully used in developing and benchmarking two of the most accurate electronic structure methods in existence, W4 [3] and HEAT III [4], both of which achieve sub-kJ/mol accuracy and otherwise could not have been evaluated in earnest. ATcT are currently involved in developing and benchmarking additional high-level theoretical methods [5, 6].

As opposed to the sequential approach underlying traditional thermochemical tabulations, ATcT are based on constructing, analyzing, correcting, and solving a Thermochemical Network (TN), and represent a new paradigm for obtaining accurate, reliable, and internally consistent thermochemical values, accompanied by uncertainties that adhere to the accepted standard. In addition to increased accuracy and statistically sound uncertainties, both of which are highly relevant to benchmarking state-of-the-art electronic structure methods, ATcT introduces a number of new commodities to the field of thermochemistry. Inter alia, the ATcT uncertainties are accompanied by a complete set of covariances. Though covariances are completely ignored in traditional tabulations, thus leaving no choice but to treat the tabulated values as if they were entirely uncorrelated, the enthalpies of formation that are obtained via a sequential approach are in fact very highly correlated. The TN approach of ATcT softens this correlation, and the superior accuracy achieved by ATcT is related to TN features that lower the inter-species correlation. In general, covariances influence the propagation of the uncertainties of the enthalpies of formation to reaction enthalpies, and thus affect, for example, the correct propagation of thermochemical uncertainties through models of complex chemical environments, such as simulations of combustion processes or atmospheric chemistry, whose chemical mechanisms involve a large number of species and reactions. Another valuable ATcT feature that is related to the treatment of uncertainties is the ability to perform variance decomposition, which allows, for example, an explicit quantification of the influence of each and every thermochemically-relevant determination present in the TN.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Contract No. DE-AC02-06CH11357.

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Monday Afternoon I, Lehár

Analytic DFT calculations of anharmonic force constants

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We present a recursive scheme for the analytic calculation of cubic and quartic force constants at the density functional level of theory[1] based on an open-ended, atomic-orbital-based scheme for calculating higher-order molecular properties.[2] All possible rules for eliminating response parameters using the $k(2n+1)$ rules[3] have been implemented, allowing for a stringent test of the correctness of the code and allowing us to explore the computational costs of different approaches for calculating higher-order molecular properties. The use of recursive programming allows for an open-ended, compact code, and we will present results for the sextic force contants at the Hartree–Fock level of theory.

The evaluation of one- and two-electron integrals differentiated with respect to geometrical perturbations follows the approach of Reine, Tellgren and Helgaker[4], integrating the differentiated integrals in Hermite rather than Cartesian orbital basis, as implemented in the Gen1Int[5] and a local two-electron integral program.[6] The contributions arising from derivatives of the exchange–correlation kernel are evaluated using automatic differentation.[7]

In addition to outlining the key features of the approach for calculating analytic DFT cubic and quartic force fields, results for anharmonic force constants obtained both for small molecules and for molecular systems containing up to 10-20 atoms will be presented. The main focus of the discussion will be on the analysis of the importance of electron correlation, as described by DFT, on cubic and quartic force constants.

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Wednesday Morning II, Bartók

Electrons in motion, or: Can we make a Hartree-Fock state?

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Recent progress in generating intense laser fields, has pushed the timescale for probing dynamical processes in atomic and molecular systems down to the attosecond domain (1 as=10^{-18} s). In parallel with experiments, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes our efforts to extend *ab initio* wavefunction based methods of stationary electronic structure theory, to the explicitly time-dependent domain. In particular, time-dependent configuration interaction (TD-CI) and time-dependent complete active space SCF method (TD-CASSCF) [1] will be introduced as systematically improvable, correlated methods for propagating electronic wavefunctions in real time.

Armed with these methods, we seek to control electron motion at will, using shaped, ultrashort laser pulses. For instance, we may ask as to whether it is possible to create *a Hartree-Fock state* – a hitherto purely theoretical concept – starting from the (correlated) ground state of an atom or molecule [3]. In particular alkaline earth atoms seem suitable for an actual experiment to realize controlled, correlated electron motion, *cf.* Fig.1. A Hartree-Fock state is an electron wavepacket, a non-stationary state whose fate is also of interest: We find that electron correlation reappears on an attosecond timescale, when starting from a Hartree-Fock reference. Finally, we also demonstrate how explicitly time-dependent methods can be used to calculate response properties of molecular systems after non-resonant or resonant, excitation with ultrashort laser pulses [2]

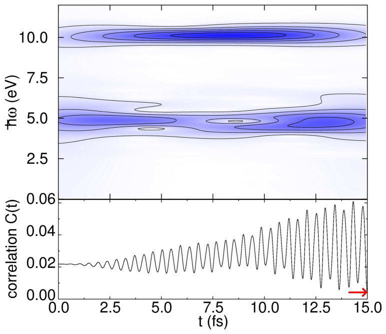

Fig.1: A series of laser pulses obtained from optimal control theory (upper), controls the amount of "correlation" in a Mg atom (below) [3].

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Monday Afternoon I, Bartók

Towards the multiscale modeling of catalysis

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We have embarked on a multistage research program on the multiscale theory, simulation, computation and understanding of catalysis along two lines: i) enzymes and ii) heterogeneous nanocatalysts.

Progress will be illustrated by one or more of the following projects:

I) **Electron transfer between proteins**[1]– the role of interfacial residues in governing the solvent dynamics to accelerate the electron transfer[2] including the effects of quantum decoherence[3]. The techniques involved are classical Molecular Dynamics combined with the Pathway Model of electron transfer (within Marcus theory), constrained Density Functional Theory (DFT), Born-Oppenheimer Molecular Dynamics and a new methodology for quantum decoherence.

II) **Nanocatalysts for in-situ upgrading of the oil sands** – We are working with Pedro Pereira's experimental bitumen upgrading group to help design new nanocatalysts that can be introduced to the oil sands in order to do some of the upgrading underground, leaving undesirable products in the reservoir. So far we are focusing on the hydrogenation of benzene as a model. Techniques include DFT on periodic (VASP)[4] and cluster (deMon)[5] models and a fast semiempirical method from the Miyamoto lab, UAQCMD – Ultra-Accelerated Quantum Chemical Molecular Dyamics.

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Wednesday Afternoon , Lehár

Oxidation states from wavefunction analysis

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The concept of oxidation state (OS) is widespread in transition metal chemistry and in the study of redox and catalytic reactions. The reactivity, spin-state, spectroscopic and geometrical features of transition metal complexes are often rationalized on the basis of the oxidation state of the metal center. In coordination chemistry, the OS is typically defined as *the charge left on the metal after all ligands have been removed in their normal, closed shell, configuration.* Thus, to formal OS are obtained by assigning integer number of electrons to the atoms/ligands according to some rules. In complicated bonding situations involving non-innocent ligands or in intermediates or transition states of catalytic reactions the formal OS assignment may be rather ambiguous.

Oxidation states are intrinsically related to electronic distribution, but the atomic charge after the formal electron counting is only imaginary; that *an atom would have under certain conterfactual conditions.*[1] Even though electronic populations do change with oxidation/reduction of the metal center, they are only a pointer of the oxidation state. Even spin populations need a previous knowledge of the electronic structure (spin state),[2] and are clearly futile in pure singlet states.

There have been several attempts to derive OS from first principles.[2, 3] In this presentation we will introduce a very simple alternative based upon an a posteriori wavefunction analysis. The method is based on the use of of the so-called effective atomic orbitals of Mayer,[4, 5] treating alpha and beta electrons separately and extending the formalism to molecular fragments (if necessary). Moreover, the occupation numbers of the effective atomic orbitals may be used to quantify to which extent a particular wavefunction conforms with the ideal OS assignation. The method is general and it can formally be applied to any molecular system. We will discuss the analysis of the intermediates and active species involved in the C-H catalytic hydroxylation carried out by a Fe(Pytacn) complex,[6] where the presence of high-valent species such as Fe^{V}-oxo was suggested.

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Monday Afternoon I, Pátria

The relativistic electron correlation problem

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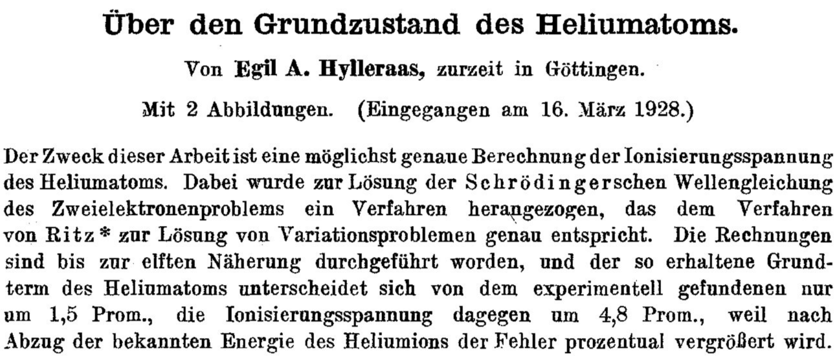

Über den Grundzustand des Heliumatoms.

Von **Egil A. Hylleraas,** zurzeit in Göttingen.

Mit 2 Abbildungen. (Eingegangen am 16. März 1928.)

Der Zweck dieser Arbeit ist eine möglichst genaue Berechnung der Ionisierungsspannung des Heliumatoms. Dabei wurde zur Lösung der Schrödingerschen Wellengleichung des Zweielektronenproblems ein Verfahren herangezogen, das dem Verfahren von **Ritz** * zur Lösung von Variationsproblemen genau entspricht. Die Rechnungen sind bis zur elften Näherung durchgeführt worden, und der so erhaltene Grundterm des Heliumatoms unterscheidet sich von dem experimentell gefundenen nur um 1,5 Prom., die Ionisierungsspannung dagegen um 4,8 Prom., weil nach Abzug der bekannten Energie des Heliumions der Fehler prozentual vergrößert wird.

In 1928 Egil Andersen Hylleraas published the first of a series of papers on the helium isoelectronic series, setting new standards for the accuracy of approximate quantum mechanical calculations. Although Hylleraas would later (1955) provide an elegant analytical solution to the relativistic one-electron atom, he did not consider relativistic two-electron atoms. This is a tougher problem since the Dirac equation has solutions of both positive and negative energy, which in turn implies that the Dirac-Coulomb Hamiltonian has no bound solutions. A solution which avoids invoking the full machinery of QED is to embed the Dirac-Coulomb Hamiltonian by projection operators, thus treating the negative-energy orbitals as an orthogonal complement. In the present contribution we explore the optimal solution to the relativistic two-electron atom within this no-pair approximation.

Tuesday Afternoon I, Bartók

Getting to Lewis electron pairs from quantum mechanical calculations: Maximum Probability Domains

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A method is presented to recover Lewis' picture from quantum mechanical calculations[1]: a spatial domain is defined by maximizing the probability to find a pair of electrons in it. This definition has not only the advantage of simplicity. It can be applied to any type of wave function (examples: Hartree-Fock, or correlated with Jastrow factors)[2]. It does not only recover Lewis' picture in trivial organic molecules, but also in crystals. In the same spirit, other questions can be asked, beyond the electron pair concept, e.g., identifying ions[3].

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Friday Morning I, Pátria

Local correlation methods for molecules and solids

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During the last two decades local correlation methods have evolved to an efficient computational tool to treat extended molecular systems and also periodic infinte systems like solids[1] beyond the realm of density functional theory. In the first part of my contribution I will discuss so called pair approximation in local coupled cluster theory: In the context of local coupled cluster theory individual pairs of occupied orbitals are usually discriminated on the basis of the inter orbital distance, or the size of the MP2 estimate of the pair energy. Only strong pairs are treated at the full coupled cluster level, while weak pairs are treated just at the MP2 level. Yet MP2 might be problematic for certain situations, for example π-stacking interactions. It will be shown that an approach based on ring-CCD including diagrams up to third order is clearly superior to MP2 and still computationally cheap.

In the second part of my contribution I will discuss recent advances in the correlated treatment of solids. First results of the recently implemented periodic local MP2 program based on orbital specific virtuals will be presented.

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Wednesday Morning I, Bartók

Formation of doubly excited states by XUV excitation and Auger spectra in presence of strong IR fields

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Doubly excited states do not have a strict mathematical correspondence in standard quantum mechanics. Rather, their energies are associated with poles of the scattering matrix in the complex plane. The time-honored method of (global) complex scaling (GCS) has been offering easy and mathematically well-defined access to these states: they can be related to square-integrable eigenfunctions of an analytically continued, non-hermitian Hamiltonian (see [1] for a recent discussion in a broader context). In the variant of "exterior complex scaling" (ECS) the method can be applied when the Hamiltonian can be analytically continued only outside a finite range. Both methods use the coordinate transformation

$$\vec{x} \longrightarrow \vec{z}_{R_0,\theta}(x) = \begin{cases} \vec{x} & \text{for} \quad |\vec{x}| < R_0 \\ \left[e^{i\theta}(|\vec{x}| - R_0) + R_0\right] \hat{x} & \text{for} \quad |\vec{x}| > R_0 \end{cases},$$

where GCS corresponds to $R_0 = 0$.

GCS has rarely been applied to time-dependent problems, because the complex continued wave function cannot easily be associated with a physical counterpart. For ECS, only recently comprehensive numerical evidence was presented that the wave function $\Psi_{R_0,\theta}(\vec{x}, t)$ resulting from propagation with the complex scaled Hamiltionian $H_{R_0,\theta}(t)$ agrees with the exact solution on $|\vec{x}| < R_0$. Also, with "infinite range" ECS (irECS) a particularly efficient discretization was found [2].

Using irECS, we are able perform *ab initio* calculations of formation of doubly excited states of He and other two-electron atoms by XUV pulses. In addition, fully differential (3d) photo-electron momentum spectra were calculated by the newly developed time-dependent surface flux (tSURFF) method [2]. Dependence of the Auger spectra on time-delayed IR fields will be shown.

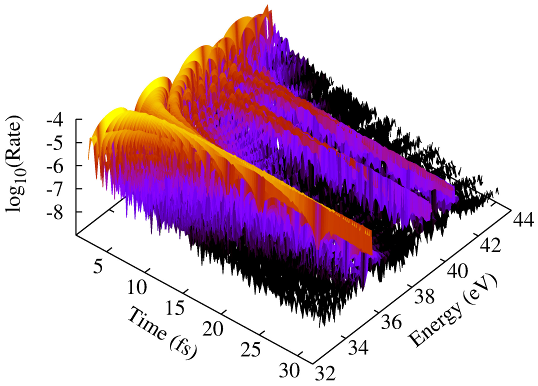

Figure: Buildup rate $d\sigma(E,t)/dt$ for the Fano-profile in the photo-emission spectrum of the lowest few doubly excited $L = 1$ states of Helium after excitation by an attosecond XUV pulse.

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Monday Morning I, Pátria

Symmetry Breaking and Restoration

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Symmetries play a crucial role in electronic structure theory. I will discuss our recent developments regarding the self-consistent variation-after-projection optimization of symmetry-projected wave functions **[1,2]** for number, spin S^2 and S_z, complex conjugation, point group, and lattice translation. The resulting method yields a comprehensive black-box treatment of static correlation with mean-field computational cost. The ensuing wave function is of high quality multireference character competitive with CASSCF. The method can be applied to excited states and spectral functions **[3]** and has been extended to non-orthogonal multi-references **[4]**. Applications to both molecules and lattice systems will be presented. The curse of the thermodynamic limit and the quest for a low-cost treatment of residual correlations will also be addressed.

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Wednesday Morning I, Bartók

The quantum dynamics experienced by a single molecular eigenstate excited by incoherent light

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Abstract

Contrary to conventional wisdom that all dynamics is a result of interference (or "dephasing") between many (at least 2) energy eigenstates, we show that when a continuum of states is present, even a single molecular eigenstate undergoes "steady-state" quantum dynamics. Moreover, this type of dynamics can be initiated by incoherent (e.g., solar) light sources. Continua are invariably involved in molecular systems due to a variety of sources such as the ever present bath modes; spontaneously emitted photons; the detachment of electrons; or the dissociation of chemical bonds. Contrary to a single bound energy-eigenfunction which is a real ("standing-waves") function that carries no flux, hence has no dynamics, a single (complex) continuum energy-eigenfunction carries "steady-state" flux given by the group velocity of the energetically narrow wave packet it represents. When this energy eigenfunction is a multi-mode resonance embedded in a continuum via a chain of intramolecular couplings, this dynamics may be initiated by any (light) source, and is controlled, contrary to coherent wave packet dynamics, by the position of the resonance rather than its width.

Tuesday Morning II, Brahms

Uncertainty Quantification and Data Discrimination in Combustion Kinetic Modeling

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Chemical mechanisms in combustion consist of large numbers of elementary reactions. Models to describe such mechanisms must therefore include many rate parameters in order to describe all of these reactions. The rate parameters cannot be determined from first principles and so must be measured. Measuring individual rate parameters can be difficult, however, and estimates from theory are known to be highly uncertain.

As computational power has increased, it has become easier to simulate complex combustion systems with large fuels. Indeed, our ability to describe the combustion mechanisms of these fuels has outstripped our ability to precisely measure individual rate parameters, which has left us with large numbers of rate parameters with large uncertainty. This has led to a tendency to tune chemical reaction models to match experimental measurements, adjusting the model rate parameters until the model can reproduce the observations. In principle, at least, such adjustments result in a model with a set of rate parameters that are closer to reality and have tighter uncertainties.

Tuning models against experimental data has two significant pitfalls, however. The experimental measurements (the training set) and the parameters for adjustment are often chosen on an ad-hoc basis. This ensures a set of model parameters that will reliably reproduce the training set. Without an estimate of the uncertainty, however, it is not possible to reliably describe the model's performance outside the training set. Furthermore, the training set may include many experiments are chemically similar, meaning that perhaps only one condition need have been measured. This has resulted in a proliferation of chemical kinetic models published by different groups.

This talk will discuss recent development of experimental and modeling methodologies, in particular the Method of Uncertainty Minimization using Polynomial Chaos Expansions. These methodologies use data analytics, uncertainty analysis, and experimental design techniques to produce a rigorously optimized model with quantified prediction uncertainty, while at the same time minimizing experimental measurement duplication. Rigorous optimization ensures that the recommended rate parameter values are indeed the best, based on the data provided. A quantified prediction uncertainty provides that the behavior of the model is known outside the training set. Experimental design ensures that the recommended model is based on best set of experimental measurements available. Examples of the application of the method will include estimating rates of radical attack on small hydrocarbons using detailed kinetics measurements in shock tubes and optimization of combustion reaction models using laminar flame speeds and ignition delay times.

Graphene, Silicene and Forgotten Lessons of Surface Science

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The nickname of a 'miracle material' has been widely accepted by the graphene community. It normally means the material superior properties. However, all the properties are only the outward manifestation of the graphene wonderful nature. The real miracle of graphene is that it is a union of two entities: the physical and chemical ones, each of which is unique in its own way. The physical superior properties of graphene are widely discussed. Much less has been told about its chemical uniqueness that is generated by carbon atoms packing in a flat honeycomb structure. The structure, based on benzenoid units, offers three neighbors to each carbon atom leaving the atom fourth valence electron on its own. These electrons form the pool of *odd* electrons whose behavior might change from the covalent bonding, characteristic for π electrons, to free electrons of radicals when the interaction between the electrons becomes weaker and weaker. The two electron states belong to different limit cases in terms of the electron correlation: π electrons are not correlated while radical electrons are strongly correlated so that two electrons with different spins occupy different places in the space. π-Electrons of the benzene molecule belong to the first limit case while odd electrons of benzenoid units of graphene (as well as fullerenes and carbon nanotubes) are correlated, which is caused by the difference in the C-C bond lengths while the critical length of 1.395Å and below marks the first limit case [1].

The odd electrons correlation and the exceptionally close relationship between the correlation extent and benzenoid bond structure make graphene material highly sensitive to any kind of external action such as morphological changing, chemical modification, mechanical loading and fixation, application of electric and magnetic field, and so forth thus making it structurally-and-electronically non stable. The “fluid” electronic structure accompanied with the flexible space structure aggravated with equal-energy topological phase transitions are the main reasons for failures of stable technologies for converting graphene from semimetal to semiconductor [2]. The way to improve the situation can be seen in inhibiting the odd electrons correlation by depositing one-layer adsorbate of either carbon (graphene) or silicon (silicene) on a proper substrate.

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Thursday Morning II, Brahms

Free energy analyses on cluster deformations by cumulant mechanics

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We have formulated extended dynamics that describe fluctuation around classical variables in terms of cumulants and applied these methodologies to quantal and statistical mechanics and dynamics [1-2]. In this study, we propose a method for the variational determination of free energy within cumulant mechanics. Within second-order approximation to cumulant variables, the free energy functional for the one-dimensional case is given as

$$F=\frac{1}{2m}\left(p_0^2+\sigma h\right)-\frac{k_BT}{2}\left(1+\ln\left(2\pi\sigma\right)\right)+\int\frac{dq}{\sqrt{2\pi\lambda}}\exp\left[-\frac{\left(q-q_0\right)^2}{2\lambda}\right]V\left(q\right)-\frac{k_BT}{2}\left(1+\ln\left(2\pi\lambda\right)\right).$$

where q (q_0) and p (p_0) are the classical position and momentum and σ and λ are the second-order cumulant variables for position and momentum, respectively. h is the Planck constant originated from the statistical normalization relation. Free energy minima are optimized as a function of q_0, p_0, λ, and σ. This method can be easily generalize to treat multi-dimensional many-body systems.

For the 7 particle Morse cluster, where particles interact with the inter-particle Morse potential $V_M\left(r_{ij}\right)=\exp\left(-2\left(r_{ij}-R_e\right)\right)-\exp\left(-\left(r_{ij}-R_e\right)\right)$, free energy landscape along the two-dimensional reaction coordinates (RCs; distances between 1 and 3, r_{13}, and 1 and 7, r_{17} are chosen) for a deformation of cluster from PBP structures (left-upper and right-lower regions) to COCT structure (right-upper region), where we set temperature as k_BT=0.01 (/unit) and mass as m=1000, is given in Figure 1. Free energy barrier from the PBP structure is 0.41 (/unit), which is in good accordance with that obtained by conventional method such as metadynamics. This method requires less computational cost than the ordinary molecular dynamics simulations indicating promising method to evaluate free energy surface s for given systems.

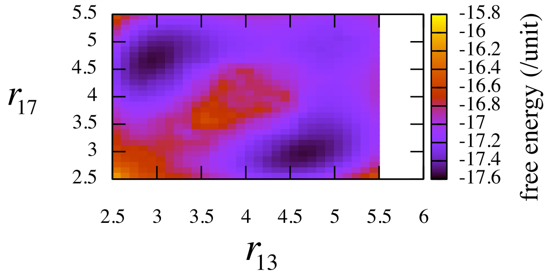

Figure 1 Free energy landscape along r_{13}-r_{17} axis

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Insights on Enzyme Catalysis

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Catalysis and enzyme design are among the most fascinating and challenging aspects of chemical and biological research. Recent years have witnessed great progress in this area with computational techniques playing a central role as manifested by several recent de-novo designs of enzymes. Unfortunately, the improvement in catalytic rates of the resulting designs leave lot to be desired, emphasizing the complexity and variability of enzymes. We believe that part of the reason is insufficient consideration of factors that control enzyme reactivity.

Here we propose a better understanding of various factors that govern enzyme reactivity. We will use the valence bond (VB) based QM/MM approach.[1-3] VB is a quantum method that provides unique chemical insights and explanations to reaction mechanisms. The distinctive abilities of VB stem from the description of the wave-function as a mixture of well-defined electronic configurations which are easily interpreted as chemical structures. Our work will emphasize the contribution and advantage of the VB based methods compared with the other QM/MM methods in providing insights into chemical reactivity and enzyme catalysis. We will show the potential of these insights to improve enzyme design. We will focus on the S_N2 reaction which is the first step in the conversion of haloalkanes into alcohols within Haloalkane Dehalogenase (DhlA), and try to better understand the effect of the protein on the catalytic behavior.

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Wednesday Morning II, Lehár

The present status of DFT studies on water oxidation in photosystem II is described. It is argued that a full understanding of all steps is close. In each S-transition, the manganese that is oxidized and the proton released are strongly implicated, and structures of all intermediates have been determined. For the S_2-state, recent important experimental findings support key elements of the structure and the mechanism. In this mechanism, the O-O bond is formed between an oxyl radical in the center of the cluster and a Mn-bridging μ-oxo ligand, which was suggested already in 2006. The DFT structure of the oxygen evolving complex, suggested in 2008, is very similar to the recent (2011) high-resolution X-ray structure.

Wednesday Afternoon , Bartók

Convergence of the bipolar expansion for the Coulomb potential

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The bipolar expansion for the Coulomb potential,

$$\frac{1}{|\mathbf{r_1} - \mathbf{R} - \mathbf{r_2}|} = \sum c_{l_1 l_2 l_3}^{m_1 m_2} \, Y_{l_1}^{m_1}(\theta_1, \phi_1) \, Y_{l_2}^{m_2}(\theta_2, \phi_2) \, Y_{l_3}^{-m_1-m_2}(\theta_3, \phi_3) \, v_{l_1,l_2,l_3}(r_1, r_2, R),$$

is a four-region expansion: in three of the regions, one distance is dominant ($R > r_1 + r_2$, $r_1 > r_2 + R$, or $r_2 > r_1 + R$); in the fourth, the radii satisfy the triangle inequality, ($r_1 + r_2 > R > |r_1 - r_2|$), and associated charge densities would be interpenetrating. The radial function $v_{l_1,l_2,l_3}(r_1, r_2, R)$ has a different functional form in each region. (See, for instance, Ref. [1].)

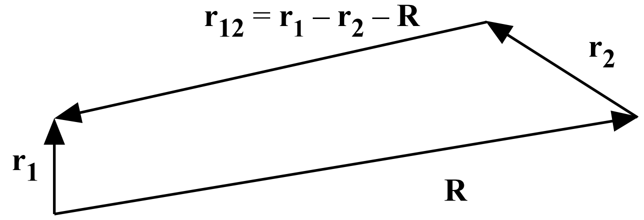

Figure 1: $\mathbf{r_1}$, $\mathbf{r_2}$, and $\mathbf{R}$, drawn for the case $R > r_1 + r_2$.

When any one distance is dominant, for example $R > r_1 + r_2$, then the bipolar expansion converges absolutely by comparison with the series

$$\frac{1}{R - r_1 - r_2} = \sum_{l_1=0}^{\infty} \sum_{l_1=0}^{\infty} \binom{l_1 + l_2}{l_1} r_1^{l_1} r_2^{l_2} R^{-l_1-l_2-1}$$

For the interpenetrating region, it has only recently been shown numerically that the convergence is conditional[2]: there are terms whose magnitudes decrease like $1/(l_1 + l_2)$, e.g., like the harmonic series. This study discusses both analytics of the interpenetrating series and numerical consequences.

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Thursday Morning II, Lehár

Nucleation and growth of methane clathrate hydrate crystal - molecular dynamics study

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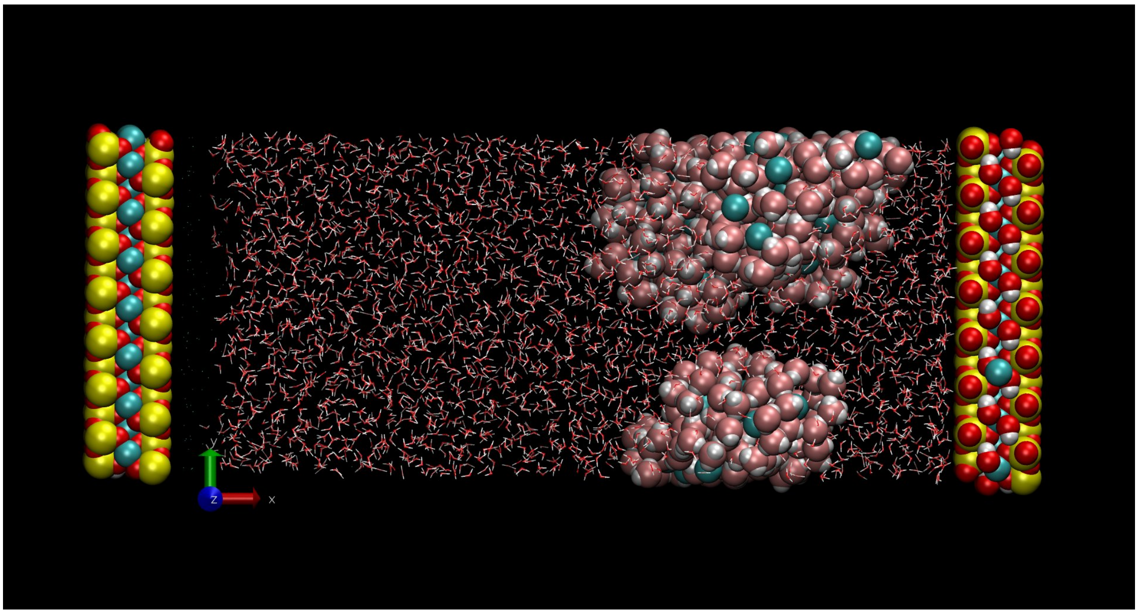
Clathrate hydrates (CH) are solid structures formed by water molecules organised in cages. Inside those cages guest molecules are encapsulated. Vast amounts of methane CH's found in marine sediments and in permafrost regions may become important source of natural gas in near future. However, still little is known about the exact mechanism of their formation and dissociation what hinders development of extraction technologies.

To fill this gap several molecular dynamics simulations of the systems containing methane dissolved in liquid water were performed. Layers of the clay were attached to the rectangular unit cell to represent the natural environment in which hydrates are being formed. The role of the temperature, concentration of methane, ionic strength of the solution and type of clay on the nucleation process was considered. Microsecond range of trajectory was collected in nVT ensemble for systems containing about 16000 atoms using TIP4P2005 for water, single L-J site for methane and CLAYFF for clay atoms.

Picture below depicts system containing water solution of methane (with methane concentration equal to 25% of methane concentration found in hydrate) after 1245ns of trajectory. Nucleation center was formed close to pyrophyllite clay surface.



Monday Morning I, Bartók

Hybrid quantum/classical and fragmentation techniques for radicals and electronic excited states

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Hybrid quantum mechanics/molecular mechanics (QM/MM) and fragmentation techniques allow rigorous description of extended systems including biological polymers and macromolecules. This work focuses on applicability of QM/MM and fragmentation methods to open-shell and electronically excited systems.

In the first part of the talk, we will focus on our recent developments in the Effective Fragment Potential (EFP) method.[1] The EFP method is a model potential designed for describing non-covalent interactions from first principles and without using fitted parameters. When combined with QM subsystem, EFP overcomes the most significant limitations of QM/MM by replacing empirical MM interactions and QM-MM coupling by parameter-free first-principles based ones, while retaining the computational efficiency of QM/MM. We will discuss QM/EFP schemes for electronic excited and ionized states as well as treatment of dispersion in QM/EFP systems.

In the second part, we will talk about our recent work on extending the energy decomposition analysis within the Fragment Molecular Orbital (FMO) method to open-shell systems.[2] In the FMO formalism, one performs fragment calculations in the electrostatic field of other fragments, mutually self-consistent with each other. Extension of the energy decomposition analysis to open-shell states allows one to quantify inter- and intra-molecular interactions in systems containing radicals or high-spin species. The new technique is applied to a tripeptide trialanine upon hydrogen abstraction (HA) from various sites, to characterize and compare the intra-molecular non-covalent interactions in the radical peptide.

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Thursday Afternoon II, Lehár

Spatial decomposition and assignment of vibrational spectra: Dipolar coupling and correlated particle motion in aqueous Li^+

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Terahertz (THz) spectroscopy has been demonstrated to be able to detect even small solute-induced changes of the hydrogen bond dynamics in aqueous solutions [1, 2]. The THz spectra reveal long-ranged dynamical correlations around solutes that can be approached theoretically by analyzing vibrational spectra in a spatially-resolved manner. Recently, it has been shown on the basis of *ab initio* MD simulations that intra- and intermolecular vibrational modes of liquid water are modulated by the solvation shells in a qualitatively different manner [3]. In order to probe these effects, novel spatial decomposition methods have been introduced that allow for deep insights into the mechanisms of this frequency-dependent dynamics and the resulting distance-dependent dipolar responses of the solvating water molecules [3, 4].

Here, several spatial decomposition schemes for infrared spectra are used to reveal the distinct distance- and frequency-dependent contributions of the solvation shells to the spectral response in aqueous solutions of Li^+, based on extensive *ab initio* MD simulations. The solvent's response to the presence of the solute is systematically disentangled and reveals important structure-spectra relationships in the THz spectral window, highlighting differences between dipolar response and correlations in particle motion [5].

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Monday Afternoon I, Bartók

Modeling of enzymatic organophosphate hydrolysis: towards design of new biocatalysts

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Some organophosphate pesticides tend to accumulate in aquatic environment and their decontamination belongs now to urgent research tasks. Enzymatic biodegradation seems to be one of the most promising options, but none of known enzymes existing in nature are sufficiently useful for this purpose, so new mutated variants started to be subject patent applications [1] and even theoretical design [2]. However, the catalytic activity of recently designed enzyme [2] could be considerably improved via directed evolution and the role of additional mutations is not completely understood. In order to explore the catalytic activity detailed molecular mechanism of diethyl-7-hydroxycoumaryinyl phosphate hydrolysis by modified adenosine deaminase [2] has been modeled within ONIOM approach. Reactant interactions with active site residues have been analyzed using ab initio and atomic multipole approximation in order to interpret observed catalytic activity changes resulting from aminoacid mutations. In addition the utility of atomic multipole expansion in exploring relative stabilities of interacting biomolecules will be also discussed [3]

Acknowledgements: Work supported in part by Wrocław Research Center EIT+ under BIOMED project “Biotechnologies and advanced medical technologies” POIG 01.01.02-002-003./08-00 and Wrocław University of Technology

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Thursday Afternoon I, Lehár

Molecular dynamics and reactive trajectory approaches to modeling of electrochemical reactions near the liquid/solid interface

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A reactive trajectory approach for the study of proton discharge at charged metal surfaces (here a simplistic model of a platinum surface is used) is discussed. The approach is based on an extension of a minimalistic empirical valence bond (EVB) model to study proton transfer in the bulk [1]. Extensive quantum mechanical density functional theory calculations were parametrized for the EVB force field. The model is used to investigate reactive (discharging) proton trajectories that were started in the bulk of a water film adsorbed on charged metal electrodes. The results indicate a transition between a reaction-dominated regime at moderate negative charges, where the rate constant increases exponentially, to a "transport limited" regime where the transfer rate is almost independent of the surface charge density (at more negative surface charge densities) [2, 3].

The results are critically analysed in view of the nature of the approximations and together with free energy calculations for quasi-stationary hydronium and Zundel ion species. Some recent results of extensions of the model whcih introduce background electrolytes with and without specific ion adsorption are also presented.

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Wednesday Afternoon , Pátria

How much do, and can, we ``understand” about the ground state of NO_3

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The ground electronic state of the nitrate radical has been of great interest to theoreticians for decades. Historically, questions centered on the geometrical structure of this strange molecule, with significant debate centering on the question of whether it is threefold symmetric (point group D_{3h}) or distorted to C_{2v}, an issue that led to significant confusion both with regards to the consistency of computational results and indeed, even the proper interpretation of the question. Another, and more recent, focus of study has been the vibrational energy level structure in the ground electronic state, both in the position of the levels and the designation of the states by the usual harmonic oscillator numbering system. The issue of the vibrational levels, especially the large (> 400 cm-1) discrepancy between calculated and assigned positions for the v_3 degenerate stretching fundamental, has been quite controversial in the past several years. This talk will review some recent results for this molecule, specifically the construction of an elaborate quasidiabatic Hamiltonian using equation-of-motion coupled-cluster theory, and its application to the calculation of energy levels and spectra involving the ground electronic state of NO_3. The degree to which one can describe the spectacularly rich infrared spectrum of this molecule (which has many characteristics of an electronic spectrum) will be emphasized, especially the limitations of trying to understand it in the conventional manner based on harmonic oscillator mode numbering and standard expectations about mode intensities.

Friday Morning II, Pátria

Local correlation-energy increments for solids – ground and excited states

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Possibilities to determine solid-state properties by means of many-body expansions in terms of finite subsystems are critically reviewed. Different variants are shown to be needed for molecular crystals, ionic solids, and semiconductors.

At the example of LiH, it is demonstrated that milli-Hartree accuracy for the cohesive energy, E_{coh}, can be obtained both for the Hartree-Fock and the correlation piece of E_{coh}, by expansions based on suitably prepared zeroth-order model systems [1].

Difficulties due to delocalization and transferability problems for incremental expansions in metals are discussed, and several suggestions to overcome these problems for group 1, 2 (11, 12) metals are compared [2].

Finally, calculation of electron correlation effects for excited states and band structures within incremental approaches is considered. While for localized excitations a direct determination of energy increments with extension of an initial orbital space is possible [3], increments for both diagonal and off-diagonal matrix elements between intermediate quasi-particle states are needed in the delocalized case. Two possible routes for the latter purpose ('correlate then localize' and 'localize then correlate') are critically compared, in the light of new results [4].

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Does Direct Perturbation Theory converge?

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Direct Perturbation Theory (DPT) is an elegant approach to treat relativistic effects in a perturbative manner. The basic idea behind DPT is to change the metric in the Dirac equation and then to employ a perturbative expansion in powers of c^{-2} with c as the speed of light. This expansion gives the correct non-relativistic limit and is in principle applicable in any order.

Implementation of DPT is facilitated if the theory is formulated in terms of energy derivatives using the method of Lagrange multipliers. In this manner, analytic derivative techniques can be exploited.

However, for any perturbative method to become a reliable tool, convergence needs to be ensured. Kutzelnigg showed that DPT converges for hydrogen-like atoms up until the nuclear charge of Z = 137 [1]. To which degree this behaviour is generalizable to atoms and molecules with more than one electron will be discussed for Hartree-Fock as well as for correlated methods.

Furthermore, a simplified "one-electron" variant of lowest-order DPT (DPT2-1e) which does not require relativistic two-electron integrals is introduced and its performance is investigated.

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Wednesday Morning II, Pátria

In memoriam Shi Shavitt: Application of MR-CI methods to describe the potential energy surfaces of O_3 and the dimer of O_2

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The contribution by Isaiah Shavitt to the development of MR-CI method is certainly dominating, as well represented by his early book [1]. For a recent review on MR-CI method see Ref. [2]. As a tribute to him, in this paper we will present some recent results obtained with MR-CISD method and it corrected versions on systems formed by oxygen atoms.

An accurate description of the complicated shape of the potential energy surface (PES) of ozone and the characterization of the highly excited vibration states is of crucial importance for dealing with various unsolved issues in its spectroscopy and dynamics. Well designed MR-CISD and MR-AQCC surfaces are presented wich describe the important features of the surface, in particular for large variations of nuclear displacements along the minimum energy path (MEP). We discuss typical problems we face when performing MR-CI type calculations. The resulting new analytical representation of PES is the most accurate available today and allows an accurate theoretical predictions for ozone vibrational band centres at the energy range near the dissociation threshold.

The other example deals with chemiluminescence of oxigene molecule: it is perhaps the most widely known of such processes, even used as demonstration experiment in high school. The currently accepted interpretation predicts the dimer of two singlet oxygen molecules to be responsible for the red light emission, however, no theoretical study could fully support this mechanism so far. In this study, the potential energy surfaces of the singlet oxygen dimer were investigated using the highest level MCSCF and multi-reference CI approaches, to locate excited state minima and structures corresponding to experimentally observed transition energies. However, no such minima could be found. Performing therefore collision simulations on these repulsive surfaces, it was indeed possible to reproduce the observed red emission.

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Multi-component molecular methods for hydrogen bonded systems and positronic compounds

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Recently, we have developed some first-principles approaches for multi-component systems including both electrons and nuclei (or positron) quantum-mechanically: (I) Multi-component molecular orbital (MC_MO) [1, 2], DFT (MC_DFT) [3], quantum Monte Carlo (MC_QMC) [4], and (II) *ab initio* path integral (PI) [5, 6] methods.

First, we demonstrated that HCN, as the simplest nitrile molecule, can bind a positron by the most accurate QMC approach [4]. We have also found that the positron affinity (PA) value of acetonitrile with electronic 6-31++G(2df,2pd) and positronic [15s15p3d2f1g] basis set with the CI scheme of MC_MO method is calculated as 4.96 mhartree [2], which agrees to within 25% with the recent experimental value of 6.6 mhartree by Danielson *et al*. [7].

Next, we will show some theoretical aspects of path integral simulation with 2nd and 4th order Trotter expansion. Then, we will show some computational results with PIMD simulation for the H/D isotope effect on deprotonated water dimer anion $H_3O_2^-$ [5,6] and muonated molecular systems.

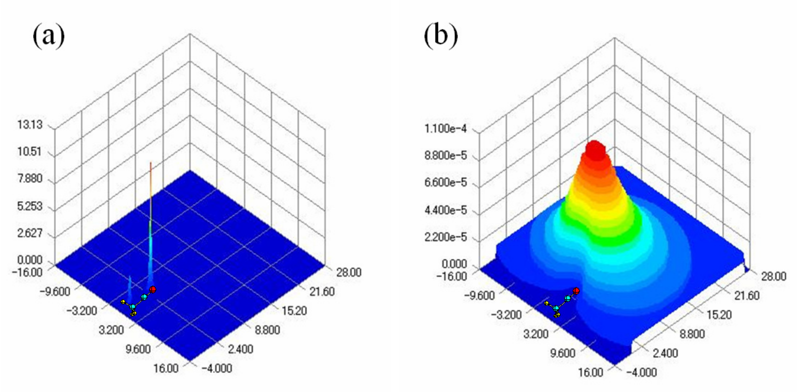

Figure 1: (a) Electronic and (b) positronic densities of [CH_3CN; e^+] species.

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Molecular Dynamics Assessment of Concentration- and Head-Size-Dependent Effects on $C_{12}E_x$ Aggregation

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Since the dawn of the application of polymeric micelles as drug delivery systems in the late 1980s [1], numerous polymer self-assemblies have been extensively investigated, designated to deliver various substances including: low-molecular-weight anticancer drugs, contrast/imaging agents, proteins, plasmid DNA, antisense DNA, and more recently short interfering RNA (siRNA). Promising building blocks of drug delivery containers are deemed nonionic surfactants of poly(ethylene glycol) alkyl ethers, abbreviated as C_nE_x, where $\boldsymbol{n}$ refers to the number of carbon atoms in the hydrocarbon backbone of the tail and $\boldsymbol{x}$ – to the number of oxyethylene units in the hydrophilic head of the molecule.

The aim of the present study is to determine the head-size effect on the geometry transitions of $C_{12}E_x$ ($\boldsymbol{x}$=3÷8) aggregates upon concentration increase. MARTINI [2] coarse-graining molecular dynamic simulations (NPT/293 K) of the self-assembly process of the listed surfactants in aqueous solution were carried out with PBC applied. Extending earlier estimates [3], aggregation numbers and aggregate shapes were defined and the concentrations at which certain shape transitions occurred were specified. The latter were quantified in terms of shape anisotropy supplemented by a detailed structural analysis of the micelles as a function of aggregation number.

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Thursday Morning II, Lehár

Intermolecular Force Field Parameterization from First Principles

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Understanding the forces acting between atoms and molecules is crucial for elucidation the organization and, as a consequence, the physicochemical properties of matter both in the gas and in the condensed phase. Equipped with the advanced intermolecular perturbation theory [1], it is now very timely to rethink a number of *ad hoc* concepts such as "π–π" or "ion–π" interactions invoked to describe the forces that drive association between molecules. Recent developments in the Symmetry Adapted Perturbation Theory (SAPT) [2] allow partitioning of the total intermolecular energy into different physically well-defined contributions (electrostatic, exchange-repulsion, dispersion and induction) against which the corresponding terms in the force field can be separately parametrized. An approach is described to include the missing *charge penetration* energy term *directly* into a force field using a sum over pairwise electrostatic energies between spherical atoms as originally suggested by Spackman [3]. This important contribution to the intermolecular potential can be further refined to reproduce the accurate electrostatic energy between monomers in a dimer by allowing for the radial contraction-expansion of atomic charge densities. This new short-range term is supplemented by a long-range electrostatic contribution described with atomic multipoles (up to quadrupoles) based on distributed multipole analysis [4, 5]. The other components of a force field (exchange-repulsion and dispersion) are parametrized to reproduce the corresponding contributions calculated within the SAPT framework. As a proof-of-concept, we have developed the force field parameters suitable for modeling intermolecular interactions between polycyclic aromatic hydrocarbons (PAH) [6]. We show that it is now possible to have a balanced force field suitable for molecular simulations of large molecules avoiding error cancellation to a large extent.

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Conformations of Small Molecules

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While the role and importance of conformations and conformational analysis for understanding the functioning of biomolecules has been recognized long ago, the relevance of presence of multiple conformers (or even isomers) for molecules routinely encountered in organic and inorganic synthesis and analysis is often overlooked. Very small molecules consisting of a dozen of atoms may possess an obvious global minimum on the potential energy surface, easily found by following chemical intuition. On the contrary, somewhat larger molecules, which have become accessible to DFT methods during the last decade, can possess multiple local minima, and determining the lowest energy one by intuition alone can yield misleading results. Furthermore, depending on the barriers on interconversion pathways, solvent, reaction temperature, etc, the different geometries may represent either isomers, or conformers, the latter being in a chemical equilibrium and giving rise to a Boltzmann distribution of the various forms.

In this contribution, several examples are presented, where only a careful conformational analysis has made it possible to understand the particular chemical or physical phenomenon. The examples include:

- pK_a calculations of organic bases (bipiperidine and bimorpholine) [1]
- Tautomeric equilibria in substituted purinamines [2]
- Assignment of *J*-coupling constants in NMR spectra of bicyclooctanes [3]
- Interpretation of Vibrational Circular Dichroism spectra of chlorooxindoles [4]
- Complex formation between Ti^{4+} and cyclic diketones (unpublished)

In all these examples, a simplistic use of a single geometry, even if representative of the lowest point on the potential energy surface, would have led to an inaccurate or even incorrect interpretation of the experimental facts being studied. Consideration of the relative abundancies of the various conformers and isomers, however, led to a significantly improved explanation of the phenomenon at hand.

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This work was supported by Estonian Science Foundation grant 8255.

Friday Morning II, Bartók

(Un)Chemical Bonding: Surprises in Non-Covalent Interactions in Molecular Systems

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Non-covalent van der Waals (vdW) interactions are ubiquitous in molecules and condensed matter, and play a crucial role in determining the structure, stability, and function for a wide variety of systems. The accurate prediction of these interactions from first principles is a substantial challenge because they are inherently quantum mechanical phenomena that arise from correlations between many electrons within a given system. We discuss the recently developed efficient method [1,2] that combines quantum and classical electrodynamics and accurately describes the nonadditive many-body vdW energy contributions arising from interactions that cannot be modeled by an effective pairwise approach. It is demonstrated that such contributions can significantly affect the behavior of biological (DNA), chemical (molecular crystals), and condensed (bulk, hybrid interfaces) systems. In most of these cases it is found that collective vdW interactions play a noticeable, if not crucial role, not just for quantitative values but also for the qualitative behavior [3,4,5,6].

