### Application of Multireference Theory: From the Photodynamics of Nucleobases to Graphene Multiradical Structures

Hans Lischka Texas Tech University

### Why Multireference (MR) Approaches?



# **Energy Surfaces**

- 1. Franck-Condon Excitation
- 2. Dynamics on the excited-state energy surface
- 3. Proceeding through the funnel to the conical intersection
- 4. Radiationless, ultrafast transition to the ground state
- 5. Dynamics on the ground state

**Conical intersections are the rule not the exception!** They form a seam in N-2 dimensions



Reliable methods for excited-state energy surfaces  $\rightarrow$  Multireference methods: MCSCF, MRCI

Nonadiabatic coupling, energy gradients  $\rightarrow$  analytic procedures



# COLUMBUS Program System



- Focus: multireference calculations on ground and excited states
- Methods: MCSCF, MR-CISD, MR-ACPF/AQCC, Spinorbit CI
- Analytic MR-CI gradients, nonadiabatic couplings, parallel CI
- Authors: R. Shepard, I. Shavitt, R. M. Pitzer, H. Lischka
  - Vienna: M. Barbatti, M. Ruckenbauer, J. Szymczak, B. Sellner, F. Plasser
  - Budapest: P. G. Szalay
  - Jülich: Th. Müller
  - USA: S. Brozell, G. Kedziora, E. Stahlberg, ...
- Web page: http://www.univie.ac.at/columbus

### Photodynamics

- Input includes the energy surfaces, energy gradients and nonadiabatic coupling vectors
- What kind of dynamics quantum (wavepacket) or surface-hopping?
- Restricted set of internal coordinates vs. onthe-fly approach with full set of internal coordinates?

Development of the surface-hopping program NEWTON-X

### **NEWTON-X**

a package for Newtonian dynamics close to the crossing seam

### **Dynamics**

General-purpose program for on-the-fly excited-state molecular dynamics, including non-adiabatic methods (Tully's surface hopping).

### Modularity

Easy and direct link to any quantum chemistry package that can provide energy gradients and (optional) nonadiabatic coupling vectors.

#### Freeware and open source

M. Barbatti, H. Lischka (Vienna), M. Persico, G. Granucci (Pisa), et al.

www.univie.ac.at/newtonx

### **Adenine Dynamics**



## Adenine dynamics

- Ring puckering is the main mechanism at picosecond level
- First step: Fast relaxation  $S_3 \rightarrow S_2 \rightarrow S_1$  (22 fs)
- Second step:  $S_1 \rightarrow S_0$  relaxation (~0.5 ps)
- After relaxation into S<sub>1</sub>: short trapping close to <sup>2</sup>E structure
- Deactivation almost exclusively at <sup>2</sup>E
- Deactivation via NH<sub>2</sub> out-of-plane motion is not a major path

### Systematic Dynamics Survey



- Comprehensive dynamics study of all five bases
- Reaction paths *from the dynamics* and time constants
- Dependence of dynamics on initial pump energy
- Unifying picture what does it mean?

M. Barbatti, A. J. A. Aquino, J. J. Szymczak, D. Nachtigallová, P. Hobza, and H. Lischka, PNAS **107** (2010) 21453

# QM/MM



QM/MM (Multiscaling) approach for excited states, including nonadiabatic effects

#### **QM: Important part:**

single nucleobase stacked dimer base pairing charged defects...

**MM**: DNA oligomer, water molecules counter ions,...

QM methods: MRCI, CASSCF, CC2, ADC(2), TDDFT(?) MM methods: Amber force field

### **DNA Dodecamer**



# **Cytosine Dynamics**



# **Guanine Dynamics**



# Cytosine vs. Guanine excitation

Cytosine QM	Guanine QM		
Gas phase			
Life time 0.58 ps	0.36ps		
68% semi-planar crossing	Strong puckering		
DNA			
Life time 0.38ps Low puckering degree	Only 9% in ground state after 0.5 ps		
	Ethyl. II		





### Multichromophore Interactions: Stacked DNA Bases



Local excitations, excitonic coupling, charge transfer

**Defect dynamics** 

### Charge Transfer in π Stacking



# Interacting Fragments Diabatic vs. Adiabatic Representation



 $\Rightarrow$  Marcus theory

### Weak Diabatic Interactions



### Individual CT Processes I



**Real CT**: Starts with the charge in the ground state on one side and finally ends with the charge in the ground state on the other side

