

A

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módszerei

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"...tunc iusti fulgebunt sicut sol in regno Patris eorum..."
(Mt 13,43).

This work has been dedicated to the memory of
Prof. Ede Kapuy (*1928 - †1999)

A**Compendium****of Modern****Quantum****Chemistry****(Theoretical Methods in Structural
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Contents:

Postulates of the Classical and the Non-Relativistic Quantum Mechanics	XIII
INTRODUCTION	2
The advantages of the theory	3
The disadvantages of the theory	3
History of Quantum Chemistry	4
ATOMIC UNITS	6
1. THE HARTREE-FOCK METHOD	6
Orbital-approximation	7
Separation of the eigenvalue problem in \mathcal{L}_2 space	8
Antisymmetry Postulate, Pauli-principle, exclusion principle	9
Slater-determinant	9
Energy expression for spinorbitals	10
Core integrals	10
Coulomb integrals	11
Exchange integrals	11
Unrestricted Hartree-Fock (UHF) method	12
Restricted Hartree-Fock (RHF) method	13
Orbital energies	14
Numerical solution for atoms	15
LCAO-approximation	15
Requirements for the basis set	16
Types of basis sets	16
Slater-type basis (STO)	17
Boys-type basis (GTO)	17
Contracted basis sets	17
Minimal basis set	17
STO-3G	18
4-31G	18
6-31G*	18
6-31G**	18
Determination of the LCAO coefficients (Roothaan-Hall)	19
One-electron integrals	20
Two-electron integrals	20
Special feature of the GTOs	21
Method of the Lagrange-multipliers	22
Overlap matrix	22
Fock-matrix	23
Roothaan-Hall LCAO-SCF equation	23
Unitary transformations	24
Canonical orbitals	25
Hartree's Self-Consistent Field (SCF) method	25
Organization of a simple quantum chemical program	26
Valuation, scaling	27
Method of shared exponents	28
Direct SCF method (Almlöf)	29
Semi-direct SCF method (Ahlrichs)	30
Multiplicative Integral Approximation, MIA (von Alsenoy, Pulay)	30

2. DERIVATIVES	31
Potential surface	31
External perturbations	31
Notations	32
Calculation of the derivatives	33
The advances of the analytical method	33
The drawbacks of the analytical methods	34
Summary of the different derivatives	34
Calculation of the derivatives	35
1.§. Variational deduction without constraints	36
2.§. Variational deduction with constraints	39
3.§. Non-variational deduction	39
4.§. First derivative of the Hartree-Fock energy	40
Popular/notable ab initio program systems	41
Gaussian (Pople's group)	41
PQS (Pulay)	41
CADPAC (Handy)	41
TurboMol (Ahlrichs)	42
Spartan (Hehre)	42
AcesII (Bartlett & Stanton)	42
Determination of the geometry	42
Example: <i>cyclo</i> -oktatetraene	44
Jahn-Teller principle	45
Standard examples for the Jahn-Teller effect	47
Estimation of the Hessian	47
Coordinates: Cartesians and internals	47
The character of stationary point	48
Saddle points	48
Second derivatives	49
Reaction paths	50
Nonorthogonal (nonunitary) transformations	51
Solutions for the lack of uniqueness of reaction path	53
Example: The HF-based SQM Force Field method	54
Yeljasevich-Wilson vibrational equation	54
SCALE3 program	55
A priori SQM Force Fields	56
Natural Internal Coordinates (NICs)	57
INTC program	60
Recommended Internal Coordinate System (pre-NICs)	61
Sample output of the INTC program	62
Internal coordinates and orthogonality	63
3. POST-HARTREE-FOCK METHODS	66
Disadvantages of the Hartree-Fock method	66
Full Configurational Interaction (Full CI)	67
Perturbation Theory	68
Møller-Plesset (MP) partition of the Hamiltonian	69
First-order correction	69
Second-order correction	69
Slater-rules	70