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A reactivity index based on orbital energies

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A reaction analysis method based on the orbital energies, which are accurately given by the long-range corrected (LC) DFT[1, 2] calculations, is presented. Although there are several methods using orbital energies in reaction analyses, these methods have used hypothetical orbital energies instead of the calculated ones in reaction diagrams. This is because there is no conventional method giving accurate orbital energies. Surprisingly, it was recently found that LC-DFT quantitatively reproduces valence orbital energies including LUMO energies for the first time.[3]

Based on the quantitative orbital energies of LC-DFT, we have developed a new reaction analysis method based on orbital energies for gas-phase reactions. To make clear the relation between reactivities and orbital energies, we have exhaustively explored the orbital energy variance on the intrinsic reaction coordinates (IRCs) for the major reactions of small light molecules. Consequently, we proposed a reactivity index using the LC-DFT orbital energies. Using this reactivity index, we found that forward reactions initially proceed through electron transfers associated with no intramolecular geometrical change except for the S_N2, symmetric, and other several reactions. By investigating these exceptional reactions, we have found that several reactions including the S_N2 and symmetric reactions are questioned about their reaction paths. We have, therefore, explored reaction paths, which are not located on the IRCs, for these reactions. As a result, we have found plausible reaction paths obeying the reactivity index, which are also consistent with experimental results, for these reactions.

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Tuesday Morning I, Brahms

Quantification of the Uncertainty of Parameters in Chemical Kinetics

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Many models in science and engineering use chemical kinetics parameters and thermodynamic data. The accuracy of simulation results and the predictive power of these models rely on the precision and level of uncertainty of the chemical kinetics and thermodynamic parameters. Several methods exist for the quantification of the uncertainty of these parameters:

(i) If the parameter is the direct result of a measurement, then the uncertainty of the measured data have to be estimated.

(ii) The parameter (*e.g.* rate coefficient at a given temperature and pressure, or the standard enthalpy of formation of a species) can be the result of a theoretical calculation. The accuracy of such calculations depends on the level of theory and the accuracy of the data used.

(iii) Optimization of chemical kinetic models or thermodynamic networks leads not only to well established parameters, but also a quantification of the uncertainty of the fitted parameters. Following the pioneering work of Michael Frenklach et al. [1], [2] and Branko Ruscic et al. [3] in chemical kinetics and thermodynamics, respectively, several groups developed the optimization methodology in both fields.

In the lecture the main features of the quantification of the uncertainty of rate parameters will be reviewed and the approach developed in our group will be presented.

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Tuesday Afternoon II, Bartók

Natural Orbital Functional Theory of the Molecular Electronic Structure

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The one-particle reduced density matrix (1-RDM) functional theory, was proposed a few decades ago [1]. One major advantage of such density matrix formulation is that the kinetic energy is explicitly defined and does not require the construction of a functional. Hence, the electron correlation functional remains as the only unknown energy functional. Since, the electron correlation is a known functional of the two-particle reduced density matrix (2-RDM), a reconstruction functional of the 2-RDM in terms of 1-RDM solves the problem on formal grounds, but poses the problem of its N-representability, not solved yet. Here we will present an explicit recontruction of the 2-RDM in terms of the spectral expansion of the 1-RDM using the cumulant expansion [3] which leads to the Piris Natural Orbital Functional (PNOF) [4]. The PNOF is based on an explicit ansatz of the two-particle cumulant $\lambda(\Delta,\Pi)$ satisfying the D-, Q- and G-necessary positivity conditions for the 2-RDM [5]. Appropriate forms of matrices $\Delta(\{n_p\})$ and $\Pi(\{n_p\})$ lead to different implementations of the PNOF [6].

In this presentation, special emphasis will be put on the spin conserving NOF theory [7]. Some examples of strongly correlated systems, where electron density functionals yield pathological failures, are shown to illustrate the capability of the NOF theory. In particular, our NOF implementation yields a remarkably accurate description of the homolitic dissociation of a number of selected diatomic molecules. It is also found that the method describes correctly their dissociation limit yielding an integer number of electrons on the dissociated atoms. Compounds with full or partial diradical character have been also considered. We have found that PNOF shows a reliable description of these species, and yields the correct trends in their occupation numbers as compared highly correlated with wave-function methods such as CASSCF. The calculations presented here have been carried out with our implementation, the PNOFID code [8], based on a recently proposed algorithm [9] which yields the natural orbitals by an iterative diagonalization of a generalized pseudo-Fockian matrix.

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Tuesday Morning I, Lehár

CCSD(T) calculations of confined systems: In crystal polarizabilities of anions.

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We present isotropic dipole polarizabilities of a series of the F^-, Cl^-, O^{2-}, and S^{2-} anions in LiF, LiCl, NaF, NaCl, KF, KCl, ZnO, ZnS, MgO, MgS, CaO, CaS, SrO, SrS, BaO, BaS and other crystals containing halogen, oxygen, or sulphur anions. The second electron in free O^{2-} and S^{2-} anions is unbound. Both are energetically stabilized in the crystal environment with respect to the singly charged anion and the neutral oxgen or sulphur atoms, respectively. Similarly, O^{2-} and S^{2-} anions are substantionally stabilized when exposed to an external harmonic-oscillator confining potential. With relatively weak confining potential both O^{2-} and S^{2-} anions represent true energy minima and all HF instabilities and the implied broken symmetry solutions disappear [1]. At the same time, polarizabilies of F^-, Cl^-, O^{2-}, and S^{2-} anions confined by an external harmonic-oscillator potential calculated by the CCSD(T) method are considerably reduced in comparison with polarizabilities of free anions. We relate the harmonic-oscillator confining potential ω to the experimental anionic polarizabilities which are known for selected crystals. We were able to find anionic polarizabilities resulting from CCSD(T) calculations with a specific confining potential ω which are the same as experimental in-crystal polarizabilities. We use these polarizabilities (our training set) as tuning quantities for predicting in-crystal polarizabilities of anions. We observe that so determined values of ω depend linearly on the ionic radius of the cation participating in specific crystals containing F^-, Cl^-, O^{2-}, or S^{2-} anions. For predicting in-crystal anionic polarizability for a crystal we only need the ionic radius of the participating cation and the CCSD(T) polarizability of an anion exposed to an external harmonic-oscillator confining potential with a specific ω as obtained from the relation between ω and the ionic radius of a cation in the training set. We predict in-crystal polarizabilities of F^-, Cl^-, O^{2-}, and S^{2-} anions in a series of crystals having similar structural features as crystals used as a training set.

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Tuesday Afternoon I, Brahms

Uncertainty quantification of the rate parameters of an ethyl iodide pyrolysis mechanism

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The optimization of a kinetic mechanism for the pyrolysis of ethyl iodide was carried out based on data obtained from reflected shock wave experiments with H-ARAS and I-ARAS detection. The experiments were conducted in a stainless steel shock tube behind reflected shock waves at temperatures between 957 K and 1397 K, and pressures between 1.3 bar and 1.8 bar with argon as bath gas [1].

The thermal decomposition reaction of C_2H_5I behind the reflected shock wave was monitored using H-ARAS and I-ARAS. In the mechanism optimization study all these measurements were taken into account together with the rate coefficients measured by Michael et al. [2] for reaction $H_2 + I \rightarrow H + HI$. The experimental data were interpreted using the following 5-step mechanism: R1: $C_2H_5I \rightarrow C_2H_5 + I$; R2: $C_2H_5+M \rightarrow C_2H_4+H+M$; R3: $C_2H_5I \rightarrow C_2H_4 + HI$; R4: $H + HI \rightarrow H_2 + I$; R5: $C_2H_5I + H \rightarrow C_2H_5 + HI$.

Arrhenius parameters A and E of reactions R1, R3, R4, and R5 were determined from the experimental data. The joint covariance matrix of the optimized Arrhenius parameters was also calculated. This covariance matrix was converted to the temperature dependent uncertainty parameters f of the rate coefficients and to the temperature dependent correlation coefficients between pairs of rate coefficients. Each fitted rate coefficient was determined with much lower uncertainty compared to the estimated uncertainty of the data available in the literature.

The C_2H_5I decomposition branching ratio, $k_{R1} / (k_{R1} + k_{R3})$, was calculated from the optimized rate parameters. The value obtained was 0.965 at 900 K, decreasing nearly linearly to 0.905 at 1400 K, and the value extrapolated to 2000 K was 0.840. This is in good agreement with the branching ratios determined by Kumaran *et al.* (0.87±0.11 at 950 K-2050 K) [3], Yang and Tranter (larger than 0.87) [4], and Miyoshi *et al.* (0.92±0.06 at 950 K-1400 K) [5].

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Thursday Morning II, Brahms

Quantum control by laser-induced conical intersections

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A few years ago we have started a systematic study of the nonadiabatic effect induced by laser waves in diatomic molecules. It has been shown that light-induced conical intersections (LICIs) can be formed in a molecular system either by standing or by running laser waves[1,2]. The energetic and internuclear positions of these CIs depend on the laser frequencies while the strength of their nonadiabatic couplings can be modified by the field intensities. The impact of these LICIs on different dynamical properties of the diatomics has been discussed in several papers[1-7].

Wave packet calculations have been performed for Na_2 dimer which demonstrate that LICIs exert strong effects on the quantum dynamics even for weak laser fields. The impact of LICIs on another process of interest has also been studied, namely on the spatial alignment of diatomics in fields of moderate intensity ($\sim 10^8$-10^{10} W/cm^2). An important message is that LICIs can substantially influence molecular alignment. Calculating the population on the first excited electronic state of aligned molecules, there is a large difference between the results obtained in the presence of the LICI and those obtained by employing the "standard rigid rotor" one dimensional model. Since the electronic population is a relevant measurable quantity, we hope that our work concerning the molecular alignment will stimulate experimental investigations in the near future.

The photodissociation dynamics of the D_2^+ molecule in an intense laser field has also been studied. The results obtained undoubtedly demonstrate the strong impact of the coupling of the rotation to the vibrational and electronic motions and hence of the LICI on the dissociation dynamics of the D_2^+ molecule.

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Tuesday Afternoon II, Bartók

Saving Sanderson's Principle?
Order of Magnitude Improvements by Equalizing Mulliken Valence-State Electronegativities χ_{VS} Instead of DFT-Based Chemical Potentials μ

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Conceptual DFT operationally assumes $\mu = -\frac{1}{2}(I_0 + A_0) = -\chi$, with I_0 and A_0 being the ground-state ionization energy and electron affinity, respectively. However, a recent empirical test of 210 molecules discloses that most molecules seriously disobey Sanderson's electronegativity equalization (ENE) principle and the μ-equalization principle [1]. In more than 150 cases, the molecular μ_{mol} falls outside the range spanned by the μ_{at} of the constituent atoms, $min\ \{\mu_{\mathrm{at}}\} \leq \mu_{\mathrm{mol}} \leq max\ \{\mu_{\mathrm{at}}\}$ [1].

I here discuss elementary thermodynamic cycles revealing the conditions for ENE and/or μ-equalization in arbitrary diatomic and selected polyatomic molecules. The cycles explain why the DFT-based operational μ is equalized in exceptional cases only, as for the H_2 molecule. A proof is given that the diatomic χ(XY) and μ(XY) cannot be generally calculated from atomic data alone, but necessarily require molecular input data, specifically, the bond dissociation energies, D_0, of molecular ions, e. g., XY^+ and XY^-. Using ground-state I_0 and A_0 frequently violates the Wigner-Witmer correlation rules [2] necessary for proper molecular symmetry. According to the correlation rules Mulliken's valence-state ionization energies, I_{VS}, electron affinities, A_{VS}, and electronegativity, χ_{VS}, [3] have to be employed for molecules and atoms alike. The differences between the molecular $\chi_{\mathrm{VS,\ mol}} = \frac{1}{2}(I_{\mathrm{VS}} + A_{\mathrm{VS}})$ and $-\mu_{\mathrm{mol}}$ and the corresponding averages from atomic values, $<\chi_{\mathrm{VS,\ at}}>$ and $<-\mu_{\mathrm{at}}>$, are expressed by observed differences in D_0. Such differences frequently cancel and an order of magnitude improvement of accuracy in ENE is achieved by the consistent use of Mulliken's valence-state χ_{VS} as opposed to the commonly used ground-state EN, or μ values. The study shows that the Mulliken electronegativity and the DFT-based chemical potential have to be accepted as two separate and distinct properties characterizing chemical systems. For conceptual DFT a **paradigm shift** is in order by replacing the dominance of ground-states and emphasising valence-states.

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Tuesday Morning I, Brahms

Multiscale Kinetic Knowledge Propagation - Combustion Chemistry of Small Hydrocarbons

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Chemical kinetic models have become indispensable to the design of low-emission, highly efficient engines using both conventional and bio fuels. At this time, the predictive uncertainties of these models remain large. While the validity of a reaction model can be checked usually against a set of fundamental combustion data, the underlying problem of model uncertainty is nonetheless ill-defined mathematically. The accuracy of the reaction rate parameters can be assessed, in principle, by examining the scatter in the experimental data and/or the results obtained in ab initio quantum chemistry methods at different levels of theory. In this talk, the rate parameter uncertainty will be illustrated using a recent theoretical study as an example. It will be shown that the best theory available still leaves a rate uncertainty as large as a factor of 3. To address the above problem, we introduce the spectral uncertainty method, and more specifically the method of Polynomial Chaos Expansions and its application in examining the effects of kinetic model uncertainty on combustion predictions. An extension of this method, termed the Method of Uncertainty Minimization, has been developed to allow for forward and backward projections of uncertainties in both the reaction model and fundamental combustion experiments. The application of this method in the development of a recent CEFRC foundational fuel chemistry model and in designing better combustion experiments will be discussed.

Wednesday Morning I, Pátria

Explicitly Correlated Multireference Electronic Structure Methods

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Recent developments of multireference electron correlation methods in our group are reviewed. In particular, we will focus on new explicitly correlated multireference perturbation theory and multireference configuration interaction methods [1,2]. The explicitly correlated (F12) terms very much reduce the basis set incompleteness errors, and typically at least quintuple-zeta quality is achieved already with triple-zeta basis sets. The additional cost is negligible. Benchmarks are presented for ground and excited states and various properties of molecules and elementary reactions. Furthermore, new implementations of analytic energy gradients for state-averaged CASSCF and CASPT2 wave functions [3] that employ density fitting techniques to speed-up the evaluation of the two-electron integrals are presented. Finally, some applications to open-shell transition metal complexes with complicated electronic structure are discussed.

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Wednesday Afternoon , Bartók

Analytical wave function of helium atom

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Schrödinger equation of the helium atom is one of the simplest problems in quantum mechanics (QM). The problem was formulated [1] soon after the discovery of QM. Highly accurate numerical estimates of the ground state energy are available [2] but the analytical structure of the wave function has not been determined until today despite of substantial effort in this direction. [3, 4, 5, 6, 7] The current talk is supposed to review the situation in the field and suggest a possible line of further development.

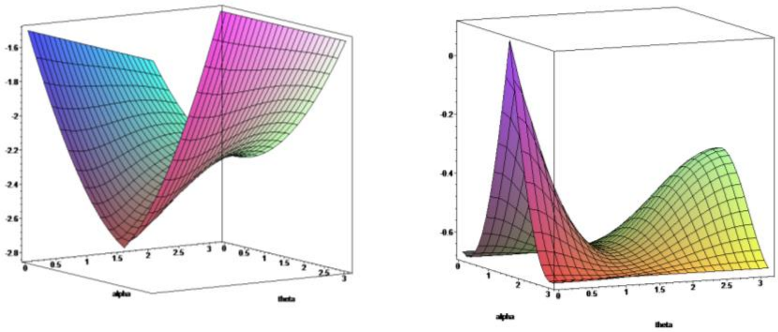

Figure 1. First-order wave function of helium atom (left) and a component of the second-order wave function of helium atom (right) in hypershperical coordinates (α,θ)

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Monday Afternoon I, Pátria

The influence of a presence of a heavy atom on spin-spin coupling constants between two light atoms in organometallic compounds and halogen derivatives.

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The importance of relativistic effects is getting widely recognized in the scientific community and more and more molecular properties are being calculated using relativistic Hamiltonians. It is known that the presence of a heavy nucleus in the molecule affects not only the Nuclear Magnetic Resonance (NMR) properties of the heavy nucleus in question, but influences also the shielding constants and indirect spin-spin coupling constants of nearby light nuclei (heavy-atom-on-light-atom, or HALA, effect). However, while the relativistic effects on the shielding constants of light nuclei neighbouring heavy atoms are relatively well investigated, the parallel phenomenon occurring for the nuclear spin-spin coupling constants is almost unexplored. There is a handful of papers dealing with the situation when a heavy atom mediates the geminal coupling between two light atoms but there are practically no studies concerning the situation where the heavy atom is not in the coupling path.

As we have shown in our previous study on heavy metal cyanides, the HALA effects on the $^{1}J_{CN}$ are sizeable [1]. These findings inspired us to look more closely at the influence of the presence of heavy atom on the one-bond spin-spin coupling constant of the nearby light nuclei.

The systems under study are aliphatic hydrocarbons substituted with I, At, Cd and Hg. This choice allowed us to study substituent effects on $^{1}J_{CC}$ and $^{1}J_{CH}$ and to explore the factors, which may influence the HALA effect on these properties: the nature of the heavy atom substituent and carbon hybridization.

The calculations are carried out using density functional theory with the zeroth-order regular approximation Hamiltonian (with the spin-orbit term included) [2] and with the four-component Dirac-Coulomb Hamiltonian [3], since our secondary aim is to compare the performance of ZORA-DFT and Dirac-Kohn-Sham methods for modelling of HALA effects on the spin-spin coupling constants.

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Selective Vibrational Mode Excitation in Nanocarbons by Tailored Intense Near-Infrared Pulses and Subsequent Intramolecular Vibrational Energy Redistributions

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Interactions between nanocarbons and intense near-infrared (NIR) pulses with femtosecond pulse length T_p and intensity $I \approx 10^{15}$ W/cm^{-2} induce structural rearrangements and fragmentations. Larrmann *et al.* experimentally showed that tailored NIR pulse trains can optimize the specific fragment yields of fullerene C_{60} [1]. We theoretically showed that selective impulsive Raman excitation of specific vibrational modes with vibrational period T_vib in C_{60} can be achieved by setting $T_\mathrm{p} \approx T_\mathrm{vib}/2$ and the fragmentation process depends on the vibrational modes initially excited [2]. These results suggest that intramolecular vibrational energy redistributions (IVR) leading to fragmentations depend on the pulse shape.

We performed the *on-the-fly* trajectory calculations on NIR-pulse-induced vibrational dynamics in C_{60} with various T_p to clarify the effects of the pulse shape on the IVR dynamics. We combined the time-dependent adiabatic state approach [3] and density-functional based tight-binding theory [4] for simulations. We found that exciting different vibrational modes drastically changes the IVR dynamics as in Figs. 1a and 1b even if the total vibrational energy E_in acquired remains the same. Exciting the $h_\mathrm{g}(1)$ mode (T_vib = 140 fs) by setting T_p = 70 fs leads to the slow IVR in Fig. 1a; fast and complex IVR between the $a_\mathrm{g}(1)$ and $h_\mathrm{g}(2)$ modes occurs as in Fig. 1b when the $a_\mathrm{g}(1)$ mode (T_vib = 60 fs) is enhanced by setting T_p = 30 fs. We will also discuss IVR dynamics in a semiconducting single-wall carbon nanotube [5].

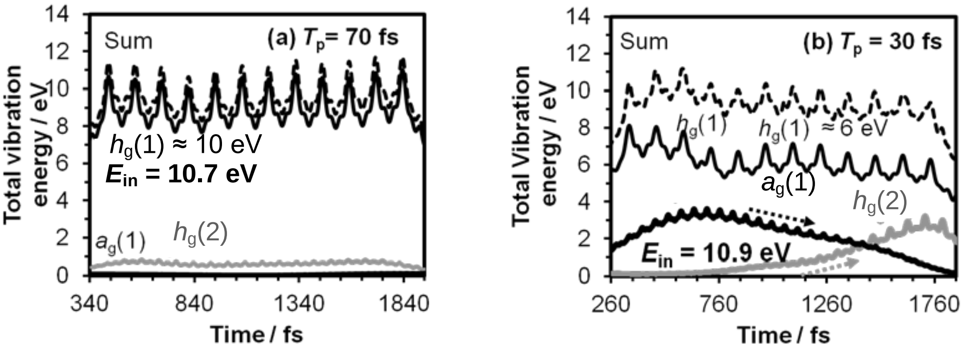

Fig. 1: Temporal change of the vibrational energies in low frequency modes of C_{60} induced by single pulse excitation ($I = 7.0 \times 10^{14}$ W/cm^2, λ = 1800 nm). (a) T_p = 70 fs: the $h_\mathrm{g}(1)$ mode (T_vib = 140 fs) is mainly excited and the IVR is slow. (b) T_p = 30 fs: the $a_\mathrm{g}(1)$ mode (T_vib = 60 fs) is relatively enhanced and fast IVR between the $a_\mathrm{g}(1)$ and $h_\mathrm{g}(2)$ modes is observed.

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Exchange-Correlation Energies from Paring Matrix Fluctuation and Particle-Particle-Random Phase Approximation

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We formulate an adiabatic connection for the exchange-correlation energy in terms of pairing matrix fluctuation. This connection opens new channels for density functional approximations based on pairing interactions. Even the simplest approximation to the pairing matrix fluctuation, the particle-particle Random Phase Approximation (pp-RPA), has some highly desirable properties. It has no delocalization error with a nearly linear energy behavior for systems with fractional charges, describes van der Waals interactions similarly and thermodynamic properties significantly better than particle-hole RPA, and eliminates static correlation error for singly bound systems. Most significantly, the pp-RPA is the first known functional that has an explicit and closed-form dependence on the occupied and unoccupied orbitals and captures the energy derivative discontinuity in strongly correlated systems. These findings illlustrate the potential of including pairing interactions within a density functional framework.

Ref: . arXiv:1306.4957 Exchange-Correlation Energy from Pairing Matrix Fluctuation and the Particle-Particle Random Phase Approximation, Helen van Aggelen, Yang Yang, Weitao Yang

Tuesday Afternoon II, Lehár

Orbital views of molecular conductance and spintronics

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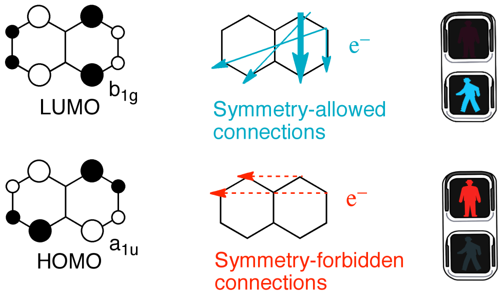
We have developed a chemical way of thinking about electron transport in molecules in terms of frontier orbital theory [1-4]. The phase and amplitude of the HOMO and LUMO of π-conjugated molecules determine the essential properties of their electron transport. By considering a close relationship between Green's function and the molecular orbital, we derived an orbital rule that would help our chemical understanding of the phenomenon. First, the sign of the product of the orbital coefficients at sites *r* and *s* in the HOMO should be different from the sign of the product of the orbital coefficients at sites *r* and *s* in the LUMO. Secondly, sites *r* and *s* in which the amplitude of the HOMO and LUMO is large should be connected. Recently we confirmed these theoretical predictions experimentally by using nanofabricated mechanically controllable break junctions to measure the single-molecule conductance of naphthalene dithiol derivatives [5]. The measurement of the symmetry-allowed 1,4-naphthalene dithiol shows a single-molecule conductance that exceeds that of the symmetry-forbidden 2,7-naphthalene dithiol by two orders of magnitude.

Spintronic properties of cyclobutadiene (CBD) systems are investigated based on a qualitative frontier orbital analysis [6]. CBD undergoes a Jahn-Teller distortion from the square triplet state to the rectangular singlet state. According to the qualitative Hückel molecular orbital analysis, the electron transport through the square triplet state is symmetry allowed while that through the rectangular singlet state is symmetry forbidden. The magnetic triplet state is a possible coexisting system of conductivity and magnetism. Sophisticated first-principles quantum chemical calculations are performed by using a realistic molecular junction model. Interesting spin filtering properties are found in the square-shaped CBD system. The high- and low-spin states of the square-shaped CBD system produce the spin-α and -β polarized conductance, respectively.



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Tuesday Morning I, Brahms

Uncertainties in *ab initio* rate coefficient calculations

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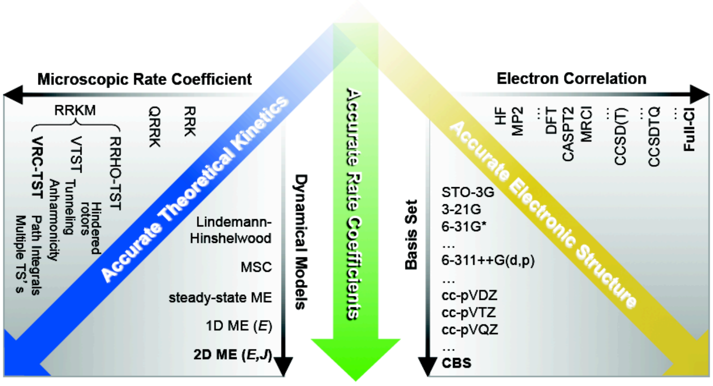
Modern chemical mechanisms describing the combustion of a single-component fuel often consist of thousands of chemical reactions. Unfortunately, only a relatively small number of rate coefficients are known experimentally, especially under conditions relevant to combustion. As the pace of the experimental investigations clearly cannot keep up with the pace of mechanism development, modelers increasingly rely on theoretical approaches to determine rate coefficients. Theoretical kinetics has a clear path to increase accuracy in the calculations, which entails accurate electronic structure methods and an accurate treatment of microscopic transition probabilities coupled to a rigorous dynamic model to describe the probabilities with which the microscopic populations evolve.



The components of theoretical kinetics, arranged in order of increasing accuracy [1].

Advances in electronic structure methods and transition state theory allow accurate *ab initio* determination of elementary gas-phase reaction rate coefficients involving several heavy atoms. Exactly how accurate these calculations are, what accuracy we need, and where most of the uncertainties lie is just beginning to unfold through the recent studies directed towards this problem. In this talk these issues will be illustrated through several examples, and the possibilities that lie in Bayesian inference [2] will be highlighted.

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Monday Morning I, Lehár

How to make Dynamical Mean Field Theory quantitative?

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In quantum chemistry, calculations for strongly correlated solids are impossible besides the smallest cases because of a prohibitive cost of the explicit treatment of periodic boundary conditions. However, in condensed matter physics, Dynamical Mean Field Theory (DMFT), which is an established method, enables the treatment of solids without explicitly imposing periodic boundary condition. The success of DMFT is based on a self-consistency cycle that takes into account the mutual interaction between a unit cell and the environment. Consequently, one of the most important steps in DMFT is the solution of a Hamiltonian that describes the unit cell and its simplified interaction with the surrounding orbitals. Because of the "frequency" dependence of the embedding DMFT includes significant correlation effects that go beyond the simpler QM/QM approaches so far used in quantum chemistry. In order to solve such a Hamiltonian, one can use any existing quantum chemistry method that allows us to treat strongly correlated electrons. Such a treatment makes possible calculations for strongly correlated solids. Thus, a hierarchy of methods similar to the one existing for treatment of molecules (MBPT2, CCSD, MRCI, DMRG) can be established for the treatment of strongly correlated solids within the DMFT framework. I will introduce our recent contributions in adapting the Dynamical Mean Field Theory (DMFT) to realistic quantum chemical calculations for solids and I will discuss how the DMFT embedding theory can be developed from a qualitative theory for model systems into a quantitative theory with quantum chemical accuracy. Finally, if time permits I will show application of DMFT to Kondo problems.

Analyzing Complex Electronic Structure Calculations on Large Molecules in Simple Chemical Terms

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In this talk we shall introduce a new scheme for chemical bond analysis [*J. Chem. Theory Comput.*, 2009] by combining the Extended Transition State (ETS) method [Theor.Chim.Acta 1977,46,1] with the Natural Orbitals for Chemical Valence (NOCV) theory [J.Phys.Chem.A. 2008,112,1933]. The ETS-NOCV charge and energy decomposition scheme makes it not only possible to decompose the deformation density, $\Delta\rho$, into the different components (such as σ,π,δ etc.) of the chemical bond, but it also provides the corresponding energy contributions to the total bond energy from these components.

Thus, the ETS-NOCV scheme offers a compact, qualitative and quantitative, picture of the chemical bond formation within one common theoretical framework. Although, the ETS-NOCV approach contains a certain arbitrariness in the definition of the molecular subsystems that constitute the whole molecule, it can be widely used for the description of different types of chemical bonds. The applicability of the ETS-NOCV scheme is demonstrated for single (H_3X-XH_3, for X = C, Si, Ge, Sn) and multiple (H_2X=XH_2, H_3CXXCH_3, for X = C, Ge) covalent bonds between main group elements, for sextuple and quadruple bonds between metal centers (Cr_2, Mo_2, W_2, $[Cl_4CrCrCl_4]^{4-}$) and for double bonds between a metal and a main group element ($(CO)_5Cr$=XH_2, for X = C, Si, Ge, Sn). Applications are also given to hydrogen- and agostic bonds as well as the interaction between adsorbates and metal surfaces. The scheme is finally used to explain the trans-effect in square planar platimum complexes.

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4. I.Seidu and T.Ziegler "A Theoretical Analysis of the Putative Triple Bond in Ar'EEAr' (E=Si, Ge, Sn; Ar'=C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$) and Ar*PbPbAr* (Ar*=C_6H_3-2,6(C_6H_2-2,4,6-$Pr^i{}_3$)$_2$)" Inorg.Chem. 2013,submitted

Chemical Reactions with two different elementary Transition States – Crypto Three-State System. Photo-/ Thermo-chemical aspects and VB rationalization.

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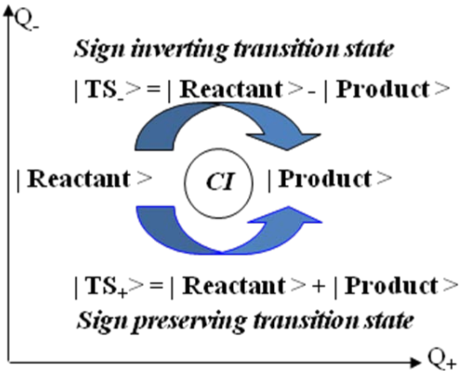
It is commonly assumed that the chemical reaction is determined by the unique transition state (TS), and the two-state approach is a basic model for the analysis of the chemical reaction. However, during the last 10 years, various examples of chemical reactions with two different TSs were reported.[1] Lucid VB arguments allow to identify reactions with two different TSs as a crypto three state system, where the Reactant and the Product are defined by the combinations of the three dominant VB structures.



2D domain based on the two minima - the Reactant (**R**) and the Product (**P**), which are connected by two different TSs can include the S_0/S_1 conical intersection according to the Longuet-Higgins theorem.[2] This is a situation which constitutes a necessary and sufficient condition for a photochemical reaction bearing a single product.[3]
Two different transition states detected (on the CAS level of calculation) for the cis-trans isomerization around polar double bonds, azo-compounds, charge shift in aliphatic radical-cations, conjugated radicals, H atom *vs.* proton-coupled electron transfer *etc*..
Symmetry allowed reactions have the $\mathbf{TS}_+$=(**R+P**). Symmetry forbidden reactions served by $\mathbf{TS}_-$=(**R-P**) which is a preferable route (lower barrier) in some of studied cases.
The principles of the design of *crypto three-state system* are represented for both types of systems – with two different and two equivalent TSs. The electronic mechanisms leading to the chemical reaction with two TSs are described.
The reduction in rate due to non-adiabatic recrossing near the conical intersection[4] is discussed in connection with a different types of the reactions with two TSs.

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Abstracts of Poster Session I

Stochastic Structure Determination for Conformationally Flexible Clusters: CrazyLego

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Ionic liquids (ILs) are a subset of molten salts distinguished by having melting points below 100°C. The physical, rheological and electrical properties of ILs may be potentially tuned through judicious choice of anion and cation structure. Of myriad possible ILs, only a small fraction will possess the desired properties to make them useful in any given application. Thus, a method towards systematically understanding IL structure and properties, that does not rely on (expensive) chemical synthesis, is required.

We present the CrazyLego method, a stochastic structure generator, that unlike previous implementations of the “Kick" algorithm[1], is fully conformer-aware. The conformer, rotation and position of each fragment are all chosen stochastically. Structures are then optimized using dispersion-corrected 3rd order SCC-DFTB (DFTB3).[2]

Using CrazyLego, we have determined the structures and properties of imidazolium-nitrate IL clusters, $([\mathrm{xMIM}]^+[\mathrm{NO}_3]^-)_n$ for x=D,E,B and alkylammonium-nitrate clusters, $([\mathrm{xAN}]^+[\mathrm{NO}_3]^-)_n$ for x=E,P,B for up to n=10 ion pairs. We compute binding energies, Radial Distribution Functions (RDFs) and hydrogen bonding properties of each IL cluster and show the emergence of bulk properties at surprisingly modest cluster sizes of only 7-10 ion pairs.

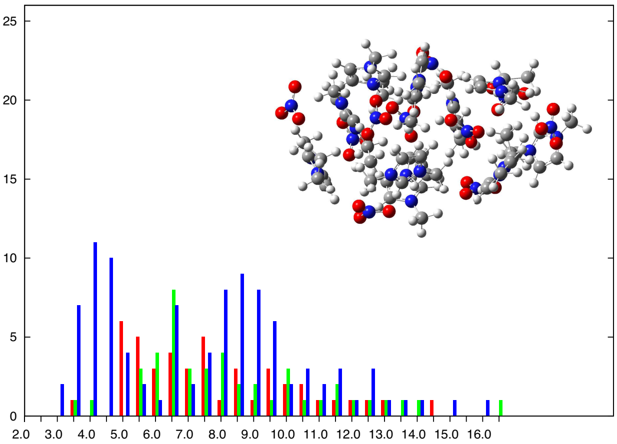

Figure 1: Cation-anion (blue), anion-anion (green) and cation-cation (red) distance distributions for inter-centroid distances of $([\mathrm{EMIM}]^+[\mathrm{NO}_3]^-)_{10}$.

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No. 2, Poster Session I

An Ab Initio Microscope: Molecular Contributions to the Femtosecond Time-Dependent Fluorescence Shift of a Reichardt-Type Dye

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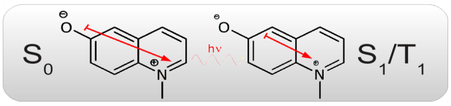
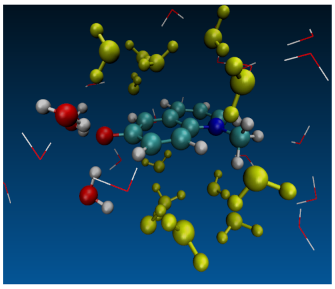
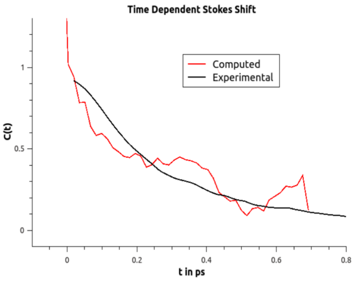
The molecular probe N-methyl-6-quinolone (MQ) gives spectroscopic access to its local environment.[1] Its experimentally observed time-dependent Stokes shift can be explained by molecular dynamics simulations in combination with DFT calculations. Decomposition of the MD trajectories shows that an important contribution to the time-dependent Stokes shift originates from a group of water molecules that strongly interact with the molecular dipole of MQ.[2]







The approach we have been taken to simulating the excited state solvation dynamics[3] is currently being applied to excited state proton transfer.

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No. 3, Poster Session I

Size-extensive wave functions for QMC: The J-LGVBn theory

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We show a new class of multideterminantal Jastrow-Slater wave functions constructed with localized orbitals and designed to describe complex potential energy surfaces of molecular systems for use in quantum Monte Carlo (QMC). Inspired by the generalized valence bond formalism, we elaborate a coupling scheme between electron pairs which progressively includes new classes of excitations in the determinantal component of the wave function. In this scheme, we exploit the local nature of the orbitals to construct wave functions which have increasing complexity but scale linearly. The resulting wave functions are compact, can correlate all valence electrons, and are size-extensive. We name these wave functions of the Jastrow linear generalized valence bond (J-LGVB) form [1]. The theory can be extended to include multiple coupling schemes characterized by different sets of localized orbitals, which enables the detailed study of large portions of the potential energy surface [2]. Moreover, for large molecular systems the method can be applied at a multi-level scheme to treat different regions of the molecule at different levels of the theory [3]. The performance has been assessed on a variety of homolytic fragmentations, on the calculation of barrier heights of five prototypical chemical reactions, and on a complex reaction path like that of the decomposition of α-hydroxy-dimethylnitrosamine.

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No. 4, Poster Session I

Combined ab initio/semi-empirical Screening Protocol for Properties of Self-Assembled Monolayers

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Organic electronic devices recently found their way into the first consumer products such as mobile phone displays. These devices take advantage of the unique properties of organic materials such as transparency, flexibility, and simple and low-cost processability. However, they always need to be incorporated into conventional inorganic electronic frameworks. This very often leads to a lower device performance and limit the choice of materials.

Self-assembled monolayers (SAMs) are a means to improve the organic-inorganic junction: dipolar organic molecules form an interlayer between the inorganic electrode and the organic semiconductor, tune the effective work function of the electrodes and adjust the metal's Fermi energy to the conduction bands of the organic semiconductor.

For a well-directed synthesis of SAMs, computational screening methods are necessary in order to search for organic molecules with given properties. The prediction of SAM-properties is possible with reasonable accuracy using plane-wave density functional theory calculations. However, the costs of these methods are too high to allow systematic in silico searches for new materials.

Here, we present a combined *ab initio*/semi-empirical protocol for predicting properties of SAMs. Taking advantage of restricted semi-empirical geometry optimizations reduces the total computation time for work-functions by more than one order of magnitude. In all cases periodic boundary conditions are taken into account.

The protocol was successfully applied to more than 15 functionalized thiols on gold and silver surfaces. Finally the robustness of the methodology was evaluated comparing the calculated work functions with experimental data.

No. 5, Poster Session I

Flexibility of Hunam Thioredoxin 1 and new biding sites using Normal Modes Analysis

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The thioredoxin (Trx) is a ubiquitous protein, present since bacteria to humans. The Thioredoxin system (thioredoxin, thioredoxin reductase and NADPH) is involved in several processes such as oxidative stress, DNA repair, apoptosis, transcription In this work, we used normal mode analysis to identify putative biding site regions for HumanThioredoxin 1 that arise from global motions of its structure. We identified three possible binding regions for inhibitors that corroborate experimental indications. We show that the motions of the protein can expose hydrophobic regions and non-active site cysteines that could constitute biding sites for new inhibitors of the Thioreoxin system. It may be concluded that NMA is an appropriate technique for the characterization of global motions allowing to identify putative binding sites in a proteins.

Word Keys: normal modes, human thioredoxin, hydrophobic pocket
Supported by: FAPESP, CNPq and CNRS

No. 6, Poster Session I

DNA – Protein interaction in the nucleosome system

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The interaction between the negative side chain of DNA and the positive side amino acids of histone protein have been characterized by Hartree-Fock and second order Møller-Plesset perturbation theory level using the triple-ζ basis set with polarization functions in the framework of the two-layer ONIOM method [1]. The strength of the intermolecular interaction and the magnitude of the charge transfer between the DNA and the histone protein is discussed considering the presence of different positive (K^+, Mg^{2+}) [2] and negative ions (Cl^-) [3] as well as water molecules. The role of the ions on the stability of the nucleosome systems and the possible consequences of the DNA unwrapping from the histone are widely discussed.

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No. 7, Poster Session I

Impact induced multifragmentation of fullerene on gold: experimentally motivated molecular dynamics simulations

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Postcollision multifragmentation phenomena for the impact of C_{60}^{-} ions on gold and nickel was recently observed over a wide range (80-900 eV) of impact energies [1]. In order to gain a deeper insight into the microscopic dynamics of the fullerene multifragmentation processes, we have carried out molecular dynamics (MD) simulations of C_{60} single impacts with an Au (001) target under nearly the same initial conditions and scattering parameters as the experimental ones. Both, near threshold (80-120 eV) and full multifragmentation (higher impact energies) regimes were studied. In the near threshold energies we have studied the dynamics of both intact scattering and onset of multifragmentation events.

The results of our simulations are in relatively good agreement with the near-threshold behavior observed in the experiment for a similar range of impact energies. The calculated multifragmentation yield curve exhibits a threshold behavior at 90-100eV as compared with the 80-100 eV experimental value. A constant relative energy loss for the intact scattered C_{60} was found, as a function of impact energy for the 80-160 eV range, for different incident angles (Θ_i=*22, 63 deg*).

The main characteristics of a postcollision multifragmentation event (300 eV) are reproduced in the calculations and found to be in qualitative and nearly quantitative agreement with the experimental results. It appears that from the moment of the initial impact induced deformation and till actual fragmentation, the deformed fullerene undergoes a sequence of structural transformations characterized by a gradual reduction in the level of coordination of the carbon atoms (decreasing connectivity). The calculated (statistically averaged) mass resolved appearance curves and the kinetic energy distributions (KEDs) of the scattered C_n fragments revealed a precursor mediated, velocity correlated fragmentation event along the outgoing trajectory. Most of the larger fragments ($n>5$) are formed within a few picoseconds after leaving the surface, at vertical distances of 20-90 Å above the surface. The precursor time dependent structural transformations resembles formerly reported high temperature phase transition like behavior of fullerenes as observed in canonical ensemble simulations [2]. A complementary microcanonical ensemble simulation of the time evolution of an initially thermalized (superheated) C_{60} cage at 8500 K, over a few picosecond timescale, revealed a dynamics which seems to be similar to that of the impact generated precursor.

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No. 8, Poster Session I

Formulation of partial triples to the electronic transition dipole moments within Fock-space multi-reference coupled cluster framework

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Abstract

Fock-space multi-reference coupled cluster method is well established to describe excited state molecular properties. In this framework, we have evaluated the electronic transition dipole moments, which depend on matrix elements between two different wave functions (e.g. ground to the excited states). We present two different ways to evaluate the transition moments. In one method, we have constructed the ground and excited state wave functions with the exponential ansatz of Fock-space coupled cluster theory. This is given by the following equation [1],

$$d_{pq}=\left[\langle\psi_{HF}\left|\Omega_{gr}^{\dagger}\hat{O}\left(\Omega_{ex}C_{\mu}^{(1,1)}\right)\right|\Phi^{(1,1)}\rangle\langle\Phi^{(1,1)}\left|\left(\tilde{C}_{\mu}^{(1,1)}\Omega_{ex}^{\dagger}\right)\hat{O}\Omega_{gr}\right|\psi_{HF}\rangle\right]^{1/2}$$

Computation of the relevant off-diagonal matrix elements from the above equation gives us the transition moment. In the second approach, we have linearized the exponential form of the wave operator by using Lagrange formulation. This gives us a linear left vector and an exponential right vector.

$$d_{pq}=\left[\langle\psi_{HF}\left|(1+\Lambda)\Omega_{gr}^{-1}\hat{O}\left(\Omega_{ex}C_{\mu}^{(1,1)}\right)\right|\Phi^{(1,1)}\rangle\langle\Phi^{(1,1)}\left|\tilde{C}_{\mu}^{(1,1)}\left(1+\tilde{\Lambda}\right)\Omega_{ex}^{-1}\hat{O}\Omega_{gr}\right|\psi_{HF}\rangle\right]^{1/2}$$

Where, $\tilde{\Lambda}$ contains the linearized left vectors of all the valence sectors [1]. The entire implementation has been done under the CCSD approximation. Transition moments and oscillator strengths of a few molecules are presented and compared with other available theoretical methods. We will be adding partial triples correction (corrected up to third order) to the above formulated transition dipole equations.

References:

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No. 8, Poster Session I

No. 9, Poster Session I

Molecular-level simulations of permeation in polymer films and fibres

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The permeability of small penetrant molecules in polymer materials is important for many applications, *e.g.*, fuel cells, gas separation and packaging. Polyethylene (PE) and polyvinylalcohol (PVA) are, for example, widely used for packaging materials and their barrier properties towards penetrants such as oxygen and water is a factor that determines the shelf-life of the packaged product. It is therefore important to identify the polymer properties that affect the permeation of penetrants. This will assist in developing new polymers that have desired barrier properties.

Molecular-level computer simulations have been performed to calculate solubility, S, and diffusion, D, coefficients of water and oxygen in PE and PVA, and to obtain a molecular-level understanding of the diffusion mechanism. The permeation coefficient, P, was calculated from the product of S and D. The figure below shows that the simulated S for water in PE yields the correct trend of increasing S with increasing temperature, although the simulated values are lower than the experimental data. The calculated diffusion coefficients are in good agreement with experimental data. The correct trend observed for the simulated S and D is reflected in the correct trend seen for P. Diffusion occurs mainly by large amplitude, infrequent jumps of the molecules through the polymer matrix.

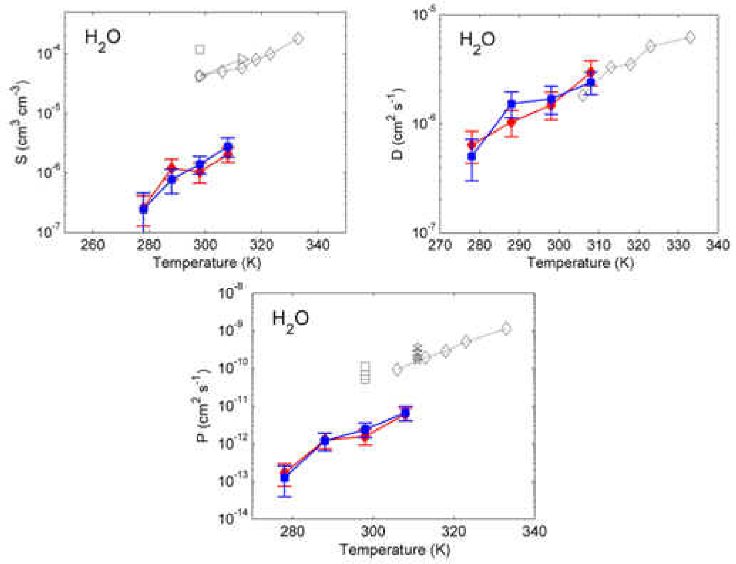

Figure: Solubility (top left), diffusion (top right) and permeability (bottom) coefficients of water in PE. The simulated results are shown with error bars (squares are when atomic charges are included in the force field) and experimental results are shown in grey.

This work is funded by the Swedish Knowledge Foundation (KK-stiftelsen).

No. 10, Poster Session I

Spin at the 2-component level of theory. The way in pain

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It will be shown that a non-relativistic unrestricted 2-component (2c) calculation of an open shell system can break the $\hat{S}_z$ "symmetry" as it is the case for a quasirelativistic unrestricted 2c calculation. Although spin itself cannot be regarded as a constant of motion at the 2c level of theory, especially when the spin-orbit coupling is accounted for, an analog of the spin contamination for an unrestricted 2c wave function will be presented. The 2c analog of the spin contamination will be evaluated by means of the overlap between the set of the original spinorbitals and the appropriate Kramers spinorbital set [1]. The comparison between the 1-component and 2-component spin density representations [2, 3, 4, 5, 6] will be presented. A "Kramers unrestricted" analog of spin density, which is based on the overlap between the original spinor set and the Kramers spinor set, will be introduced [1].