#### Transition state (TS) passage:

single passage over the TS with a sign change in the generalized reaction coordinate ξ; FCD: Fragment charge difference

#### Active charge transfer (CT):

This is a charge transfer event in the "active" state related to a single *TS passage* 

#### TS global:

Starts in the ground state with the charge on one side; overall process of reaching the TS and finally arriving in one of the potential wells of the ground state again

## Individual CT Processes II



To remain on the same diabatic surface: surface hopping is required from the lower to the upper state Will be numerically difficult if the nonadiabatic coupling region is narrow

## Surface Hopping Methods in NEWTON-X

Electronic Schroedinger equation

$$\frac{\mathrm{d}}{\mathrm{dt}}c_{j}(t) = -\mathrm{i}\hbar^{-1}c_{j}(t)E_{j}(t) - \sum_{i=1}^{N_{s}}c_{i}(t)\sigma_{ji}(t)$$
$$\sigma_{ji}(t) = \left\langle\varphi_{j}\left(\mathbf{R}(t)\right)\right|\frac{\partial}{\partial t}\left|\varphi_{i}\left(\mathbf{R}(t)\right)\right\rangle$$
$$\sigma_{ji}(t) = \dot{\mathbf{R}}(t)\cdot\left\langle\varphi_{j}\left(\mathbf{R}\right)\left|\mathbf{\nabla}\right|\varphi_{i}(\mathbf{R})\right\rangle_{\mathbf{R}=\mathbf{R}(t)}$$

- Compute nonadiabatic coupling vector directly (e.g. COLUMBUS) NAC
- 2. Compute nonadiabatic interaction from wavefunction overlap **OVL**

$$S_{ji}(t) = \left\langle \varphi_j \left( \mathbf{R}(t - \Delta t) \right) \middle| \varphi_i \left( \mathbf{R}(t) \right) \right\rangle$$
  
$$\sigma_{ji}(t) \approx \frac{1}{4\Delta t} \left( 3S_{ji}(t) - 3S_{ij}(t) - S_{ji}(t - \Delta t) + S_{ij}(t - \Delta t) \right)$$

### Local Diabatization (LD)

Granucci, G.; Persico, M.; Toniolo, A. J. Chem. Phys. 2001, 114, 10608

 $\eta_i(t) = \phi_i(t)$ diabatic adiabatic

$$\{\eta_i(t + \Delta t)\} = \{\varphi_i(t + \Delta t)\}\mathbf{T}^{-1}$$

**T** is obtained from a Loewdin orthogonalization of the overlap matrix  $S_{ji}(t) = \langle \varphi_j (\mathbf{R}(t - \Delta t)) | \varphi_i (\mathbf{R}(t)) \rangle$ 

Propagation and back transformation

$$\mathbf{c}(t + \Delta t) = \mathbf{T}^{-1} \exp\left(-\mathrm{i}\hbar^{-1}\frac{\mathbf{E}(t) + \mathbf{H}(t + \Delta t)}{2}\Delta t\right) \mathbf{c}(t)$$



#### Electronic transmission factor ( $\kappa_{el}$ ) for [Et.-Et.]<sup>+</sup>

	[EtEt.] <sup>+</sup> 5.0 Å <sup>a</sup>	[EtFA-Et.] <sup>+ a</sup>	[EtEt.] <sup>+</sup> 7.0 Å
Simulation	0.671	0.401	0.010
Model	0.891	0.471	0.010

<sup>a</sup> Plasser, F.; Lischka, H. J. Chem. Phys. 2011, 134, 034309

$$P_{12} = 1 - \exp\left(\frac{-(H_{if}^{\text{diab}})}{h\nu}\sqrt{\frac{\pi^3}{\lambda kT}}\right) \qquad \kappa_{\text{el}} = \frac{2P_{12}}{1 + P_{12}}$$

Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. J. Am. Chem. Soc. 1980, 102, 5798

### Pyridone Dimer as Model for HB in DNA

Excitation Energy Transfer (EET)

Proton transfer/proton coupled electron transfer (PCET)

(a) Pyridone dimer  $(2-PY)_2$ 

(b) PT structure



Muller, A.; Talbot, F.; Leutwyler, S. *J. Chem. Phys.* **2002**, *116*, 2836 Sagvolden, E.; Furche, F. *J. Phys. Chem. A* **2010**, *114*, 6897

Computational method: TDDFT/BHLYP, nonadiabatic dynamics with LD time step 0.5 fs