Brillouin-theorem	71
Many Body Perturbation Theory	72
MP2	73
Coupled Cluster (CC) methods	73
Variational (truncated) CI method	74
Size-consistency (size-extensivity)	75
Computational requirements	76
Scaling of different post-HF methods	77
Categories of the electron correlation (Sinanoglu)	77
Dynamic correlation	77
Nondynamic correlation	78
Example: ethylene	78
When the nondynamic correlation is important?	79
Example: Dissociation of H₂	80
RHF determinant	81
Heitler & London (Valence Bond VB)	82
Multiconfigurational Hartree-Fock (MC-SCF)	83
Doubly occupied, active (fractionally occupied), unoccupied orbitals	85
Complete Active Space (CAS-SCF)	85
Generalized Valence Bond (GVB) method	86
Projected UHF	88
First-order reduced density matrix	89
Second-order reduced density matrix	89
Natural spinorbitals (Löwdin)	90
First-order reduced spinless density matrix	90
Natural orbitals (Löwdin)	90
UHF start orbitals for CAS-SCF	92
Rule for fractionally occupied (active) orbitals	93
Linnett's theory (double quartet)	95
UNO-CAS method (Pulay)	96
Problematic features of the MC-SCF method	97
4. DENSITY FUNCTIONAL METHODS	99
New partition of the Hamiltonian	100
Hohenberg-Kohn I. theorem	101
Consequences	102
Holographic electron density theorem (Mezey)	103
Hohenberg-Kohn II. theorem	103
Kohn-Sham method	105
X_α-method (Slater)	109
Scattered Wave X_α-method (Johnson)	110
Valuation	110
Hartree-Fock-Slater (HFS) method	111
Basis sets in DFT	111
Gauss, Slater, Augmented Plane Waves	112
Fitted density	113
Exchange-correlation (XC) energy	113
Becke's procedure	114

Non-local functional approximations	115
Becke	115
Lee-Yang-Parr (LYP) correlation functional	115
B-LYP	116
B3-LYP	116
Problems of DFT methods	116
Example: DFT-Based SQM Force Field method for N ₂ O ₄	117
Natural Internal Coordinates and Scale Factors for N ₂ O ₄	119
Primitive valence coordinates for N ₂ O ₄	120
Theoretical and experimental structural parameters for N ₂ O ₄	121
Calculated and experimental vibrational spectra for N ₂ O ₄	122
5. MAGNETIC PROPERTIES; NMR CHEMICAL SHIFTS	123
Electric field, magnetic induction, vector potential	124
External fields	124
Homogeneous magnetic field	124
Nuclei: magnetic dipoles	125
Implementation into the Hamiltonian	125
Chemical shift (shielding)	127
Isotropic and anisotropic parts	127
Gauge-invariance	127
Gauge Invariant Atomic Orbitals (GIAO, London)	129
GIAO-GTO basis set (Pulay)	129
Individual Gauge for Localised Orbitals (IGLO, Kutzelnigg)	130
Localised Orbital Local Origin (LORG)	130
EPILOGUE	131
Problems in the future	131
Suggested reading	132
ACKNOWLEDGMENT	133
APPENDIX I	134
The Born-Oppenheimer approximation	134
APPENDIX II	155
GDIIS - Geometry Optimization by Direct Inversion in the Iterative Subspace	143
APPENDIX III	
Avoided crossing, conical intersection	163
APPENDIX IV	
A brief description of the independent particle (Hartree-Fock) model	173
ERRATUM	
To the Born-Oppenheimer approximation	179

POSTULATES OF THE CLASSICAL MECHANICS (CM):

I. Physical observables:

Two different sets of the physical observables are distinguished: dynamical variables and parameters. Dynamical variables are represented by continuous and differentiable functions which are real functions of real variables. In CM each dynamical variable can be expressed by the Cartesian $\underline{r}_1 = \underline{r}_1(t)$, $\underline{r}_2 = \underline{r}_2(t), \dots, \underline{r}_N = \underline{r}_N(t)$ position vectors and $\underline{p}_1 = \underline{p}_1(t)$, $\underline{p}_2 = \underline{p}_2(t), \dots, \underline{p}_N = \underline{p}_N(t)$ linear momentum vectors (at t point in time) of the m_1, m_2, \dots, m_N masses of points of mass constructing a system (N is the number of the points of mass):

$$A = A(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N, \underline{p}_1, \underline{p}_2, \dots, \underline{p}_N; t)$$

Notes: 1. The mass and the time are not dynamical variables rather parameters. 2. Even if the time does not appear in the expression of a dynamical variable in an explicit mode, it can be considered as the function of the time implicitly (via the position and linear momentum vectors). 3. In principle, infinite number of dynamical variables can be defined. 4. Thus, any system of units can be defined by fixing the units of \underline{r} , \underline{p} and t (or, of any three independent observables, like in the CGS system). 5. The position vectors can be called as trajectories, or orbital-functions. The later name is in an antagonistic relationship with the quantum mechanical/chemical "orbitals". 6. Introducing the concept of the electric charge (as a new parameter, in the electrostatics), and giving the form of the attraction between the charged points of mass (i.e., the Coulomb-law), with the use of the corresponding potential function (Coulomb-potential) we could apply the CM (i.e., it does not matter where the potential function was originated). Due to the introduction of the electric charge the use of a new physical substantial observable could be necessary.