Acknowledgements
The author (LB) is grateful to Patrick Cassam-Chenaï (Nice, France) for wonderful and stimulating discussions in different aspects of the presented work. The financial support was obtained from APVV (contract No. APVV-0202-10) and VEGA (contract No. 1/0327/12).

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No. 11, Poster Session I

Theoretical DFT, FT-IR and NMR studies of 2-methoxy-6-(5-F/Cl/Br-1*H*-benzimidazol-2-yl)-phenols

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2-(1*H*-benzimidazol-2-yl)phenol and its derivatives are known to be chelating agents and biologically active compounds. For example, some benzimidazolyl-phenol type ligands and their Fe(III), Cu(II) and Zn(II) complexes showed broad spectrum of antimicrobial activity that were either more active or equipotent the references[1,2].

In this study, theoretical DFT, FT-IR and NMR spectral studies of 2-methoxy-6-(5-F/Cl/Br-1*H*-benzimidazol-2-yl)-phenols (**I-III**) were performed. The optimized molecular geometry, dipole moment and total energy were calculated using Hartree-Fock and density functional method (B3LYP) with 6-31G(d,p) basis set. The vibrational wavenumbers and the infrared intensities were calculated scaled quantum mechanics (SQM) methodology by using Parallel Quantum Solutions (PQS) program. According to the calculations, the compounds are nearly planar (Fig. 1). The global minimum energy values of the compounds are −899.68, −1260.04 and −3371.44 a.u. for **I**, **II**, **III**, respectively. Dipole moment value of the compounds **I**, **II** and **III** are 5.01, 6.07 and 5.06 Debye, respectively. Also, charge distribution of the compounds was determined (Fig. 1).

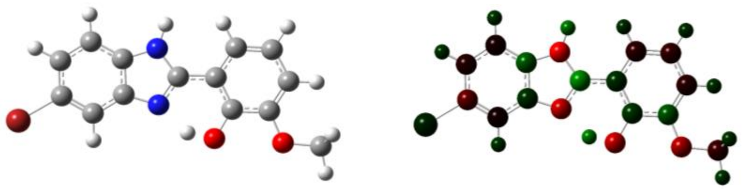

Fig. 1. Geometric optimization (left) and charge distribution (right) of **III**

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No. 12, Poster Session I

Visualization and characterization of intermolecular interaction based on the electron difference density

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Noncovalent interactions (NCI) play an important role in chemistry and biochemistry. Since these are usually weak and obscure compared with covalent bonding, some extra efforts are needed to characterize and visualize it. Johnson et al. developed a noncovalent interaction index[1] based on the electron density and its derivatives(reduced density gradient in density functional theory), which is an effective tool for biological system. We investigated the intermolecular NCI by a simple and straightforward method based on the so-called difference density for molecular complexes

$$\Delta\rho(\boldsymbol{r}) = \rho_{complex-AB}(\boldsymbol{r}) - \left[\rho_{molecule-A}(\boldsymbol{r}) + \rho_{molecule-B}(\boldsymbol{r})\right]$$

where ρ is not only electron density, but also its laplacian and electrostatic potential(ESP). These difference quantities represent the NCI-induced change of electronic structure straightforwardly. We calculated these quantities for a few kinds of molecular complexes bound by van der Waals interactions such as the Hydrogen bonding and dispersion interactions. The difference densities of the electron and the laplacian represent the NCI-induced electron transfer, concentration or depletion visually although they look somewhat complicated. These pictures are also emphasized in the motion of intermolecular vibration (Some of animated illustrations are found in Ref. 2). On the other hand, the difference ESPs, which indicate a change of local polarity, make the existence of the NCI clear and distinct. These three difference quantities amplify the buried character of the NCI, and provide direct information for understanding it.

(This work was supported by JSPS KAKENHI Grand Number 23730842.)

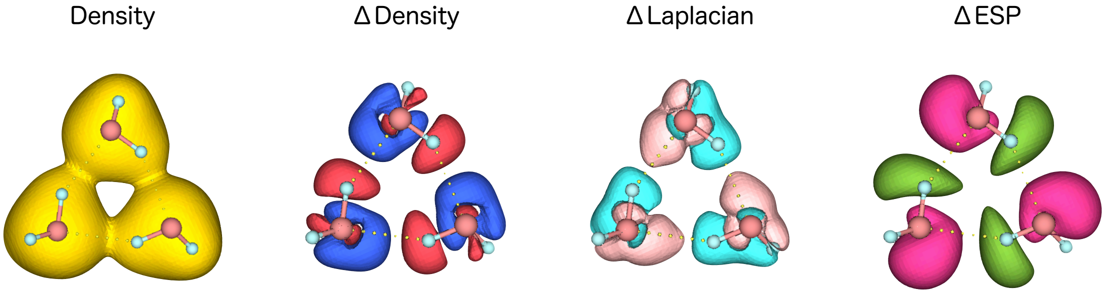

Figure 1. Molecular difference quantities of water trimer at the HF/aug-cc-pVTZ levels.

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No. 13, Poster Session I

Halogen–halogen interaction in light of many–body approach.

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The many–body theory was applied in order to estimate the character of interaction in quadruple complex consisting of four bromomethane molecules. The scheme of such system is shown in the Figure.

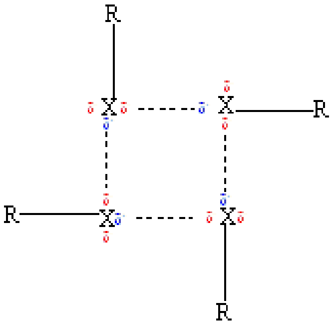

Figure. The scheme of the structural motif that occurs in the system under investigation.

The tetrameric complex used as a model system was found in the crystal structure in which the halogen bonds were stabilizing the solid state structure.[1] Decomposition of interaction energy[2] on two–, three– and four–body terms allowed to conclude that the individual halogen bonds very weakly cooperate forming the complex. The non–additive contribution to interaction energy is negative, but of very small value in respect to total interaction energy (less than 0.01%), indicating very weak cooperativity of halogen bridges. Moreover, a few Basis Set Superposition Error (BSSE)[3] schemes (namely: SSFC,[4] PAFC,[4] and VMFC[5]) were applied in order to study the influence of BSSE on the interaction energy and its terms. Both structural and energetic consequences of complexation were investigated. The importance of the chemistry model used in calculations was also studied.

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No. 14, Poster Session I

Noncovalent Interactions: Quantum Monte Carlo Approaches CCSD(T) to 0.1 kcal/mol

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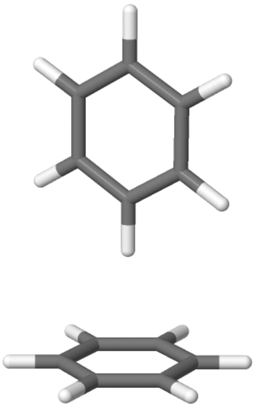
An accurate description of noncovalent molecular interaction energies is one of the most challenging tasks in computational quantum chemistry. Typically, nonempirical CCSD(T)/CBS values have been used as a benchmark reference. The practical use of the CCSD(T) is however fairly limited due to the rapid growth of its computational cost ($O(N^7)$) with the number of considered basis functions N. Here we show, that the fixed-node diffusion Monte Carlo (FN-DMC) method with a more favourable scaling ($O(M^3)$), with the number of electrons M, is capable of reaching the CCSD(T)/CBS within subchemical accuracy ($<\ 0.1$ kcal/mol) on a testing set of six small noncovalent complexes. These include dimers of ammonia, water, hydrogen fluoride, methane, ethene and ethene/ethyne complex. In larger complexes, where we test the identified protocol, i.e. benzene/water, benzene/methane, and the T-shape benzene dimer, FN-DMC provides interaction energies that agree within 0.25 kcal/mol with the best available CCSD(T)/CBS estimates. The demonstrated predictive power in conjunction with the favourable scaling of the FN-DMC thus provides new opportunities for studies of the vast and important class of medium/large noncovalent complexes.



No. 15, Poster Session I

A novel framework for deriving triples and quadruples corrections to the CCSD energy

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Using the coupled cluster energy Lagrangian technique, we have performed a perturbation analysis, in which the CCSD state is considered as the unperturbed reference state and the fluctuation potential and the effect of triple and quadruple excitations as perturbations. By counting orders in the fluctuation potential in the expansion away from the CCSD energy point towards the CCSDT or CCSDTQ energies (depending on truncation level), amplitudes and Lagrange multipliers that carry orders are derived and used in conjunction with Wigner's $2n + 1$ and $2n + 2$ rules to determine energy corrections from the energy Lagrangian. The analysis reveals that approximate triples and quadruples may be introduced in a hierarchical fashion at different levels of accuracy; the models resulting form this hierarchy encompass— to lowest order—the models of the CC(m)PT(n) hierarchy. However, the two hierarchies begin to differ at higher orders owing to the different pictures in which they are derived and established, namely EOM–CC and coupled cluster energy Lagrangian theory, respectively. In the present work, we seek to uncover these differences.

No. 16, Poster Session I

Modeling of Phytochrome Absorption Spectra

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Phytochromes constitute a family of red/far-red absorbing photosensory proteins that function as control systems for several physiological and developmental processes in response to light conditions in plants, bacteria, cyanobacteria and fungi. Despite their important roles in Nature, comparatively few computational studies have been devoted to these proteins.

In this work [1], we assess the performance of hybrid quantum mechanics/molecular mechanics (QM/MM) methods for calculating the UV-vis absorption spectrum of the first phytochrome to be resolved by crystallography. We investigate how the choice of QM method and the size of QM system affect the computed spectrum, and demonstrate that good agreement (~0.15 eV) between calculated and experimental absorption maxima can be achieved for both the Q and Soret bands. Furthermore, for the Q band underlying the primary photochemistry of phytochromes, the calculations suggest that the overall long-range electrostatic effect from the protein environment tends to *red-shift* the intrinsic absorption of the bilin chromophore, whereas short-range chromophore-protein interactions overall *blue-shift* this peak.

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No. 17, Poster Session I

The proteolytic reaction of papain: ONIOM-type hybrid QM/MM calculations and Poisson-Boltzmann electrostatic correction

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Owing to the numerous experimental and theoretical works have been carried out on the papain (Fig. 1.) during the last two decades, a semi-quantitative model for the cysteine protease reactions could be derived. Nevertheless, some details, especially the exact sequence of bond breakage and formation and the relative energies of the stationary points on the potential energy surfaces have to be revealed.

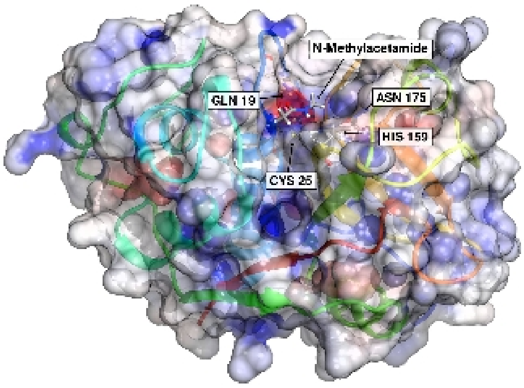

Figure 1. The structure of papain (ribbons), N-Methylacetamide and the catalytic triad (licorice). Visualized with Chimera (http://www.cgl.ucsf.edu/chimera/), the ESP surface was calculated with DelPhi (http://compbio.clemson.edu/delphi.php).

Our aim was to determine a feasible reaction path for the protease reaction of papain. ONIOM-type hybrid QM/MM calculations with electronic embedding approximation [1, 2] were used to map the potential energy surfaces and to find the local minima and first order saddle points on its. The existences of these specific points were proven by frequency analysis. MP2 method and modern density functional theories using standard basis sets with and without diffuse functions were applied throughout the study. Only the vicinity of catalytic site and the catalytic site itself were allowed to move during optimization. Poisson-Boltzmann (PB) model was used to calculate the electrostatic part of solvent effect on energy differences.

Besides the "exact" (at the levels of theories we used) stationary point geometries, energies and relative energies the most important results we obtained the instability of the "classical" tetrahedral intermediate state. The finding that the PB reaction field theory without any specific hydrogen bond is sufficient to favor the zwitterionic catalytic center [3] over the neutral one can be emphasized as well.

Acknowledgement. This work was supported by hungarian scientific research grants (OTKA K-106294, NIIy - 1057, TÁMOP-4.2.2.A-11/1/KONV-2012-0045 and TÁMOP-4.2.2.C-11/1/KONV-2012-0010)

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No. 18, Poster Session I

A Polarizable Continuum Model of solvation designed for QMC: ground and excited states of solutes.

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We show a novel Polarizable Continuum Model (PCM) scheme we have developed to include both surface and volume polarization of the dielectric medium. In particular, the treatment of volume polarization, due to quantum mechanical penetration of the solute charge density in the solvent domain, is based on quantum Monte Carlo techniques. The method allows to accurately solve Poisson's equation of the solvation model coupled with the Schrödinger equation for the solute [1,2]. The performance of the approach has been verified on a representative set of solutes in water as solvent [2] and in the transfer of glutamic acid and related ions from a lipidic phase to water [3]. The present model has been recently extended to treat the effects of solvation in solute vertical electronic transitions. Some results on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ vertical transition of s-trans-acrolein in water are here presented [4].

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No. 19, Poster Session I

POSTER /

A combined experimental and theoretical study on the structure of genipin in solution

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ABSTRACT : Today the design of new low-impact materials mimicking structures and/or functions of natural systems is a challenge in research. So in the field of food, fabric and hair coloring, large efforts have been made in such a goal. For instance, starting from naturally colored molecules, new technologies have been developed to obtain natural, not toxic and effective final products.

Among the natural sources of colorants, the fruit of *Gardenia jasminoides* provides a series of yellow blue and red colorants already used in food industry [1]. Blue and red pigments can be obtained from one of primary actives of gardenia fruits, the iridoid glycoside geniposide [1, 2]. In particular, the product of the enzymatic hydrolysis of geniposide is the aglycone genipin, well known to easy react with primary amines [3, 4] yielding blue pigments [5, 6]. Despite the applicative and industrial interests of genipin, its experimental characterization is still far to be complete.

In such a scientific context characterized by a lack of information and contrasting mechanistic hypotheses, theoretical modeling can be a powerful tool to support experimental data in unambiguously identifying molecular structures and better understanding of their stability in solution. With this aim at scope, a combined experimental and theoretical work is here presented with regard to the analysis of the tridimensional structure of genipin in solution through ^{1}H-NMR spectroscopy and modeling. Starting from these results, the equilibrium between the different genipin forms in solution has been then investigated at theoretical level, by also taking into account also the possible role of the solvent (ethanol and/or water).

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No. 20, Poster Session I

The quartet-quartet crossing in Ir...benzene half-sandwich complex

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The adsorption of aromatic molecules on metal surfaces is an important process in surface science, catalysis, molecular electronics, and spintronics. Theoretical calculations can provide essential understanding of the nature of binding between various aromatic adsorbates and metals.

In our previous study[1] we found out, that the resulting MS-CASPT2-SO/ANO-RCC-VQTZP curve showed the double minimum. While the first minimum corresponds to the interaction of singlet closed-shell $^1S_0$ state of Pt atom, the second minimum which appears after inclusion of spin-orbit coupling corresponds to the interaction of $^3F_4$ state of Pt atom with benzene molecule.

The Ir...benzene was studied at the single- and multi-reference WFT level. The two different single-reference WFT approaches used include the MP2 and more accurate spin-adapted CCSD(T) method with restricted open-shell Hartree–Fock (HF) reference functions. The multireference CASPT2 with RASSI-SO and MRCI with Breit-Pauli-SO operator were also utilized.

The nature of bonding and stability of Ir...benzene is similar to the interaction between Pt metal atom with benzene molecule. The double-minimum potential curve for Ir...benzene complex corresponds to the quartet-quartet spin-crossing and it is not neccessary to include the SOC effects.

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No. 21, Poster Session I

Theoretical and spectral characterization of 5,6-dichloro-2-(2’,3’/2’,4’/2’,5’/3’,4’/3’,5’-dimethoxyphenyl)-1*H*-benzimidazoles

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Benzimidazole and its derivatives are known to play crucial roles in the structures and functions of a number of biologically important molecules [1]. The benzimidazole ring system is present in clinically approved anthelmintics, antiulcers, antivirals and antihistamines [2].

In this study, theoretical and spectral characterizations of 5,6-dichloro-2-(2’,3’/2’,4’/2’,5’/3’,4’/3’,5’-dimethoxyphenyl)-1*H*-benzimidazoles (**I** - **V**, Fig. 1) were studied. FT-IR, FT-Raman, NMR, mass and fluorescence spectra of the compounds were investigated. Theoretical calculations were performed by using Density Functional Method (DFT, B3LYP) with 6-32G(d,p) basis set.

According to the calculations the benzimidazole and the phenyl rings are nearly perpendicular to each other (Fig. 1). The highest dipole moment value is belonging to the compound **V** (8.24 D), and the lowest dipole moment with 6.92 D is belonging to **I**.

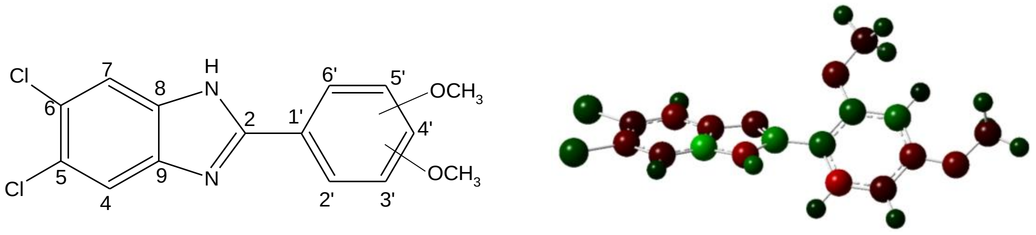

Fig. 1. General formula of the compounds in the study (left) and charge distribution of **II** (right).

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No. 22, Poster Session I

DFT Study of the Stereo-Selectivity of Oxygenated Hetero-cycles from 10 to 12 Links

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Intra-Molecular Diels-Alder (IMDA) reactions of tethered trienes can furnish two distinct diastereoisomeric products. The cis (i.e. endo) stereoisomer and the trans (i.e. exo) stereoisomer. Experimental evidences shows a quite high cis stereo-selectivity for 10 links compounds (cis/trans = 70:30) while 11 and 12 links exhibit no particular selectivity. DFT (B3LYP/6-31G*)[1,2] computations provide useful insights into the origins of this amazing stereo-selectivity. The cyclization path towards trans stereo-isomer is always thermodynamically favored whatever the size of the system. The high cis stereo-selectivity displayed by the 10 links system is kinetically controlled by a tug of war between ring strain and electronic effects in the transition structure. The dual descriptor[3,4] of chemical reactivity, a conceptual DFT based descriptor designed to delineate electronic effects, has been used to unravel the stabilizing processes that take place at the TSs.

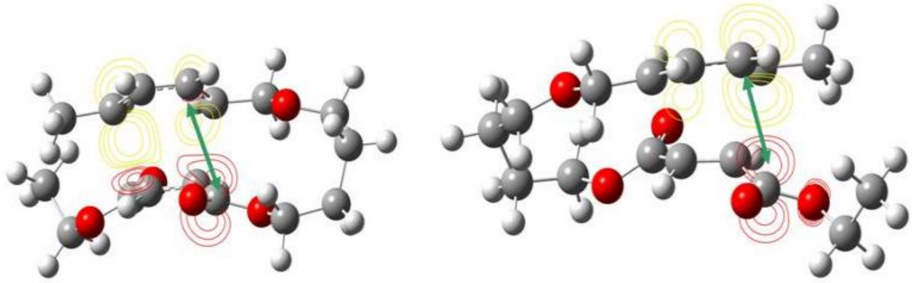

Figure. Δf maps calculated at the B3LYP/6-31G(d) for the **TS**s and projected on a plan that intersects the carbon involved in the secondary interactions.

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No. 23, Poster Session I

Cu on ZnO: alternating Cu charge states and accurate adsorption energy calculations upon charge transfer

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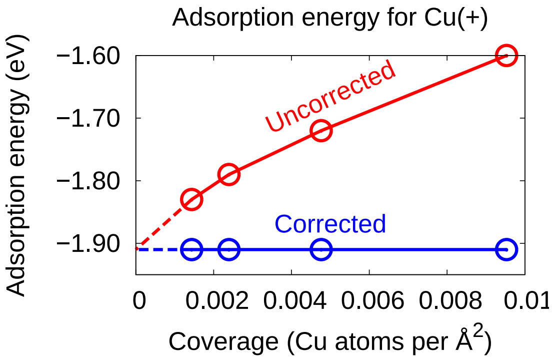
Cu/ZnO catalysts are used in industry to catalyze methanol synthesis and the water-gas shift reaction. It has been suggested that the morphology of the Cu particles influences the catalytic activity. For this reason, understanding and possibly controlling the growth of Cu particles on ZnO is of great interest.

This contribution has two messages: (i) as Cu adatoms diffuse across the ZnO($10\bar{1}0$) surface, their oxidation state repeatedly switches, and (ii) in order to accurately model the adsorption of the positively charged Cu species in a supercell, a “band-filling correction” is needed.

We recently studied the migration of two Cu atoms on the ZnO($10\bar{1}0$) surface and the formation of a Cu dimer using hybrid density functional theory [1]. We found that, depending on the adsorption site, Cu atoms adsorb with either oxidation state 0 or +1. In the latter case, the Cu atom has donated an electron to the ZnO conduction band. Single Cu atoms diffuse across the ZnO($10\bar{1}0$) surface with small migration barriers (0.3-0.4 eV), *repeatedly switching their oxidation states*. The formation of a Cu dimer from two adsorbed Cu atoms is energetically favorable with two competing structures of similar stability, both being charge neutral.

We have subsequently studied the coverage dependence of the Cu/ZnO adsorption energy (E_{ads}) in detail, and found that due to the charge transfer between Cu and ZnO it is necessary to invoke a correction scheme to calculate accurate E_{ads} values in the low-coverage limit. *The calculated adsorption energy of the Cu(+) species is highly coverage dependent*, which could possibly be attributed to electrostatic repulsion between the positively charged Cu species, but also to the "filling-up" of the ZnO conduction band that occurs as a result of the charge transfer from Cu to ZnO. We propose a simple method, the *band-filling correction*, to calculate E_{ads} in the low-coverage limit from calculations performed for finite coverage [2].



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No. 24, Poster Session I

The Equation of Motion Coupled Cluster Approach as Implemented in ORCA

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Equation of Motion Coupled Cluster (EOM-CC) theory allows for the description of the lowest few excited states of molecular systems. It provides accurate results at a cost ($\mathcal{O}(N^6)$ for EOM-CCSD) still feasible for the study of small and medium size species.

The purpose of the present work is on the one hand to shortly describe the variants of EOM-CC implemented in the development version of the ORCA quantum chemistry program package. On the other hand, by introducing various approximations we wish to find the most efficient treatment for a given EOM variant corresponding to a desired accuracy. A road map of the project will be presented here, with much of the work still in progress.

The canonical EOM equations are reformulated as a dressed CI problem, where the precomputed dressed quantities allow for an efficient factorization. Left and right hand solutions are both available, enabling the calculation of various properties. Other than the electron excitation (EE) variant, the Electron Attachment (EA) and Ionization Potential (IP) EOM variants are also discussed. In order to further reduce the cost requirements of EOM, the versatile tool of many body similarity transformations is evoked in the form of the similarity transformed EOM (STEOM) theory, which will also be considered in some detail here.

As far as approximations are concerned, we plan to focus on the following approaches: the resolution of identity/density fitting (RI/DF) approximation, the Chain of Spheres (COS) algorithm, and the pair natural orbital (PNO) expansion of the virtual space. The latter approach has proven useful in CC theory, as demonstrated by the success of the LPNO (localized PNO) and the DLPNO (domain based LPNO) CC variants. Possibilities of extending these schemes to EOM are also considered.

No. 25, Poster Session I

Natural Correlation Orbitals in Local Laplace Transformed Triples (T) Correction

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The coupled cluster (CC) singles and doubles method (CCSD) with perturbative triples correction (CCSD(T)) [1] became the most successful tool for routine and accurate calculations of dynamical correlation effects in medium-sized molecules. It is size consistent, almost variational, and captures the most of the dynamical correlation energy.

The O(N^7) scaling of CCSD(T) makes it difficult to apply it routinely to large molecules. Recent advances in parallel computation (e.g., [2]) has extended its applicability to systems with more than 100 correlated orbitals but the steep scaling precludes applications, for instance, to macromolecules of biological interest. For large systems, most computational effort is spent on the O(N^7) scaling triple substitutions; CCSD scales formally as O(N^6). Local correlation methods, leading to linear scaling, were very successful for CCSD [3]. The triples part is more challenging, as it based on Møller-Plesset perturbation theory, and the noniterative (T) formula uses canonical, i.e., delocalized Hartree-Fock orbitals. An impractical iterative procedure is required in localized orbital basis.

An elegant alternative to the latter, the Laplace transform method [4] enables separate unitary transformations within the occupied and virtual spaces while preserving the simplicity of the canonical formulation. Localizing the occupied MOs reduces the scaling of the triples calculation in two ways: (1) it allows the elimination of triplets *ijk* where the occupied orbitals are distant, and, more importantly, (2) it makes it possible to reduce the dimension of the local virtual space. Methods which truncate the virtual space at the canonical level [5] can diminish the computational effort of the triples significantly but do not affect the scaling.

Localization of virtual space is difficult. In our 2010 program [6] we used a set of optimized virtual orbitals for each occupied MO *i*, obtained as the pseudonatural orbitals (PNOs, [7,8]) of the *diagonal* pair *ii.* These are not as efficient, particularly for dispersion, as PNOs but require many fewer orbital transformations. These orbitals were also used by Schütz *et al.* [9] under the name of Orbital-Specific Virtuals. In a program under development we use Natural Correlation Orbitals (NCOs) which combine the advantages of OSVs and PNOs, by using a hierarchy of virtual spaces (two or three levels) for each occupied orbital.

We demonstrate the efficiency and scaling of our current code which uses only a single virtual space per occupied orbital. Although it requires (a) numerical quadrature at 4-5 points in the Laplace transformation and (b) overlap matrices and transformations between different virtual spaces, it is very efficient. It can recover a very high fraction of the triples correlation energy which is important to avoid artifacts on energy surfaces.

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No. 26, Poster Session I

Analytic Derivatives of Quartic-Scaling Doubly Hybrid XYGJ-OS Functional: Benchmark for Nonbonded Complexes

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Analytic gradients of XYGJ-OS[1], an opposite-spin (OS) ansatz[2] applied doubly hybrid functional with quartic scaling, is derived and implemented into Q-Chem quantum chemistry package[3]. The calculation of the first gradients scales quartically as the functional itself, with aid of Laplace transformation and resolution-of-identity technique. The assessment of XYGJ-OS optimized geometries for nonbonded complexes was performed by direct comparison with CCSD(T) geometries firstly, and CCSD(T)-F12 energy comparison with M06-2X and RI-MP2 geometries. The result showed that XYGJ-OS produced high quality geometries comparable to CCSD(T) ones, for both weakly bound complexes and molecules in S66 benchmark set[4], and were the most stable among the geometries obtained by three aforementioned methods.

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No. 27, Poster Session I

Calculation of response properties using Extended Coupled Cluster Method

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Extended Coupled Cluster (ECC) Method is used for calculation of response properties. Due to double linking nature of the functional, there are no disconnected terms present in the calculation of energy and energy derivatives and the series gets naturally terminated. Double linked nature of the functional ensures that we always have size extensive properties. ECC being variational is best suited for the property calculations.

Spectroscopic properties such as IR intensities, Raman intensities and viberational frequencies are calculated using ECC approach. We have used semi-numerical approach for these calculations[1] . IR and Raman intensities are the derivatives of energy with respect to electric field and geometric perturbation while, viberational frequencies are the derivatives of energy with respect to geometry. Recently, the analytic ECC approach has been applied for evaluating dipole-quadrupole polarizability [2]. Dipole-quadrupole polarizability, is the second derivative of energy with respect to field and field gradient.

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No. 28, Poster Session I

Symmetry breaking in a nutshell.
The *odyssey* of a pseudo problem in molecular physics.
The $\tilde{X}\,^2\Sigma_u^+$ BNB case revisited.

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The $\tilde{X}\,^2\Sigma_u^+$ BNB state considered to be of symmetry broken (SB) character has been studied by high level multi reference variational and full configuration interaction methods. We discuss in great detail the roots of the so called SB problem and we offer an in depth analysis of the unsuspected reasons behind the double minimum topology found in practically all previous theoretical investigations. We argue that the true reason of failure to recover a $D_{\infty h}$ equilibrium geometry lies on the lack of permutational symmetry of the wavefunctions employed and is by no means a real effect.[1]

[1] Apostolos Kalemos, submitted for publication to J. Chem. Phys.

No. 29, Poster Session I

A density functional investigation of ethylene adsorption on graphene and VIIIB metal-doped graphene surfaces

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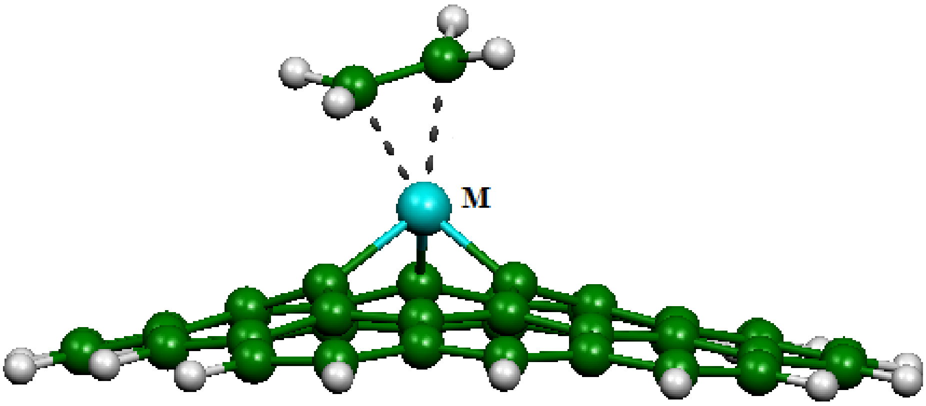
The ethylene adsorption on graphene and VIIIB metal-doped graphene (Fe-, Ru-, Os, Co-, Rh-, Pd-, Ir-, Ni- and Pt) sheets was investigated by means of density functional theory at the B3LY/LanL2DZ theoretical level. The graphene model composed of 14 benzene rings with the edge carbons terminated by hydrogen atoms ($C_{42}H_{48}$). For metal-doped graphene model, the carbon atom at the center of the sheet was replaced with metal atom ($MC_{41}H_{48}$). It is found that all metal-doped graphene sheets can adsorb ethylene molecule via exothermal process. Structural and energetic properties are also reported.



The configuration of ethylene adsorbed on metal–doped graphene sheet.

No. 30, Poster Session I

Non-covalent Interactions to Graphene: Theory and Experiment

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Graphene is a two-dimensional π-conjugated material having extraordinary physical properties, which makes its a perspective material in catalysis, energy storage, nano(opto)electronics and sensor applications.[1] The application potential of graphene can be enormously enhanced by its covalent and non-covalent functionalization.[2] An exact quantification of interaction between graphene and guest molecules as well as thorough understanding of the nature of interaction between graphene and guest molecules have not been yet achieved. We analysed nature of interaction between Ag, Au, Pd, Pt metal atoms and clusters to benzene, coronene and graphene, by quantum chemical calculations [3,4] The silver atom is bound weakly by London dispersion forces, while interaction of palladium and platinum is significantly stronger and involves some covalent character. Involvement of relativistic effects is required for a reasonable description of interactions involving Au and Pt. We measured the interaction force between metalized AFM tips (Cu, Ag, Au, Pt and naturally Si were considered, Figure) and graphene and correlated the results with theoretical calculations carried out by density functional theory (DFT). The theoretically calculated interaction forces agree with the experimental data, only when non-local electron correlation and exact Hartree-Fock electron exchange is explicitly treated.[5] The AFM tip covered by copper displayed the highest affinity to graphene among the metals considered. We also quantified the adsorption enthalpies between graphene and several organic molecules and compared the experimental results with theoretical calculations carried out by DFT, SCS(MI)-MP2 and CCSD(T) calculations.[6]

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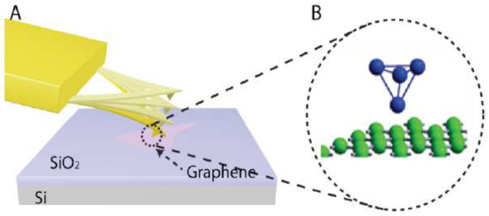
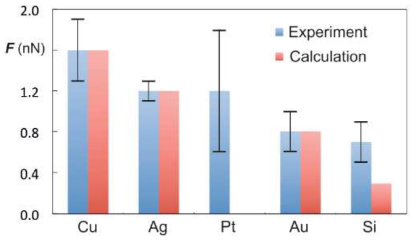


Adopted from Ref. [5].



No. 31, Poster Session I

Metal-substituted rubredoxin - theoretical prediction of the spin-spin coupling constants using ZORA

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The indirect nuclear spin-spin coupling constants between hydrogen atom in amid group in cysteine and metal cation in rubredoxin molecule have been calculated by means of density functional theory with zeroth order regular approximation Hamiltonian (DFT-ZORA). The mercury and the cadmium cations were chosen as metal cation -same as in the experimental work of Blake and coworkers [1].

The metal atom and four molecules of cysteine were selected as a model system - Figure 1.

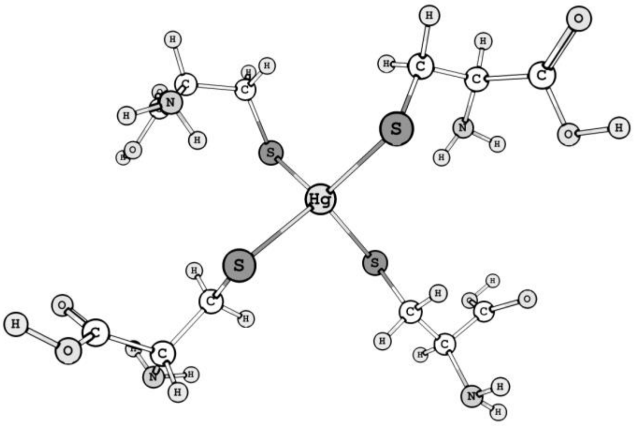

Figure 1. Model system of mercury substituted rubredoxin

Various functionals and basis sets have been tested on the model system. We have also checked how the predicted coupling constant value depends on the level of theory. It has been modeled how these values are affected by rotation of some groups in the model system.

The measured spin-spin coupling constants are in 0,29-0,56Hz range for Cd and in 0,57-2,20Hz range for Hg. The calculated values are in the similar range.

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No. 32, Poster Session I

Characterization of protein-ligand complexes using molecular dynamics simulations by consideration of $GABA_A$ protein as receptor and Lavender compounds as ligand

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Abstract:

$GABA_A$ receptors are a class of receptors that respond to the neurotransmitter gamma-aminobutyricacid (GABA), the chief inhibitory neurotransmitter in the vertebrate central nervous system, which are ligand-gated ion channels and are known as ion tropic receptors [1-5]. Lavender is a species of flowering plants in the mint family and is native to the mountainous zones of the Mediterranean and flourishes throughout southern Europe, Australia, and the United States. This herb has been used as a remedy for a range of ailments from insomnia and anxiety to depression and fatigue. This plant is grown mainly for the production of lavender's oil which has antiseptic and anti-inflammatory properties. A number of studies have reported that this oil may be beneficial in a variety of conditions, including insomnia, hair loss, anxiety, stress, and postoperative pain [6, 7]. This plant is being studied for antibacterial and antiviral properties [8]. In this work, we have simulated and studied the complexes of different chemical compounds found in the lavender extract with GABA protein as receptor. Our Simulations are based on molecular dynamics (MD) approach through force fields and GROMACS package is used to do MD simulations to locate sites with favorable interaction energy.

Keywords: $GABA_A$ receptors, Lavender plant, Molecular dynamics, GROMACS

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No. 33, Poster Session I

Proteolysis mechanism in matrix metalloproteinases suggested by molecular modeling

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The matrix metalloproteinases (MMPs) comprise a family of zinc-dependent endopeptidases which play key roles in tumour growth of metastasis. Their proteolytic activities in living organisms are regulated by tissue inhibitors of metalloproteinases (TIMPs) and disruption of this balance results in different diseases. Numerous of resent studies are devoted to the rational design of the artificial inhibitors of the MMPs based on the results of molecular docking. We suppose that a complex analysis of this problem involving modeling of the mechanism of proteolysis in the active site of the MMPs by means of combined quantum mechanics/molecular mechanics (QM/MM) approaches considerably expands the current knowledge. Application of quantum based approaches allows one to overcome shortcomings in using conventional force field parameters in molecular mechanics modeling and to proceed to simulations of chemical reactions in the enzyme active sites. Combined quantum mechanics/molecular mechanics (QM/MM) approach was applied to calculate energy profiles for the rate limiting step of the proteolysis of the native oligopeptide substrate Ace-Gln-Gly-Ile-Ala-Gly-Nme by MMP-2. The QM calculations were carried out in density functional theory (DFT) approximation with hybrid functional BB1K and the double-ζ 6-31G** basis set for all atom except Zn and 6-31G* for Zn. MM region was treated with the AMBER force field. According to our calculations, the first step, corresponding to the nucleophilic addition of OH- to the carbonyl carbon atom of the substrate coupled to proton transfer from the water molecule to the carboxyl group of the glutamate is rate limiting and has activation barrier 12 kcal/mol.

This work was supported by a Dynasty Foundation Fellowship to Maria Khrenova.

No. 34, Poster Session I

A simple and accurate non-emperical doubly-hybrid density functional using quadratic approximation of adiabatic connection formula

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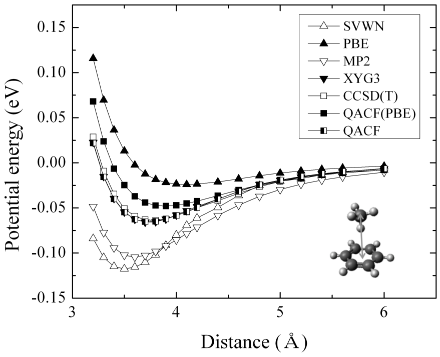
The Kohn-Sham density functional theory(DFT) has been used to predict various properties of molecular system. However most of the density functional, such as LDA, GGA, and hybrid functional, cannot reproduce the heat of formation energy within chemical accuracy of 0.05 eV. Doubly hybrid density functionals (DHDFs) are presently the most accurate density functional due to the inclusion of nonlocality for both exchange and correlation terms, but these functionals are empirically obtained to reproduce experimental data. In this poster, we present an analytic derivation of DHDF based on Becke's adiabatic connection formula. Using quadratic approximation of adiabatic connection formula we obtain a simple analytic expression for a new DHDF whose accuracy reaches 0.1 eV. The test using a methane-benzene complex shows that the new functional also yields an excellent description of the entire potential energy curve that is nearly identical to CCSD(T).



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No. 35, Poster Session I

Theoretical investigation of the binding of a positron to vibrational excited states of hydrogen cyanide molecule

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Positrons are widely used in both scientific and technological areas such as physics, chemistry, material science, medicine, and their interdisciplinary areas. A positron affinity (PA), which is a binding energy of a positron to an atom or molecule, have now been experimentally measured by Surko and co-workers for many molecular species such as some hydrocarbons (alkanes, alkenes, and aromatics), alcohols, and halogenated hydrocarbons [1-3]. Recently, Danielson *et al*. [4] have experimentally measured the binding of a positron to acetonitrile with the vibrational Feshbach resonance (VFR) technique and estimated its PA value as 180 meV. There is, however, no direct experimental evidence for the positron binding to hydrogen cyanide molecule (HCN) that is the simplest molecule including the nitrile (-CN) functional group. In this study, thus, we analyzed the characteristic features of the binding of a positron to HCN molecule with both quantum Monte Carlo (QMC) and *ab initio* molecular orbital calculations in order to theoretically predict the PA value of HCN molecule.

A positron should be able to form an infinite number of bound states with molecules if the molecule has a dipole moment with a value greater than 1.625 debye (the critical dipole moment). As is well known, nitrile molecules have strong dipole moments greater than 3 debye. Recently, we show that HCN molecule with a dipole moment of 3.3 debye, has a small PA value of 38 (5) meV at its equilibrium structure by the QMC calculation [5]. However, the effect of molecular vibrations must be taken into account for theoretically predicting an *observable* PA value, because the most of the experimental PA values are measured through the VFR, in which a positronic molecular complex can be formed at the molecular vibrational excited states. Thus, in this presentation, we will report the vibrational averaged PA values of HCN molecule for several vibrational excited states. In this analysis, the PA values at many molecular geometries are calculated with the configurations interaction (CI) calculation including electronic single excitation, positronic single excitation, and double excitations of single electronic - single positronic excitation configurations, and are averaged with a weight of vibrational probability density obtained with multi-dimensional unharmonic vibrational state analysis based on vibrational QMC technique.

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No. 36, Poster Session I

Methods for the accurate description of Platinum-DNA interaction

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Paul Ehrlich, who initiated an extensive search for the "Zauberkugel" a selective anti-infective drug in the beginning of the 20th century, introduced the age of inorganic chemotherapeutics.[1] Sixty years later Rosenberg discovered the biological activity of cis-diamminedichloridoplatin(II) and in 1969 reported its anti-tumor activity in mice.[2] Meanwhile Iridium, Rhodium, Ruthenium, Gold and other transition metal complexes have been screened for cytostatic and cytotoxic activity on cancer cells, some of them with very promising results.[3,4,5]

Cisplatin is still a widely used chemotherapeutic drug in case of cancer, but due to serious adverse effects the search for new platinum compounds with increased selectivity for cancer cells is continued.

Molecular modeling is a powerful tool to support and guide this research. As the accurate description of transition metal complexes puts high demands on the applied methods, we created a representative dataset of platinum complexes and performed a thorough benchmarking of available ab initio methods. For the future we are aiming on the detailed description of the interaction between Platinum complexes and biomolecules by QM/MM methods.

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No. 37, Poster Session I

Automated optimisation of quantum chemical algorithms within an integrated tensor framework

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The manual implementation of quantum chemical ab initio methods can become unpractical and error-prone once a certain degree of complexity is exceeded. Therefore, automation tools that help simplifying method implementation processes are increasingly important.

Along these lines, we present a tool to optimise high-level algorithms towards memory and I/O efficiency in the context of the Integrated Tensor Framework (ITF) [1, 2] developed by G. Knizia. In this tensor framework, algorithms are composed of abstract high-level instructions, e.g. to access tensors, create loops or to perform tensor contractions, and these algorithms are executed on a virtual machine (VM) within the ITF at runtime.

In order to assemble memory and I/O efficient algorithms for complex methods consisting of many interconnected binary contractions, the optimisation tool makes particularly use of the following algorithmic manipulations: (1) the introduction of loops, (2) the reuse of tensors and (3) the optimisation of the contraction order. Starting from sets of coupled binary tensor contractions and corresponding tensor properties, a combination of dedicated heuristics and Simulated Annealing is then used for optimisations in the present large optimisation space. This optimisation strategy can be applied to a large range of methods within the ITF; including CCSD, CCSD gradients, DF-CASPT2 gradients [3] and MRCIC [1].

Selected benchmark examples furthermore present the usefulness of this optimisation approach for various ab initio methods available within the ITF.

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No. 38, Poster Session I

Ab Initio Molecular Dynamics Simulations of H_2 Formation inside POSS Compounds

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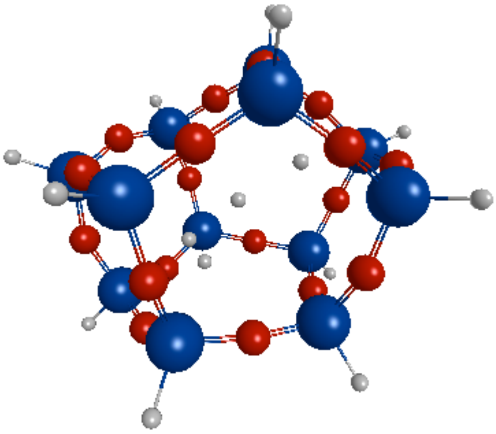
Polyhedral oligomeric silsesquioxanes (POSS), $[RSiO_{1.5}]_n$ (n = 4, 6, 8, 10, 12, …), referred to as T_n, have been the focus of considerable experimental and theoretical interest because of their wide variety of practical uses for many years. Especially, making use of the cage cavities for encapsulation of atoms and ions is one of the very exciting research areas of POSS compounds. The present study applies the ab initio molecular dynamics (AIMD) method to examine the mechanism and dynamics for H_2 formation process inside some POSS compounds in various situations.

Three types of H_2 formation were considered here : (I) $H + H@T_n \rightarrow H_2@T_n$[1], (II) $H + H_2@T_n \rightarrow (H + H_2)@T_n$, and (III) $H + (H + H_2) \rightarrow 2H_2@T_n$; n=8 and 12. The host molecules are T_8 with a cubic structure and the larger T_{12}. The various reactions, such as H_2 formation ($H + H \rightarrow H_2$), H-H exchange ($H + H_2 \rightarrow H_2 + H$) and escaping of a H or H_2 from the cage, take place depending on the initial condition.



The state of two hydrogen atoms and one hydrogen molecule moving inside T_{12} at a time of the AIMD trajectory for the reaction of $H + (H + H_{2)}@T_{12} \rightarrow 2H_2@T_{12}$

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No. 39, Poster Session I

Theoretical studies of possible routes for the synthesis of amino acids in space

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One of the most interesting debates in interstellar chemistry concerns the possibility of finding biomolecules in astronomical sources. Among them, amino acids are of particular relevance in Astrobiology. It has been argued that interstellar amino acid formation could precede the syntheses of more complex molecules. In particular the search for interstellar glycine, the simplest amino acid, has been a recurrent subject in recent years. However, despite several radioastronomical searches, no conclusive identification of glycine has been possible so far. Nevertheless, the recent detection in space of related molecules such as amino acetonitrile, has prompted the search for interstellar glycine. In addition, experimental studies [1] have shown that precursors of glycine and alanine can be formed under laboratory conditions by the gas-phase reactions of protonated and ionized hydroxylamine with acetic and propanoic acids.

Within this context computational studies can be valuable to ascertain whether there are plausible and efficient synthetic routes toward interstellar glycine. Different theoretical studies [2,3] on these and related processes have been carried out in recent years to evaluate their feasibility under interstellar conditions. In the present communication we will present a theoretical study of different ion-molecule processes which have been proposed as possible routes toward the synthesis of precursors of glycine in the interstellar medium. Reactions involving chemical species such as acetic acid, formic acid, hydroxylamine, and ammonia derivatives, all of them of astrophysical significance, are considered.