- Start in S<sub>2</sub>, after 11 fs in S<sub>1</sub>, localization on Pyridone 1
- At ~130 fs jump into S<sub>2</sub> and EET to Pyridone 2
- At ~235 fs another nonadiabatic event, no EET



- Hopping from S<sub>2</sub> to S<sub>1</sub>, back S<sub>2</sub>, then S<sub>3</sub>
- 14 fs: proton transfer, zwitterionic
- 20 fs: back proton transfer
- 30 fs: remaining in S<sub>1</sub> state, FCD 0, simultaneous transfer of electron and proton
- Ultrafast internal conversion to the ground state



#### Proton coupled electron transfer (PCET)



- Initial conditions: 75%
  S<sub>2</sub>, 25% S<sub>1</sub>, according to ratio in osc. strengths
- Fast decay to the S<sub>1</sub> state, S<sub>2</sub> state remains occupied by ~10%
- Initial sharp rise of PCET, after 50 fs ~17%, then significant slowdown of the increase in PT



EET transfer time: 207 fs (exp. 318 fs)



Important modes:  $v_4$  (106 cm<sup>-1</sup>, "shearing") and  $v_6$ (166 cm<sup>-1</sup>, "stretching")  $v_{15}$  (581 cm<sup>-1</sup>) and  $v_{26}$  (896 cm<sup>-1</sup>), in-plane ring deformation  $v_{35}$  (1067 cm<sup>-1</sup>), in-plane CH bending  $v_5$  (108 cm<sup>-1</sup>, "opening") of  $B_u$ symmetry – leads to localization of the excitation

 $v_4$  and  $v_6$  which were also observed most prominently in two-color resonant twophoton ionization spectra  $v_5$  was reported as well



### **Transport Properties and Defects in Graphene**

### From multireference theory to tight binding

armchair

Develop TB parameter sets that describe a defect based on ab initio methods Distribution of defects in a graphene sheet bulk values from DFT band structure

Cooperation with J. Burgdoerfer and Florian Libisch, Technical University of Vienna

H<sub>2</sub> defect zigzag corner нн vacancy

## Methods

- CASCF (8,8) reference wavefunction
- Extended reference space for open shell systems (CAS(8,8) quasi-degeneracies)
- Dynamic electron correlation with Multireference Averaged Quadratic Coupled Cluster (MR-AQCC)
- Fixed molecular structure (MP2)
- $\sigma$  orbitals frozen
- Basis set 6-31G; 6-31G\* for smaller systems

## **Polyradical Chain**

- CAS(8,8) reference is not enough → intruder states in MR-AQCC, the weight of the reference decreases steadily
- RAS(4)CAS(4,4)AUX(4)-1ex reference: in total 12 internal orbitals, 1-ex from RAS to CAS/AUX, 1-ex CAS to AUX
- Significant increase of the weight of the wavefunction
- $\sigma$  orbitals frozen after SCF step

# Poyradical character: n-acenes



MR-AQCC: a) RAS(4)/CAS(4,4)/AUX(4), b) CAS(8,8)/6-31G

### **Orbitals**



### Polyacenes



# $n \times m$ periacenes



MR-AQCC(8,8)/6-31G

# 2-dim. pericacenes $(n \times 3)$



# 2-dim. circumacenes $(5 \times n)$



much less pronounced

### Conclusions

- Tools are available for multireference calculations and nonadiabatic dynamics
- Photodynamical simulations of DNA bases provide a concrete and detailed picture
- QM/MM is a feasible way to extend the calculations to realistic environments
- QM region has to be large enough to contain the relevant photo-excited processes
- Many other applications: graphene defects, excitation energy transfer (EET)⇒photovoltaics
- COLUMBUS new directions: localized orbitals

### Acknowledgments

Vienna: D. Tunega, (J. Szymczak, M. Ruckenbauer, B. Sellner, H. Pašalić) F. Plasser, A. Ramert TU: J. Burgdoerfer, F. Libisch (Graphene) **Argonne/USA**: R. Shepard (COLUMBUS) **Juelich**: Th. Mueller (COLUMBUS) **Mülheim:** M. Barbatti (NEWTON-X) **Pisa**: M. Persico, G. Granucci (NEWTON-X) Budapest: P. Szalay (AQCC) Prague: P. Hobza, D. Nachtigallova **T. Zeleny** (DNA etc.); J. Pittner (Dynamics) Lubbock: Adelia Aquino, Bill Hase

Lubbock 2011