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No. 40, Poster Session I

Integrating the Laplacian of electron density in fuzzy overlap space as a measure of covalent bond order

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Bond order is an important concept for understanding the nature of chemical bond. In this work, we propose a novel definition of covalent bond order based on the Laplacian of electron density $\nabla^2\rho$ in fuzzy overlap space, called Laplacian bond order (LBO).[1] The LBO between atom A and B can be simply written as

$$\mathrm{LBO}_{A,B} = -10 \times \int_{\nabla^2\rho<0} w_A(\mathbf{r}) w_B(\mathbf{r}) \nabla^2\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

Where w is a smoothly varying weighting function and represents fuzzy atomic space, hence $w_A w_B$ corresponds to fuzzy overlap space between A and B. Note that the integration is only restricted to negative part of $\nabla^2\rho$. The physical basis of LBO is that the larger magnitude the integral of negative $\nabla^2\rho$ in the fuzzy overlap space, the more intensive the electron density is concentrated in the bonding region, and therefore, the stronger the covalent bonding.

The reasonableness and usefulness of LBO were demonstrated by applying it to a wide variety of molecules and by comparing it with many existing bond order definitions.[1] It is shown that LBO has a direct correlation with the bond polarity, the bond dissociation energy and the bond vibrational frequency. The computational cost of LBO is low, also LBO is insensitive to the computational level used to generate electron density. In addition, since LBO is inherently independent of wavefunction, one can in principle obtain LBO by making use of accurate electron densities derived from X-ray diffraction data.

LBO has been implemented in our wavefunction analysis program Multiwfn,[2] which can be freely downloaded.

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No. 41, Poster Session I

Relativistic and correlation effects on heavy molecules containing Sn and Pb atoms

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A new procedure that was recently published[1], which mix together accurate experimental chemical shifts (δ) and theoretical magnetic shieldings (σ) of heavy atom containing molecules, was applied on a family of heavy-halogen containing molecules to calculate the absolute value of σ(Sn) and σ(Pb). We found out that the absolute magnetic shielding σ(Sn; $SnMe_4$) in gas phase shall be close to 3852.38 ppm ± 20,33 ppm. In the case of Pb, σ(Pb; $PbMe_4$) shall be close to 14067.10 ppm ± 501.90. Such values correspond to the RPA level of approach within relativistic polarization propagators, that seems to be the more accurate as compared with DFT calculated values.

We also studied the dependence of such shieldings with 4-component functionals as implemented in the DIRAC code. To our knowledge there are no previous studies on these matters. We show that RPA results are more reliable than the DFT ones. We argue that DFT functionals should be modified to give better results of NMR magnetic shieldings within the relativistic regime. There is a dependence between electron correlation and relativistic effects that should be introduced in one way or another in the functionals. They were parameterized in a nonrelativistic context and so cannot be used properly within the relativistic regime.

In the $XY_{4-n}Z_n$ (X = Sn, Pb; Y, Z = H, F, Cl, Br, I; n = 0, 1, 2) family of compounds there should appear the newest heavy-atom effect on vicinal heavy atoms, HAVHA[2, 3]. We found that such effects are among the most important relativistic effects in compounds were the central atom is surrounded by three or four halogen atoms belonging to the fourth or fifth row of the Periodic Table.

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No. 42, Poster Session I

Structure and Dynamics of ionic liquids from first principles simulations: Effects of dispersion corrected density functionals and charge density cutoff

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The thermodynamics, structural and transport properties of an Ionic liquid(IL) were investigated through first principles molecular dynamics simulations. The simulations were carried out using different generalized gradient approximation functionals and the charge density cutoff in the isobaric-isothermal and canonical ensembles. The effects of dispersion interactions on the various properties of cations and anions were investigated. Thermodynamic properties of IL are sensitive to the details of the electronic structure calculations. Subsequently, the calculations were extended to the time dependent vibrational spectroscopy and preliminary results were discussed in terms of correlation between spectral signature and hydrogen bond dynamics.

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No. 43, Poster Session I

Electronic structures and hydrogen absorption properties of Pd/Pt clusters: What is the difference from bulk?

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[Introduction] Bulk Pd is a well-known hydrogen storage material. On the other hand, bulk Pt, which belongs to the same group 10, does not store hydrogen inside but only adsorb them on the surface. Recently, Yamauchi *et al.* investigated hydrogen storage ability of Pd/Pt nano cluster from pressure-composition (PC) isotherm. They expected the enhancement of the hydrogen storage ability by enlarging surface area of the material. The amount of hydrogen absorbed by the Pt nano cluster was enhanced as expected, however that by the Pd nano cluster was much smaller than that by the bulk Pd [1]. The experimental observations mean that the abilities for hydrogen absorption of the metal clusters are precisely controlled by the surface electronic structure of them. In this study, we investigated the differences of the hydrogen absorption properties between Pd and Pt clusters using electronic structure calculations.

[Methods] Resolution of identity DFT (RI-DFT) calculations with PBE exchange correlation functional and def-SV(P) basis sets were performed to investigate the electronic structure of the Pd/Pt clusters [2]. First, structures of the Pd_{55} and Pt_{55} were optimized with cubooctahedral (O_h) symmetry that was observed by X-ray diffraction experiments [1] (See Fig. 1). Then, the potential energy of H atom in/on the Pd/Pt clusters at grid points of a total number of 17×17×17 (a grid interval is 0.25 Å) were calculated to obtain hydrogen absorption potential energy surface. Natural population analysis was also performed at each grid point.

[Results] Fig. 2 shows that 2D views of potential energy surface (PES) cutting along the Y-Z plane of clusters (See Fig. 1). Figs.2 (a) and (b) show contour plot of the adiabatic potential energy surface for the hydrogen atom, at x = -0.25 and at x= -1.0, respectively. As shown in Fig. 2(a), we could observe much broader stable funnel for Pd_{55} than for Pt_{55}. We also found that the octahedral site of Pd (Fig. 2(b)-left) is more stable than that of Pt. These results indicated that the hydrogen atom in the Pd_{55} cluster can diffuse into the further inside more easily compared with Pt_{55}. The differences of enhancement of the hydrogen storage ability between Pd and Pt clusters will be further discussed in the poster session.

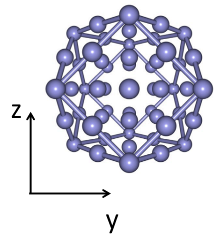

Fig.1 Optimized Pd $_{55}$ with cuboctahedral symmetry (Oh)

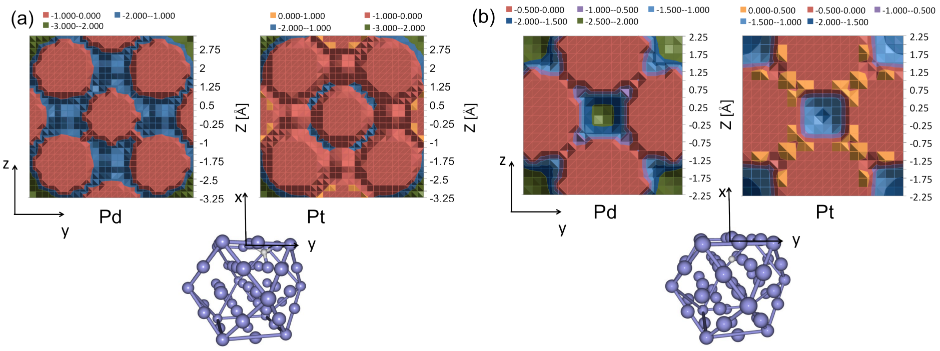

Fig.2 contour plot of the adiabatic potential energy surface for the hydrogen atom, at (a) x=-0.25 (b) x=-1.0

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Acknowledgment One of the author (A.M.) has been supported by JSPS scholarship for young researcher. She is grateful for the support.

No. 44, Poster Session I

Microscopic mechanism of band-gap variations in SiC polytypes based on *ab initio* calculations: Roles of peculiar electron state floating in internal space

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Silicon Carbide (SiC) is a promising material for power electronic devices. In spite of the vigorous studies for SiC, some unaccountable SiC properties are still remained: Some properties cannot be understood by the conventional semiconductor theories. For example, SiC exhibits hundreds of polytypes, and their structural differences come from the differences of the stacking structures. Though their local atomic structures are identical to each other, their band gaps vary substantially as much as 40%: e.g., 3.33 eV for *2H* (AB-stacking) structure, and 2.40 eV for *3C* (ABC-stacking) structure. The microscopic mechanism of the band-gap variations is lacking, and is remained to be a longstanding problem. We have studied the mechanism, based on the density-functional theory (DFT) calculations.

We have found that the band-gap variation is deeply related to the peculiar electron state at the conduction-band minimum (CBM) [1]. The wave function at the CBM has Nearly-Free-Electron (NFE) like character: The electron state at the CBM distributes not near atomic sites, but extends in internal space broadly, thus *floating* in internal space. Therefore, the energy level of the floating state depends on the electrostatic potential at the interstitial sites, thus showing dramatic variations in band gap in *3C* structure. In addition, we have found that the largeness of the spreading space and its symmetry also have great effects on the changes in band-gap. In fact, we have found that band-gap variations can be completely analyzed by an electron-energy level in the 1-dimensional quantum well with its width being “channel length”, representing the largeness of the spreading space of the floating state. Thus, we have clarified that “channel length” is an essential parameter to describe the band-gap variations [2].

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No. 45, Poster Session I

Electronic Structure of Iron Complexes Containing Bipyridine-based PNN Pincer Ligans

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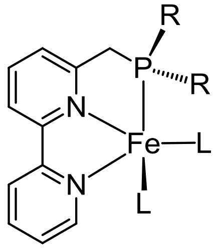
Pincer ligands are used in many transition metal complexes, and these complexes serve as effective catalysts for various reactions. In particular, a complex of Ru and a bipyridine-based pincer ligand was shown to catalyze various environmentally benign reactions, such as the hydrogenation of amides to the corresponding alcohols and amines[1] and the hydrogenation of urea derivatives to amines and methanol[2]. This broad application of the Ru pincer complex encourages investigation of bipyridine-based pincer ligands coordinated to an iron center. Herein, we present a study in which we examine the electronic structure of iron pincer complexes containing the bpy moiety. Our attention is especially concentrated on answering the question of whether the bpy moiety is a spectator ligand or a redox-active ligand. This question arises from study by Scarborough *et al.*[3] who showed several examples of complexes containing bypiridine (bpy) that behave as non-innocent ligand and the complexes have a biradical character.



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No. 46, Poster Session I

Edge Effect in Finite-length Pentaheptite Nanotubes

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Stone-Wales bond rotation[1] transforms four adjacent hexagons into two pentagons and two heptagons. Pentagon /heptagon defects may strongly affect the electronic properties of nanotubes. Crespi[2] applied the SW transformation to graphene in order to modify the hexagonal honeycomb lattice to form another lattice with only heptagons and pentagons (known as pentaheptite). A pentaheptite carbon nanotube PHCNT can be derived by rolling up pentaheptite layer. The one of main structural factors which determine the electronic properties of carbon nanotubes is the periphery structure of the hydrocarbons. It was found that zigzag edges in CNT raise the HOMO energy of the system (the edge effect). In this paper we theoretically study the effects of edges on the electronic properties of PHCNTs by using PM3 method.

We construct PHCNT with the units of azulen belt which is composed from azulene (a pair of pentagon and heptagon). Finite-length PHCNTs have the ends which are armchair edge or zigzag edge. PHCNT can be classified into the following three-types; (a) A-A type : the two ends are armchair edges, (b) Z-Z type : the two ends are zigzag edges, (c) A-Z type : one end is armchair edges and the opposite end is zigzag edges. The PHCNTs in Fig.1 are, from the left side, A-A type, Z-Z type and A-Z type.

We calculated the HOMO and LUMO energies of PHCNTs of the three types with various lengths and diameters. From the obtained results it is found that at each length in units of azulene belt, the HOMO energy for A-A PHCNT is lower than that for Z-Z PHCNT and the HOMO energy for A-Z PHCNT is in the midst of HOMO energies for A-A and for Z-Z PHCNT. This result means that the edge effect on HOMO energy found for pristine CNT holds also for PHCNT. However the edge effect on HOMO-LUMO gap is not found. The discrepancy between the edge effects on HOMO energy and on HOMO-LUMO gap in PHCNT is due to non-alternancy of the system.

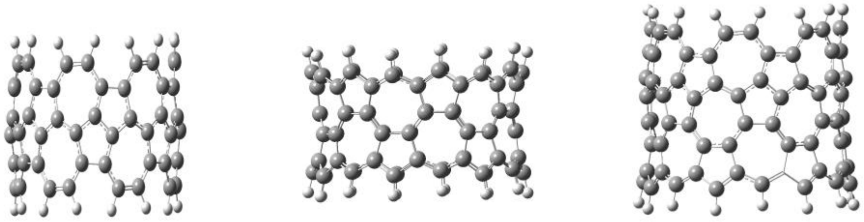

Figure 1 Three types of PHCNT; A-A, Z-Z, A-Z

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No. 47, Poster Session I

Solvation of *tert*-Butyl Alcohol in Water: An Effective Fragment Potential Study

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Recent theoretical and experimental studies of alcohol-water solutions provide evidence for incomplete mixing at the molecular level and retention of the structure of bulk water. To predict the level of mixing and other thermodynamic properties, it is necessary to investigate the intermolecular interactions of liquids. Structure and clustering patterns of tert-butyl alcohol (TBA) aqueous solutions are analyzed using molecular dynamics simulations with the effective fragment potential method (EFP). EFP is a polarizable model potential in which all parameters are obtained from a set of preparatory *ab initio* calculations on isolated fragment molecules. Thus, EFP does not contain any empirical fitted parameters and provides first-principles-based description of intermolecular interactions. TBA solutions with 0.01, 0.03, 0.06 TBA mole fractions are investigated to identify aggregation patterns of TBA molecules and behavior of bulk water as perturbed by the TBA molecules. Radial distribution functions and vibrational frequency calculations are utilized to analyze the results of these simulations.

No. 48, Poster Session I

Electronic Band Structure Calculations on Thin Films of the L2$_1$ Full Heusler Alloys X_2YSi (X, Y = Mn, Fe, and Co): toward Spintronic Materials

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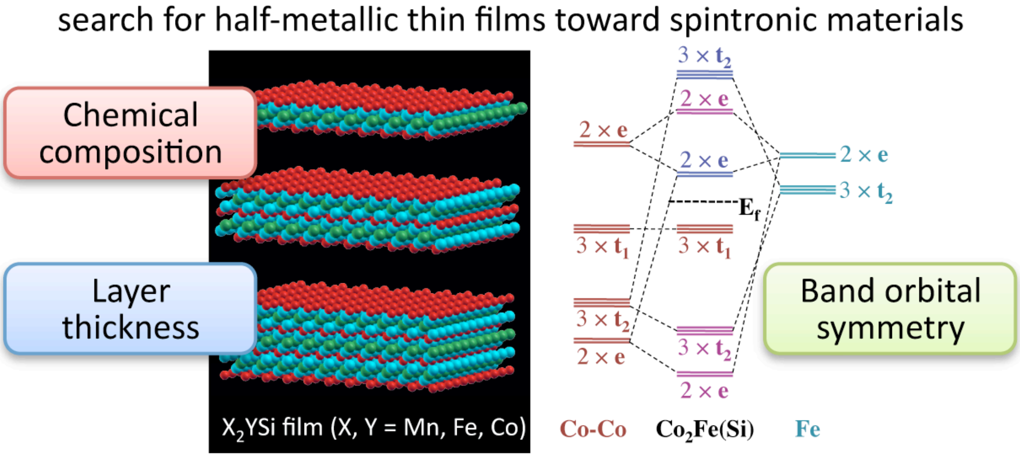
To design half-metallic materials in thin film form for spintronic devices, the electronic structures of full Heusler alloys (Mn_2FeSi, Fe_2MnSi, Fe_2FeSi, Fe_2CoSi, and Co_2FeSi) with an L2$_1$ structure have been investigated using density functional theory calculations with Gaussian-type functions in a periodic boundary condition. Considering the metal composition, layer thickness, and orbital symmetries, a 5-layered Co_2FeSi thin film, whose surface consists of a Si layer, was found to have stable half-metallic nature with a band gap of *ca.* 0.6 eV in the minority spin state. Using the group theory, the difference between electronic structures in bulk and thin film conditions will be discussed.



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No. 49, Poster Session I

Analytical gradients of Random Phase Approximation correlation energies in Range-Separated-Hybrid context : theory and implementation

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In view of the recent revival of interest in the Random Phase Approximation (RPA) in a range-separated hybrid (RSH) context as a method to calculate ground-state correlation energies of electronic systems, in particular systems where long-range electron-electron interaction play an important role, we propose a method to obtain the gradient of RSH-RPA energies.

Taking advantage of the Lagrangian formalism and using several versions of the Riccati equations associated to the RPA problem (which are in some cases equivalent to the rCCD expressions), we obtain a compact matrix formulation for the energy gradient. The resulting algebra is implemented in the Molpro program suite, exploiting analogies with the analytical gradient of the Møller–Plesset (MP2) energy.

Simple test cases and examples of geometry optimization of intermolecular complexes are shown.

No. 50, Poster Session I

Optical activity spectra of carbon nanostructures via a novel π-electron model

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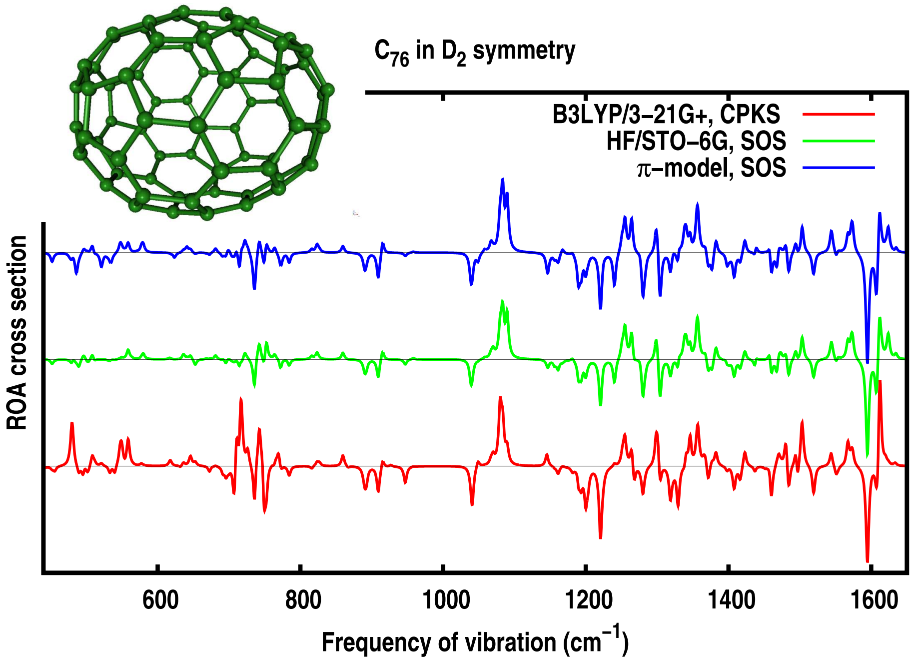
Characterization of chiral carbon nanostructure samples, such as fullerenes and carbon nanotubes are still a challenging task, since the spectroscopical tools are limited to electronical and vibrational optical activity (OA).

To interpret the OA spectra of these systems quantum chemical methods are necessary. Due to large system size, we choose a cost-effective, one-particle π-electron method. Our studies focus on spectral line intensities of inelastic light scattering, i.e. Raman and vibrational Raman Optical Activity (VROA).

We find that π-electron methods, relying on the first neighbour approximation (Hückel-model) describe the Raman spectra of fullerenes well, but one has to include one-particle integrals between all sites to obtain reliable VROA spectra.

Parameters of the π-model are derived from ab initio calculations in a system-specific manner, in the spirit of the Bloch-equation. Standard linear response theory is used to calculate spectral intensities.



No. 51, Poster Session I

Adaptive refinement of wavelet based solutions of the Schrödinger equation by independent estimation of the fine resolution coefficients

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Multiresolution analysis (MRA) [1] or wavelet analysis is a successful tool for data compression and it can also be used – similarly to the Fourier analysis – for solving differential equations. Wavelets, the basis functions of MRA, divide the Hilbert space into subspaces, each of which can be characterized by a resolution level index. The wavelet expansion of the functions contain high resolution level wavelets only at those locations, where the function is more rapidly varying, the smoother parts can be expanded by only rough resolution level basis functions. This fact is behind the enormous success of wavelet-based data and image compressing methods, in most of the cases the functions or distributions to be compressed are smooth in most locations, and high resolution is needed only in very restricted domains.

In electron structure calculations the wave functions are usually unevenly detailed, some parts, like the cusps need high spatial resolution to be sufficiently precisely described, while the parts further away from the cores are smooth, they require less fine resolution. According to this fact, and the uniformness of the wavelets, the basis functions of the MRA seem to be successful candidates for basis functions of electron structure calculations [2, 3]. Operators that contain differentiation and multiplications with polynomials can usually be represented in wavelet basis very well[5, 4], the exception is clearly the Coulomb potential. A method is presented here to solve electron structure calculations using wavelets as basis functions, this method automatically adapts to the required resolution level, i.e., it uses higher resolution level basis functions only in those spatial domains, where they are necessary. With the method it is also possible to predict the next, finer resolution level coefficients, if we have a given resolution solution. This property can be used either for estimating the error of the given solution, or for refining it.

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No. 52, Poster Session I

Structure Optimization of Molecules Consisting of up to Period 5 Elements by Discrete Variational Xα Method

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Discrete variational method utilizes very natural and adaptive basis functions[1], which will be advantageous to calculate various chemical and physical quantities. But numerical integration accompanying this method causes rather serious numerical errors. Especially energy gradient seemed to be very difficult to calculate with practical accuracy. The author succeeded to cancel major part of its numerical error by the following way.

$$F_B = \left(F_B^{H-F} + F_B^{LCAO}\right)_{MOL} - \left(F_B^{H-F} + F_B^{LCAO}\right)_B$$

Here F_B denotes a force acting on atom B in the molecule, $(F_B{}^{H\text{-}F}+F_B{}^{LCAO})_{MOL}$ denotes Hellmann-Feynman force and the correction for LCAO approximation calculated in the molecule and $(F_B{}^{H\text{-}F}+F_B{}^{LCAO})_B$ denotes the counterpart calculated in only atom B. As no force can act on the isolated atom, calculated value of the latter part must be just numerical error and it cancels mostly numerical errors included in the former part.

By applying this way to MOs obtained by DV-Xα method[2], the force acting on each atom in the molecule consisting of up to period 3 elements could be calculated. Further by the procedure adopted by McIVER and KOMORNICKI[3], those molecules could be optimized with practical accuracy. But there still remained large numerical errors for molecules including period 4 and 5 elements.

The author has developed the new numerical integration method, where sample points are arranged like the face centered cubic lattice instead of quasi random number distribution in the unit cube and are mapped into the real 3D space. Further the mapping function is adjusted to distribute sample points far more densely near nuclei in the real 3D space. By these improvements, molecules consisting of up to period 5 elements can be optimized. The followings are its small examples, where 37600 points/atom for I atom and Sb atom and 56400 points/atom for In atom were used.

This method can be applied also for calculations of other quantities and will add new applications to Discrete Variational method.

AB_3	InI_3 (D_{3h})		SbI_3 (C_{3V})	
	Experimental	Optimized	Experimental	Optimized
R(AB)	2.64 Å	2.67～2.68 Å	2.719 Å	2.730～2.789 Å
∠BAB	120.0°	117.2～122.4°	99.1°	99.4～102.3°

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No. 53, Poster Session I

Quantum chemical study of binding affinity of the purine inhibitor and its bioisosteres to cyclin-dependent kinases

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The aim of this work is to explain the difference in binding affinity of the purine inhibitor Roscovitine and its pyrazolopyrimidine bioisosteres to cyclin-dependent kinases (CDK) 2 and 9. The increased activity of CDK significantly contributes to the loss of control over cell proliferation, which is one of the basic properties of cancer cell formation. They thus represent an interesting target of cancer chemotherapy. The accurate description of binding mechanism enables us to design specific inhibitors. The binding affinity between the inhibitor and the protein is estimated by using the scoring function, which is based on the semi-empirical quantum mechanical (SQM) PM6-D3H4 method with corrections for dispersion energy (D) and hydrogen bonding (H) [1,2,3]. The calculated scores correlate well with experimental binding data (R^2=0.92). The interaction 'free' energy between fragments of the inhibitor and the whole protein is computed in the same way, and it correlates well with experimental data too (R^2=0.81). The ligand fragmentation, NBO analysis and electrostatic potential of the studied inhibitors rationalize changes in binding affinity. Gas phase interaction energy (IE) between the fragments of the protein and the whole inhibitor is described by the PM6-D3H4, DFT-D3 and MP2 methods. IE calculated by PM6-D3H4 agree well with DFT-D3/def2-QZVP (R^2=0.99). On the other side, the sum of interaction 'free' energies between the inhibitor and the protein fragments does not correspond to the experimental data. This result shows that it is important to consider whole protein.

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No. 54, Poster Session I

Electronic rearrangements during the inversion of lead phthalocyanine

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Application of metal phthalocyanines (MPc’s) as molecular switches is based on the possibility to control the conformational changes of the adsorbed molecules as well as their electronic and magnetic states. Particularly, PbPc can adsorb on a range of different substrates in two orientations due to its shuttlecock shape: either having the central metal atom towards (PbPc↓) or away from (PbPc↑) the surface [1-2]. The reversible switching between these configurations can be triggered by small but energetic nanomechanical motions. As a result, one can use the effect for constructing molecular memories and sensors at the nanoscale.

Here we present work devoted to studying of the mechanism of PbPc inversion from the bonding evolution theory standpoint, enabling one to monitor the electronic structure rearrangements in the course of elementary reaction [3]. It was found that reorganization of Pb’s ELF basins with pronounced role of core ones is the basis of the catastrophes identified, whereas ELF basins belonging to other atoms are almost not involved in the electronic structure changing [4]. The results obtained provide the new topological picture of processes underlying the conformational transitions of shuttlecock shaped MPc’s adsorbed on surfaces.

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No. 55, Poster Session I

Comparison of the monomer structure of the FMN binding protein from *Desulfovibrio vulgaris* obtained by NMR and molecular dynamics simulation approaches

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Flavin mononucleotide (FMN)-binding proteins (FBPs) play an important role in the electron transport process in bacteria. In this work, the structures of the FBP from *Desulfovibrio vulgaris* (Miyazaki F) (*Dv*FBP) were compared between those obtained experimentally by nuclear magnetic resonance (NMR) spectroscopy and those derived from molecular dynamics simulations (MDSs). A high residue root of mean square deviation (*RMSD*) was observed in residues located at both sides of the wings (Gly22, Glu23, Asp24, Ala59, Arg60, Asp61, Glu62, Gly75, Arg76, Asn77, Gly78, and Pro79), whilst a low residue *RMSD* was found in residues located in a hollow of the structure (Asn12, Glu13, Gly14, Val15, Val16, Asn30, Thr31, Trp32, Asn33, Ser34, Gly69, Ser70, Arg71, and Lys72). Inter-planar angles between the Phe7 and Iso and between the Phe7 and Trp106 residues were remarkably different between the MDS- and NMR-derived *Dv*FBP structures. Distribution of the torsion angles around the covalent bonds in the aliphatic chain of FMN were similar in the MDS- and NMR-derived structures, except for those around the C1’-C2’ and C5’-O5’ bonds. Hydrogen bond formation between IsoO2 and the Gly49 or Gly50 peptide NH was formed in both the NMR- and MDS-derived structures. Overall, the MDS-derived structures were found to be considerably different from the NMR-derived ones, which must be considered when the photoinduced electron transfer in flavoproteins is analysed with MDS-derived structures.

No. 56, Poster Session I

Theoretical Study on Internal Alkyne/Vinylidene Isomerization on Group 8 Transition Metal Complexes

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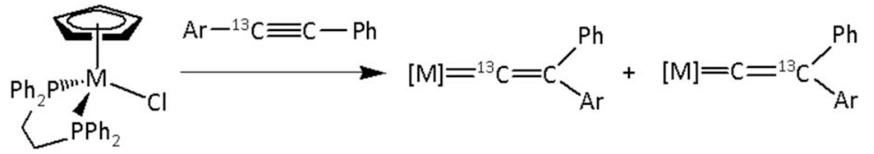
Alkyne/vinylidene isomerization in transition metal complexes has been exploited in the synthesis of a wide range of vinylidenes. Recently, Ishii and his co-workers reported the internal alkyne/vinylidene isomerization of $[CpM(PhC{\equiv}CC_6H_4R\text{-}p)(dppe)]^+$ (M = Fe, Ru; R = OMe, Me, H, Cl, and CO_2Et) [1,2], and our DFT study on the Ru complexes clarified that the migration reaction is nucleophilic[3]. However, effects of the central metal on the reaction remain unrevealed. Herein, we report the results of DFT calculations on the transformation of internal alkyne complexes having group 8 transition metals, $[CpM(PhC{\equiv}CC_6H_4R\text{-}p)(dppe)]^+$ (M = Fe, Ru, Os; R = OMe, CO_2Et, and Cl), and discuss the metal effects on the reaction.



Geometry optimization followed by frequency calculations and intrinsic reaction coordinate (IRC) calculations were performed with the B3PW91 functional. The ECP and basis set used are SDD for the metals and 6-31G(d) for the remaining nonmetal atoms. The combined basis set is denoted by SDD+6-31G(d) in the present study. NBO analysis was carried out at the HF level of theory.

Two types of 1,2-migration pathway were obtained for each metal complex, which are paths 1 and 2 in the Fe complex and paths 1 and 3 in the Ru and Os complexes. The activation free energies for paths 2 and 3 were smaller than that for path 1, respectively. Thus, the isomerization reaction of internal alkynes to vinylidenes proceeds through paths 2 and 3. The difference between path 2 (Fe complex) and path 3 (Ru and Os complexes) is in geometry of the reactants. The difference in the reactant structures is due to the different characteristics of the valence d orbitals of Fe in the complex from those of the other metals, which lead to different types of overlap between the d orbitals of the metal and the π orbital of the alkyne. To assess the stability of alkyne and vinylidene complexes for three kinds of metals, orbital interaction energies between the alkyne/vinylidene moiety and the other parts of organometallic complex were calculated by NBO analysis. It was revealed that the Os complex has the strongest interaction for both cases, followed by the Ru and Fe complexes.

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No. 57, Poster Session I

Chemistry of defects in solids

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The properties of materials are strongly influenced by the defects of crystal structure such as two-dimensional planar interfaces as grain boundaries or one-dimensional dislocations. Those are regions with different atomic structures and consequently implementing new properties of solids. Due to segregation of impurities and their accumulation at the defects, the grain boundaries can become weaker and susceptible to intergranular fracture with catastrophic effects on the operation of machines and devices. Hence the chemistry of grain boundaries is of primarily importance for the safe utilization of all kinds of transportation and other facilities. Nitrogen and phosphorus due to their chemical resemblance display a similar enrichment of grain boundaries. Surprisingly, carbon and silicon despite of their chemical resemblance behave entirely unlikely.

No. 58, Poster Session I

Structural and Electronic Contributions to Redox-noninnocent Behavior

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Ligands that are capable of accepting or providing electrons during redox reactions of transition metal complexes, called redox-noninnocent ligands, can profoundly modulate the overall reactivity of the corresponding complex. Recent efforts focus on the application of such ligands as electron reservoirs to promote multi-electron processes and triggering redox-noninnocence to yield reactive ligand radicals to establish ligand-based catalysis. Our approach is distinctively different in that it is governed and heavily guided by chemical concepts that are derived from first principle computations allowing the full understanding and the development of a unified concept of this behavior. Our most recent investigation focuses on the structural and electronic requirements of ligand noninnocent behavior using DFT based techniques. Octahedral Fe and Co and square planar Co and Ni complexes containing benzoquinonediimine-based noninnocent ligands were selected for this systematic, whereas the analogues Ru and Pd systems serve as references. We analyzed how the coordination of ligand to the metal center makes the ligand-based reduction energetically more favorable to the free ligand. Using square schemes we determined that the major component of this stabilization has electronic origin and structural relaxation – one of the most salient feature of noninnocence – plays only a minor role. We further analyzed the origin of this electrostatic stabilization using various techniques including interaction energy decomposition analysis. A simple measure based on the electron density is introduced to quantify ligand redox-noninnocence.

No. 59, Poster Session I

Carbon–Carbon bond activation of epoxides by a (dtbpm)Pt fragment - A theoretical study.

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Platinum complexes with the bis(di-tert-butylphosphino)-ligand (dtbpm) are the only known complexes that selectively activate epoxides at the carbon-carbon bond. Here we study this reaction theoretically using the random phase approximation. We find that the reactivity is kinetically controlled and is caused by the formation of a monodentate (dtbpm-$\kappa^1 P$)Pt fragment rather than the (dtbpm-$\kappa^2 P$)Pt chelate complex. Insertion into the epoxide C-C bond occurs without energy barrier. The competing reactions, C-O and C-H activation, both proceed via formation of a σ-complex, followed by small but significant barriers for the insertions. A reversible formation of the σ-complexes would perfectly explain the observed reactivity. For an irreversible formation we find that intramolecular rearrangement of these σ-complexes towards C-C activation is faster than both C-O and C-H activation. The same reactivity is expected for other mono-coordinated platinum phosphine complexes. However, only the specific properties of dtbpm make the formation of this intermediate and the subsequent, rapid closing of the chelate ligand favourable.

No. 60, Poster Session I

Towards a multireference coupled-cluster method based on a unitary transformation

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The application of a unitary transformation to be able to describe a set of strongly interacting real particles as a set of weakly interacting quasi-particles is a frequently used tool in the many-body theory. Our aim is to adapt such a transformation in the multireference coupled-cluster (MRCC) framework. The main idea behind the new method is to use a unitary transformation which allows to describe a set of orthogonal basis functions – showing multirefence (MR) character – by single determinants. The elements of the MR basis are defined by the solutions of complete active space (CAS) problems and one element of the MR basis is the reference CAS function itself. Using this unitary transformation quasi-particle operators ($\hat{Q}$) are defined. These operators allow us to represent the CAS reference function or any other elements of the MR basis in a determinant-like form, $|\Phi_{\mathrm{CAS}}\rangle = \hat{Q}_n^+ \dots \hat{Q}_2^+ \hat{Q}_1^+ |\rangle$, where the quasi-particle creation and annihilation operators satisfy the fermion anti-commutation relations. On the basis of these quasi-particles a possible generalization of the normal ordered operator products for MR problem can be introduced.

As a consequence of the formal simplicity of the reference function, the definition of an MRCC approach on the unitary transformed basis is straightforward and this approach retains several beneficial properties of the single reference CC approach. On the other hand we have to handle two obvious difficulties, namely the ambiguity of the definition of the unitary transformation and the more than two particle nature of the Hamiltonian expressed through the quasi-particles.

Test results for small systems are presented using a pilot implementation of our method. The results are compared to the MRCC theory originally published by Oliphant and Adamowicz [J. Chem. Phys 94 (1991) 1229] and later generalized by Piecuch and co-workers [J. Chem. Phys 99 (1993) 1875 , J. Chem. Phys 110 (1999) 6103], which is reminiscent of our approach in the sense that in both methods the single reference CC framework is applied in the MRCC context.

No. 61, Poster Session I

Binding mode and binding affinity prediction of inclusion complex between flavonoid and ß-cyclodextrin

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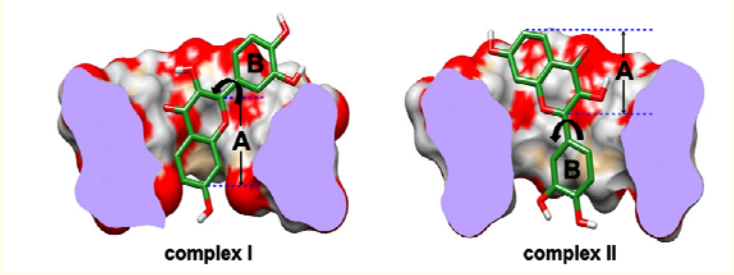
Although fisetin, a flavonoid compound, possess a wide range of important pharmacological activities, its low water solubility is a major problem for pharmaceutical application. β-cyclodextrin (βCD) can be used to improve the solubility of poorly soluble organic compounds by encapsulating hydrophobic molecule inside its cavity. Herein, the multiple molecular dynamic simulations were applied to study the binding mode and affinity between the fisetin guest molecule and the βCD host molecule. Fisetin was firstly docked into the βCD cavity using molecular docking approach and the four different fisetin/βCD complexes (I-IV) resulted were consequently used as the starting structures for classical molecular dynamics study in aqueous solution for 70 ns. The complexes III and IV are relative complexes I and II with 180 degree rotated torsion angle. For complex I, translocation of fisetin molecule inside the cavity was observed. In contrast, the B-ring strongly interacts with the βCD in complexes II and IV. The radial distribution function indicated that the water solubility of fisetin is significantly increased by complexation with βCD. Based on MM/PB(GB)SA and QM/PB(GB)SA calculations, complexes II and IV are likely more stable than the others.



complex I complex II

No. 62, Poster Session I

Formulation of an Internally Contracted Multi-Reference Coupled-Cluster Based Linear Response Theory to Study Excited States

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Linear Reponse (LR) theory is an effective tool to calculate the excitation energies of chemical systems which have a proper ground state description. For systems having prominent Multi-Reference (MR) characters in their electronic ground state, a number of different MR theories have been developed in the past years which can be divided into two broad categories: (a) Theories where the different model functions are used as the reference states. (b) Theories which use a contracted description, i.e., a linear combination of the model functions are exploited. The second class of theories are known as 'Internally Contracted MR' (IC-MR) theories.

In our present formulation, we have developed and implemented a linear response theory based on internally contracted multireference coupled-cluster theory (ic-MRCC-LRT, [1]). Excitation energies can be obtained, using LRT framework, as the poles of the response function when an external field acts on its ground state. The formulation of the ic-MRCC-LRT can be approached differently by treating the external field in a time-dependent [2] or time-independent manner [3]. These two approaches lead to different final expressions as here the cluster operators are non-commuting and have been truncated after doubles excitations.

We will present some pilot numerical applications of the above mentioned ic-MRCC-LRT. Our results indicate that the ic-MRCC response functions are well-behaved and the resulting excitation energies turn out to be very accurate. The method is particularly promising for the description of doubly excited states and photochemical pathways.

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No. 63, Poster Session I

Structure- and ligand-based drug design of novel p38 alpha MAPK inhibitors in the fight against the Alzheimer's disease.

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Alzheimer's disease (AD) was first characterized in 1907 by the german neuropathologist Alois Alzheimer, whose clinical symptoms includes cognitive, physiological and behavioral dysfunctions, memory loss, eventually incontinence, dementia, and death. It is a neurodegenerative disease of the central nervous system that usually affects individuals group in older age. This is characterized microscopically by the presence of amyloid plaques, which are accumulations of beta-amyloid protein inter-neurons, and neurofibrillary tangles formed predominantly by highly phosphorylated forms of the microtubule-associated protein, tau, which form tangled masses that consume neuronal cell body, possibly leading to neuronal dysfunction and ultimately death. p38α MAPK has been implicated in both events associated with AD, tau phosphorylation and inflammation. p38α MAPK pathway is activated by a dual phosphorylation at Thr180 and Tyr182 residues. Drug design of p38α MAPK inhibitors is mainly focused on small molecules that compete for ATP in the catalytic site. Here, we used different approaches of structure- and ligand-based drug design and Medicinal Chemistry strategies based on a selected p38α MAPK structure deposited in the PDB in complex with inhibitor, as well as other reported in literature. As a result of the virtual screening experiments here performed, as well as molecular dynamics, molecular interaction fields study, shape and electrostatic similarities, activity and toxicity predictions, pharmacokinetic and physicochemical properties, we have selected 7 compounds that meet criteria of low or no toxicity potential, good pharmacotherapeutic profile, predicted activities calculated values comparable to those obtained for the reference compounds, while maintaining the main interactions observed for the most potent inhibitors. These compounds must be acquired for *in vitro* inhibition studies against the enzyme p38α MAPK, as potential leads for Alzheimer's disease treatment.

Key words: Alzheimer's disease, p38 alpha MAPK, drug design.

No. 64, Poster Session I

Probe molecule transformations for staining techniques in zeolites – A periodic DFT study

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The so-called probe molecules for staining techniques facilitate the direct experimental investigation of the acid site distribution and strength by generating UV active species in situ inside the zeolite. We investigated the formation of such fluorescent (oligo)thiophene derivatives in three characteristic sites of acidic ZSM-5 zeolite. The acidic sites were modeled in the straight and sinusoidal channels and in their intersection by substituting one silicon atom to Al at the T5, T10 and T12 sites (Si/Al ratio of 95), respectively, and neutralizing the remaining negative charge with a proton. First, the most plausible acid catalyzed decomposition/oligomerization pathways of thiophene were determined using a cluster model, which were then implemented into the various channels of the zeolite using MFI framework with periodic boundary conditions. We found that the adsorption of thiophene on the acidic site is followed by the protonation at C1 carbon atom in an energetically uphill process. The generated carbocationic species, however, readily reacts with excess neutral thiophene molecules to form bithiophene and terthiophene carbocations. The modeled adsorption and emission peaks of the latter species show very good agreement with the experimentally observed and utilized characteristic bands of the staining experiments [1,2]. The specific weak interactions between the zeolite framework and neutral and carbocationic (oligo)thiophene derivatives were also scrutinized with the recently introduced Non-Covalent Interaction method [3,4].

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No. 65, Poster Session I

Jahn–Teller, pseudo-Jahn–Teller, and spin-orbit coupling effects in cerium trihalide molecules

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Low-lying spin-orbit states of cerium trihalide molecules CeX$_3$ (X = F, Cl, Br, I) are studied using single-reference CCSD(T) and multireference MRCI and MRPT2 methods with the basis sets of quadruple-ζ quality. Scalar relativistic effects are incorporated in all-electron calculations using Douglas–Kroll–Hess Hamiltonian. Spin–orbit coupling is treated either with the Breit–Pauli spin-orbit operator $\hat{H}_{SO}$ or with spin–orbit pseudopotentials. The spin-orbit eigenstates are obtained by diagonalizing $\hat{H}_{el} + \hat{H}_{SO}$ in a basis of eigenfunctions of $\hat{H}_{el}$.

The originally degenerate 4f-orbitals of Ce^{3+} split into a_2'', e', e'', a_1', a_2' orbitals in the ligand field of D$_{3h}$ symmetry. The energy difference of the highest and lowest CeX$_3$ electronic states corresponding to different f electron occupation of these orbitals amounts to 2200, 1400, 1300, and 1100 cm^{-1} for X = F, Cl, Br, I, respectively, with the first excited state $^2E'$ lying above the ground state $^2A_2''$ by 100, 40, 20, 10 cm^{-1}. An accounting for spin-orbit coupling of the states changes this pattern dramatically. The energy splitting grows to 4000, 3400, 3200, and 3100 cm^{-1}. The relative energy of the first excited spin-orbit state $^2E_{3/2}$ with respect to the ground state $^2E_{5/2}$ amounts to 370 – 470 cm^{-1}.

The Jahn–Teller (JT) and pseudo-Jahn–Teller (PJT) effects are studied in detail for CeF$_3$. The JT distortion (D$_{3h}$ $\rightarrow$ C$_{2v}$) in the $^2E'$ state yields the Y-shaped structure with α_e(F-Ce-F) = 115° and the JT stabilization energy E_{JT} = 75 cm^{-1}. The JT effect in the $^2E''$ state is very weak: α_e(F-Ce-F) = 119.5°, E_{JT} = 2 cm^{-1}. The PJT coupling $(A_2'' + E'') \otimes e'$ results in strongly anharmonic adiabatic potential energy surface (APES) in the $^2A_2''$ ground state. The SO coupling enhances the anharmonic character of APESs due to both SO-quenching of JT distortions and the $^2A_2''$ state mixing in spin-coupled states. In all of the spin-orbit states the CeF$_3$ molecule is non-planar (C$_{3v}$) with the C$_{3v}$ $\rightarrow$ D$_{3h}$ $\rightarrow$ C$_{3v}$ inversion barrier height h = 90–330 cm^{-1}.

The vibronic model Hamiltonian $(A_2'' + E' + E'' + A_1' + A_2') \otimes (a_1' + e' + e' + a_2'')$ is constructed and parametrized for CeF$_3$. The JT and PJT coupling constants are determined by a fitting of the calculated APESs. To describe the complicated vibronic coupling of the electronic states by the out-of-plane bending mode a_2'', the relevant coupling constants are evaluated via the fitting of quasidiabatic MRCI potential energy surfaces generated by an approximate diabatization procedure. To include SO coupling of the $A_2'' + E' + E'' + A_1' + A_2'$ electronic multiplet in the model Hamiltonian, the zeroth-order SO coupling constants are evaluated.

The eigenstates of the spin-vibronic Hamiltonian are calculated variationally and compared with the published infrared absorption spectrum of CeF$_3$. The assignments of the observed spectral features are suggested.

The authors acknowledge support from the Russian Foundation for Basic Research, Grant No. 13-03-01051.

No. 66, Poster Session I

The quantum chemical study of isotropic and anisotropic magnetic properties of molecular magnets

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The field of molecular magnetism grows essentially over the past two decades. Significant progress has been achieved in the synthesis and investigation of different types of molecular magnetic materials. Note, that nowadays quantum chemistry plays a crucial role in the understanding and analysis of the magnetic properties.

In most cases, the magnetic properties of three-dimensional bulk molecular magnets can be described using isotropic spin-Hamiltonian ($\hat{H} = -2\Sigma J_{ij}\hat{S}_i\hat{S}_j$), where only isotropic exchange spin coupling is taken into account. In contrast, in the case of anisotropic systems, such as single molecular magnets, the anisotropy caused by electron spin-orbit coupling in metal centers determines the magnetic properties [1].

Here we report results of our calculations for both the isotropic and anisotropic molecular magnets.

The first investigated system is the anion radical salt of [1,2,5] thiadiazolo [3,4-c] [1,2,5] thiadiazolidyl with bis(toluene)chromium. Parameters of the Heisenberg spin-Hamiltonian have been calculated at the CASSCF/NEVPT2 and broken-symmetry DFT levels, and the complex magnetic motifs featuring the dominance of the antiferromagnetic (AF) interactions have been revealed.

The second system of interest is the heterometallic cluster $[Co_2^{III}Mn_2^{II}(hmp)_6Br_2(CH_3CN)_2]$ $Mn^{II}Br_4$. The DFT calculations of the exchange interactions revealed that AF interactions between core Mn^{II} cations determine the magnetic properties.

The third system under study is a layered $[Co_3^{II}(2,2'-bpdo)_4(H_2O)_4[W^V(CN)_8]_2]\cdot 8H_2O$ network [2]. In this system, the bulk magnetic anisotropy is confronted with a local anisotropy of Co complexes. According to the CASSCF/RASSI/SINGLE_ANISO *ab initio* calculations this material is characterized by a strong axial anisotropy of the trans,cis,cis-$[Co^{II}(\mu-NC)_2(H_2O)_2(2,2'-bpdo)]$ moieties represented by g_x = 2.06, g_y = 2.95 and g_z = 7.30, and a planar anisotropy of the trans,cis,cis-$[Co^{II}(\mu-NC)_2(H_2O)_2(2,2'-bpdo)_2]$ moieties represented by g_x = 5.40, g_y = 4.82 and g_z = 2.28. These values well reproduce the anisotropy of magnetic properties observed in the experiment.

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No. 67, Poster Session I

Isomerization effect on the dynamics of the H + O_2 collision

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The reaction of H atom with dioxygen has been termed the "single most important" elementary step in combustion. It is important to explore the factors that play crucial role in the dynamics of the reaction. We have employed the quasiclassical trajectory (QCT) method and the first excited potential energy surfaces of Guo and coworkers [1].
Most reactive trajectories in the HO_2 system undergo isomerization (1,2-H-atom shift) through the barrier at the C_{2v} arrangement on both PES. Furthermore, in reactive collisions the O-O breakage occurs right after the isomerization, if the isomerization takes place in the appropriate O-O vibrational phase (when the O-O distance increases). The products of trajectories that isomerized before the bond breaking are rotationally hot and vibrational cold. We found that if no isomerization happens in reactive collisions the picture the final state distribution is the opposite: the products are rotationally cold and vibrationally hot. This means the dynamics of isomerization involves a torque that is missing if there is no isomerization. The sharp difference of the behavior of different kinds of trajectories indicates that the internal phase space of electronically excited HO_2 is far from ergodic.

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No. 68, Poster Session I

An efficient linear-scaling CCSD(T) method based on local natural orbitals

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An improved version of our general-order local coupled-cluster (CC) approach [1] and its efficient implementation at the CC singles and doubles with perturbative triples [CCSD(T)] level is presented. The method combines the cluster-in-molecule approach of Li and co-workers [2] with frozen natural orbital (NO) techniques. To break down the unfavorable fifth-power scaling of our original approach a two-level domain construction algorithm has been developed. First, an extended domain of localized molecular orbitals (LMOs) is assembled based on the spatial distance of the orbitals. The necessary integrals are evaluated and transformed in these domains invoking the density fitting approximation. In the second step, for each occupied LMO of the extended domain a local subspace of occupied and virtual orbitals is constructed including approximate second-order Møller–Plesset NOs. The CC equations are solved and the perturbative corrections are calculated in the local subspace for each occupied LMO using a highly-efficient CCSD(T) code, which was optimized for the typical sizes of the local subspaces. The total correlation energy is evaluated as the sum of the individual contributions. The computation time of our approach scales linearly with the system size, while its memory and disk space requirements are independent thereof. Test calculations demonstrate that currently our method is one of the most efficient local CCSD(T) approaches and can be routinely applied to molecules of up to one hundred atoms with reasonable basis sets.

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No. 69, Poster Session I

Parallel Evaluation of Two-Electron Integrals using a Wavelet Approach on the Graphics Processor Unit

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In high precision electron structure calculations of chemical and solid-state physics, traditionally atom-specific basis functions are used to compute one- and two-electron integrals of the Coulomb interaction potential. In the present study we show, that using a wavelet approach, the evaluation of such integrals can lead to a much more economical scheme compared to the atomic basis function (LCAO) based calculations. Using the wavelet (scaling function) basis set gives a general, system independent, therefore more efficient solution.

However, the calculation of such integrals is a highly time-consuming and CPU-intensive task. Therefore, we propose a method to reduce significantly the evaluation time by introducing parallel processing techniques.

Recently, the graphics processor unit (GPU) has become a powerful platform for parallel computing and a new approach was offered to evaluate specific tasks in computational chemistry. In this study, we describe the implementation of calculating two-electron integrals using a GPU to improve the computation time. The algorithm was developed on an Nvidia Tesla M2070 GPU using the compute unified device architecture (CUDA).

A theoretical study of the interaction between a lectin called Siglec-7 and its glycan ligand in the immune system

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Siglecs (sialic acid-binding immunoglobulin superfamily lectins) are a group of receptors in the immune system, which specifically recognize glycans that contain sialic acids (Neu5Ac). Siglec-7 belonging to CD33-related siglecs was mainly expressed on natural killer cell. More attention has been paid to its potential role in natural killer cells as part of cancer research in addition to its major role in the innate immune system. Siglec-7 has been reported to recognize α(2,8)-disialyl residue (Neu5Acα2-8Neu5Ac) preferentially[1], the mechanism of which, however, has not been elucidated. In order to investigate the specificity of glycan recognition of siglec-7, we analyzed the intermolecular interaction between siglec-7 and its ligand.

We clarified in detail the theoretical features of the interaction between the glycan ligand and Siglec-7 by *ab initio* Fragment Molecular Orbital (FMO) calculations [2] and classical molecular dynamics (MD) simulations. We utilized the X-ray crystal structure of siglec-7 complexed with GT1b analog, α (2,8)-disialyl glycolipid (PDB ID: 2HRL) [3]. By comparing the ligand-Siglec-7 interaction of the wild-type Siglec-7 and those of mutant-Siglec-7s, we herein describe the protein-glycan interaction thoroughly, and provide fundamentals to elucidate ligand-recognition mechanism [4].

The interaction energies obtained by the FMO method were consistent with the experimental ligand-binding results. The glycan ligand preferentially interacted with Siglec-7 via sialic acid residues. The stabilization by the dispersion interaction between the neutral parts of the ligand was also considerable in the binding.

The experimentally observed decrease in ligand binding produced by mutagenesis at residues in non-active site was explained with MD simulations; both Trp85 and Trp74 residues are fundamental in structural stability of the Siglec-7, which is involved in the binding of the glycan ligand (Figure 1).

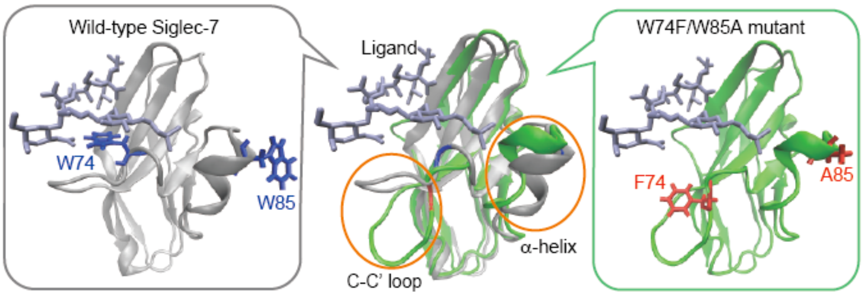

Figure 1 The structure of the double mutant W74F/W85A (depicted in green, the snapshot at 9 ns in the MD simulation) is superposed with the X-ray structure of wild-type Siglec-7 (silver, PDB ID: 2HRL).

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[4] K. Ueno-Noto *et al. J. Theor. Comp. Chem. in press*, 2013

No. 71, Poster Session I

Theoretical DFT, FT-IR and NMR studies of 2-methoxy-6-(5-H/Me/NO_2-1*H*-benzimidazol-2-yl)-phenols

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Benzimidazolyl-phenol ligands known to be strong chelating agents are potential N,O donors and they react easily with the metal ions to give stable chelate complexes. Various transition metal chelate complexes of benzimidazolyl-phenol type ligands were reported[1,2].

In this study, theoretical DFT, FT-IR and NMR spectral studies of 2-methoxy-6-(5-H/Me/NO_2-1*H*-benzimidazol-2-yl)phenols (**I** - **III**) were performed. The optimized molecular geometry, dipole moment and total energy were calculated using Hartree-Fock and density functional method (B3LYP) with 6-31G(d,p) basis set. The vibrational wavenumbers and the infrared intensities were calculated scaled quantum mechanics (SQM) methodology by using Parallel Quantum Solutions (PQS) program.

According to the calculations the compounds are nearly planar (Fig. 1). The global minimum energy values of the compounds are −800.47, −840.05 and −999.97 a.u. for **I**, **II**, **III**, respectively. Dipole moment value of the compounds **I**, **II** and **III** are 4.42, 4.22 and 7.56 Debye, respectively. Also, charge distribution of the compounds was determined (Fig. 1).

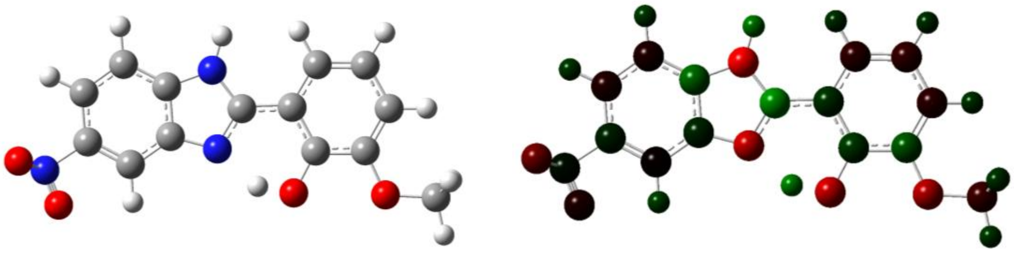

Fig. 1. Geometric optimization (left) and charge distribution (right) of **III**

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No. 72, Poster Session I

Approximate lower bounds via Löwdin's bracketing function

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In quantum chemistry the usage of upper bounds to the energy is well spread. In contrast to upper bounds, lower bounds are barely used, because they are much more complicated and can only be applied if appropriate conditions are fulfilled.

Löwdin's bracketing function[1], $f(\varepsilon)$ gives a lower bound if the argument ε is an appropriate upper bound. In general the argument and the value of the function „brackets" at least one eigenvalue. Taking a normalised reference function φ, the bracketing function is expressed as:

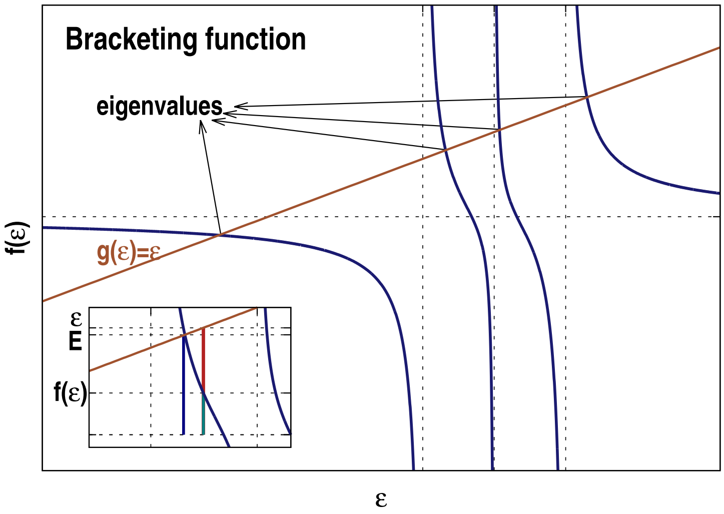
$$f(\varepsilon) = \langle\varphi|H + H\frac{P}{\varepsilon - H}H|\varphi\rangle, \qquad P = 1 - |\varphi\rangle\langle\varphi|.$$

The bracketing function can be written in the alternative form:

$$f(\varepsilon) = \varepsilon + \langle\varphi|(H-\varepsilon)^{-1}|\varphi\rangle^{-1}$$

Calculation of the lower bound is computionally demanding due to the operator inverse. To explore practical approaches we used several numerical approximations. The approximate formulae are evaluated at each step of a Davidson full CI iteration sequence on the example of simple molecules.

Based on a variational principle which holds for this lower bound we studied constrained optimization of the reference function by maximizing the lower bound. We showed that solving the linearised simultaneous equations for the wave function, the nonsymmetric formula results the CEPA0 energy.



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No. 73, Poster Session I

Molecular dynamics study on the substrate binding free energy of Threonine Synthase

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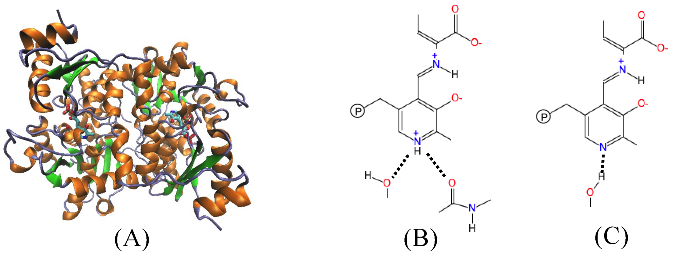
Threonine Synthase (TS) catalyzes a L-threonine formation reaction from O-phospho-L-homoserine (OPHS). TS contains a pyridoxal phosphate (PLP) and a phosphate ion in the active site. The reaction of TS is full of regiospecific and stereospecific steps, and the complicated reaction mechanism is not yet elucidated. It is sill unclear even for the protonation form at the PLP-pyridine nitrogen, though it seems to be critically important for the reactivity.

In this study, molecular dynamics (MD) calculations were performed and the substrate binding free energies are evaluated at the protonated and unprotonated state. MM-GBSA method was used for the binding free energy calculations. In the MM-GBSA formulation, total free energy is decomposed into an internal protein energy (G_{gas}) and a solvation free energy (G_{solv}). G_{solv} is the sum of the electrostatics and the nonpolar contributions, which are evaluated by the Generalized Born and surface accessible area calculations, respectively. GROMACS program package was used for MD simulations. By the 20ns MD simulations, the protonated PLP formed a minor hydrogen bond to Ala289 backbone oxygen atom at 5.78%. The unprotonated PLP formed a stable hydrogen bond to Thr317 side chain, which is observed in X-ray structures (Fig.1). These results suggest that the pyridine nitrogen is unprotonated in the X-ray structure. Calculated pKa value is 8.0 (cf. pKa = 5.8 in water), which indicates that protonated state is more stabilized in the protein environment.



(A) (B) (C)

Fig.1 structure of TS (A) and molecular structure of pyridoxal phosphate (PLP) at the protonated form (B) and the unprotonated form (C).

No. 74, Poster Session I

Theoretical investigations of Ag/SiO_2 interface

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Ag(111)/SiO_2 system is of a great interest in optics, synthesis of new heterostructures, etc. In our work this interface was investigated by means of Density Functional Theory. All calculations were done using Quantum Espresso [1] package with plane-wave basis set and ultrasoft pseudopotentials for the treatment of the core electrons.

Different structures of Ag(111)/SiO_2 interface were considered and the size of lattices was chosen to reduce the strain at the interface. The influence of SiO_2 structure on the adhesion properties was investigated.

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No. 75, Poster Session I

Potential of mean force of association of hydrophobic particles: dependence on size and temperature

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We carried out molecular dynamics (MD) simulations with AMBER force field for three pairs of dimers (neopentane, bicyclooctane, fullerene-C_{60} molecules) using TIP3P model of water as a solvent. To asses entropy contribution to the Gibbs free energy MD simulations were then run at three temperatures 273K, 323K, and 348K using umbrella-sampling/WHAM method. The stability of dimers is described by potential of mean force (PMF). The shape of PMF curves is characteristic for hydrophobic interactions with a contact minimum, a solvent-separated minimum and a desolvation maximum. The depth and position of the contact minimum for each pair changes with the size of nonpolar particle, consequently the larger molecules shifted to larger distances. Additionally, the contribution of Lennard-Jones potential to PMF increases simultaneously with increase of the particles' size. It is shown, the hydrophobic surface between two interacting particles, entrapes water molecules. We observed, that the contact minima on PMF curves increase with temperature. This means that the association entropy is positive. The dimensionless PMF curves showed low tendency (near contact minima area) of temperature effect, the association entropy is low.

No. 76, Poster Session I

Modified New Carbon K4 and Metal-Organic Framework Structures: A Theoretical DFT Study

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In the present talk we would like to bolster advantages of the cluster approach (being relatively very simple but complementary to other periodic slab model calculations) in proper modeling of extended systems [1-3]. Especially, the structure and chemical activity of the selected transition metal and metal oxide catalysts would be thoroughly discussed [3-5]. In line with combining of metal oxide connectors with organic linkers into extended metal-organic framework (MOF) networks, some solutions is given to stabilize and characterize modified new carbon K4 [6] and related new IRMOF structures. Based on these DFT cluster calculations results, some discrepancies with the results of other theoretical investigations and studies in literature have been critically pointed out.

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No. 77, Poster Session I

Linearized Coupled Cluster Corrections to Antisymmetrized Product of Strongly Orthogonal Geminals: role of dispersive interactions

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A linearized multi-reference Coupled Cluster (MR-LCC) theory is formulated based on the Antisymmetrized Product of Strongly Orthogonal Geminals (APSG) reference state. The role of dispersive interbond interactions is discussed. The presented theory has lead to qualitatively correct potential curves for the case when both OH bonds dissociate in H_2O, a result that cannot be achieved by adding only perturbative corrections to APSG. The potential curve obtained for the He...He problem practically coincides with the full CI (FCI) result, showing the unexpected accuracy of the MR-LCC approach in this case. We recently presented our results in the Journal of Chemical Theory and Computation [1].

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Abstracts of Poster Session II

No. 1, Poster Session II

Real-time TDHF/TDDFT calculation with efficient time evolution

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Electron dynamics, which is an ultrafast phenomenon occurring in femtoseconds, was recently observed by experiments and has attracted much attention. To theoretically describe electron dynamics, we can use real-time propagation (RT) method of time-dependent theories, such as the time-dependent Hartree-Fock (TDHF) method and the time-dependent density functional theory (TDDFT). However, the RT-TDHF/TDDFT calculations[1-3] have limited applications than the conventional frequency-domain TDHF/TDDFT for evaluating excitation spectra and frequency-dependent polarizabilities, because evaluation of the time evolution operator is computationally demanding. The Chebyshev expansion technique in real space[4,5] is one of the efficient methods for evaluation of the time evolution operator. This method has been applied to time-dependent Schrödinger equation for nuclear wave packet dynamics and succeeded in decreasing computational cost. In this study, we applied this Chebyshev expansion method to RT-TDHF calculation to achieve efficient time evolution.

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[2] Yam, C. Y., Yokojima, S., Chen, G. H. *J. Chem. Phys.*, 119:8794-8803, 2003.
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No. 2, Poster Session II

Modeling Spin Crossover Complexes

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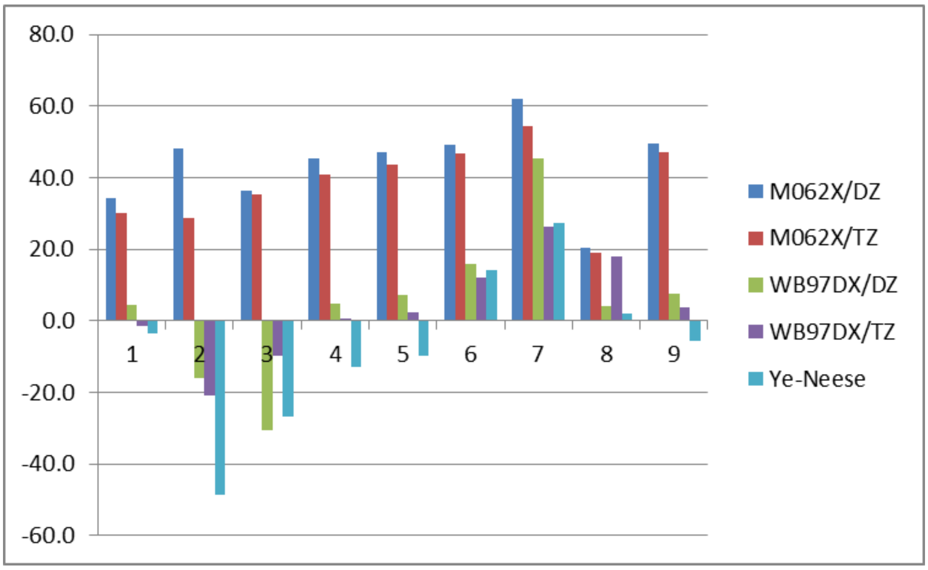
A class of inorganic compounds called spin crossover systems have spin states so nearly degenerate that changes in temperature, pressure, and environment can change their relative stability and thus interconvert ground states [1]. We report computations complementing and extending the work of Ye and Neese [2] on the prototype Fe(phenanthroline)$_2$(NCS)$_2$ (**1** in the figure below) and related quasi-octahedral species, [Fe(L)(NHS$_4$)] with L = NO$^+$(**2**), CO(**3**), PMe$_3$(**4**), PH$_3$(**5**), N$_2$H$_4$(**6**), NH$_3$(**7**)] with NHS$_4^{2-}$ = 2,20-bis(2- mercaptophenylthio)diethylamine dianion]. In addition we describe Fe(III)PCl (P = porphyrinate) (**8**) and Fe(phenanthroline)$_2$(CN)$_2$ (**9**).

The spin state preferences of set of reference compounds employed in [2] are well described by the ωB97XD functional with the cc-pVTZ basis, substantially smaller than the def2-QZVPP recommended for use with the B2PLYP functional. [2]



Spin state energies (kcal/mol, high spin state relative to low spin state) for Fe complexes.

We will present descriptions of the effect of relativistic (SO-ZORA) corrections and alternative choices of functional on the temperature response of crossover systems' state preferences and describes spin crossover in several four-coordinate systems.

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Electron Transfer Pathway in Biomolecules: FMO-LCMO and Tunneling Current Analysis

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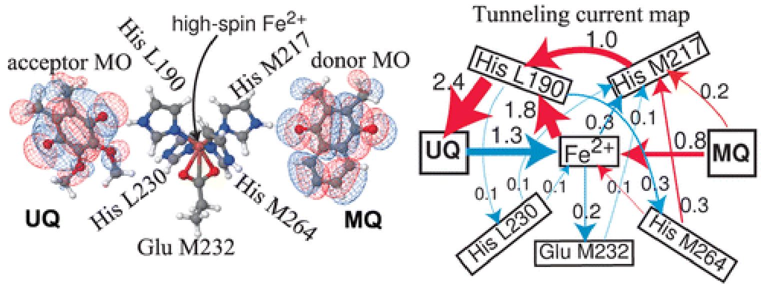
Biological energy conversions such as photosynthesis and respiration involve long-distance electron transfers (ETs) as key processes. However, the role of protein environment has not been fully understood; for instance, it is unclear whether they are simply holding the redox centers at appropriate locations, or they play some specific roles to mediate the long-distance ETs. While biological long-distance ETs can be regarded basically as single-electron processes, the effective one-electron potentials or orbitals should be derived via many-electron calculations, which is apparently formidable for realistic large proteins. To address this, we deploy the linear combinations of fragment molecular orbitals (FMO-LCMO) [1]. We then compute the electronic coupling energy of ETs by the generalized Mulliken-Hush and bridge Green function methods, and carry out tunneling current pathway analysis at atomic or fragment resolution.

The scheme has been applied to ET steps in the reaction center of photosynthetic bacteria *Blastochloris viridis*. Figure shows the molecules involved in the ET step from menaquinone (MQ) to ubiquinone (UQ) via Fe^{2+} complex with four histidines (His) and one glutamate (Glu). The right panel shows the result of tunneling current analysis. In contrast with the previously prevailing suppositions from mutagenesis experiments that exhibit weak dependence of the ET rate on metal substitution and depletion, a major pathway involves Fe^{2+} ion and one of the His ligands (L190). When the metal ion is replaced by Zn^{2+}, another pathway via two His ligands (M217 and L190) opens. These two His ligands take up the major role when the metal ion is depleted. The computed values of electronic coupling are consistent with experiments.



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No. 4, Poster Session II

Theoretical Study of Glucose Transformation to 5-Hydroxymethylfurfural using RISM-SCF-SEDD

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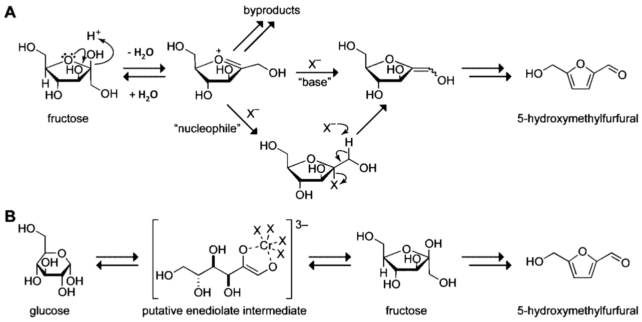
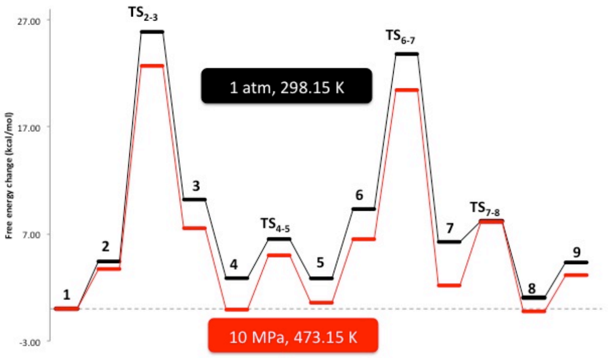
Hydrolysis of hexose into 5-(Hydromethyl)furfural (HMF) is believed to be one of the many key reactions for ‘green chemistry’. Previous proposed mechanisms, as shown in Scheme 1, suggests that formation of HMF from glucose occurs after the isomerization into fructose (**B**), which would be directly dehydrated into HMF (**A**).[1] Open ring mechanism, also given in Scheme 1, is the most likely pathway of isomerization from glucose into fructose. Besides the open ring mechanism, cyclic or closed ring mechanisms have been proposed by experimental and theoretical works as the reaction pathway for transforming 6-membered ring pyranose xylose molecule into the 5-member ring furanose furfural.[2]



Scheme 1. Previous proposed mechanism via open ring

In the present work, we considered both open ring and cyclic mechanisms for the isomerization reaction and further dehydration to produce HMF. We applied the coupled-cluster level of theory using RISM-SCF-SEDD [3] as the solvation model. We found that our energetics produced by RISM-SCF-SEDD shown good agreement with experimental studies. Furthermore, RISM-SCF-SEED allows to treat the system in high pressure and temperature conditions which shown in Scheme 2.



Scheme 2. Free energy surface of glucose isomerization for cyclic mechanism

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No. 5, Poster Session II

The hydrolysis of α-iminocarbonyls – a quantum chemical mechanistic study

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We present our DFT investigations of the hydrolysis mechanism of α-iminocarbonyl compounds. The aim of the present study is to explain the experimental observations by providing a deeper understanding of the complex processes taking place in the reaction mixture.

The α-arylation of α-aminocarbonyl compounds can be achieved through oxidative deprotonation with transition-metal catalysts.In a one-pot reaction a 1,2-dioxo compound can be obtained in the presence of copper(II) chloride catalyst, atmospheric oxygen and an excess amount of TBHP through an imine intermediate. [1] Remarkably, modification of the reaction conditions leads to the formation of the α-iminocarbonyl derivate. It has been also shown that the catalyst, the oxidizing agent and the presence of air can enhance the hydrolysis in a synergistic fashion.

Our calculations have revealed two possible mechanisms for the imine hydrolysis: a catalytic route by $CuCl_2$ and an oxidative mechanism with TBHP. Along the catalytic route $CuCl_2$ plays a twofold role: it acts as a Lewis acid and also as a catalyst for autoprotolysis. On the oxidative path TBHP acts as an OH-radical source which induces radical pathways. Our findings also explain the observed synergistic effect: the oxidant regenerates the copper catalyst from its complexated form by oxidizing the aromatic amine derivates whereas the copper salts catalyze the formation of the hydroxyl radicals.

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No. 6, Poster Session II

Reactivity of first-row transition metal monocations with methyl fluoride: a computational kinetic study

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The study of gas-phase reactions between metal cations and organic substrates has been the focus of a great deal of attention in the last few years. Its importance is mainly attributable to gas-phase reactions relevance in synthetic chemistry and their applications in several fields including catalysis, biological activity, atmospheric chemistry, and in the study of potential semiconductor materials. Among the organic substrates methyl fluoride deserves a special interest, since it constitutes a simple molecule to analyze the Carbon-Fluorine bond activation as well as the competition between C-F and C-H activation. In this context, reactions of first-row transition-metal single-charged cations with methyl fluoride become fundamental processes. Previous theoretical works within this field [1,2] proved very useful to fully understand this type of reactions.

In the present communication the gas-phase reactivity of methyl fluoride with selected first-row transition metal monocations has been investigated. Our thermochemical and kinetics study shows that early transition-metal cations exhibit a much more active chemistry than the latest transition metal monocation Zn^+. In the present computational study we combine the characterization of the PESs for the $M^+ + CH_3F$ reactions and kinetics calculations, allowing us to compute rate constants to be compared with available experimental data [3]. The present systematic study does provide valuable mechanistic information about a number of reaction paths leading to different products, thus complementing the experimental information available.

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No. 7, Poster Session II

Structure and Spectra modeling of CsRg (Rg=Ar, Xe, Kr) van der Waals Complexes

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[2]Physics Department, College of Science, King Khalid University,
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The potential energy interactions of the ground state and many excited states of the CsRg van der Waals complexe have been determined using [Cs^+] and [e-Rg] pseudopotentials [1-3] with the inclusion of core polarization operators on atoms. This has reduced the number of active electrons of the CsRg dimer to only one valence electron, permitting the use of large basis sets for the Cs and Xe atoms. Potential energy curves of the ground state and many excited states have been performed at the SCF level. The core-core interactions for Cs^+Rg are included using the accurate CCSD potential of Hickling et al [4]. Spectroscopic constants for the ground and excited states of CsRg are derived and compared with the available theoretical and experimental results. In addition, the transition dipole moment have been evaluated in order to simulate the $X^2\Sigma^+$---$A^2\Pi_{1/2}$, $X^2\Sigma^+$---$A\Pi_{3/2}$ and $X^2\Sigma^+$--$B^2\Sigma_{1/2}^+$ absorption spectra and to predict molecular transition shift and the Cs atomic spectrum broadening requested for development of powerful Alkali metal vapor lasers that are pumped by diode lasers [5-6].

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No. 8, Poster Session II

Limitations of reaction barrier benchmarks with fixed geometries

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A sizable fraction of the advancements in accuracy for density functionals over the last two decades have been due to insights from benchmarking studies. These studies are usually done at frozen geometries due primarily to computational cost. This works extremely well for some properties such enthalpy of formation, for example; a given density functional will give about the same error bar in ΔH_f if the molecules in question are optimized with that functional or not. However, fixed geometries are not very good when benchmarking barrier heights except at the high end of the accuracy range. Functionals with high accuracy in predicting barrier heights with frozen geometries tend to produce good transition state geometries, so optimization is not required for functional ranking at the low error end of the scale. At the lower accuracy end of the spectrum, this is not the case, and we demonstrate here that in some cases the functionals when used to optimize the geometries actually do significantly worse in predicting barrier heights, including a few cases where transition states disappear completely, which makes numerical value for these errors inappropriate. This work emphasizes the necessity of using high accuracy functionals for reaction modeling in spite of the slightly higher expense.

No. 9, Poster Session II

CANCELLED

No. 10, Poster Session II

Hydrogen dissociation on aluminum cluster interacting with carbon surfaces by first principle calculations

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Dissociation of H_2 on bare Al_n clusters (n=2,4,6) has recently been studied theoretically [1], where transition states, reaction paths, and the effect of the two low spin states of Al_n have been considered. Comparison of theory with experimental results agrees regarding the high reactivity of the Al_6 cluster.

Moreover theoretical studies of the dissociation of H_2 on carbon materials such as graphene[2] and single and double walled nanotubes[3] have recently demonstrated the catalytic effect of these carbon surfaces on the dissociation of the hydrogen molecule.

From these encouraging results, we aim to study the combined effect that Al_n clusters (n=2,4,6) and carbon surfaces such as coronene (C) and graphene (G) have on the dissociation energy of the hydrogen molecule.

We studied the interaction of H_2 with Al_n (n=2,4,6) clusters on the G and C surfaces using Density Functional Theory. To study physisorbed states we account for vdW interactions in DFT using the methods of Langreth and Grimme [4,5]. Various H_2 physisorbed configurations on the Al_n cluster on C and G surfaces were considered.

The analysis of the interaction of Al_n cluster on G show that the presence of Carbon atoms promotes the dissociation of H_2 over the small Al_n clusters with n=2 and 4. Results of Al_n on C show that coronene stabilizes the Al_n clusters in the singlet state. This result turns out quite interesting considering that the bare Al_2 and Al_4 clusters, without carbon materials, are more stable in the triplet state and the dissociation of H_2 molecule has eventually to follow a triplet pathway on these systems.

Reaction paths, leading from the physisorbed state to the dissociated chemisorbed state for Al_n clusters interacting with both C and G have been studied by Nudged Elastic Band (NEB) [6] calculations.

Our study demonstrates the catalytic effect that combining carbon surfaces and Al_n clusters has on the dissociation of Hydrogen molecule. The case of the H_2 on Al_4 on C turns out to be a particularly interesting system since dissociate the hydrogen molecule barrierless. The electrostatic energy, charge transfer and molecular orbital analysis explain the observed phenomena.

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No. 11, Poster Session II

Theoretical investigation of molecular switch properties of several quinoline compounds

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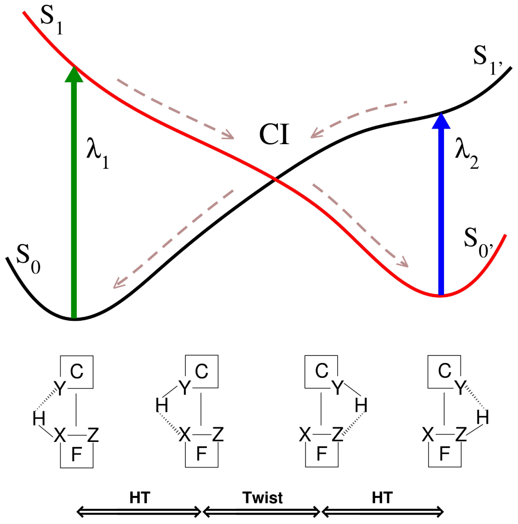
Molecular switches, being the simplest molecular level devices, are of great interest nowadays [1]. They have wide range applications, maybe the most important is in informatics: by representing an elementary bit memory unit they allow high density data storage on molecular level [2].

In this study we investigate the effect of chemical substitutions on the functional properties of a molecular photoswitch [3] by means of theoretical tools. Molecular switches are known to be consisting of so-called frame and crane components. Several functional groups are substituted to the 7-hydroxyquinoline molecular frame at position 8 as crane fragments. The impact of π-electron donating NH_2 groups attached to the frame is also investigated. Excited state intramolecular hydrogen transfer mediated by the frame-crane torsion has been considered as a possible reaction mechanism.

For all the investigated systems, we present the resulting CC2 potential energy profiles of the ground and first excited states. The presence of conical intersections around the 90 degree twist was shown using the CASSCF method. Vertical excitation energies and oscillator strengths of the 5 lowest-lying excited electronic states calculated at the two terminal points of the reaction path are also presented [4].



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No. 12, Poster Session II

Dissociation of the fluorine molecule: A benchmark study

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A small but notable discrepancy exists between the two most recently published [1, 2] dissociation energies for the fluorine molecule and, consequently, heats of formation for the F atom. The difference between the two atomic heats of formation in question is 0.20 kJ/mol, which is considerably larger than the sum, 0.11 kJ/mol, of the error bars associated with the corresponding results. In addition, in a theoretical study [3] the existence of a small and uncertain barrier along the dissociation curve of the molecule with a height of approximately $+40\ \mu\mathrm{E}_h$ ($\sim$0.10 kJ/mol) has been reported near the internuclear separation of 4 Å, while in another computational investigation [4] no such barrier has been found. In the case of its negligence during the evaluation of the raw experimental data, the barrier may introduce and additional error to the results which may be at least as high as the barrier height itself.

In order to resolve the discrepancies between the dissociation energy [$D_0(\mathrm{F}_2)$] and atomic heat of formation [$\Delta_f H_0^\circ(F)$] values, a highly accurate coupled-cluster based composite theoretical model chemistry has been utilized. The protocol involves contributions of up to pentuple excitations in coupled-cluster theory amplifying with additional corrections beyond the non-relativistic and Born–Oppenheimer approximations. The augmented core-valence counterparts of the correlation consistent basis set families, aug-cc-pCV*X*Z, have been used up to octuple-ζ quality. Our best theoretical estimates for $D_0(\mathrm{F}_2)$ and $\Delta_f H_0^\circ(\mathrm{F})$ obtained in this study are 154.95 ± 0.48 and 77.48 ± 0.24 kJ/mol, respectively. The relatively high error bars are mostly due to the considerably large contributions from the relativistic effects carrying large uncertainties.

In order to prove or disprove the existence of the small barrier on the dissociation curve of F_2, extensive multi-reference configuration interaction and coupled-cluster calculations based on all-electron CASSCF reference orbitals have been performed. The extrapolated results from aug-cc-pCV*X*Z (X=T,Q,5) calculations clearly indicate that the barrier indeed exists. It is located at 3.80 ± 0.20 Å along the dissociation curve with a height of $42\pm10\ \mu\mathrm{E}_h$ ($\sim$$0.11\pm0.03$ kJ/mol).

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No. 13, Poster Session II

Analytic gradients for general non-iterative coupled-cluster approaches

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It is fair to say that the coupled-cluster (CC) approach popularized by Bartlett and his associates [1] in the field of computational chemistry became an inevitable tool for quantum chemists. The level of accuracy that can be achieved heavily depends on the truncation applied to the cluster operator. Due to the steep scaling of the CC(n) approach, $\mathrm{n_o^n n_v^{n+2}}$, where the cluster operator truncated at n-tuple excitations and $\mathrm{n_o}$ is the number of occupied while $\mathrm{n_v}$ is the number of virtual orbitals, facilitated the development of the non-iterative [CC(n)(n+1)] methods where the highest excitations are treated approximately including the most important contributions only. Well-known methods such as the CC(2)(3) a.k.a. CCSD(T) and CC(3)(4) a.k.a. CCSDT(Q) approximations including non-iterative triples and quadruples excitations, respectively, belong to this category.

The calculation of energy for the CC(n)(n+1) approximation has already been coded for arbitrary excitations using a string-based algorithm [2]. Nevertheless, the efficient calculation of first-order properties requires analytic gradients. Although analytic first derivatives are implemented for the general iterative CC(n) approaches they are not readily available for the non-iterative CC(n)(n+1) methods. So far, analytic gradients have been developed for CCSD(T) only [7]. Here, we present the first general implementation of analytic gradients for the CC(n)(n+1) approaches. It is coded into the development version of the MRCC suite of programs utilizing its general string-based formalism. The details of the implementation are presented as well as the performance of the CCSDT(Q) method for first-order molecular properties, such as equilibrium structures and dipole moments has been assessed investigating several small molecular systems and compared the results with those obtained by CCSD(T), CCSDT and CCSDTQ calculations.

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No. 14, Poster Session II

The substituent effect in the doubly-charged benzene

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The substituent effect belongs to the one of the most important aspects of the general and the physical organic chemistry. Usually, it is considered as an effect associated with interaction between a specific chemical group (the substituent), possessing some given electron donating/withdrawing power, and the aromatic ring or other π-conjugated system. The interaction between the substituent and the substituted ring usually leads to important changes in various physical and chemical properties of the chemical compound. On the other hand, the substitution, although, it changes significantly, e.g. reactivity of the given aromatic ring, leads to very limited changes in the degree of π-electron delocalization. For instance, the substitution of the benzene ring with -NO or -OH group results in reduction of π-electron delocalization of the benzene ring by less than 1% (as shown by HOMA index [1]). This is due to the fact, that benzene ring, as distinct from its nonaromatic counterparts [2,3] tends to keep its aromatic character, and thus, is relatively resistant for substituent effect.

Here, we present the results of the investigation on the substituent effect in doubly positively charged benzene derivatives. The benzene dication, being 4n Hückel system, seems to be much more sensitive for the substituent effect when compared with its neutral counterpart. The interaction of several various substituents, possessing different electron donating/withdrawing properties, and interacting via the substituent effect with mono- and disubstituted benzene dications in its singlet and triplet states will be discussed. The changes in π-electron structure of the systems under investigation will be assessed by means of the Substituent Effect Stabilization Energy (SESE) parameter [4] and by the set of commonly used aromaticity indices.

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No. 15, Poster Session II

Products of quinoline thermal decomposition and theirs further reactions. Quantum chemical calculations and kinetic modeling.

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The initiation step in the thermal decomposition of quinoline and isoquinoline is the H-atom ejection from the pyridine ring, where the ortho-position is preferred. In the decomposition process the formation of ortho-quinolyl or ortho-isoquinolyl radicals via H-atom abstraction reactions by hydrogen atom and other radicals plays a very important role.

The product distribution [1] shows that three of the main decomposition products that contain the benzene ring, namely, benzene, benzonitrile and phenyl acetylene undergo further destruction at high temperatures. It is result mainly in two types of the reactions:

1) opening of the benzene ring, followed by breaking down into two parts, and
2) dissociative attachment of –C≡N and -C≡CH groups by hydrogen atom.

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No. 16, Poster Session II

Integral direct and memory conservative CCSD residual algorithm

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A novel implementation for the coupled cluster singles and doubles (CCSD) vector equations is presented. The algorithm is designed for low memory consumption and moreover it is efficiently parallelizable for several nodes. The recently developed divide-expand-consolidate (DEC) method is a linear scaling approach for coupled cluster methods, taking the local character of correlation into full account. In this approach the calculation is split into independent fragment calculations and the precision is determined by only one single input threshold, the fragment-optimization-threshold (FOT). Given that the fragments do not exceed a certain size the presented algorithm is suitable for large scale calculations of coupled cluster energies on large supercomputer systems. Hereby the time to solution will be drastically reduced compared to standard implementations. It will be shown how the presented algorithm performs compared to convenient implementations and how it is used within the DEC method. A further step of parallelization can be introduced by employing parallel distributed memory, which reduces the calculation time and broadens the range of application for the algorithm, since larger fragments and larger basis sets can be treated.

No. 17, Poster Session II

Revisiting the aromaticity concept: electrostatic effects are responsible for the stability of benzene towards ring distortions

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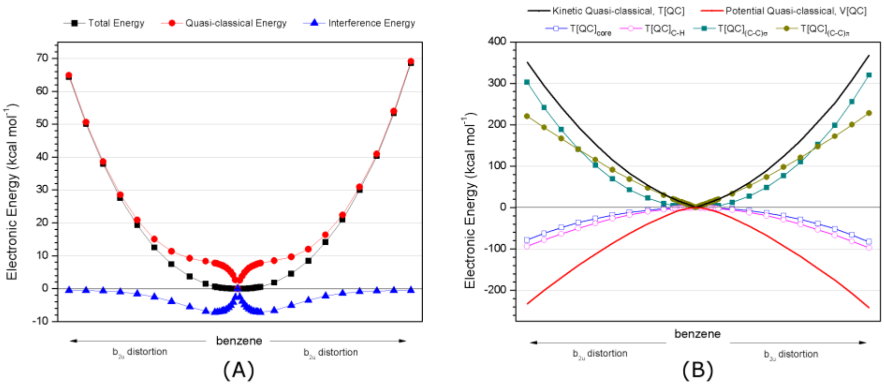
The concept of aromaticity lacks of a precise or general definition, even nowadays, due to the fact that is neither an observable quantity nor directly measurable. Furthermore, the question of which electrons are responsible for the stabilization of the D_{6h} structure of benzene is still matter of subject. For many decades delocalization of π electrons was pointed as the stabilizing factor responsible for stabilization of benzene, but recent works admit this effect is a by-product of the (C-C)σ frame's propensity to possess identical bond lengths [1]. This work revisits the aromaticity concept using the GPF-EP methodology [2] energy partitioning scheme that allows a proper evaluation of covalent and quasi-classical effects in different bonds and their role in the stability of the molecule. The method was applied to investigate how these contributions vary along vibration modes that distort the ring, including the b_{2u} mode that leads to a cyclohexatriene-like structure. The results show that, except for the symmetric breathing ring mode, quasi-classical effects are the main responsible for the stabilization of benzene towards distortion. For the b_{2u} mode, interference stabilizes a distorted structure (Figure 1A), while the partitioning of quasi-classical energy (Figure 1B) shows that the stability comes from the kinetic part of (C-C)σ and (C-C)π quasi-classical energies related to the polarization of the GVB orbitals associated to σ and π electrons. This shows that the σ and π electrons are equally important to the planarity and stability of the D_{6h} benzene – and therefore to aromaticity – but by quasi-classical effects, and not covalent ones.



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No. 18, Poster Session II

Is DFT reliable for beryllium containing systems? The example of the Be – π system interaction

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Beryllium is known to be difficult to handle by the quantum chemistry methods currently available. The small 2s - 2p energy interval leads to quasi-degenerated electronic sates described by a multi-references wave function. In the gas phase, beryllium interacts through weak van der Waals (vdW) interactions as a consequence of its closed shell electronic configuration ($1s^2$ $2s^2$). In the bulk, it hybridizes and standard methods based on DFT and post-HF theory are given to be correct [1].

We herein investigate the ability of DFT based methods to describe the interaction between beryllium atom and graphitic systems. Recent DFT investigation [2] established that atomic beryllium is physisorbed on graphene while it chemically binds in a bilayer of graphite.

The critical case of the weak interaction that take place between an isolated beryllium atom and graphene is investigated at different level of theory: (i) density functional calculations with Grimme correction (ii) Single reference post Hartree-Fock methods: second-order Møller-Plesset (MP2) perturbation theory and coupled cluster method with the inclusion of single, double and perturbative triple excitations (CCSD(T)) (iii) Multi reference post Hartree-Fock methods: complete active space self consistent field (CAS-SCF) and complete active space with perturbation theory truncated at the 2nd order (CAS-PT2) (iv) Periodic density functional computations using the Perdew-Burke-Ernzerhof functional with the Grimme correction of the dispersion forces (PBE-D2).

The combined (i)-(iii) approaches allow us to select an accurate functional to describe the beryllium – graphene interaction (PBE-D2) and understand the electronic mechanisms that occur when beryllium interacts with the surface. Finally mechanisms of the beryllium - graphite interaction are understood and the validity of DFT based methods is established.

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No. 19, Poster Session II

A new look at the electronic structure of the $\{\mathrm{RuNO}\}^6$ moiety using density-fitting CASSCF calculations and localised orbitals

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Nitrous oxide (NO) has been found to play a role in neurotransmission, blood pressure control and even control of tumor growth. Therefore, various transition metal nitrosyl complexes have been employed in targeted NO delivery to biological tissues such as photodynamical therapy (PDT)[1] . Understanding the electronic structure of the metal-NO moiety is crucial for the understanding of the mechanisms of the NO liberation and delivery in these complexes.

However, the metal-nitrosyl coordination has been known to be difficult to describe. NO is known as a non-innocent ligand in coordination chemistry, leading to complicated and ambiguous electronic structures of transition metal nitrosyls. Enemark and Feltham [2] have suggested to describe the electronic structure of this moiety as $\{\mathrm{M(NO)}\}^{\mathrm{n}}$, with n being the total number of electrons in the metal d and nitrosyl π^* orbitals. However, within this concept it is neither possible to assign a particular oxidation state to the metal nor to the NO. For example, it is unclear whether $\{\mathrm{RuNO}\}^6$ should be treated as $\mathrm{Ru^{II}{-}NO^+}$ or $\mathrm{Ru^{III}{-}NO^0}$.

In this work we attempt to resolve the ambiguity of the electronic structure of the $\{\mathrm{Ru(NO)}\}^6$ moiety with the help of density-fitting CASSCF (DF-CASSCF) calculations and localised natural orbitals, similarly to the approach of Radoń et al. [3] on {Fe(NO)} complexes. We optimise the S_0 and T_1 structures with the DF-CASSCF method using the newly developed analytical gradients with atomic compact Cholesky Decomposition (acCD) basis sets[4]. Subsequently, we describe the electronic structure of a $\{\mathrm{Ru(NO)}\}^6$ complex with a CASSCF wavefunction expansion in terms of localised orbitals, and conclusions about the electronic structure such as the formal oxidation state of Ru and the charge of NO are drawn from the total contribution of certain classes of electronic configurations to the multiconfigurational wavefunction.

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No. 20, Poster Session II

Analytical energy gradients for explicitly correlated second-order Møller–Plesset perturbation theory

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We present algorithms for computing analytical energy gradients for explicitly correlated second-order Møller–Plesset perturbation theory (MP2-F12) using the 3*A and the 3*C approximations with fixed amplitude ansatz. In order to simplify the formulation of the theory, equations are derived without using the complementary auxiliary basis set (CABS) approach. A variant of the 3*A approximation has been derived from the 3*C approximation to avoid computing the troublesome commutator integrals. It is identical to the common 3*A approximation within the assumption that the resolution-of-the-identity (RI) space is complete. For efficiency, the density fitting (DF) approximation is used for evaluating all two-electron integrals and their derivatives.

No. 21, Poster Session II

On the Association of the Base Pairs on the Silica Surface based on Free Energy Biased Molecular Dynamics Simulation and Quantum Mechanical Calculations

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The adsorption of the DNA bases and base pairs on the hydrophobic silica surface has been investigated by ab initio quantum mechanical (QM) methods (DFT-D) and molecular mechanics (MM) and also by biased molecular dynamics (MD) simulations (metadynamics). The structures of all the clusters (surface with single-bases and base pairs) predicted by means of the force field are compared with the results of direct QM calculations. The MM interaction energies for all clusters agreed well with the QM ones, which justifies the use of MM methods in the evaluation of accurate adsorption free energies. Rigid rotor-harmonic oscillator-ideal gas (RR-HO-IG) calculations based on QM and MM entropies as well as biased metadynamics (MTD) simulations based on MM demonstrated that mA-mT (Adenine-Thymine) and mG-mC (Guanine-Cytosine) base pairs are adsorbed on a fully solvated silica surface in different H-bonded forms. Both QM and MM techniques convincingly demonstrated that adsorptions of any H-bonded (Watson-Crick (WC), non-WC and Hoogsteen) structures on the surface are stronger than that of any π-π stacked structures.

No. 22, Poster Session II

Stabilization mechanisms at polar ZnO surfaces in ideal vacuum conditions: a SCC-DFTB study

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We present a study of a variety of surface reconstructions for the most abundant polar ZnO surfaces, namely the Zn-terminated (0001) and the O-terminated $(000\bar{1})$ surfaces [1]. Our method is quantum-mechanical calculations of the tight-binding DFT type. More precisely, we use a SCC-DFTB approach [2] in conjunction with a recently developed parameter set [3]. The applicability, transferability and quality of the chosen set of parameters were thoroughly tested by comparison with results obtained from DFT calculations as well as with earlier experimental and theoretical work, see e.g. [4, 5, 6]. These tests show that, using SCC-DFTB, the polar surfaces of ZnO are described astonishingly well, and at a low computational cost which allows for the investigation of larger - and more realistic - surface structures compared to previous studies. In particular, we find that the different surface terminations demonstrate different reconstruction patterns as a result of minimizing the dipole moment across the surface. At the ZnO(0001) surface, the reconstruction results in a high density of triangular defects with O-terminated step edges, whereas the $\mathrm{ZnO}(000\bar{1})$ surface favors ordered hexagonal defect patterns. Finally, through an extensive analysis of the SCC-DFTB-generated energetics and electronic structures of surfaces exhibiting many different step defect patterns, we have developed a simple geometric model that manages to predict the favored surface reconstruction patterns for the ZnO(0001) and $\mathrm{ZnO}(000\bar{1})$ surface terminations.

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No. 23, Poster Session II

Local response dispersion method in periodic systems: Implementation in the package based on a plane-wave basis set

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A number of dispersion correction methods have been developed to make density functional theory (DFT) applicable to noncovalent interactions. Our group has proposed and extended the local response dispersion (LRD) method,[1-5] which evaluates density-dependent dispersion coefficients using the result of DFT calculation. The LRD method was implemented in the program based on Gaussian basis functions. The availability of the LRD method was investigated not only for conventional hydrogen-bonded and dispersion-dominated molecular complexes but also for open-shell systems[4] and excited states.[5] Since the implementation in the program based on a plane-wave basis set was not reported, this study implements the LRD method into Quantum Espresso and examines the accuracy of the LRD method for periodic systems.

As a primary application, we optimized lattice parameters and cohesive energies of urea. Here, the LRD method is combined with the revised Perdew-Burke-Ernzerhof (revPBE) functional.[6] According to Table 1, significant improvements in structure and energetics are achieved. Numerical results of other periodic systems and details of the implementation will be explained in the poster session.

Table 1. Optimized lattice parameters and cohesive energies of urea. Differences from the experiments are shown in parentheses.

	revPBE		revPBE+LRD		Expt.
Lattice parameter					
a (Å)	6.055	(0.490)	5.638	(0.073)	5.565[7]
c (Å)	4.768	(0.084)	4.722	(0.038)	4.684[7]
V (Å^3)	174.8	(29.7)	150.1	(5.1)	145.1[7]
Cohesive energy (kcal/mol)	13.49	(-9.75)	23.26	(0.02)	23.24[8]

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No. 24, Poster Session II

CNDO/2 and Tamm-Dancoff methods for electronic structure evaluation of aluminum porphyrins involved in photodynamic therapy

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The porphyrins are known as ideal singlet oxygen sensitizers, being recognized as most efficient drugs in photodynamic therapy of cancer [1,2]. Metallo-substituted porphyrins yielded promising results when used as photosensitisers in photodynamic therapy (PDT). The addition of a central diamagnetic metal ion such as aluminium or zinc to the core structure of porphyrins changes their photophysical properties by enhancing singlet oxygen production and longer triplet states, while sulphonation increases the solubility of the molecules, increases their antitumoral properties and decreases the tendency of the compounds to aggregate, consequently improving their photosensitising efficacy [3].

In this paper we initiate a study on the mechanistic aspects involved in photochemical processes (Jablonski diagram) for aluminato-porphyrins (Al(III) X TPP) with different axial ligands (X= C2H5, C4H9, C8H17, C12H25).

Calculations were performed by means of semi-empirical CNDO / 2 electronic structures, evaluating the influence of the electronic structure (axial ligand) on the photochemical reactivity of aluminato-porphyrins (constant of photosensibilization reaction rate) by evaluating the deactivation energies, the direct and indirect mixtures and the states involved in electronic transitions. The calculations were performed for the equilibrium geometry of aluminato-porphyrins in the excited state electron, the Tamm-Dancoff approximation approximation, highlighting a radical dissociation of the porphyrin-ligand fragments during photochemical processes. Some correlations between the electronic structure, energy levels and photodynamic activity of these sensitizers, are discussed, too.

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No. 25, Poster Session II

Theoretical Study of Protein Flexibility During Molecular Docking

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Understanding the protein interaction has huge capability to improve drug development process. Flexibility of the protein plays important key role to generate active binding sites and orientation for favorable docking over a wide rage of energy. In the present study, we have studied the variation of flexibility of protein and its influeance during the molecular docking. The vibrational density of states of protein in the range from 2.3 to 10.3 nm is studied with the help of molecular-dynamics simulations. Our particular interest is in the behaviour of flexibility of protein during the moleculare docking, which is very important in microscopic behaviour of protein.

In the process of drug development molecular dynamics(MD) simulation has become a popular method in the investigation of protein dynamics and has successfully been integrated into virtual screening efforts to optimise lead discovery. In this study we have adopted the flexibility of protein as very important parameter which has key contribution in protein-ligand interaction.In our study , we choose the protein which responsible for Alzheimer deices (pdb code is 1fkn.pdb) [2]. This protein chain contain more then 1000 atoms so for reduces simulation efforts we consider only atoms (hydrophobic active sites) of the protein those are responsible for active molecular docking. Moreover, we can explore and analysis the process during molecular docking in new dimensions those are not possible by laboratory experiments. In the present study, we used NWchem [1] for MD simulation at 128 node based Unix cluster and in 6 hours for completing the single calculation.

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No. 26, Poster Session II

Theoretical study on ternary complex stability and Michael addition reactivity of Thymidylate synthase/mTHF/XdUMP

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Keywords: thymidylate synthase, cancer, Michael addition,

Thymidylate synthase (TS) catalyzes the reductive methylation of dUMP to dTMP during the DNA synthesis process. Herein, binding affinity, and activation energy of Michael addition and a covalent complex formation of TS/mTHF/XdUMP (where X is -H, -F, -Cl or -Br) were investigated using molecular dynamics (MD) and high level quantum mechanics-molecular mechanics (QM-MM) methods. Note that FdUMP is metabolite form of available anticancer agent, 5-FU, targeted at this enzyme. In MD results, the unique H-bonding between Y94 and the substituted fluorine of FdUMP was detected whereas the other systems share almost similar pattern in the overall H-bonding interactions. The B3LYP/6-31+G*-CHARMM potential energy surface according to the two reacting distances, d1: S-(C14)-C6(dUMP) and d2: C5(dUMP)-CH_2(mTHF) suggested that the Michael addition and covalent complex formation occurred in the concerted mechanism. In addition, the SCS-MP2/cc-pVTZ-CHARMM//B3LYP/6-31+G*-CHARMM barriers of this mechanism were 19.7, 23.6 and 25.1 kcal/mol for dUMP, FdUMP and CldUMP complexes.

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No. 27, Poster Session II

Reusable software for quantum chemistry applications

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The notion of reusable software libraries was around for a long time in the software development community. However, despite multiple advantages, a practice of reusing software is uncommon among computational chemists. We present *libefp* [1] – a full implementation of the effective fragment potential (EFP) method as a portable software library which brings reusable high-performance EFP implementation to the quantum chemistry community. The EFP method has emerged as a promising technique for performing simulations on extended molecular systems by substituting computationally expensive integral evaluations by first-principles derived formulas with parameters obtained from preparatory *ab initio* calculations. When electronic degrees of freedom are important, e.g., in case of a chemical reaction or electronic excitation, a part of the system where the electron rearrangement takes place can be described by quantum mechanical methods in a spirit of QM/MM schemes. *libefp* is the first software of its kind used by several major quantum chemistry packages such as NWChem [2], PSI4 [3], and Q-Chem [4] allowing a straightforward extension of unique electronic structure methodologies designed for accurate simulations in the gas phase to condensed phases via QM/EFP.

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No. 28, Poster Session II

Theoretical Study of the Dispersive Interactions Effects on the Adsorption properties of 4,4'-Bipyridine in H-ZSM-5 Zeolite

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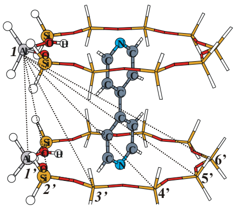
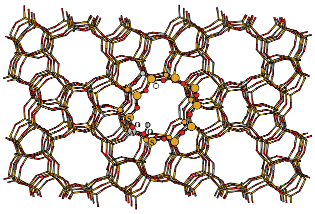
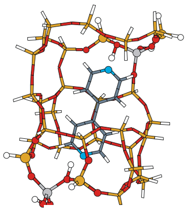
The effects of the zeolite framework on the adsorption of bidentate 4,4'-bipyridine (44BPY) ligand in the straight channel of H-ZSM-5 (Z) has been investigated by DFT calculations using M06-2X functional to account for dispersive interactions [1].
The straight channel is simulated by two clusters constituted of 20 and 32 tetrahedra (T). These clusters have two Al atoms located at positions sufficiently distant from each other allowing the bidentate 44BPY to interact with the two Brønsted acid sites of the zeolite.



44BPY / 20T



H-ZSM-5



44BPY / 32T

The minimum energy pathways of the double proton transfer from H-ZSM-5 to 44BPY ligand were calculated. The potential energy surfaces are characterized by two minima corresponding to the monodentate $44BPYH^{+}/Z^{-}$ and bidentate $44BPYH_2^{2+}/Z^{2-}$ ion pair complexes. No energy minimum is found for neutral hydrogen bonding structure.
Two monodentate ion pair complexes differing by the protonated pyridyl ring may be formed, which leads then to the formation of the bidentate $44BPYH_2^{2+}/32T^{2-}$ complex via two distinct pathways. The relative stability between all adsorption complexes involved in this double proton transfer does not exceed 5 kcal mol^{-1}.
Our results clearly show that the adsorption energy of 44BPY is mainly due to the effects of the zeolite framework executed through dispersive van der Waals interactions. These interactions decrease the relative stability of mono and bidentate complexes and stabilize the transition state connecting them. Consequently, an equilibrium between the two mono- and bidentate minima can be established on a flat potential energy surface.
The calculated vibrational frequencies and frequency shifts of 44BPY adsorbed as mono- or diprotonated species are in good agreement with available experimental data.

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No. 29, Poster Session II

Development of MPI/OpenMP hybrid parallel algorithm of resolution of identity second-order Møller–Plesset perturbation calculations for massively parallel multicore supercomputers

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Second-order Møller–Plesset perturbation theory (MP2) is the simplest but robust electron correlation method to account for the non-covalent interactions that play important roles in the chemical phenomena of nano and biological molecules. However, the computational cost of MP2 calculations scales $O(N^5)$ with respect to the size of molecules (N), and practical applications are limited to molecules of moderate size. To make the MP2 calculations applicable to the large nano and biological molecules, development of efficient computational techniques is desired.

We have developed a MPI/OpenMP hybrid parallel algorithm of resolution of identity MP2 (RI-MP2) calculations suitable for the massively parallel calculations on muticore supercomputers such as K computer by improving the previous algorithm [1] developed by authors. In the previous algorithm, the occupied orbital pairs are distributed to processors for the calculation of four-center two-electron integrals. However, the number of occupied orbital pairs is small, and this makes the load balancing problems in the cases of the massively parallel computations. We have changed to use the virtual orbital and its pair for the MPI parallel task distribution in order to use more large number of CPU cores with the efficient load balancing. Generally, the number of virtual orbitals is more than four times larger than the number of occupied orbitals, and the load valancing is considerably improved from the original algorithm. Computationally demanding tasks inside of MPI parallelized loops are mainly matrix-matrix multiplications and efficiently parallelized by OpenMP version of optimized BLAS libraries such as Intel MKL and AMD ACML. The algorithm is also designed for the massively parallel calculations by avoiding the I/O overheads and reducing network communication overheads. We have implemented the parallel RI-MP2 algorithm into NTChem quantum chemistry software. The new implementation has been supplied as library software on K computer.

Using the new MPI/OpenMP hybrid parallel RI-MP2 codes in NTChem, MP2 calculations of large molecules having up to 300 atoms and 7000 atomic orbitals can be performed with high parallel performance and in modest times on K computer. We successfully performed a RI-MP2/cc-pVTZ calculation of π-π stacked two-layer nanographene sheets $(C_{96}H_{24})_2$ (6432 atomic orbitals) on K computer. The calculation was finished in 33 minutes using 2048 node and 16384 CPU cores of K computer.

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No. 30, Poster Session II

Quantum-Chemical Calculations of ^{195}Pt-NMR Chemical Shifts in Platinum(IV) Porphyrins with Axial Ligands (Cl^{-}, Br^{-}, I^{-}, SCN^{-})

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Platinum(IV) porphyrin derivatives with two various axial ligands such as halide and thiocyanate anions shown in Figure 1 have been synthesized and their ^{195}Pt-NMR chemical shifts have been also measured by us and others. In this study, we calculated the optimized geometries and the ^{195}Pt-NMR chemical shifts of these complexes. We also confirmed the relativistic effect of the Pt-NMR chemical shifts.

The level of theory is the DFT-ZORA, and the DFT functional is OPBE0. The basis set is TZ2P for Pt and N, TZP for the axial ligand atoms, and DZP for the other atoms. We used abbreviation L-L' for platinum(IV) porphyrin with the two axial ligands L and L' in Figure 1, for example, Cl-Br.

The calculated ^{195}Pt-NMR chemical shifts reproduced well the trend of the observed ones. The contribution of the paramagnetic term (σ^{para}), which is the orbital response term, mainly determines the total chemical shifts in the present complexes. Because we have already known that the correlation between the Hammett substituent constants and the ^{195}Pt-NMR chemical shifts breaks down in SCN-SCN, we showed the relation between the reciprocal orbital-energy difference (ΔE^{-1}) and the paramagnetic contribution (σ^{para}) as an alternative analysis in Figure 2. We found that σ^{para} was linearly correlated with ΔE^{-1}, although on the SCN-SCN and I-I complexes there was significant deviation from the linear correlation.

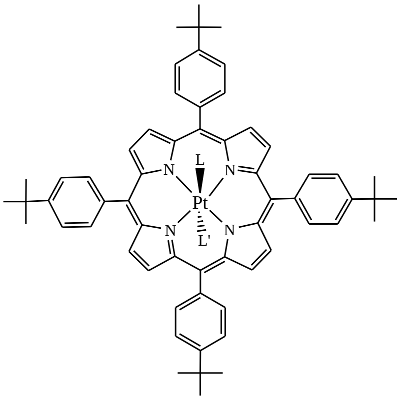

Figure 1. Platinum Porphyrins with axial ligands (Cl^{-}, Br^{-}, I^{-}, SCN^{-})

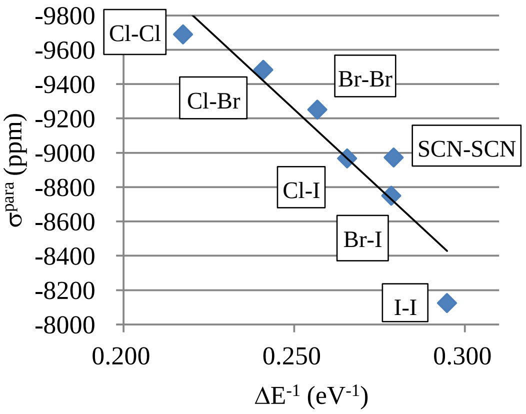

Figure 2. Relation between σ^{para} (ppm) and ΔE^{-1} (eV^{-1})

No. 31, Poster Session II

The effect of non-linear variational parameters on the energy convergence of Coulomb three-body systems

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Cox *et al.* [1] applied the series solution method, developed by Pekeris [2] for the Schrödinger equation for two-electron atoms and generalized by Frost *et al.*[3] to handle any three particles with a Coulomb interaction, to calculate the ^{1}S and ^{3}S states of helium and low Z helium-like systems with nucleus fixed and with nucleus in motion and showed that a non-linear variational parameter accelerated convergence of the energy. The wavefunction is expanded in a triple orthogonal set in three perimetric coordinates. The perimetric coordinates are defined as $z_i = r_j + r_k - r_i$ where the r_i are interparticle distances, and the z_i have the advantage of being independent over their range of 0 to ∞. The wavefunction takes the form

$$\psi(z_1, z_2, z_3) = e^{-\frac{1}{2}(\alpha z_1 + \beta z_2 + \gamma z_3)} L_l(\alpha z_1) L_m(\beta z_2) L_n(\gamma z_3)$$

Previous work fulfilled the condition $\alpha = \beta = \frac{1}{2}\gamma = \sqrt{-E}$ corresponding to an exponential dependence of the form $e^{-\alpha(r_1+r_2)}$ without any dependence on r_3, which is in principle an exact form as the exponential term contains the correct asymptotic behaviour of the solution of the Schrödinger equation for two electron atoms.

However, the convergence of molecular-type systems (such as H_2^+, HD^+, *etc.*) was very slow compared to that of atomic-type systems (such as H^-, He, *etc.*). Following the work of Gálvez *et al.* [4], [5], we have recently implemented a second and third non-linear parameter, whilst preserving the orthogonality of the Laguerre basis functions. Here we present the results of these studies, evaluated in terms of the rate of energy convergence and the accuracy of various expectation values. It is found that an explicit exponential dependence on r_3 is crucial for obtaining reasonable convergence of molecular-type systems.

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No. 32, Poster Session II

AIMPAC2: A next-generation QTAIM code

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The Quantum Theory of Atoms in Molecules (QTAIM) originated by Professor R.F.W. Bader and colleagues over 30 years ago, has seen growing acceptance and use in the chemistry, physics, and materials science communities, and has spawned multiple independent software implementations. This project addresses the need for a flexible common core of QTAIM and QCT (Quantum Chemical Topology) functionality, to encapsulate the best available algorithms and discourage unnecessary duplication of effort. The new collaboratively developed AIMPAC2 code (evolving directly from the Bader group's original AIMPAC code), will also allow a vastly extended range of analyses to be performed across a wide range of fields in the physical sciences, yielding deeper insights into behavior and properties of molecules and materials. This talk will outline the current state, development roadmap and future of AIMPAC2, before its general release to the scientific community, including theoretical developments such as our new Ehrenfest Force partitioning [1-4].

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No. 33, Poster Session II

Acceleration of basis set convergence of ACFDT-RPA and MP2 correlation energies using effective energy techniques

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Evaluation of total energies using correlated methods, such as the adiabatic-connection fluctuation-dissipation theorem method within the random phase approximation (ACDFT-RPA), are receiving more and more interest in the computational materials community. However, the applicability of ACFDT-RPA is to a large extent limited by the cost of evaluating the response function where many unoccupied bands need to be included to obtain sufficiently converged results. This issue is equivalent to the slow convergence encountered in standard quantum chemistry methods, such as coupled cluster or Møller-Plesset perturbation theory (MP). In fact, second order of the ACFDT-RPA expression corresponds to the so-called direct MP2 energy term [1]. A promising way to speed-up the convergence is to use the resolution of identity (ROI) and replace the sum over an infinite number of unoccupied states by an effective correction [2, 3]. However, the available schemes have been formulated only for norm-conserving pseudopotentials and lead to spurious errors when ultrasoft pseudopotentials (US-PPs) or the projector augmented-wave (PAW) method are used. We present and evaluate two modifications that allow to use the ROI correction within US-PPs or the PAW schemes. Furthermore, we show how the convergence of one of the schemes, the so-called effective-energy technique given in Ref. [3], can be further improved. Finally, the efficiency of the methods for ACFDT-RPA calculations and the prospect of using them to speed-up the convergence of other methods, such as MP2, are discussed.

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No. 34, Poster Session II

The Early Phase of the Conformational Transition at Vertebrate Transglutaminases; Can We See it From Molecular Dynamics Simulations?

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The main physiological role of transglutaminases is to form inter- or intramolecular ε(γ-glutamyl)-lysyl crosslinks. The atomic resolution 3D structure for the "open" (assumed to be "active") conformation, fixed with substrate analog inhibitor [1], is available only for human TG2. The difference between the "closed" ("inactive") and "open" X-ray structures is surprisingly large. Nevertheless, only the relative orientation of the constituting domains were changed while the domains kept their substructures.

Because of the structural and functional similarity of the "inactive" ("closed" conformation) vertebrate transglutaminases, significant similarity between their "open" conformations can be assumed as well. It was the basis of the theoretical model we proposed [2] for the "open" conformation of FXIII-A_2*.

While the whole conformational transition can be considered as „rare events" on the time scale can be reached even on nowadays high-end supercomputers, simulations can provide us valuable data on the early phase of conformational changes. Therefore our aim was to extract information from molecular dynamics trajectory on how these large Ca^{2+}-dependent conformational changes begin. Our aim was also to gain information on the binding mode of Ca^{2+} and to reveal their role in triggering the large scale conformational transition.

1μs NPT molecular dynamics simulations using explicit solvent molecules and periodic boundary condition have been carried out on the „closed" form of human TG2 in the presence and in the absence of Ca^{2+} ions. The long range electrostatic interactions were calculated by means of the particle mesh Ewald protocol implemented in the GROMACS molecular dynamics package. OPLS-AA/L force field was used for the protein while for the solvent the TIP3P water model was applied. The low frequency modes were extracted from the covariance matrices which were constructed from the trajectories of dynamic simulations. They represented motions along which the conformational changes are assumed to occur. The most probable Ca^{2+} binding sites were proposed from simulation and they are in a good accordance with those ones which were obtained from systematic mutational experiments [3]. In addition to the primary Ca^{2+} binding sites were found experimentally and which were found characteristic ones even from simulations, other, less characteristic Ca^{2+} binding sites were obtained as well.

Acknowledgments: This work was supported by Hungarian Scientific Research Fund (OTKA K-106294, NIIF-1057, TÁMOP-4.2.2.A-11/1/KONV-2012-0045 and TAMOP-4.2.2.C-11/1/KONV-2012-0010 grants.

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No. 35, Poster Session II

Predicting excitation energies from short-range density functionals combined with the long-range strongly orthogonal geminal theory

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Predicting excitation energies from time-dependent density functional theory (TDDFT) can be performed at relatively low computational cost and often leads to satisfactory results, in particular for low-lying single excitations. However, some excitations (i.g. double excitations) remain beyond the reach of conventional approaches to TDDFT based on the adiabatic approximation.

Recently, we have proposed a formalism based on the Rowe's equation of motion that employs reduced density matrices obtained from the antisymmetrized product of strongly orthogonal geminals (APSG) model [1]. It leads to obtaining accurate excitation energies of molecules when static correlation effects are of importance. Unfortunately, close to equilibrium geometries of the investigated molecules the accuracy of the excitation energies is often only comparable or even inferior to that of the TDHF method [2].

We show that applying the principle of action and the linear response theory for the APSG functional leads to equations of the similar structure as the structure of equations obtained from the equations of motion. It opens an avenue to combining the TD-DFT and APSG approaches by range-separating of the electron-electron interaction and restricting density functionals to short-range and the APSG to long-range regimes, similarly to what has been proposed in the context of density matrix functionals [3] and MC-SCF [4]. Illustrative calculations of potential energy curves of excited states confirm that the short-range-TDDF – long-range-APSG approach leads to significant improvement over TDDFT.

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No. 36, Poster Session II

Electric-dipole properties of spatially confined water molecule

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Since the recent experimental work of Kurotobi and Murata [1], who demonstrated the so-called molecular surgery approach for the isolation of a C_{60} fullerene containing a single trapped H_2O molecule, the properties of spatially limited water are intensively studied. Particularly interesting is the change in the dipole moment of H_2O upon encapsulation in the fullerene cavity. Theoretical reports regarding to this topic lead to rather opposite conclusions, indicating that the dipole moment value of the $H_2O@C_{60}$ complex is significantly smaller [2,3], slightly bigger [4] or almost equal to that of an isolated H_2O molecule [1].

In this study the confinement-induced changes in the dipole moment of water have been reinvestigated. Additionally, the effect of the orbital compression on the polarizability (α) and first hyperpolarizability (β) was also analyzed. In order to render the influence of the spatial confinement on the properties in question two model spherical confining potentials, mimicking a topology of fullerene cage, were considered. The magnitudes of relevant components of μ, α and β were computed within the finite field method (FF). The calculations have been performed using a wide range of *ab initio* techniques, including Hartree-Fock approximation (HF), the second-order Møller-Plesset perturbation theory (MP2), as well as the coupled-cluster (CCSD and CCSD(T)) methods. Our results demonstrate that depending on the nature of the applied confining potential predicted changes in the analyzed electric-dipole properties differ.

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To appear in *Molecular Physics*
Vol. 00, No. 00, Month 2013, 1–1

No. 37, Poster Session II

POSTER ABSTRACT FOR ISTCP-VIII CONFERENCE

The Divide-Expand-Consolidate MP2 scheme goes massively parallel

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(*Received 00 Month 200x; final version received 00 Month 200x*)

For large molecular systems conventional implementations of second order Møller-Plesset (MP2) theory encounter a scaling wall, both memory- and time-wise. We describe how this scaling wall can be removed. We present a massively parallel algorithm for calculating MP2 energies and densities using the Divide-Expand-Consolidate scheme [1–6] where a calculation on a large system is divided into many small fragment calculations employing local orbital spaces. The resulting algorithm is linear-scaling with system size, exhibits near perfect parallel scalability, removes memory bottlenecks, and does not involve any I/O. The algorithm employs three levels of parallelization combined via a dynamic job distribution scheme [6]. Results for two molecular systems containing 528 and 1056 atoms (4278 and 8556 basis functions) using 47120 and 94240 cores are presented. The results demonstrate the scalability of the algorithm both with respect to the number of cores and with respect to system size. The presented algorithm is thus highly suited for large super computer architectures and allows MP2 calculations on large molecular systems to be carried out within a few hours – for example, the correlated calculation on the molecular system containing 1056 atoms took 2.37 hours using 94240 cores.

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ISSN: 00268976 print/ISSN 13623028 online

DOI: 10.1080/0026897YYxxxxxxxx
http://www.informaworld.com

No. 38, Poster Session II

Specific interactions between lactose repressor protein and DNA: classical MD and *ab initio* MO calculations

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Lactose repressor (LacR) protein controls the transcriptional mechanism of gene information from DNA to mRNA in a ligand-dependent manner. Although the ligand-binding to LacR was found to change the mechanism drastically, the effect of ligand-binding on the conformation of LacR-DNA complex has not been clarified at atomic and electronic levels. In our previous study [1], molecular simulations combined with classical molecular mechanics (MM) and *ab initio* fragment molecular orbital (FMO) methods were performed to elucidate the specific interactions between LacR monomer, DNA and ligand. In the present study, we investigated the change in conformation of the solvated complex of LacR dimer and DNA induced by the ligand-binding by molecular dynamics (MD) simulations.

The initial structure of the complex with LacR dimer, DNA and anti-inducer ONPF, which is defined as LacR-DNA-ONPF, was constructed based on the PDB structure (PDB ID: 1EFA). The structure of LacR-DNA without ligand was constructed by deleting ONPF, while that of LacR-DNA-IPTG with inducer IPTG was constructed by replacing ONPF by IPTG. These structures were optimized in water by the MM method based on AMBER99SB-ILDN and TIP3P force fields, and 100 ns MD simulations were performed to elucidate the conformational change of LacR-dimer+DNA complexes.

We first analyzed the time evolution in RMSD of Cα atoms of LacR during the MD simulation. In LacR-DNA and LacR-DNA-ONPF, the conformation of LacR dose not change significantly. In contrast, LacR in LacR-DNA-IPTG has large conformational change at 7.7 ns, indicating the remarkable effect of inducer IPTG on the LacR-DNA complex. To elucidate the effect, the structures of LacR-DNA-IPTG at 1.5 and 7.7 ns are compared in Figure 1. LacR dimer tilts 12.8 degree to the left relative to DNA at 7.7 ns. We furthermore investigated which parts of LacR are affected by the IPTG binding to find that the conformation of the α-helix including Asp149 and Asn125 residues is changed significantly. These residues contribute to the specific binding between LacR and IPTG. Therefore, it is elucidated that the information of IPTG binding transfers to the α-helix, leading to the change in its conformation. This change is expected to influence the conformation of the DNA-binding domain of LacR and the binding affinity between LacR and DNA. The specific interactions between LacR and DNA investigated by *ab initio* FMO calculations will be shown at the conference.

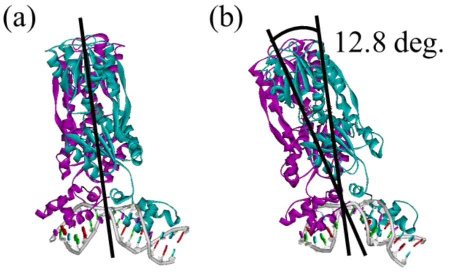

Fig. 1 Structure of LacR-DNA-IPTG at (a) 1.5 ns and (b) 7.7 ns of MD.

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No. 39, Poster Session II

Comparison between the contact and effective electron/spin densities at the IOTC quasirelativistic level of theory

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Effective electron density can be obtained via the derivative of electronic energy by means of the size of nucleus [1, 2]. Alternatively, the electronic energy can be replaced with the matrix representation of the nuclear potential, considering the homogenously charged sphere nucleus model [3]. Another approach, which is able to obtain both the electron and spin densities in the same way, is based on weighting of the density by the normalized Gaussian distribution of the nucleus [3]. All these approaches are considered, hand in hand with the comparison to contact electron/spin densities for two different models of nucleus (point charge nucleus and Gaussian finite model of nucleus).

The calculated values of contact and effective electron/spin densities for the Cu, Ag, Au atoms and the chemical shifts related to their cations are presented. The influence of PCE correction, the use of finite model of nucleus and the sensitivity to the quality of basis set is considered as well. All the calculations have been performed at the IOTC quasirelativistic level of theory, using the TONTO package [4]

Acknowledgements
The financial support was obtained from APVV (contract No. APVV-0202-10) and VEGA (contract No. 1/0327/12). We are grateful to the HPC center at the Slovak University of Technology in Bratislava for the computational time and resources made available. We are also grateful to Markus Reiher (ETH Zürich) for valuable comments and suggestions.

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No. 40, Poster Session II

On the Excitation Energy Transfer Dependency on Pigment–Protein Interactions in the Fenna–Matthews–Olsen Complex.

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Most models of dissipative energy transfer in protein–pigment complexes assume that the local environments of each chromophore are identical, despite the often significant local differences in protein structure. In this contribution I will introduce the use of a model where chromophore excitation energies depend on their surroundings. The model is developed using results from ground state molecular mechanics simulations together with a partial charge difference calculation for the long–range contributions to the chromophore excitation energies fluctuations. The widely studied Fenna–Matthews–Olsen (FMO) [1, 2] "excitonic wire" protein–pigment complex is used as a benchmark system. I will show how the resulting chromophore dependent spectral densities, and the local differences in environmental fluctuations determined by these quantities, influence energy transfer processes in this system. In particular, the calculations reveal that chromophores that are close to the protein–water interface experience strongly dissipative environmental interactions characterized by solvent reorganization energies that can be as much as two–three times those of chromophores that are buried deep in the hydrophobic protein scaffolding. Using a linearized density matrix quantum propagation method [3] the inhomogeneous system–bath model obtained from the site–dependent spectral density calculations give results consistent with experimental dissipation and dephasing rates. [4]

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No. 41, Poster Session II

A Density Functional Theory Based Protocol to Compute the Redox Potential for Transition Metal Complexes

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Toward the design of new materials at molecular level, it is helpful to understand the property of a single molecule. The redox potential is one of the most fundamental quantities of transition metal complexes (TMCs), which clarifies whether the target molecule can easily take an electron or not. The importance of measuring the redox potential of TMC is not limited to inorganic chemistry. The redox potential is one of the key information for a metal cluster to understand its catalytic property. It is also meaningful to investigate the redox potential of significant metallo-proteins, which play a crucial role for electron transfer process in biomolecules.

Recently, we have proposed a scheme to evaluate redox potential of a wide variety of transition metal complexes by adding a charge-dependent correction term for a counter ion around the charged complexes, which is based on Generalized Born theory, to the solvation energy [1]. The mean absolute error (MAE) toward experimental redox potentials of charged complexes is considerably reduced from 0.81 V (Maximum error 1.22 V) to 0.22 V (Maximum error 0.50 V). We found a remarkable exchange-correlation functional dependence on the results rather than the basis set ones. Moreover, long-range corrected (LC)-DFT well reproduces the experimental standard hydrogen electrode potentials (4.44 V).

The combination of Wachters+f (for metal) and 6-31++G(d,p) (for other atoms) with the B3LYP functional gives the least MAE 0.15 V for the test complexes. This scheme is applicable to other solvents, and heavier transition metal complexes such as $M_1(CO)_5(pycn)$ (M_1=Cr, Mo, W), $M_2(mnt)_2$ (M_2=Ni, Pd, Pt), and $M_3(bpy)_3$ (M_3=Fe, Ru, Os) with the same quality.

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No. 42, Poster Session II

Classical and advanced molecular dynamics study on ligand-protein interactions targeted at HCV NS3/4A protease

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Hepatitis C virus (HCV) infection is the global health problem leading to liver inflammation which can develop to hepatocellular carcinoma. Even if the commercial anti-HCV drugs are available, the side effects have shown up and the mutations have caused the drug resistance. Therefore, understanding of the drug-target interactions and searching potent compound against HCV are needed for further drug design and development. Since NS3/4A protease has an essential role in viral replication, it becomes a major drug target. Using the classical molecular dynamics (MD) simulation, the ligand-protein interactions between the known anti-HCV drugs (boceprevir and telaprevir) and inhibitors (danoprevir and BI201335) and NS3/4A protease were explored. These four ligands displayed a strong hydrogen bonding interaction with A157, while the hydrogen bonding interaction with backbone of R155 was decreased in both drugs. This result was supported by the MM-GBSA binding free energies in which the two known inhibitors showed higher efficiency than the two anti-HCV drugs. Meanwhile, the steered MD was employed to screen the potent compounds against NS3/4A out from ZINC database. It was found that **59500093**, **59784724**, **13527817** and **26660256** compounds come to be the candidates of potent HCV inhibitor and van der Waals interaction is the main contribution in stabilizing the NS3/4A complex.

No. 43, Poster Session II

Photoswitching of the kindiling fluorescent protein: a theoretical study

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Fluorescent protein asCP (also known as kindling fluorescent protein) is a member of photoswitchable fluorescent proteins class. Its ability to be reversibly switched between a nonfluorescent “off”-state (λ_{abs} = 565 nm) and a fluorescent “on”-state (λ_{abs} = 576 nm, λ_{em} = 610 nm) upon intense green light irradiation has been attributed to photochemical E→Z isomerization of its chromophore. A reverse isomerization proceeds either thermally or photochemically by irradiation at 445 nm. The details of this interconversion remain poorly characterized. Here, by using high-level quantum chemistry methods we explore the asCP photocycle at atomic level.

Structures, spectra and properties of asCP have been modelled by using *ab initio* based QM/MM and molecular cluster approaches. The results of these simulations favour a mechanism describing a majority of photoinduced asCP transformations solely relying on protein structures with the anionic form of the chromophore. The computed energies of $S_0 \rightarrow S_1$ (561 nm) and $S_1 \rightarrow S_0$ (605 nm) vertical electronic transitions for the model system with the anionic chromophore, as well as calculated vibronic structure of the absorption band correlate well with the available experimental data. Internal conversion is shown to proceed through two competing radiationless channels in the off-state of the protein corresponding to twisted S_0/S_1 conical intersections. Both conical intersections are related to internal rotation of the chromophore in the central bridge moiety. One of them corresponds to the photoinduced E→Z isomerization, and the other leads to relaxation back to the “off”-state. Small quantum yield of the asCP photoactivation originates from different topographies of S_1 along the two branches in internal conversion. Photochemical quenching of the “on”-state of asCP is traced to the excited-state Z→E isomerization of the neutral form of the chromophore. The estimated value of the absorption maximum (437 nm) is in close agreement with the experimental maximum of quenching efficiency (445 nm). Furthermore, the neutral chromophore concentration increases upon “off”-“on” photoswitching as it has been shown by the QM/MM-based molecular dynamics study, whereas the ground state Z→E isomerization proceeds exclusively through the anionic form of the chromophore.

This work is supported by the RFBR (grants 11-03-01214 and 13-03-00207). The use of computational facilities of the Supercomputing Center of Lomonosov Moscow State University is acknowledged.

No. 44, Poster Session II

A second-order multi-reference perturbation method for molecular vibrations

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We will present a multi-reference method in vibrational structure theory. Quantum nature of molecular vibrations plays important roles in a variety of chemical phenomena. Theory for vibrational wavefunctions, so called vibrational structure theory, is thus a vital tool to understand them at atomistic level. So far, various mean-field-based (i.e. single-reference) models have been developed for a system consisting of weakly-correlated vibrational motions. [1] These methods are capable of efficiently describing quantum dynamics when a targeted system or phenomenon includes no strongly-coupled motions. There exist, however, many chemical phenomena that contain strongly-coupled motions such as floppy hydrogen stretching and wide-amplitude motions. We develop a multi-reference vibrational wavefunction model to obtain accurate descriptions of small to medium size molecules with such motions.

Our approach is based on a mixed configuration-interactions (CI) and mean-field (SCF) wavefunction ansatz. In this scheme, vibrational coordinates are divided into active and bath space: active space includes a targeted strongly-coupled modes and bath space consists of the other modes; CI wavefunction is used for active space and SCF wavefunction for bath space; a system's wavefunction is defined as a direct product of active and bath wavefunctions. Although this procedure considers strong correlation within active space, it neglects weak correlation among bath modes and between bath and active modes. In order to take into account the weak correlation, we introduce a second-order perturbation to this multi-reference reference function. The method is named as Vibrational Active Space Second-Order Perturbation Theory (VASPT2). VASPT2 allows us to quantitatively evaluate vibrational energy levels of a system including either resonances or strong mode coupling in a cost effective way.

We will show some pilot applications of VASPT2 method. For example, VASPT2 has been employed to compute fundamental bands of *trans*-formic acid with a new semi-global potential energy surface at CCSD(T)(F12*)/cc-pVTZ-F12 level of theory; [2] the results exhibit that the root mean squared deviation of VASPT2 from experimental values is 7 cm^{-1}, while that of the widely-used vibrational MP2 method is 20 cm^{-1}.

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No. 45, Poster Session II

Probing the effect of the environment on the excited state dynamics of biological chromophores by *ab initio* quantum chemistry.

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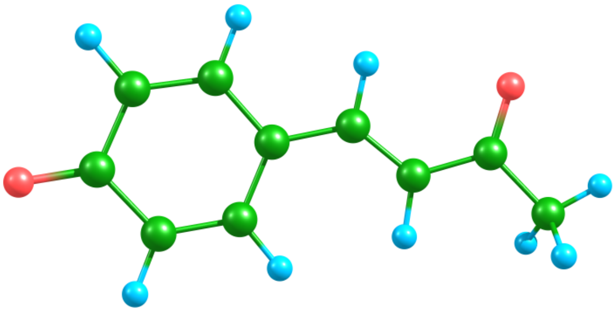
The key step in activation of many photoreceptors is photoisomerization of a conjugated chromophore inside the protein matrix. To reveal the atomistic details of the photo-isomerization process we use computer simulations. In our work, we use the multi-configurational self-consistent field (CASSCF also with multi-configurational perturbation theory) level of *ab initio* theory to model electronic structure of biological chromophores in gas phase and solution. We characterize reactant, product and intersection geometries as well as the minimum energy pathways that connect these structures. We also compute absorption spectra of these structures, with which we assign measured time-resolved photon-absorption spectra. To understand also the factors controlling the isomerization, we incorporate the effect of the environment (i.e. solvent) at different levels of sophistication, including continuum models, forcefields (MM), Effective Fragment potentials (EFP) and *ab inito*, as well as combination of these. Finally, to explore the role of dynamics, we compare minimum energy pathways to molecular dynamics trajectories. New results on the deactivation of the photoactive yellow protein chromophore in different solvents as well as the explanation for the large difference in the photochemistry of the chromophore in these solvents that were observed experimentally by Changenet-Barret and co-workers [1] will be reported.



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No. 46, Poster Session II

Performance of Density Functionals in Modeling the Decomposition of CH_3OH by Cu_4 Cluster

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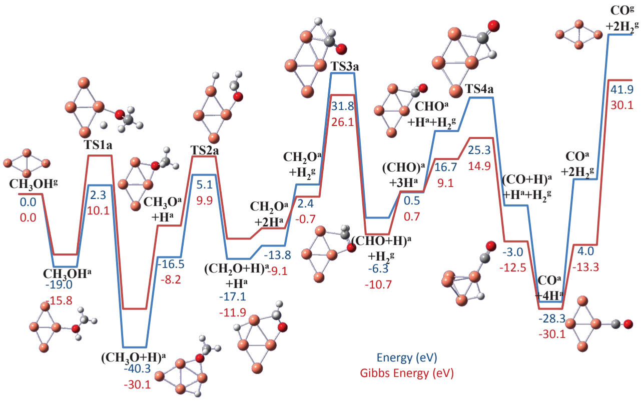
Heterogeneous catalysts are a critical part of industrial chemistry, primarily as a tool for more economically and ecologically efficient chemical processes. The activation of small abundant organic molecules such as methanol, catalyzed by metals, leads to hydrogen gas with a high atomic economy, which gives to the reaction the potential role in the development of such a promising source of energy. It is thus desirable to develop theoretical methods that can predict trends in catalytic activity and predict active catalyst for industrially important reactions. We are interested in the efficacy of DFT for modeling heterogeneous catalysis; this has to be ascertained through benchmark studies. In this study, the mechanism of the dissociation of CH_3OH by Cu_4 clusters is computed with DFT and with CCSD(T)/CBS-extrapolated. Adsorption energies of all possible decomposition products, reaction barriers for the cleavage of all possible bonds, and the reaction energies of those cleavages have been computed.We have undertaken a benchmarking study of various methods on the decomposition of methanol on small copper clusters with a wide range of DFT methods. The simulation of the reactivity of such small metal clusters is interesting both for elucidating the participation of the small clusters and also as model for the molecular-metal interactions in nanoparticles and surfaces.



No. 47, Poster Session II

Development of Relativistic quantum Monte Carlo method: Theory and parallel program

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The Quantum Monte Carlo (QMC) method is a suitable method for massively parallel computation of electron-correlation effects in physical and chemical problems. While the target of molecular orbital theory or density functional theory has been extended to systems including heavy elements, the QMC method has been limited to systems with light elements. To treat molecular systems with heavier elements, the inclusion of relativistic effects – scalar relativistic and spin-orbit effects – is required.

To treat the scalar relativistic effect, we have developed relativistic quantum Monte Carlo methods based on the zeroth order regular approximation (ZORA) Hamiltonian, whose kinetic term is suitable for the real space MC integration. The scalar ZORA QMC method includes three extensions to the nonrelativistic QMC method – (1) the ZORA local energy expression, (2) the ZORA cusp correction scheme, and (3) the ZORA approximate Green's function. Combined with the spin-orbit treatment of Ambrosetti *et al.*[4], the developed methods are implemented in a QMC program "R4QMC", a QMC part of "NTChem" software. The details of theory and implementation of the relativistic extension of the QMC methods for general molecular systems are presented.

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No. 48, Poster Session II

Origin of the surface-induced first hyperpolarizability in the C_{60}/SiO_2 system: a SCC-DFTB insight.

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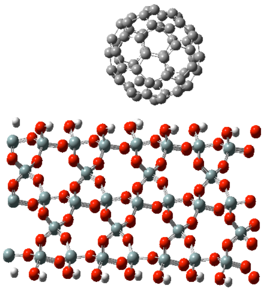
In last decades, nonlinear optical (NLO) properties have been widely used to design efficient devices in different fields, like sensing, communication, or medical imaging. Nevertheless, some phenomena need further investigations to be totally understood, especially interface NLO properties. Here we investigate the second-order NLO response of buckminsterfullerene adsorbed on a silica surface. The macroscopic property of interest is the second-order NLO susceptibility, $\chi^{(2)}$, whereas at the molecular scale, the property is the first hyperpolarizability, β. Isolated C_{60} molecule is a centrosymmetric molecule and is therefore NLO inactive. However, once it is adsorbed on a silica surface, it displays a second-order NLO response. This has been observed experimentally: C_{60}/SiO_2 surfaces exhibit a $\chi^{(2)}$ response [1]. This result has been confirmed theoretically a few years ago, for C_{60} films as well as for single molecules adsorbed [2]. This surface-induced hyperpolarizability has first been attributed to geometric deformations or vibrational coupling at the interface.



We propose here to extend this characterization by performing quantum chemistry calculations. Owing to the size of the system, we adopt the self-consistent charge density functional tight binding (SCC-DFTB) model. This semi-empirical model permits fast calculations on periodic large systems, with a DFT-like quality. Preliminary, it was demonstrated that the SCC-DFTB method is suitable to describe the variations of first hyperpolarizabilities as a function of the structure of model compounds. Then, it is applied to the characterization of the NLO responses of the C_{60}/SiO_2 interface and its analysis as a function of charge transfers, energy level alignment, and polarization effects.

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No. 49, Poster Session II

Theoretical and Experimental Investigations of an Aldol-type Reaction with Rh Complex

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The chemical transformation of nitrile groups plays an important role in the field of organic synthesis. Goto *et al.* reported an aldol-type reaction of organonitriles under mild conditions in 2008 [1] with a Rh catalyst. In the present study we theoretically and experimentally investigate the origin for its high catalytic efficiency, leading to the observed high yield of the corresponding β-hydroxynitrile product.

In the theoretical investigations, all stationary points on the potential energy surfaces, including transition states, were optimized using the density functional theory (DFT) with the B3PW91 functional. The PCy_3 (Cy = cyclohexyl) ligand is explicitly treated. We chose a moderate basis set size (6-31G(d) for non-metal elements and LanL2DZ for Rh) for geometry optimization, and the refined energies were computed using ONIOM(DF-LCCSD(T):DF-SCS-LMP2) with a larger basis set ((aug-)cc-pVTZ and ECP28MWB). To evaluate the solvent effect (dimethyl sulfoxide (DMSO)), we performed RISM-SCF-SEDD [2] calculations at RI-SCS-MP2/(aug)-cc-pVTZ+cc-pVDZ, and the energetic contribution due to the solvation was added to the ONIOM free energy. We investigated several reaction pathways with monomer and dimer catalysts, and proposed a plausible catalytic cycle as shown in Figure 1.

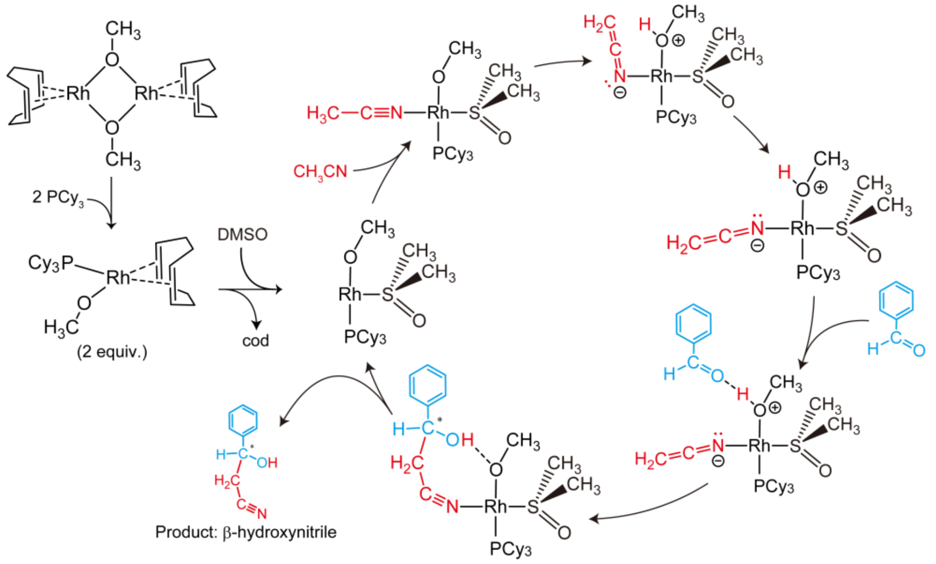

Figure 1. Proposed catalytic cycle

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No. 50, Poster Session II

Fragment molecular orbital and MD calculation study: Interaction analysis of HIV-1 antibody 2G12 and glycan Ligand

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I. Introduction

In HIV-1 infection, human antibody 2G12 is capable of recognizing the high-mannose glycans on the HIV-1 surface glycoprotein, gp120 [1]. To investigate the ligand binding mechanisms of antibody 2G12 with glycans aiming for the contribution to the medications, we carried out classical molecular dynamics (MD) simulations and ab initio fragment molecular orbital (FMO) calculations [2] on the antibody 2G12 complex with its high-mannose ligand ($Man_9GlcNAc_2$).

II. Method

The X-ray crystal structure of the Fab region of the antibody 2G12 with the ligand $Man_9GlcNAc_2$ was utilized as the calculation model (Fig. 1, PDB ID 1OP5 [1]). The 2G12-ligand complex extracted from classical MD simulations at several time steps and evaluated the glycan-antibody affinities with MP2/6-31G level of FMO calculations.

III. Results and discussion

Our calculation results showed that monosaccharide Man D1 in the high-mannose ligand was the most important moiety of the ligand binding to the antibody 2G12, which supported the experimental results. In addition to Man D1, significant roles of Man D4 and D4' in the ligand binding was theoretically indicated (Fig.2). We concluded that the high binding affinity of oligosaccharide $Man_9GlcNAc_2$ was dominated by terminal monosaccharide Man D1. Branched structure of Man 4 and Man 4' could provide more flexibility to the ligand binding to the Fab 2G12 [3].

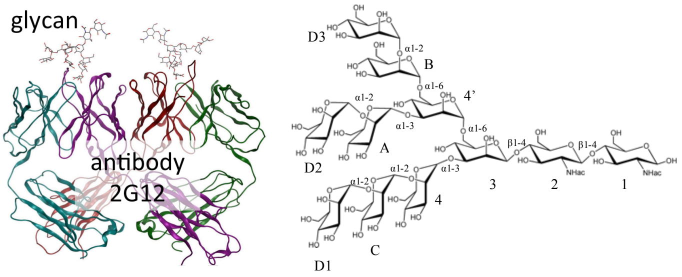

Fig.1 The crystal structure of antibody 2G12 and the ligand ($Man_9GlcNAc_2$) (PDB ID :1OP5 [1])

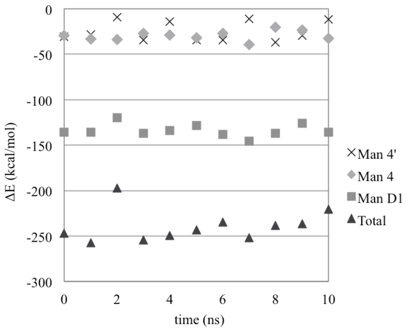

Fig.2 Total interaction energy of the antibody with $Man_9GlcNAc_2$ and the ligand moieties (Man D1, Man 4, and Man4') (kcal/mol) (MP2/6-31G*)

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No. 51, Poster Session II

Acceleration of the vibrational structure calculation with optimized vibrational coordinates

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Theoretical vibrational analysis plays an important role to interpret the observed vibrational spectrum and to elucidate the dynamical behavior of molecules. One of the standard method to compute the spectrum is the vibrational self-consistent field (VSCF) and post-VSCF methods. These methods, combined with ab-initio electronic structure theory to generate the anharmonic potential, provide an accurate prediction of the spectrum for small to medium size of molecules. Nonetheless, the cost of these calculations grows steeply with respect to the size. For example, generation of a quartic force field (QFF) requires the Hessian calculation at $2f^2+1$ geometry points for f-mode systems. Therefore, theoretical development is still needed to make the application feasible to large molecular systems.

Recently, one of the author proposed a new algorithm to optimize the vibrational coordinates for anharmonic systems based on the VSCF (oc-VSCF) [1]. In this method, successive transformations of all pairs of coordinates are carried out iteratively to minimize the VSCF energy until convergence. However, the number of the pairs increases rapidly with system size.

In this work, in order to reduce the computational cost, we propose a rational index that selects pairs of coordinates to mix. We also investigate the performance of oc-VSCF with a cubic force field (CFF) requiring the Hessian matrices at $2f + 1$ points, which reduces the computational effort to obtain an anharmonic potential from quadratic to linear in f. We show that the proposed pair-selection scheme with CFF significantly reduce the computational cost without loss of accuracy [2]. Our method is applied to ethylene and *trans*-1,3-butadiene combined with vibrational quasi-degenerate perturbation theory [3]. Calculated fundamental frequencies have been found to be in good agreement with experimental results.

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Theoretical study of DNA with unnatural base pair system using order-N DFT calculations

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We present our recent theoretical study on DNA with unnatural base pair, called Ds-Pa, (7-(2-thienyl)-imidazo[4,5-b]pyridine (Ds) and pyrrole-2-carbaldehyde (Pa)) systems using our order-N density functional theory (DFT) calculations. Previously we have reported the intermolecular interactions of the unnatural base pair Ds-Pa molecule in the gas phase by DFT and HF-MP2 using the quantum chemical method [1]. We have found that the interaction between Ds and Pa molecules is very weak and mainly governed by the dispersion forces. This result suggests that the stabilization of unnatural base pair within DNA double helix structure, which is observed in experiments, should depend on the environment such as the frame spacing of DNA backbone, the interaction of the unnatural base with its upper and lower base pairs, and/or the existence of solvent.

Based on these results, we have applied our order-N DFT code, CONQUEST [2] to hydrated DNA system including one unnatural Ds-Pa base pair (see figure). The system consists of 11,912 atoms (763 atoms for a DNA including one Ds-Pa pair, 22 Na counter ions and 3,709 water molecules). We can employ accurate and robust SCF calculations on such a complex system using our order-N DFT methodology. As in our previous study on hydrated DNA systems [3], we have calculated the atomic forces and the total energies. We also discuss the van der Waals effect on the total energies and the atomic forces.

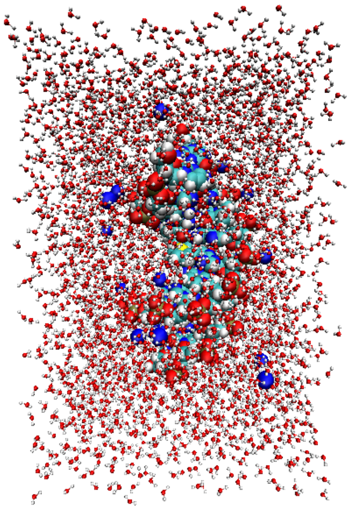

Figure.
DNA including one unnatural base pair, Ds-Pa system, which contains 11,912 atoms.

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No. 53, Poster Session II

THEORETICAL INVESTIGATION OF YTTERBIUM TRI-CHELATES COMPOUNDS

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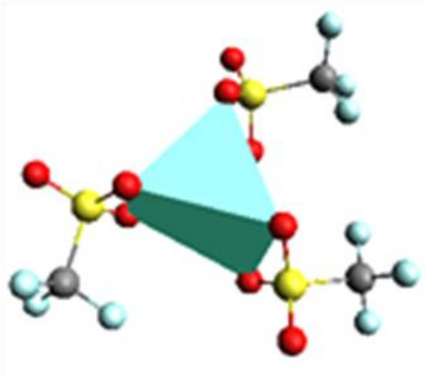
Abstract

Theoretical studies on ytterbium tri-chelates, Yb(L)$_3$ (L= **trifluoromethanesulfonate (OTF), perchlorate (ClO$_4$), p-toluenesulfonic (TOS), nitrobenzenesulfonic (NBSA), and dodecylsulfate (DOS),** are carried out using density functional theory (DFT) method at the PW91/TZP level, for the first time. All ligands are bidentate and the compounds exhibit a distorted trigonal prismatic structure, with a maximum twist angle obtained for ytterbium p-toluenesulfonic compound Yb(TOS)$_3$. The quantum theory of atoms in molecules (AIM) and energy decomposition analysis reveal the dominant ionic character in ytterbium–oxygen bonding with a little covalent character. According to the Pearson therminology, the Yb(NBSA)3complex reveals the higher acidity.



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No. 54, Poster Session II

THE NATURE OF THE METAL-ACETYLIDE INTERACTION IN THE TERNARY TRANSITION METAL ACETYLIDE COMPLEX $C_5ME_5TI[\eta\text{-}C_2(SNME_3)_2]$

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Abstract

The metal–acetylide bonding in the transition metal acetylide $C_5Me_5Ti[\eta\text{-}C_2(SnMe_3)_2]$ complex have been studied at the density functional theory (DFT) level using natural bond orbital (NBO)[1], energy decomposition analysis (EDA)[2], atoms in molecule (AIM)[3] and electron localization function (ELF)[4] methods. The NBO analyses show that there is a single bond between each M-$C_{acetylide}$ bond, and all of them are polarized toward the C atoms. These bonds were associated with the intermediate atomic interaction type in terms of the Bader topological theory, whereas, both EDA and ELF methods support the classification of the metal-$C_{acetylide}$ bonding as mainly ionic.

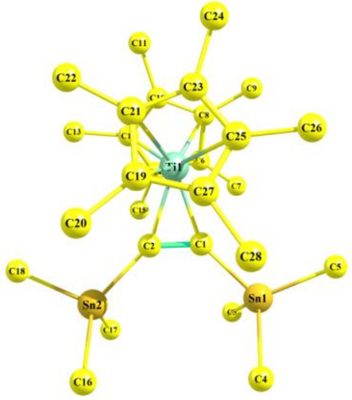

Figure 1: Molecular structure of the parent complex $C_5Me_5Ti[\eta\text{-}C_2(SnMe3)2]$.The hydrogen are removed for clarity

Keywords:
Transition metal acetylide, polymetallic acetylide compounds, (NBO), (EDA), (AIM), (ELF) methods

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No. 55, Poster Session II

Quantum Chemistry-based Docking and Scoring for Design of Protein Kinase Inhibitors

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In silico drug design relies on i) correct prediction of the structure of the protein-ligand complex and ii) accurate ranking of alternative structures. For the first task we used molecular docking enhanced by QM calculations in order to correctly describe halogen bonding [1,2]. The second problem was tackled using a quantum-chemistry based scoring function [3]. This scoring function uses semi-empirical quantum chemical method, PM6, augmented with advanced dispersion, hydrogen-bonding and halogen bonding corrections (PM6-D3H4X) [4]. This method reliably describes different types of non-covalent interactions and is thus generally applicable. The scoring function is constructed as a sum of physical terms, i.e. interaction free energy including solvation effects, the interaction entropy, and the change of the conformation free energy of the ligand and protein upon binding. The scoring function has already been successfully applied to series of HIV protease, CDK2 and CK2 inhibitors [3,5,6,7].

Here, we present a project aiming at discovery of new halogenated inhibitors of CK2 kinase which is implicated in various cancer types. A series of brominated compounds has been designed using the above methodologies, synthesized and tested *in vitro* for inhibition activity. In summary, we propose a general computational strategy to guide rational drug design.

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No. 56, Poster Session II

Studies on halogen bonding

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Halogen bond currently belongs to one of most intensively investigated noncovalent interactions. This is due to the fact that, similarly like in the case of hydrogen bond, it is relatively strong, directional and may play important role in various physical, chemical and biological processes. [1] The mechanism of formation of the halogen bond is rooted directly in anisotropy of electron charge distribution. Due to this anisotropy of charge density the halogen atom may exhibit dual character when it contributes in noncovalent interaction. It may act as both Lewis acid (in e.g. halogen bonding) and as Lewis base (in e.g. hydrogen bonding or another halogen bonding). Therefore, one may expect that in specific conditions the same halogen atom can interact *via* both such interactions, playing the role of Lewis base and Lewis acid, simultaneously. A few examples of such interactions will be presented. What is more, anisotropy of halogen atom was usually reported on the basis of analysis of various contacts observed in crystal state. [2] It will be shown that such observations may significantly depend on the molecular fragment used as a criterion in search through CSD. Thus, the analysis of electron density distribution around the halogen nucleus will be revisited. Finally some interesting cases of interactions, which can be considered as untypical halogen bonds, will also be presented.

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No. 57, Poster Session II

Employing ensemble variational principle to calculate electron excitation energies of molecules: a range-separated approach

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We propose a method of calculating electronic excitation energies that is both computationally inexpensive and able to capture states of multiconfigurational character (single and double excitations are recovered). It exploits the ensemble variational principle [1, 2] (EVP) which states that if $\psi_1, \ldots, \psi_m$ are orthonormal trial functions and $\omega_1 \geq \omega_2 \geq \ldots \geq \omega_m \geq 0$ then for m lowest eigenstates of Hamiltonian H corresponding to eigenvalues E_1, E_2,..., E_m the following relation holds: $\sum_{i=1}^{m} \omega_i E_i \leq \sum_{i=1}^{m} \omega_i \langle \psi_i | H | \psi_i \rangle$. In principle, EVP allows for finding a desired number of lowest excited states of a system with a variational method of choice, e.g. ensemble Hartree-Fock [3] or DFT [4]. Unfortunately, the existing methods based upon EVP [1, 3, 4, 5] have difficulties with describing accurately both static and dynamic correlation.

We start with relating the ensemble variational theory with the minimization of the free energy of the canonical ensemble. This leads us to proposing to use Boltzmann factors as weights in the ensemble functional. Our method relies on minimization of the range separated ensemble functional with Boltzmann weights [6]. The dynamic correlation energy is recovered by orbital relaxation and the presence of the short-range density functional, whereas the long-range static effects are expected to be captured by going beyond the single-determinantal description of states.

Two approaches are considered. Either the density functional is dependent on the ensemble density or on the densities of the components of the ensemble. The latter approach removes the spurious "ghost" [4] terms from the interaction between electrons. Both versions of the method are applied to predicting potential energy curves of a few low-lying states of a number of small molecules. We show that the proposed method is indeed able to capture different types of excitations and produces the dissociation curves of correct shape.

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Exactly-solvable position-dependent mass Schrödinger equation for the Thomas-Fermi and Harmonic Oscillator potentials.

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Abstract

The aim of this work, is to obtain the exactly-solvable position-dependent mass Schrödinger equation (PDMSE) for the Thomas-Fermi and Harmonic Oscillator potentials. To attain that purpose, the PDMSE in the variable x is transformed into a standard Schrödinger-like equation with constant mass (CMSE), in a new the variable u, by means of a point canonical transformation scheme. This approach applied to the PDMSE, allow us to obtain the transformation that should be used to find the exactly solvable CMSE. In that case, the former potential associated to the PDMSE and the potential involved in the CMSE are related through a Riccati-type relationship that includes the equivalent of the Witten superpotential that determines the position-dependent mass distribution $m(x)$ leading to exactly-solvable PDMSE. As a useful application of the proposal, we assume that the Witten superpotential is constant to find $m(x)$ and consequently the exactly-solvable $V(x)$ Thomas-Fermi and Harmonic Oscillator potentials. In that case, it is considered an exponential-type $V(u)$ potential leading to Bessel-type eigenfunctions for the Thomas-Fermi and to Laguerre-type solutions for harmonic oscillator potentials for the PDMSE, as particular cases. Beyond the worked example, the approach is general and can be useful in the study of the electronic properties of materials in which the carrier effective mass depends on the position as well as its application in the search of new potentials suitable for the study of quantum systems.

Keywords : Position-dependent mass, Point canonical transformation, Thomas-Fermi potential, Schrödinger equation.

No. 59, Poster Session II

Fluorescence of PRODAN in Water: a Computational QM/MM MD Study

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PRODAN (6-propionyl-2-dimethylaminonaphthalene) and its derivatives are fluorescent probes which are known for a strong dependence of their emission spectra on the solvation state. They are commonly used in many time dependent solvent relaxation studies, in particular in those focused on hydrated bio-membranes. Despite the extensive use, the fluorescence spectra of PRODAN were not yet theoretically resolved. We studied fluorescent properties of PRODAN in water by means of excited state molecular dynamics simulations employing a combined quantum mechanical and molecular mechanical (QM/MM) approach with the time-dependent density functional theory. State of the art coupled cluster method (CREOM-CCSD(T)) was used to benchmark the density functional theory calculations. The issue of the molecular geometry of the excited state PRODAN molecule in water was addressed. The planar conformer is predominantly responsible for the fluorescence; the twisted conformer is strongly stabilized in water, but it does not suffice to explain the experimental spectra due to its low oscillator strength. The influence of the water environment on PRODAN emission was investigated within several computational schemes with varying description of the solvent. The experimental emission spectra are successfully reproduced only after including the polarization effects by employing a polarizable force field into our QM/MM approach.

No. 60, Poster Session II

Photophysical Properties and Photochemistry of Substituted Cinnamates for UVB Blocking: Effect of Hydroxy, Nitro, and Fluoro Substitutions at *ortho*, *meta*, and *para* Positions

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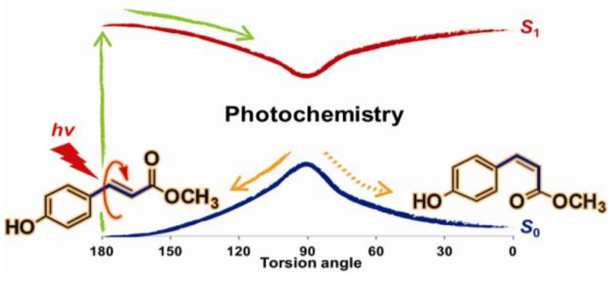
Cinnamate derivatives, an important class of organic UV filters, are widely used as ultraviolet B (UVB) blocking compounds in cosmetic sunscreens. The photophysical properties and photochemistry of various substituted cinnamates have been investigated theoretically. This series includes monohydroxy-, -nitro, and -fluoro derivatives at the *ortho*, *meta*, and *para* positions. The absorption spectra of these compounds were satisfactorily reproduced by the direct symmetry-adapted cluster-configuration interaction (SAC-CI) method with the experimental absorption bands. The transition character of the low-lying two ππ* and σπ* states for these 9 derivatives were analyzed in detail. The *para* derivatives have a different transition character of the ππ* transitions compared with those of the *ortho* and *meta* derivatives. To evaluate the UVB blocking of these derivatives, the calculated radiative lifetimes indicate that the *ortho*- and *meta*-substituted derivatives have longer lifetimes for emission than the *para* derivatives. The potential energy curves of the ground (S_0) and excited (S_1) states of the hydroxy derivatives were examined to investigate *cis–trans* photoisomerization. The *ortho* and *meta* derivatives have an energy barrier to the conical intersection resulting in fluorescence, whereas *para* derivatives show nonradiative decay because they have no energy barrier. The hydroxy derivatives were found to be excellent UV absorbers because of their broad absorption in both the UVA and UVB regions as well as their higher photostability. The present work provides important information for the design of UVB blocking compounds and for the possibility of photoactive molecules in the UV–Vis wavelength domain.



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No. 61, Poster Session II

Dispersion-only approximation for long-range RPA correlation contributions to DFT intermolecular interaction energies

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Dispersion interactions can be included in DFT calculations in a range-separated framework by standard correlation methods from perturbation or coupled-cluster theory. One appealing possibility is the random-phase approximation (RPA), which is based on the interaction of mono-excitations. When employed for fragmented molecular systems, a classification of occupied and virtual orbitals on monomers[1] allows us to identify dispersion-type coupled mono-excitations contributing to inter-fragment interaction energies. A first study[2] pointed out that the combination of localized orbitals and range-separated DFT provides an appropriate framework for this approximation, too crude in a standard correlation calculation context based on a Hartree-Fock reference.

We apply the approach to a larger variety of systems, in order to assess the applicability in different contexts, ranging from highly ionic interactions to charge transfer complexes. The efficiency and potential gains of the approximations will be discussed.

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No. 62, Poster Session II

Vibronic and Resonance Raman Spectra of Extended Viologens Modelled by Multireference Approaches

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Due to the unique combination of electronic, optical, and magnetic properties, extended viologens are regarded as very promising materials with potential applications in electrochromic devices and field-effect transistors [1,2]. These compounds can undergo two consecutive one-electron reductions to form a stable radical cation in the first step and then a neutral state with multireference character. The redox behavior is even more complex because a dimerization of the radical cations may compete with the second reduction step. The product of the side reaction has similar absorption properties as the neutral state. Therefore, a reliable structural identification of the neutral state is required.

The experimental characterization of electrogenerated species in solution can be done by in-situ absorption and resonance Raman spectroscopy. However, the interpretation of the experimental spectra and the unraveling of the photophysical properties can be hampered by the complexity of the vibrational structures, which call therefore for the use of well-designed theoretical models and of accurate first principles calculations. In this study, multireference approaches are employed to simulate and interpret the absorption and resonance Raman spectra of extended viologens. The structures of the ground and the brightest excited state were obtained by state-specific and state-averaged complete active space self-consistent field theory (CASSCF). Multiconfigurational second-order perturbation theory (CASPT2) was applied to take into account the remaining dynamic correlation effects on the electronic transition energies. The quantum-chemical calculations were performed by the MOLPRO package, while the vibronic and resonance Raman spectra were simulated by a program developed locally.

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No. 63, Poster Session II

Two-photon absorption spectra of the spiropyran and merocyanine pair: A comparative study of solvation models

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In their seminal paper, Parthenopoulos and Rentzepis demonstrated the potential application of a photochromic molecule embedded in a polymer matrix for three-dimensional optical storage memory [1]. The device employed two-photon writing and reading. Since then, many follow-up studies have been devoted to optical properties of other photochromic systems for numerous applications including optical data storage (see Ref. [2, 3, 4] and references therein). Computer-aided design of two-photon active media has proven its appreciable role in molecular nonlinear optics. In fact, first-principles quantum chemical calculations allow to ivestigate (electronic) structure-property relationships and their results are often stimulus for experimental studies. However, the reliability of the predictions heavily depends on the level of theoretical approximation. In the present study, we report the one- and two-photon absorption spectra of the spiropyran/merocyanine pair in aqueous and chloroform solutions. The spiropyran molecule in question exhibits photochromism both in solution and in the crystalline state [5]. In order to study the linear and nonlinear absorption spectra in solutions, we employ several computational strategies, with an eye towards their comparison. In particular, the set of studied approaches includes the polarizable continuum model and a newly developed polarizable embedding self-consistent scheme (linear in the solvent polarization) [6]. The results of the calculations are compared to experimental data obtained with the aid of the Z-scan technique.

The work was financed by a subsidy from the Polish Ministry of Science and Higher Education within "Iuventus Plus" programme (Grant No. 0628/IP3/2011/71).

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No. 64, Poster Session II

THEORETICAL INVESTIGATION ON HOMOLEPTIC YTTRIUM TRI-GUANIDINATES:

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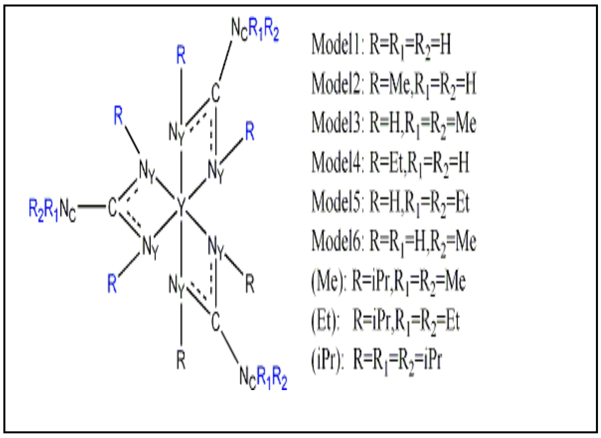
The electronic and molecular structures of the homoleptic yttrium tris-guanidinates complexes $Y[(N^{i}Pr)_2CNR_1R_2]_3$, [$R_1=R_2=Me$, Et and iPr] have been investigated employing DFT calculations in order to understand the structures, bonding and energies of the interactions between yttrium metal and a guanidinate ligands. The effect of the substitution on nitrogen position of guanidinate on these complexes has been also investigated employing DFT and TDDFT calculations for 6 kinds of models obtained by alternative substitution of alkyl on nitrogen of guanidinate ligands. The results reveal that the substitution position plays a crucial role in the geometry structure by affecting the torsion angle and the HOMO-LUMO transitions. The energy decomposition analysis indicates a majority of ionic bonding in all systems; the exception is in the model4 ($Y[(N_YR)_2CN_CR_1R_2]_3$; R=Et, $R_1=R_2=H$) which present a significant degree of covalency.



Model1: $R=R_1=R_2=H$
Model2: $R=Me, R_1=R_2=H$
Model3: $R=H, R_1=R_2=Me$
Model4: $R=Et, R_1=R_2=H$
Model5: $R=H, R_1=R_2=Et$
Model6: $R=R_1=H, R_2=Me$
(Me): $R=iPr, R_1=R_2=Me$
(Et): $R=iPr, R_1=R_2=Et$
(iPr): $R=R_1=R_2=iPr$

No. 65, Poster Session II

A Quantum Monte Carlo and CIPSI case study: Magnetic Coupling of a meta-xylylene diradical.

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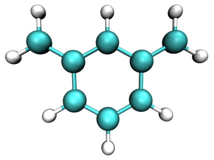
Calculating accurate magnetic couplings has been, and is, a difficult and challenging endeavor [1]. Even so, successful strategies for calculating diradical conjugated hydrocarbons have been devised in previous works using CASSCF level calculations [2].

Our work intends to conceive such a strategy for a meta-xylylene diradical *(Fig. a)* under a Quantum Monte Carlo framework, and eventually to be able to treat bigger and more general magnetic systems *(Fig. b)*. Due to the intrinsic multiconfigurational character of the wavefunction and the weakness of the magnetic coupling magnitude, good correlation energy is paramount to provide a precise account of this phenomena.

Starting from Hartree Fock we build a multiconfigurational wavefunction by selecting configuration interactions according to a perturbative criteria. This is done with the CIPSI algorithm [3]. Many parameter were explored to devise the best approach: Number of Determinants, stoping criteria, use of Dressed CI [4]) and type of orbitals (fock, natural, localized), among others.

The resulting wavefunction is then treated with Fixed-Node Diffusion Monte Carlo with the QMC=CHEM [5] software. As a result we have designed a perturbation based stoping criteria that provides accurate results for this system.



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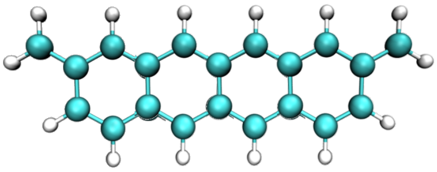

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No. 66, Poster Session II

Theoretical investigation on the absorption spectrum of photosystem as a biomarker on extrasolar planets

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Over 900 extrasolar planets have been discovered, and more than 3,000 candidates have been detected. Moreover, planets in habitable zone were observed, and the discovery of Earth-like planets has been expected. Great attentions have been paid to the detection of life in extrasolar planets. For the detection, several indicators have been proposed as biomarkers. One important indicator is red edge [1], which is a characteristic steep gradient observed in the near-infrared region around 750 nm [2]. Actually, red edge is observed in the reflection spectrum of the Earth via the Moon (earthshine [3]). Red edge is affected by many factors, and precise predictions of the red edge are not easy, though the origin of red edge is absorption of plant's chlorophyll [2]. In the Earth, photosynthetic organisms have evolved under the sunlight condition. On the other hand, on extrasolar planets, photosynthetic organisms should evolve differently in many parts, such as pigment types and the arrangements depending on the spectra of the primary star.

Before predictions of biomakers of extrasolar planets, we investigated on the absorption spectrum of chlorophylls in photosystems. Chlorophylls are concentrated in chloroplast, and form pigments-protein complexes in the photochemical systems. Quantum mechanics/molecular mechanics (QM/MM) calculations were performed to calculate the absorption spectrum. Each chlorophyll was included in the QM region. We found that absorption wavelengths are shifted about +10 nm by the effects of protein environment. Similar influence was observed by the effect of amino acid coordination to the central Mg ion in chlorophyll. These results indicate a fine modulation character of adsorption wavelength for photosystem. Current study will be important for understanding photosystems in extrasolar plants as well as diverse photosystems in the Earth.

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No. 67, Poster Session II

Reaction Energetics of the Diels-Alder Reactions: A Long-range Corrected Density Functional Theory Study

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Diels-Alder reactions have been important targets especially in chemical reactivity calculations. We present the possibility of quantitative reaction analysis on the long-range corrected density functional theory (LC-DFT) [1]. In this study, we first found that the long-range correction for exchange functionals is principally required to quantitatively reproduce the Diels-Alder reaction enthalpies, which have been poorly given by conventional DFTs. Next, It was noticed that the LC-DFTs somewhat overestimate the barrier height energies. However, these overestimations are drastically improved by taking dispersion forces into account by the local response dispersion (LRD) method. We therefore proposed that the dispersion correction is also needed to investigate the overall Diels-Alder reaction processes. Based on the remarkable accuracies of the LC-DFT in the calculations of the Diels-Alder reactions and orbital energies, the behaviors of the global hardness response (GHR), the halves of the HOMO-LUMO gaps, along the intrinsic reaction coordinates were examined. Consequently, we found that the LC-DFTs give suggestive GHR behaviors: GHR is almost constant for the initial processes and then rapidly increases for the subsequent processes. This suggests that orbital energies play a significant role in chemical reactions.

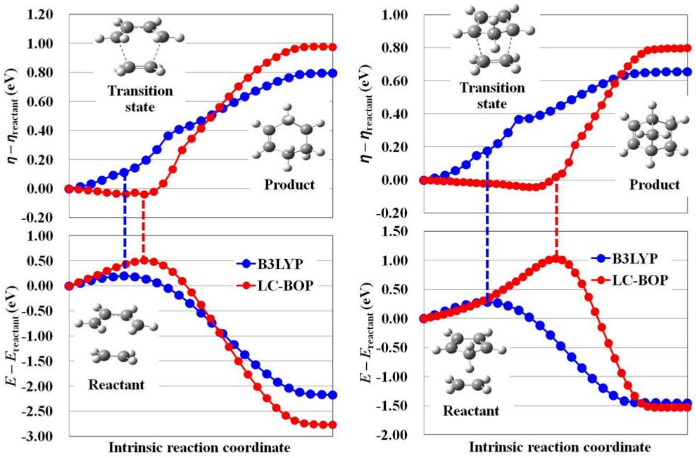

Figure 1: Global hardness responsesη and total energies E along the intrinsic reaction coordinates for the reactions of both butadiene and cyclopentadiene with ethylene.

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No. 68, Poster Session II

Generalization of the Non-Redundant Fockian for N>2 electronic systems: Application to Excited States of Be Atom

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A recently developed technique of the non-redundant Fock operator for calculation of excited states of He atom [1,2] has been generalized also for N-electron systems where N>2 [3]. The method generates a set of virtual orbitals that more properly describe electronic excitations than the standard Hartree-Fock orbitals.

Recently, we used this one-electron approach to develop an exponentially-tempered Gaussian basis set scheme (ExTG), which more properly describe atomic excited states than other Gaussian sets. Such a basis set scheme proved particularly suitable for complex scaling calculations, so far being tested on helium Rydberg states, Feshbach resonances [1], and dynamical simulations of the helium atom in strong XUV laser field [2].

Here, the generalized non-redundant Fockian technique has been applied to excited states of Be atom. We compare electronic spectra obtained by employing either the regular or the non-redundant Fockian for generating virtual orbitals. The spectra are calculated at CIS level and for truncated MO space also by FullCI. Several standard quantum chemistry basis sets are compared to the ExTG basis.

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No. 69, Poster Session II

Towards accurate ab initio thermochemistry and spectroscopy of lanthanide compounds: Quantifying basis set, electron correlation, and spin-orbit coupling effects in lanthanide species

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The importance of theoretical electronic structure investigations for the study of lanthanide compounds is well known, however, accurate quantum chemical calculations are still a quite difficult task for these systems. There are at least three reasons for that. First, the electron correlation problem in such a system is extremely demanding. Second, the resulting accuracy of any correlated electronic structure calculation can be highly dependent on the quality of 1-particle basis set used to represent the underlying molecular orbitals. Third, a proper account of both scalar relativity and spin-orbit coupling (SOC) can be very important.

All these issues are addressed in the study on a 26-molecules test set containing 17 diatomic LnX (Ln = La, Ce, Eu, Yb, Lu; X = O, F, Cl, Br, I) and 9 polyatomic species YbX_2, CeX_3 (X = F, Cl, Br, I), LaF_3. Bond lengths r_e, bond angles, vibrational frequencies ω_e, barriers to linearity in YbX_2, inversion barriers in LnX_3, and atomization energies D_0 have been calculated at sophisticated levels of theory including coupled cluster CCSD, CCSD(T), EOM-, FS-CCSD, configuration interaction MRCI, and perturbation theory MRPT2. Using the sequences of systematically convergent correlation consistent triple-ζ, quadruple-ζ, and quintuple-ζ basis sets the complete basis set (CBS) limit has been accurately estimated. Core-valence (CV) electron correlation effects involving the Ln outer-core 4s,4p,4d electrons and the X atom outer-core (n-1)s,(n-1)p,(n-1)d electrons were evaluated separately. The Douglas-Kroll-Hess Hamiltonian and the Breit-Pauli spin-orbit operator, or the 2-component methods with relativistic core pseudopotentials were used to account for and to separate the scalar relativistic and SOC effects.

The molecular properties of diatomics for which the experimental values are well established, have been reproduced at the CCSD(T)(CV)/CBS level with mean absolute deviation of 2.0 kcal mol^{-1} for D_0 (7 comparisons), 0.0048 Å for r_e (13 comparisons), 5.3 cm^{-1} for ω_e (16 comparisons). The capability of T1 and D1 diagnostics of a multireference character of wave function to give indication of the quality of results to be expected from the single-reference CCSD(T) calculation has been verified. A composite scheme for accurate calculation of thermochemical and spectroscopic properties of lanthanide compounds is proposed.

The authors acknowledge support from the Russian Foundation for Basic Research, Grant No. 13-03-01051.

No. 70, Poster Session II

Atomistic Study of the incorporation effect of guest ions Mg^{2+}, Al^{3+} y Fe^{3+} in crystalline structures models of cementitious phases like alite (C_3S) and belite (C_2S)

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The presence of chemical substitutions is believed to play a crucial role in the hydration reactions, structure, and elastic properties of cement clinker phases. Hence, substitutions are of great technological interest, as more efficient production of cement clinkers would result in a reduction of CO_2 emissions, as well as possible economic benefits. Here we use a combination of classical and quantum mechanical simulation methods to study the detailed physicochemical changes of the clinker phases alite (Ca_3SiO_5) and belite (Ca_2SiO_4) when Mg^{2+}, Al^{3+} and Fe^{3+} guest ions are incorporated into their structure. Using classical force field methods [1], we considered random substitutions among possible sites and different compositions in order to identify the preferential substitution sites on the crystalline structures. Then, the resulting structural changes that take place to accommodate the guest ions are investigated and discussed in detail. Using quantum mechanical density functional theory calculations [2] the electronic structure of representative configurations has been computed to determine the potential impact of impurities on the reactivity.

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No. 71, Poster Session II

Cheap HEAT protocol: CHEAT1

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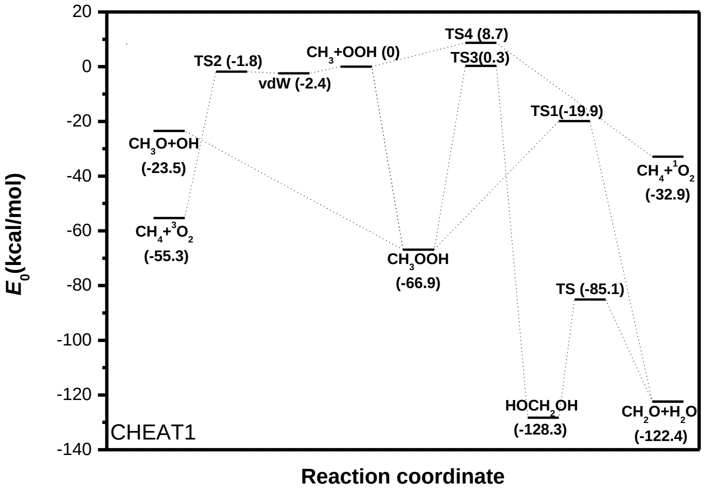
An effective simplification of the HEAT protocol [1], CHEAT1 is to provide accurate potential energy surface for relevant combustion or atmospheric reactions. The performance of CHEAT1 protocol is demonstrated to provide a comprehensive, robust and highly accurate single reference based description of the system. At high T_1 diagnostic values, multi-reference treatment for species in reaction system is often recommended. However, accurate single reference solution to the problem can also be applied involving higher excitation terms. In the case of the CH_3+HO_2 reaction system, the performance of the CHEAT1 is demonstrated within an absolute deviation (AD) from literature values of <0.6 kcal/mol. Such results infer the proposed method to be appropriate for accurate theoretical kinetic calculations. Furthermore, it has found that energetics of the system studied could not be reproduced accurately using any popular standard composite methods due to their inability to provide transition state structures (e.g. CBS-QB3, G3MP2B3, G4, W1U and W1BD) or the finding that the accuracy of the calculated activation energy was too small for CBS-4M and G2 (AD=29.0 and 10.0 kcal/mol, respectively).



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No. 72, Poster Session II

Theoretical research on the substrate specificity of uridine-cytidine kinase

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Uridine-cytidine kinase (UCK) catalyzes phosphorylation of uridine and cytidine. This reaction is important in the salvage pathway of pyrimidine-nucleosides as sources of energy and materials for biosynthesis of DNA/RNA. Because cells take in some agents through this pathway, UCK is the target of some anticancer drugs. UCK from *Thermus thermophilus* HB8 (ttCK) has specificity to only cytidine, and this character depends on only a single amino-acid residue (Y93)[1]. The molecular mechanism of substrate specificity in ttCK has not yet been elucidated.

In this study, the mechanism of substrate specificity of UCK was investigated by using molecular dynamics (MD) simulations and free energy analyses. Molecular Mechanics - Poisson Boltzmann Surface Area (MM-PBSA) method is used to evaluate the substrate binding free energy. We have succeeded to reproduce the strong interaction between ttCK and cytidine and weak interaction between ttCK and uridine (Fig.1). On the other hand, a sufficient binding free energy is not calculated for Y93H mutant-uridine interaction. Thus, possibilities for other protonation states are investigated. Mixed quantum mechanics / molecular mechanics (QM/MM) calculations are also used.

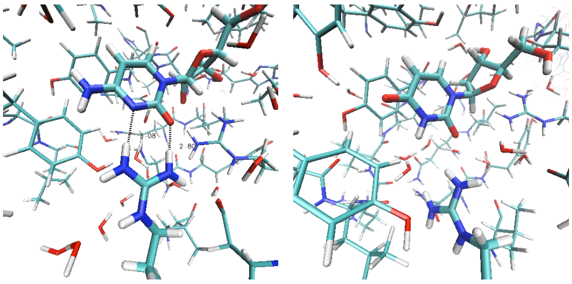

Fig.1 : The interaction between ttCK and cytidine (left) and between ttCK and uridine (right)

[1] Tomoike, F.et al. *Biochemistry* 50, 4597-4607 (2011)

No. 73, Poster Session II

Prolapse-Free Relativistic Adapted Gaussian Basis Sets for $_{87}$Fr up to $_{118}$Uuo

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The variational prolapse problem in relativistic Gaussian basis sets is attributed to an ill description of atomic orbital symmetries close to the nucleus, which leads to increasing total energy values during the addition of tight functions and may result in total energies from Dirac-Fock-Coulomb (DFC) calculations below the correspondent ones from numerical Dirac-Fock (NDF) results [1, 2].

Hence, we generated relativistic adapted Gaussian basis sets (RAGBSs) for Francium through Ununoctium atoms without variational prolapse by means of a polynomial version of the Generator Coordinate Dirac-Fock (p-GCDF) method [3], where the resolution of Dirac-Fock integral equations is done through the integral discretization (ID) technique with a polynomial expansion for each w atomic orbital symmetry,

$$\Theta_i^{(w)} = \frac{\ln \gamma_i^{(w)}}{A} = \Theta_{\min}^{(w)} + \Delta\Theta_1^{(w)}(i-1) + \Delta\Theta_2^{(w)}(i-1)^2 + \ldots + \Delta\Theta_q^{(w)}(i-1)^q \,, \qquad (1)$$

in which $i = 1, 2, \ldots, N$ (N = number of discretization points), A is a scaling parameter and $\Theta_{\min}^{(w)}$ and $\Delta\Theta_q^{(w)}$ are parameters respectively known as the initial point of the mesh and the increment of order q applied to obtain discretization points. A slight adjustment of these parameters after an initial optimization process was capable to eliminate completely variational prolapse.

Two finite nucleus models were employed, the Gaussian and the uniform sphere models. The basis set sizes, for the 7*s*, 7*p*, 6*d* and 5*f* block elements are, respectively, 33s27p17d11f, 33s30p19d14f, 33s27p19d14f and 33s27p17d14f functions. The largest difference between the DFC energies obtained with our RAGBSs and NDF values is 15.4 mE$_h$ for $_{118}$Uuo. Such study complements a series of prolapse-free relativistic Gaussian basis sets from $_1$H up to $_{118}$Uuo atoms obtained with the p-GCDF variant [4, 5].

This work is supported by FAPESP.

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No. 74, Poster Session II

Computational Thermochemistry of Superbases Derived from the Cyclopropene Imine Core

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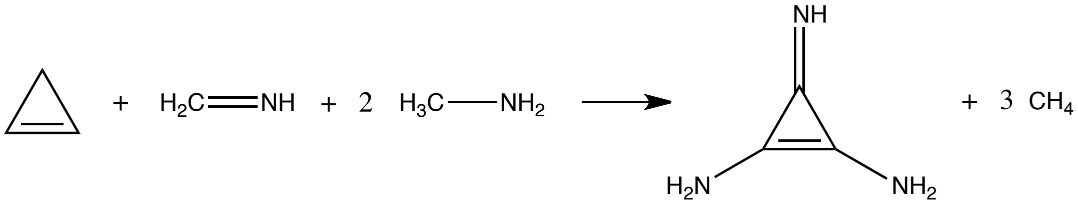
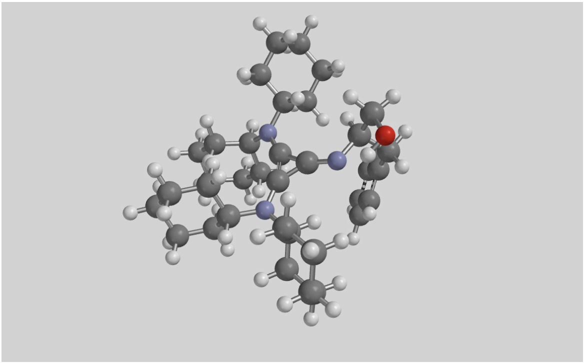
The thermochemical properties of superbase species derived from cyclopropene imine (CPI) [1] are estimated by computations on isodesmic reactions, e.g.:

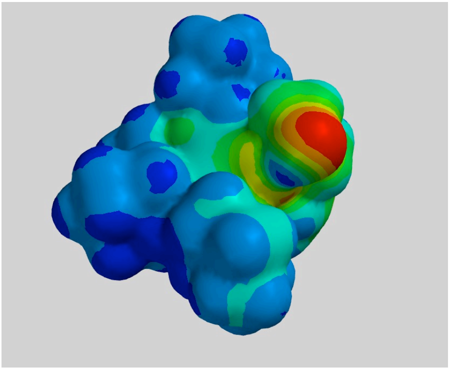


Gas phase proton affinities and basicities, as well as enthalpies of formation of gas phase superbases, guanidines and the parent 1, 2-diamino cyclopropene imine shown above are well represented by the thermochemical schemes W1BD, G4, and CBS-QB3. DFT calculations with modern functionals M06-2X and wB97DX in the cc-pVTZ Dunning basis allow characterization of larger systems.

We compute pKa values of the conjugate acid of N(imino)-*tert*-butyl-N, N, N, N(amino)-*tetra*-isopropyl CPI in acetonitrile, in fair agreement with the experimental value of 26.9 reported by Bandar and Lambeth [2]. More approximate calculations describe the Bandar-Lambert catalyst shown below.



Structure of the Bandar-Lambert Catalyst



Electrostatic field on an isodensity surface

[1] Maksić, Z. B., Kovačević, B. J., *J. Phys. Chem. A*, 103:6678-6684, 1999.
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No. 75, Poster Session II

Theoretical investigation of the electron transfer process in water

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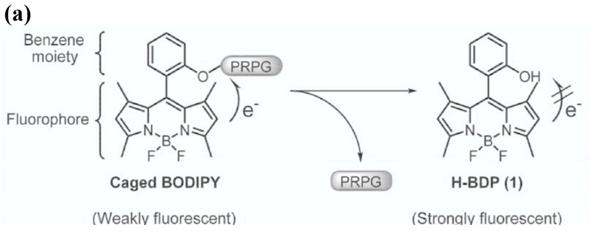
Recently, light emitting molecules in aqueous solution draw a lot of attention and have been synthesized for applications related to bioimaging. Urano and coworkers reported a new class of caged fluorophores which can emit only when photoremovable protecting groups (PRPGs) are removed by UV light irradiation. They found that the acceptor strength of PRPG is correlated to the efficiency of emission quenching [1]. Their fundamental strategy of the molecular design was emission quenching by the efficient intramolecular charge transfer (CT) from BODIPY to PRPG after the excitation (see **Fig. 1a**). Theoretical understanding of this process is necessary to improve the accuracy of molecular design.

In the present study, the importance of solvent fluctuation in the CT process is discussed in terms of the free energy change. The RISM-SCF-SEDD method [2], which combines quantum chemistry and statistical mechanics, is employed to describe the solvent effect. The non-equilibrium treatment of solvation with a hypothetical charge distribution [2] allowed us to compute free energy profiles. As a representative example, we show simulated free energy curves in **Fig. 1b**. As the acceptor strength increases (*p*-DCB < NB < *p*-QN), the charge transfer state curve shifts to lower energies, and the activation free energy becomes smaller. These findings compare well to the observed trends in experimentally determined redox potentials. As the charge transfer mostly occurs from a donor molecule in the excited state to an acceptor in the ground state, we also applied our approach to the “true” excited state, which allows us to discuss the energy relaxation path.



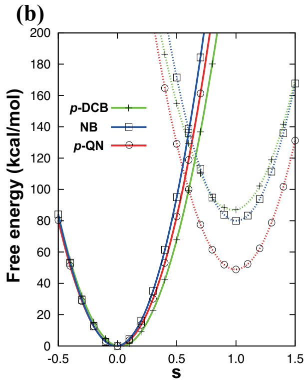


Figure 1. (a) Synthesized bio-marker. PRPG can be removed by UV irradiation. **(b)** Simulated free energy curves (solid : ground state, broken : charge transfer state) for phenol with *p*-dicyanobenzene (*p*-DCB), nitrobenzene (NB), and *p*-quinone(*p*-QN) systems. *s*, is a mixing coefficient to reproduce the hypothetical charge distribution.

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Determine damage depth profiling by high-energy ion channeling in Monocrystalls

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RBS analytical technique in channeling mode can be used to study the dependences of the radiation damage with ion implantation energy, direction and temperature.

The channeling implantation and elevating temperature implantation results in the decrease of the damage. The RBS/channeling technique is often used for defect depth profiling. The energy loss of channeled particles differs from the random case. If the defects are located in a well defined depth, deviations have been observed between the measured and expected defect depth, that may be attributed to the reduction of the stopping power in the channeling direction [1].

The stopping power of channeled particles differs markedly from that of particles following random trajectories. In ion channeling measurements, the ions are directed upon a single crystal along a major crystallographic direction as compared to a random direction during standard RBS measurements. Prior to being backscattered, incident ions are steered preferentially into the interstices of the lattice by a series of correlated small-angle collisions with the target atoms. Therefore, the channeled ions preferentially probe the interstices of the crystal and are sensitive to the location of impurity atoms. The redistribution of the ion flux provides RBS with structure-sensitive capabilities useful for probing defects and lattice strain.

Furthermore, the average energy loss and the straggling are influence the depth resolution of the damage depth profiles. In an amorphous solid the straggling is described approximately by the Bohr theory. According to this theory the spread in energy loss is a Gaussian with a width increasing with the square root of depth.

In a single crystal when the incident beam is aligned with a channel the energy loss is different for the different kinds of trajectories and the width of the energy loss distribution increases roughly linearly with depth.

In a Monte Carlo calculation different trajectories have different energy losses if one includes impact parameter dependent energy losses. The deflection by the nearest atom is treated as a binary collision in the impulse approximation. The influence of the more distant strings of atoms is taken into account in the continuum string approximation. To simulate the channeling spectra, the Monte Carlo program include the energy dependent cross section for backscattering. If combines existing theories on the dependence on the impact parameter of the energy loss with a Monte Carlo program calculating the trajectories of channeled particles it is possible to compare measured and calculated energy loss distributions. Measured channeling spectra are compared with computer simulations.

Rutherford backscattering and channeling spectrometry (RBS/C) studies are performed with 2.0MeV 4He+ ion beam. In order to conduct RBS/channeling measurements, the sample must be mounted on a goniometer, so that the crystal axis direction can be aligned with the incident beam.

At Institute of Applied Physics of NAS of Ukraine equipment for location of impurity atoms and damages in monocrystals is being developed. The facility is based on recoil nuclei [2] of analytic accelerating facility on electrostatic accelerator with ion energy up to 2 MeV. The main purpose of the channel is quantitative non-destructive investigation of hydrogen in materials by elastic recoil detection technique.

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No. 77, Poster Session II

Acceleration of divide-and-conquer method on GPU

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I. Introduction

The conventional Hartree-Fock (HF) calculations have the bottleneck at the diagonalization and construction of the Fock matrix, of which computational costs formally scale as N^3 and N^4, respectively, where N represents the size of the system under consideration. As the acceleration of diagonalization of the Fock matrix, we have implemented and assessed the divide-and-conquer (DC) self-consistent field (SCF) method. DC method is a linear-scaling scheme by dividing a total system into several subsystems originally proposed by Yang [1,2]. On the other hand, the almost 90% of computational cost is the construction of the Fock matrix. Unlike to the diagonalization, the construction has the high parallelization efficiency and the wall time could be cut down by graphical processor units (GPUs). Furthermore, the resolution-of-identity (RI) approximation [3] could reduce the construction costs. In this presentation, we will report the implementation of the DC method with GPU and show some performances.

II. Divide-and-conquer based resolution-of-identity Hartree-Fock

In the DC-HF method, we solve the Roothann-Hall equation corresponding to individual subsystem $S(\alpha)$. The local Fock matrix is constructed in the usual manner:

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{\alpha} + \sum_{\alpha} \sum_{\lambda\sigma \in S(\alpha)} \left[D_{\lambda\sigma}^{a} (\mu\nu|\lambda\sigma) - 1/2\, D_{\lambda\sigma}^{a} (\mu\lambda|\nu\sigma) \right]$$

$\mathbf{F}^{\alpha}$, $\mathbf{H}^{\alpha}$, and $\mathbf{D}^{\alpha}$ are the local Fock, core Hamiltonian, and density matrices. RI technique involves approximation the costly four-center two-electron integrals with the use of two-center and three-center integrals.

$$(\mu\nu|\lambda\sigma) = \sum_{P,Q} (\mu\nu|P)(P|Q)^{-1}(Q|\lambda\sigma)$$

Hereafter, indices μ, ν, λ, and σ refer to atomic orbitals (AOs), P and Q refer to auxiliary AOs.

III. Results

The present DC-RI-HF method with GPU was assessed in calculations of a oligoglycine $(\text{gly})_{10}$. In the DC calculations, one amino acid was adopted as a central region and several adjacent left-and-right 2 units were treated as the corresponding buffer region. Table 1 shows the wall time [min] of each SCF parts (the construction of Fock matrix and diagonalization of SCF equation) by the direct-SCF and RI-SCF. The utilization of GPU reduced drastically the construction time. By the hybrid of GPU and the RI method, we achieved 10.6x speeding up of the construction time. On the other hand, the DC method could speed up the diagonalization time, which it is difficult to parallel. In the presentation, we will report the DC-based correlation methods: DC-MP2 and CCSD.

Table 1. The wall time [min] of construction of Fock matrix and diagonalization of SCF equation by direct-SCF and RI-SCF on CPU and GPU.

	Construction	Diagonalization	Total time	Speed up
Direct-HF(CPU)	124.2	3.8	128.5	-
Direct-HF(GPU)	26.7	3.8	30.7	4.2x
RI-HF(GPU)	11.7	3.8	15.9	8.1x
DC-RI-HF(GPU)	11.7	2.5	14.7	8.8x

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Addicoat	Matthew	Monday	Evening		Aula	18 : 00
Akama	Tomoko	Thursday	Evening		Aula	18 : 00
Allen	Wesley	Thursday	Afternoon		Brahms	15 : 00
Allolio	Christoph	Monday	Evening		Aula	18 : 00
Altun	Zikri	Thursday	Evening		Aula	18 : 00
Amovilli	Claudio	Monday	Evening		Aula	18 : 00
Ando	Koji	Thursday	Afternoon	II	Bartók	17 : 40
Ando	Koji	Thursday	Evening		Aula	18 : 00
Angelova	Iva	Monday	Evening		Aula	18 : 00
Angyan	Janos	Friday	Morning	I	Bartók	8 : 30
Arifin		Thursday	Evening		Aula	18 : 00
Ayers	Paul	Wednesday	Morning	II	Pátria	11 : 30
Babinszki	Bence	Thursday	Evening		Aula	18 : 00
Barbour Scott	Luis Paulo	Monday	Evening		Aula	18 : 00
Barrientos	Carmen	Thursday	Evening		Aula	18 : 00
Bartlett	Rodney	Thursday	Morning	I	Bartók	8 : 30
Basilevsky	Mikhail	Thursday	Afternoon		Brahms	15 : 30
Becke	Axel	Tuesday	Morning	I	Bartók	9 : 00
Bende	Attila	Monday	Evening		Aula	18 : 00
Bende	Attila	Thursday	Afternoon		Brahms	14 : 30
Bernstein	Victor	Monday	Evening		Aula	18 : 00
Berriche	Hamid	Thursday	Evening		Aula	18 : 00
Bhattacharya	Debarati	Monday	Evening		Aula	18 : 00
Bhatt	Jayesh	Thursday	Afternoon	I	Lehár	15 : 00
Bil	Andrzej	Thursday	Morning	I	Lehár	10 : 10
Bolton	Kim	Monday	Evening		Aula	18 : 00
Brändas	Erkki	Wednesday	Morning	II	Bartók	11 : 00
Broer	Ria	Monday	Afternoon	I	Pátria	15 : 30
Brothers	Edward	Thursday	Evening		Aula	18 : 00
Bucinsky	Lukas	Monday	Evening		Aula	18 : 00
Cailliez	Fabien	Tuesday	Afternoon	I	Brahms	15 : 30
Cammi	Roberto	Monday	Afternoon	I	Lehár	16 : 00
Carsky	Petr	Monday	Morning	II	Lehár	11 : 00

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Castro	Miguel	Friday	Afternoon	I	Bartók	15 : 30
Chai	Jeng-Da	Tuesday	Morning	II	Bartók	12 : 10
Champagne	Benoit	Tuesday	Morning	I	Lehár	10 : 10
Chen	Feiwu	Monday	Morning	II	Lehár	11 : 50
Cheng	Lan	Monday	Morning	II	Pátria	12 : 00
Cinarli	Adem	Monday	Evening		Aula	18 : 00
Costanzo	Francesca	Thursday	Evening		Aula	18 : 00
Cox	Hazel	Wednesday	Afternoon		Bartók	15 : 00
Crawford	Daniel	Friday	Afternoon	I	Pátria	15 : 30
Cremer	Dieter	Monday	Morning	II	Pátria	11 : 30
Csehi	András	Thursday	Evening		Aula	18 : 00
Csontos	Botond	Thursday	Evening		Aula	18 : 00
Csontos	Jozsef	Thursday	Evening		Aula	18 : 00
Cui	Qiang	Monday	Morning	II	Bartók	11 : 00
Daigoku	Kota	Monday	Evening		Aula	18 : 00
Daru	Janos	Thursday	Afternoon	II	Lehár	17 : 20
de Wergifosse	Marc	Monday	Afternoon	I	Bartók	15 : 20
Dobson	John	Friday	Morning	II	Bartók	11 : 30
Doltsinis	Nikos	Thursday	Afternoon	II	Lehár	16 : 30
Domagala	Malgorzata	Thursday	Evening		Aula	18 : 00
Dominikowska	Justyna	Monday	Evening		Aula	18 : 00
Dopieralski	Przemyslaw	Thursday	Morning	II	Lehár	11 : 30
Draxl	Claudia	Tuesday	Morning	I	Lehár	9 : 00
Dubecky	Matus	Monday	Evening		Aula	18 : 00
Dubnikova	Faina	Thursday	Evening		Aula	18 : 00
Efremenko	Irena	Wednesday	Morning	I	Lehár	10 : 10
El-Azhary	Adel	Thursday	Morning	I	Brahms	8 : 50
Engin	Selma	Wednesday	Morning	I	Lehár	9 : 30
Ensing	Bernd	Thursday	Morning	I	Lehár	9 : 10
Eriksen	Janus	Monday	Evening		Aula	18 : 00
Ernzerhof	Matthias	Friday	Afternoon	I	Bartók	15 : 00
Ettenhuber	Patrick	Thursday	Evening		Aula	18 : 00
Falklöf	Olle	Monday	Evening		Aula	18 : 00
Fantuzzi	Felipe	Thursday	Evening		Aula	18 : 00
Fdez. Sanz	Javier	Tuesday	Afternoon	I	Lehár	16 : 10
Fekete	Attila	Monday	Evening		Aula	18 : 00
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Filatov	Michael	Wednesday	Morning	II	Bartók	11 : 50

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Floris	Franca Maria	Monday	Evening		Aula	18 : 00
Freitag	Leon	Thursday	Evening		Aula	18 : 00
Frenking	Gernot	Tuesday	Afternoon	I	Bartók	14 : 30
Frenklach	Michael	Tuesday	Morning	I	Brahms	9 : 00
Friedrich	Joachim	Friday	Morning	I	Pátria	10 : 10
Fromager	Emmanuel	Friday	Morning	I	Bartók	9 : 30
Furtenbacher	Tibor	Tuesday	Morning	II	Brahms	12 : 10
Gadre	Shridhar	Friday	Morning	II	Pátria	11 : 30
Geerlings	Paul	Tuesday	Afternoon	II	Bartók	18 : 30
Ghysels	An	Tuesday	Morning	I	Lehár	9 : 30
Gill	Peter	Tuesday	Morning	I	Bartók	8 : 30
Gokhberg	Kirill	Monday	Afternoon	I	Lehár	15 : 00
Gomar	Jerome	Monday	Evening		Aula	18 : 00
Goos	Elke	Tuesday	Morning	II	Brahms	11 : 50
Góra	Robert	Wednesday	Morning	I	Lehár	9 : 50
Granatier	Jaroslav	Monday	Evening		Aula	18 : 00
Gromov	Evgeniy	Wednesday	Morning	I	Lehár	8 : 50
Gürbüz	Demet	Monday	Evening		Aula	18 : 00
Gyorffy	Werner	Thursday	Evening		Aula	18 : 00
Hafida	Merouani	Monday	Evening		Aula	18 : 00
Haldar	Susanta	Thursday	Evening		Aula	18 : 00
Halet	Jean-Francois	Tuesday	Afternoon	I	Lehár	14 : 30
Hanrath	Michael	Friday	Afternoon	I	Pátria	15 : 00
Hedegård	Erik Donovan	Monday	Morning	II	Bartók	11 : 50
Helgaker	Trygve	Wednesday	Morning	II	Pátria	12 : 00
Hellström	Matti	Monday	Evening		Aula	18 : 00
Hermansson	Kersti	Thursday	Morning	I	Lehár	8 : 30
Hermansson	Kersti	Tuesday	Morning	II	Lehár	11 : 30
Hirata	So	Friday	Morning	I	Pátria	8 : 50
Hobza	Pavel	Friday	Afternoon	II	Pátria	17 : 00
Hoffmann	Mark	Thursday	Morning	II	Bartók	11 : 00
Hoggan	Philip	Tuesday	Afternoon	II	Lehár	17 : 30
Høyvik	Ida-Marie	Friday	Morning	I	Pátria	9 : 50
Huber	Stefan	Thursday	Evening		Aula	18 : 00
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Janowski	Tomasz	Monday	Evening		Aula	18 : 00
Jansen	Georg	Friday	Morning	I	Bartók	9 : 00
Jenkins	Samantha	Friday	Afternoon	I	Pátria	14 : 30
Jensen	Jan Halborg	Monday	Morning	I	Bartók	10 : 00
Jeszenszki	Péter	Tuesday	Afternoon	I	Brahms	16 : 10
Jeziorski	Bogumil	Friday	Morning	II	Bartók	11 : 00
Ji	Hyunjun	Monday	Evening		Aula	18 : 00
Joergensen	Poul	Wednesday	Morning	I	Pátria	8 : 40
Joshi	Sayali	Monday	Evening		Aula	18 : 00
Kaiyawet	Nopporn	Thursday	Evening		Aula	18 : 00
Kalemos	Apostolos	Monday	Evening		Aula	18 : 00
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Kamolphop	Uraiwan	Monday	Evening		Aula	18 : 00
Kapralova	Petra Ruth	Wednesday	Afternoon		Lehár	15 : 40
Karadakov	Peter	Tuesday	Afternoon	I	Bartók	15 : 50
Karlicky	Frantisek	Monday	Evening		Aula	18 : 00
Karlicky	Frantisek	Tuesday	Afternoon	I	Lehár	15 : 50
Kassab	Emile	Thursday	Evening		Aula	18 : 00
Katouda	Michio	Thursday	Evening		Aula	18 : 00
Kauch	Małgorzata	Monday	Evening		Aula	18 : 00
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Kazemi Babhydari	Ali	Monday	Evening		Aula	18 : 00
Kertesz	Miklos	Tuesday	Afternoon	I	Lehár	15 : 00
Khrenova	Maria	Monday	Evening		Aula	18 : 00
Kim	Jaehoon	Monday	Evening		Aula	18 : 00
King	Andrew	Thursday	Evening		Aula	18 : 00
Kirk	Steven	Thursday	Evening		Aula	18 : 00
Kiselev	Vitaly	Thursday	Morning	I	Brahms	9 : 30
Kita	Yukiumi	Monday	Evening		Aula	18 : 00
Klimes	Jiri	Thursday	Evening		Aula	18 : 00
Kobayashi	Masato	Thursday	Afternoon	II	Bartók	17 : 00
Kokoschka	Malte	Monday	Evening		Aula	18 : 00
Komáromi	István	Thursday	Evening		Aula	18 : 00
Köppl	Christoph	Monday	Evening		Aula	18 : 00
Kowalski	Piotr	Thursday	Evening		Aula	18 : 00
Kozłowska	Justyna	Thursday	Evening		Aula	18 : 00

List of Contributors cont'd

Family name	**Given Name**	**Scheduled on**				
Kraft	Markus	Tuesday	Afternoon	I	Brahms	15 : 00
Kraka	Elfi	Tuesday	Morning	II	Bartók	11 : 30
Kristensen	Kasper	Thursday	Evening		Aula	18 : 00
Krylov	Anna	Wednesday	Morning	I	Pátria	10 : 10
Kudo	Takako	Monday	Evening		Aula	18 : 00
Kurita	Noriyuki	Thursday	Evening		Aula	18 : 00
Kürti	Jenő	Tuesday	Afternoon	II	Lehár	18 : 00
Kutzelnigg	Werner	Monday	Morning	I	Pátria	10 : 00
Largo	Antonio	Monday	Evening		Aula	18 : 00
Legeza	Ors	Monday	Morning	II	Lehár	11 : 30
Lendvay	György	Monday	Afternoon	I	Lehár	14 : 30
Lindgren	Ingvar	Friday	Afternoon	II	Pátria	17 : 30
Li	Shuhua	Friday	Morning	I	Pátria	8 : 30
Liu	Wenjian	Monday	Morning	II	Pátria	11 : 00
Lu	Tian	Monday	Evening		Aula	18 : 00
Magyarfalvi	Gábor	Thursday	Morning	II	Brahms	12 : 10
Ma	Haibo	Thursday	Afternoon	II	Lehár	17 : 40
Ma	Jing	Monday	Afternoon	I	Lehár	15 : 20
Malček	Michal	Thursday	Evening		Aula	18 : 00
Maldonado	Alejandro Fabián	Monday	Evening		Aula	18 : 00
Mallik	Bhabani	Monday	Evening		Aula	18 : 00
Martyna	Glenn	Friday	Morning	I	Bartók	10 : 10
Marzari	Nicola	Tuesday	Morning	II	Lehár	11 : 00
Masia	Marco	Thursday	Evening		Aula	18 : 00
Masia	Marco	Thursday	Morning	I	Lehár	8 : 40
Matsuda	Aya	Monday	Evening		Aula	18 : 00
Matsui	Toru	Thursday	Evening		Aula	18 : 00
Matsushita	Yu-ichiro	Monday	Evening		Aula	18 : 00
Maurer	Reinhard	Tuesday	Afternoon	I	Lehár	15 : 30
Mayer	Istvan	Tuesday	Afternoon	II	Bartók	18 : 00
Mazumdar	Sumit	Tuesday	Morning	I	Lehár	8 : 30
Meeprasert	Arthitaya	Thursday	Evening		Aula	18 : 00
Mezey	Paul	Wednesday	Morning	II	Bartók	12 : 10
Michl	Josef	Friday	Afternoon	II	Pátria	16 : 30
Milko	Petr	Monday	Evening		Aula	18 : 00
Mironov	Vladimir	Thursday	Evening		Aula	18 : 00
Mitschker	Jan	Thursday	Morning	I	Brahms	9 : 50
Mizoguchi	Noriyuki	Monday	Evening		Aula	18 : 00

List of Contributors cont'd

Family name	**Given Name**	**Scheduled on**				
Mizukami	Wataru	Thursday	Evening		Aula	18 : 00
Moiseyev	Nimrod	Wednesday	Afternoon		Bartók	14 : 30
Moncho Escriva	Salvador	Thursday	Evening		Aula	18 : 00
Moon	Alena	Monday	Evening		Aula	18 : 00
Mori	Hirotoshi	Monday	Evening		Aula	18 : 00
Morozov	Dmitry	Thursday	Evening		Aula	18 : 00
Mukherjee	Debashis	Wednesday	Morning	I	Pátria	9 : 40
Musial	Monika	Monday	Morning	I	Lehár	10 : 10
Mussard	Bastien	Monday	Evening		Aula	18 : 00
Nagy	Ágnes	Friday	Afternoon	I	Bartók	14 : 30
Nagy	Péter	Monday	Evening		Aula	18 : 00
Nagy	Szilvia	Monday	Evening		Aula	18 : 00
Nakagawa	Katsumi	Monday	Evening		Aula	18 : 00
Nakai	Hiromi	Wednesday	Afternoon		Pátria	15 : 30
Nakano	Masayoshi	Thursday	Morning	II	Brahms	11 : 50
Nakatsuka	Yutaka	Thursday	Evening		Aula	18 : 00
Náray-Szabó	Gábor	Monday	Afternoon	I	Bartók	15 : 00
Nascimento	Marco	Tuesday	Afternoon	I	Bartók	15 : 30
Naumkin	Fedor	Wednesday	Afternoon		Lehár	15 : 20
Nebgen	Ben	Thursday	Afternoon	I	Lehár	15 : 20
Neese	Frank	Wednesday	Afternoon		Pátria	15 : 00
Nekardova	Michaela	Monday	Evening		Aula	18 : 00
Nemeth	Karoly	Tuesday	Morning	II	Lehár	11 : 50
Nemukhin	Alexander	Wednesday	Morning	II	Lehár	11 : 30
Nénon	Sébastien	Thursday	Evening		Aula	18 : 00
Nicolaides	Cleanthes	Wednesday	Morning	I	Bartók	8 : 30
Nishimoto	Yoshio	Thursday	Evening		Aula	18 : 00
Nizovtsev	Anton	Monday	Evening		Aula	18 : 00
Noga	Jozef	Thursday	Afternoon	II	Bartók	16 : 30
Nordlund	Kai	Thursday	Morning	II	Lehár	11 : 00
Noto	Kaori	Thursday	Evening		Aula	18 : 00
Nunthaboot	Nadtanet	Monday	Evening		Aula	18 : 00
Nyman	Gunnar	Thursday	Morning	I	Lehár	9 : 40
Ochsenfeld	Christian	Thursday	Morning	I	Bartók	9 : 00
Olivares-Amaya	Roberto	Thursday	Afternoon	II	Bartók	17 : 20
Olm	Carsten	Tuesday	Morning	II	Brahms	11 : 30
Olsen	Jeppe	Thursday	Afternoon	I	Bartók	14 : 30
Otaki	Hiroki	Thursday	Evening		Aula	18 : 00
Otsuka	Miho	Monday	Evening		Aula	18 : 00

List of Contributors cont'd

Family name	**Given Name**	**Scheduled on**				
Otsuka	Takao	Thursday	Evening		Aula	18 : 00
Ouddai	Nadia	Thursday	Evening		Aula	18 : 00
Ounissi	abdelhamid	Thursday	Evening		Aula	18 : 00
Paidarova	Ivana	Monday	Evening		Aula	18 : 00
Paidarova	Ivana	Wednesday	Morning	I	Bartók	10 : 00
Palanisamy	Deepa	Thursday	Evening		Aula	18 : 00
Palusiak	Marcin	Thursday	Evening		Aula	18 : 00
Pápai	Imre	Thursday	Morning	I	Brahms	9 : 10
Pastorczak	Ewa	Thursday	Evening		Aula	18 : 00
Pecul	Magdalena	Monday	Morning	II	Bartók	11 : 30
Peña	José Juan	Thursday	Evening		Aula	18 : 00
Pernal	Katarzyna	Thursday	Morning	II	Bartók	11 : 30
Piecuch	Piotr	Thursday	Afternoon	I	Bartók	15 : 30
Pierloot	Kristine	Tuesday	Morning	I	Bartók	9 : 30
Pinter	Balazs	Monday	Evening		Aula	18 : 00
Piris	Mario	Thursday	Morning	II	Bartók	12 : 10
Pittner	Jiri	Thursday	Evening		Aula	18 : 00
Pittner	Jiri	Thursday	Morning	II	Bartók	11 : 50
Pleßow	Philipp Nikolaus	Monday	Evening		Aula	18 : 00
Podeszwa	Rafal	Friday	Morning	I	Bartók	9 : 50
Prezhdo	Oleg	Wednesday	Morning	II	Lehár	12 : 00
Promkatkaew	Malinee	Thursday	Evening		Aula	18 : 00
Pulay	Peter	Monday	Afternoon		Pátria	16 : 50
Pyykkö	Pekka	Monday	Afternoon	I	Pátria	14 : 30
Rassolov	Vitaly	Thursday	Afternoon	I	Bartók	15 : 00
Reinhardt	Peter	Thursday	Evening		Aula	18 : 00
Rolik	Zoltán	Monday	Evening		Aula	18 : 00
Romanova	Julia	Thursday	Evening		Aula	18 : 00
Romera	Elvira	Monday	Morning	II	Lehár	12 : 10
Rosta	Edina	Monday	Morning	II	Bartók	12 : 10
Roztoczyńska	Agnieszka	Thursday	Evening		Aula	18 : 00
Rungrotmongkol	Thanyada	Monday	Evening		Aula	18 : 00
Rupnik	Kresimir	Monday	Afternoon	I	Bartók	16 : 00
Ruscic	Branko	Tuesday	Afternoon	I	Brahms	14 : 30
Ruud	Kenneth	Monday	Afternoon	I	Lehár	15 : 40
Saalfrank	Peter	Wednesday	Morning	II	Bartók	11 : 30
Salahub	Dennis	Monday	Afternoon	I	Bartók	14 : 30
Salima	Lakehal	Thursday	Evening		Aula	18 : 00

List of Contributors cont'd

Family name	Given Name	Scheduled on				
Salvador	Pedro	Wednesday	Afternoon		Lehár	14 : 30
Samanta	Pradipta Kumar	Monday	Evening		Aula	18 : 00
Sanchez Lengeling	Benjamin	Thursday	Evening		Aula	18 : 00
Saue	Trond	Monday	Afternoon	I	Pátria	15 : 00
Savin	Andreas	Tuesday	Afternoon	I	Bartók	15 : 00
Schuetz	Martin	Friday	Morning	I	Pátria	9 : 20
Scrinzi	Armin	Wednesday	Morning	I	Bartók	9 : 30
Scuseria	Gustavo	Monday	Morning	I	Pátria	8 : 30
Shapiro	Moshe	Wednesday	Morning	I	Bartók	9 : 00
Sheen	David	Tuesday	Morning	II	Brahms	11 : 00
Sheka	Elena	Wednesday	Morning	I	Lehár	8 : 30
Shigeta	Yasuteru	Thursday	Morning	II	Brahms	11 : 30
Shoji	Mitsuo	Thursday	Evening		Aula	18 : 00
Shurki	Avital	Tuesday	Morning	II	Bartók	11 : 50
Siegbahn	Per	Wednesday	Morning	II	Lehár	11 : 00
Silva	Carlos	Monday	Evening		Aula	18 : 00
Silverstone	Harris	Wednesday	Afternoon		Bartók	15 : 20
Singh	Raman	Thursday	Evening		Aula	18 : 00
Siuda	Paweł Artur	Thursday	Morning	II	Lehár	11 : 50
Skara	Gabriella	Monday	Evening		Aula	18 : 00
Slipchenko	Lyudmila	Monday	Morning	I	Bartók	9 : 30
Smiechowski	Maciej	Thursday	Afternoon	II	Lehár	17 : 00
Šmydke	Jan	Thursday	Evening		Aula	18 : 00
Sokalski	Andrzej	Monday	Afternoon	I	Bartók	15 : 40
Solomonik	Victor	Monday	Evening		Aula	18 : 00
Solomonik	Victor	Thursday	Evening		Aula	18 : 00
Spohr	Eckhard	Thursday	Afternoon	I	Lehár	14 : 30
Stanton	John	Wednesday	Afternoon		Pátria	14 : 30
Stoll	Hermann	Friday	Morning	II	Pátria	11 : 00
Stopkowicz	Stella	Monday	Morning	I	Pátria	9 : 30
Surga	José	Thursday	Evening		Aula	18 : 00
Suturina	Elizaveta	Monday	Evening		Aula	18 : 00
Szabó	Péter	Monday	Evening		Aula	18 : 00
Szalay	Péter	Wednesday	Morning	II	Pátria	11 : 00
Szegedy	Lóránt	Monday	Evening		Aula	18 : 00
Szegletes	Luca	Monday	Evening		Aula	18 : 00
Szőri	Milán	Thursday	Evening		Aula	18 : 00
Tachikawa	Masanori	Wednesday	Afternoon		Lehár	15 : 00
Tadjer	Alia	Thursday	Morning	I	Brahms	10 : 10

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Family name	**Given Name**	**Scheduled on**				
Tafipolski	Maxim	Thursday	Morning	II	Lehár	12 : 10
Takano	Keiko	Monday	Evening		Aula	18 : 00
Tamm	Toomas	Thursday	Morning	I	Brahms	8 : 30
Tanaka	Wataru	Thursday	Evening		Aula	18 : 00
Tavman	Aydin	Monday	Evening		Aula	18 : 00
Teodoro	Tiago	Thursday	Evening		Aula	18 : 00
Tkatchenko	Alexandre	Friday	Morning	II	Bartók	12 : 00
Tóth	Zsuzsanna	Monday	Evening		Aula	18 : 00
Trindle	Carl	Thursday	Evening		Aula	18 : 00
Tsuneda	Takao	Tuesday	Morning	I	Bartók	10 : 10
Turányi	Tamás	Tuesday	Morning	I	Brahms	8 : 30
Ugalde	Jesus	Tuesday	Afternoon	II	Bartók	17 : 00
Ujiie	Yuzuru	Monday	Evening		Aula	18 : 00
Urban	Miroslav	Tuesday	Morning	I	Lehár	9 : 50
Usui	Kosuke	Thursday	Evening		Aula	18 : 00
Vakula	Nikita	Monday	Evening		Aula	18 : 00
Varga	Tamas	Tuesday	Afternoon	I	Brahms	15 : 50
Vibók	Ágnes	Thursday	Morning	II	Brahms	11 : 00
Vnuchenko	Anna	Thursday	Evening		Aula	18 : 00
v. Szentpaly	Laszlo	Tuesday	Afternoon	II	Bartók	17 : 30
Wang	Hai	Tuesday	Morning	I	Brahms	10 : 00
Werner	Hans-Joachim	Wednesday	Morning	I	Pátria	9 : 10
Wiśniewska	Marta	Monday	Evening		Aula	18 : 00
Witek	Henryk	Wednesday	Afternoon		Bartók	15 : 40
Wodyński	Artur	Monday	Afternoon	I	Pátria	16 : 00
Yamazaki	Kaoru	Thursday	Afternoon	I	Lehár	15 : 40
Yang	Weitao	Tuesday	Morning	II	Bartók	11 : 00
Yoshikawa	Takeshi	Thursday	Evening		Aula	18 : 00
Yoshizawa	Kazunari	Tuesday	Afternoon	II	Lehár	17 : 00
Zádor	Judit	Tuesday	Morning	I	Brahms	9 : 30
Zgid	Dominika	Monday	Morning	I	Lehár	9 : 30
Zhanpeisov	Nurbosyn U.	Monday	Evening		Aula	18 : 00
Ziegler	Tom	Tuesday	Afternoon	I	Bartók	16 : 10
Zilberg	Shmuel	Tuesday	Morning	I	Bartók	9 : 50
Zoboki	Tamás	Monday	Evening		Aula	18 : 00

List of Participants

Given name	**Family Name**	**Affiliation**	**Country**
Matthew	Addicoat	Jacobs University Bremen	Germany
Tomoko	Akama	Sophia University	Japan
Wesley	Allen	University of Georgia	USA
Christoph	Allolio	MLU Halle	Germany
Zikri	Altun	Marmara University	Turkey
Claudio	Amovilli	University of Pisa, Department of Chemistry and Industrial Chemistry	Italy
Koji	Ando	Kyoto University	Japan
Iva	Angelova	BASF SE	Germany
Janos	Angyan	CNRS and Université de Lorraine	France
Arifin		Nagoya University	Japan
Paul	Ayers	McMaster University	Canada
Bence	Babinszki	Eotvos Lorand University	Hungary
Luis Paulo	Barbour Scott	UFABC-BRAZIL / ENS CACHAN	BRAZIL
Carmen	Barrientos	Universidad de Valladolid	Spain
Rodney	Bartlett	University of Florida	USA
Mikhail	Basilevsky	Photochemistry Center, Russian Academy of Sciences	Russian Federation
Axel	Becke	Dalhousie University	Canada
Attila	Bende	National Institute for Research and Development of Isotopic and Molecular Technologies	Romania
Victor	Bernstein	Technion - Israel Institute of Technology	Israel
Hamid	Berriche	King Khalid University	Saudi Arabia
Debarati	Bhattacharya	CSIR - National Chemical Laboratory (NCL)	India
Jayesh	Bhatt	University of Surrey	UK
Andrzej	Bil	Institute of Physical Chemistry, University of Zürich	Switzerland
Kim	Bolton	University of Boras	Sweden
Erkki	Brändas	Dept. Chemistry, Uppsala University	Sweden
Ria	Broer	University of Groningen	The Netherlands
Edward	Brothers	Texas A&M University at Qatar	Qatar

List of Participants cont'd

Given name	Family Name	Affiliation	Country
Lukas	Bucinsky	Slovak University of Technology	Slovakia
Fabien	Cailliez	Université Paris-Sud	France
Roberto	Cammi	University of Parma, Department of Chemistry	Italy
Petr	Carsky	J.Heyrovsky Institute of Physical Chemistry	Czech Republic
Miguel	Castro	Universidad Nacional Autonoma de Mexico	México
Jeng-Da	Chai	National Taiwan University	Taiwan
Benoit	Champagne	University of Namur	Belgium
Feiwu	Chen	University of Science and Technology Beijing	P. R. China
Lan	Cheng	Department of Chemistry and BioChemistry, University of Texas at Austin	United States of America
Adem	Cinarli	Istanbul University	Turkey
Francesca	Costanzo	Leiden Institue of Chemistry	Netherlands
Hazel	Cox	University of Sussex	UK
Daniel	Crawford	Virginia Tech	USA
Dieter	Cremer	Department of Chemistry, SMU	USA
András	Csehi	University of Debrecen	Hungary
Botond	Csontos	Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics.	Hungary
Jozsef	Csontos	Budapest University of Technology and Economics	Hungary
Qiang	Cui	UW-Madison	USA
Kota	Daigoku	Kitasato University	Japan
Janos	Daru	Eötvös Loránd University, Physical Chemistry Department	Hungary
Marc	de Wergifosse	Université de Namur	Belgium
John	Dobson	Griffith University	Australia
Nikos	Doltsinis	University of Münster	Germany
Malgorzata	Domagala	Department of Theoretical and Structural Chemistry, University of Lodz	Poland
Justyna	Dominikowska	Department of Theoretical and Structural Chemistry, University of Lodz	Poland
Przemyslaw	Dopieralski	Lehrstuhl für Theoretische Chemie, Ruhr–Universität Bochum	Germany
Claudia	Draxl	HU Berlin, Physics Department	Germany
Matus	Dubecky	Palacky University Olomouc	Czech Republic

List of Participants cont'd

Given name	Family Name	Affiliation	Country
Faina	Dubnikova	The Hebrew University of Jerusalem	Israel
Bo	Durbeej	Division of Computational Physics, Linkoeping University	Sweden
Irena	Efremenko	Weizmann Institute of Science	Israel
Adel	El-Azhary	King Saud University	Saudi Arabia
Selma	Engin	Laboratoire de Chimie Physique - Matière et Rayonnement	France
Bernd	Ensing	University of Amsterdam	Netherlands
Janus	Eriksen	Aarhus University	Denmark
Matthias	Ernzerhof	University of Montreal	Canada
Patrick	Ettenhuber	Aarhus University	Denmark
Olle	Falklöf	Linköping University	Sweden
Felipe	Fantuzzi	Universidade Federal do Rio de Janeiro	Brazil
Javier	Fdez. Sanz	University of Seville	Spain
Attila	Fekete	Clinical Research Center, Medical and Health Science Center, University of Debrecen	Hungary
Nicolas	Fernandez	Aix-Marseille University	France
Michael	Filatov	University of Bonn	Germany
Reinhold	Fink	Physical and Theoretical Chemistry, Tübingen	Germany
Franca Maria	Floris	University of Pisa, Department of Chemistry and Industrial Chemistry	Italy
Géza	Fogarasi	Institute of Chemistry Eotvos University, Budapest	Hungary
Leon	Freitag	Institute of Theoretical Chemistry, University of Vienna	Austria
Gernot	Frenking	Philipps-Universität Marburg	Germany
Michael	Frenklach	UC Berkeley	USA
Joachim	Friedrich	Institute for Chemistry	Germany
Emmanuel	Fromager	University of Strasbourg	France
Tibor	Furtenbacher	Eotvos University	Hungary
Shridhar	Gadre	IIT Kanpur	India
Jürgen	Gauss	Institut für Physikalische Chemie, Universität Mainz	Germany
Paul	Geerlings	Vrije Universiteit Brussel	Belgium
An	Ghysels	Center for Molecular Modeling, Ghent University	Belgium
Peter	Gill	Australian National University	Australia
Kirill	Gokhberg	Heidelberg University	Germany

List of Participants cont'd

Given name	**Family Name**	**Affiliation**	**Country**
Tomasz	Janowski	University of Arkansas	USA
Georg	Jansen	University Duisburg-Essen	Germany
Samantha	Jenkins	Hunan Normal University	China
Jan Halborg	Jensen	University of Copenhagen	Denmark
Péter	Jeszenszki	Eotvos Lorand University	Hungary
Bogumil	Jeziorski	Department of Chemistry, University of Warsaw	Poland
Hyunjun	Ji	KAIST	Republic of Korea
Poul	Joergensen	Aarhus University	Denmark
Sayali	Joshi	CSIR National Chemical Laboratory	India
Nopporn	Kaiyawet	Chulalongkorn University	Thailand
Apostolos	Kalemos	Department of Chemistry, University of Athens	Greece
Ilya	Kaliman	Purdue University	USA
Mihály	Kállay	Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics	Hungary
Uraiwan	Kamolphop	Department of Chemistry, Faculty of Science, Mahasarakham University	Thailand
Petra Ruth	Kapralova	J. Heyrovsky Institute of Physical Chemistry, The Academy of Sciences of the Czech Republic	Czech Republic
Peter	Karadakov	University of York	UK
Frantisek	Karlicky	Palacky University Olomouc	Czech Republic
Emile	Kassab	CNRS	France
Michio	Katouda	RIKEN Advanced Institute for Computational Science	Japan
Małgorzata	Kauch	Faculty of Chemistry, University of Warsaw	Poland
Joanna	Kauczor	Linköping University	Sweden
Toshiaki	Kawamura	Tokyo Metropolitan University	Japan
Ali	Kazemi Babhydari	Department of Physical Chemistry, Islamic Azad University	Iran
Miklos	Kertesz	Georgetown University	USA
Maria	Khrenova	.N.Bach Institute of Biochemistry, Russian Academy of Sciences	Russia
Jaehoon	Kim	KAIST	Republic of Korea
Andrew	King	University of Sussex	England
Steven	Kirk	Hunan Normal University	China
Vitaly	Kiselev	Institute of Chemical Kinetics and Combustion SB RAS	Russia
Yukiumi	Kita	Yokohama City University	Japan

List of Participants cont'd

Given name	Family Name	Affiliation	Country
Jiri	Klimes	Faculty of Physics, University of Vienna	Austria
Masato	Kobayashi	Waseda University	Japan
Malte	Kokoschka	Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic	Czech Republic
István	Komáromi	Clinical Research Center, Medical & Health Science Center, University of Debrecen	Hungary
Christoph	Köppl	Institute of Theoretical Chemistry, University of Stuttgart	Germany
Piotr	Kowalski	Institute of Applied Radiation Chemistry	Poland
Justyna	Kozłowska	Theoretical Chemistry Group, Chemistry Department, Wroclaw University of Technology	Poland
Markus	Kraft	University of Cambridge	United Kingdom
Elfi	Kraka	Southern Methodist University	USA
Kasper	Kristensen	Department of Chemistry, Aarhus University	Denmark
Anna	Krylov	Dept. of Chemistry, USC	USA
Takako	Kudo	Gunma University	Japan
Noriyuki	Kurita	Toyohashi University of Technology	Japan
Jenő	Kürti	Institute of Physics, Eötvös University	Hungary
Werner	Kutzelnigg	Theoretical Chemistry, Ruhr Universitat Bochum	Germany
István	Ladjánszki	Department of Physical Chemistry and Material Science, Budapest University of Technology and Economics	Hungary
Antonio	Largo	Universidad de Valladolid	Spain
Ors	Legeza	Wigner Research Centre for Physics	Hungary
György	Lendvay	Institute of Materials andEnvironmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences	Hungary
Ingvar	Lindgren	Department of Physics, University of Gothenburg	Sweden
Shuhua	Li	Nanjing University	China
Wenjian	Liu	Peking University	China
Andre	Lomaka	Chair of Molecular Technology, Tallinn University of Technology	Estonia
Tian	Lu	University of Science and Technology Beijing	China
Gábor	Magyarfalvi	Institute of Chemistry, Eötvös Loránd University	Hungary
Haibo	Ma	Nanjing University	China

List of Participants cont'd

Given name	**Family Name**	**Affiliation**	**Country**
Jing	Ma	Nanjing University	China
Mariusz	Makowski	Faculty of Chemistry, University of Gdansk	Poland
Michal	Malček	Slovak University of Technology in Bratislava	Slovakia
Alejandro Fabián	Maldonado	IMIT - CONICET, UNNE	Argentina
Bhabani	Mallik	Department of Chemistry, Indian Institute of Technology Hyderabad	India
Glenn	Martyna	IBM TJ Watson Research Center	USA
Nicola	Marzari	EPFL	Switzerland
Marco	Masia	Boston University	USA
Aya	Matsuda	Ochanomizu University	Japan
Toru	Matsui	RIKEN Advanced Institute for Computational Science	Japan
Yu-ichiro	Matsushita	Max-Planck Institute of Microstructure Physics	Germany
Reinhard	Maurer	Technische Unversitaet Muenchen	Germany
Istvan	Mayer	Research Centre for Natural Sciences, Hungarian Academy of Sciences	Hungary
Sumit	Mazumdar	University of Arizona	United States
Arthitaya	Meeprasert	Chulalongkorn University	Thailand
Paul	Mezey	Memorial University of Newfoundland	Canada
Josef	Michl	Institute of Organic Chemistry and Biochemistry AS CR, v.v.i.	Czech Republic
Petr	Milko	Weizmann Institute of Science	Israel
Vladimir	Mironov	M.V.Lomonosov Moscow State University	Russia
Jan	Mitschker	University Oldenburg, Theoretical Chemistry	Germany
Noriyuki	Mizoguchi	Meiji Pharmaceutical University	Japan
Wataru	Mizukami	University of Bristol	UK
Nimrod	Moiseyev	Technion	Israel
Salvador	Moncho Escriva	Texas A&M University at Qatar	Qatar
Alena	Moon	Purdue University	USA
Hirotoshi	Mori	Ochanomizu University	Japan
Dmitry	Morozov	University of Jyvaskyla	Finland
Sebastian	Mosbach	Department of Chemical Engineering and Biotechnology, University of Cambridge	United Kingdom
Debashis	Mukherjee	Indian Association for the Cultivation of Science, Kolkata	India
Monika	Musial	University of Silesia	Poland

List of Participants cont'd

Given name	**Family Name**	**Affiliation**	**Country**
Bastien	Mussard	Universite de Lorraine	France
Ágnes	Nagy	University of Debrecen	Hungary
Péter	Nagy	Eötvös University	Hungary
Szilvia	Nagy	Széchenyi István University	Hungary
Katsumi	Nakagawa	MO BASICS Research	Japan
Hiromi	Nakai	Department of Chemistry and Biochemistry, Waseda University	Japan
Masayoshi	Nakano	Osaka University	Japan
Yutaka	Nakatsuka	RIKEN Advanced Institute for Computational Science	Japan
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