Examples (for simplicity, the $N = 1$ case is given):

Dynamical variable:	Notation:	Function:
Position	\underline{r}	$\underline{r}(t) = x(t)\underline{e}_1 + y(t)\underline{e}_2 + z(t)\underline{e}_3$
Linear momentum:	\underline{p}	$\underline{p}(t) = p_x(t)\underline{e}_1 + p_y(t)\underline{e}_2 + p_z(t)\underline{e}_3$
Velocity:	\underline{v}	$\underline{v}(t) = (1/m)\underline{p}(t)$ Although $\underline{v}(t)$ can be expressed as the first derivative of the position vector, has to be considered as independent dynamical variable: a function and its derivative are linearly independent.
Force:	\underline{F}	Here we confine ourselves to the so-called conservative force fields: in this case the force is the only function of the position [$\underline{F} = \underline{F}(\underline{r})$], moreover, a V potential function exists whose negative gradient is the force [$\underline{F} = -\underline{\nabla}V$]. Such a system is called as conservative system.
Potential energy:	V	$V = V(\underline{r})$ (see above)
Angular momentum:	\underline{l}	$\underline{l} = \underline{r} \times \underline{p}$
Momentum of force:	\underline{N}	$\underline{N} = \underline{r} \times \underline{F}$
Kinetic energy:	T	$T = \underline{p}^2/2m$
Total energy:	H	$H = \underline{p}^2/2m + V(\underline{r})$ In the case of a conservative system H is time-independent)

II. The physical state:

The physical state of a conservative system is completely characterized by giving the Cartesian $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N$ position vectors and $\underline{p}_1, \underline{p}_2, \dots, \underline{p}_N$ linear momentum vectors (at a t point in time).

Notes: 1. The physical state of a system can be represented (at a t point of time) by a point of the hypothetical $6N$ -dimensional 'phase space' constructed by the $3N$ Cartesian position coordinates and $3N$ linear momentum coordinates. 2. In case of a probability description of the physical state of a system, at a certain t point of time a solely point of the phase space could possess a non-zero (1.000) value (confidence).

III. The measurement:

In case of an ideally accurate measurement, at a t point in time the observed values of the dynamical variables are the values of the functions which represent them. In principle, the measurement can be carried out with arbitrary accuracy, even simultaneously for any number of the dynamical variables if needed.

IV. Equation of motion:

The description of the behavior of a system in time (i.e., the change of its physical state) can be described by the Newtonian equations of motion:

$$\underline{F}_i = m_i \ddot{\underline{r}}_i, \quad (i = 1, 2, \dots, N),$$

where \underline{F}_i is the force vector acting on the i th point of mass, and $\ddot{\underline{r}}_i$ is the second derivative (according the time) of the position vector of the i th point of mass.

Notes: 1. We have to solve 3 second order differential equation for each point of mass, totally $3N$ second order differential equations, with completely $6N$ parameters which fix the initial physical state of the system. 2. The subsequent physical state of the system can be computed unambiguously (causality, what is more, determinism). 3. There is no distinguished system of coordinates (only useful, or less useful); in the axioms I-IV the Cartesian coordinate system has been applied. Instead of that we could choose arbitrary curvilinear q_1, q_2, \dots, q_f (so-called generalized) coordinates and p_1, p_2, \dots, p_f generalized linear momenta (here f is the degree of mechanical freedom; if the number of the restrictions imposed to the system is m , than $f=3N-m$). In this case the Newtonian equations of motion are changed to the so-called Hamiltonian ones. In the latter equations the $H = H(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f, t)$ Hamiltonian function of the system plays a central role. The Hamiltonian function of a conservative system is time-independent and it is equal to the total mechanical energy of the system. 4. The aforementioned equations of motion are time-reversal; i.e., changing the direction of time (substituted its value to $-t$) they yield the same results.

THE AXIOMATIC SUMMARY OF THE NON-RELATIVISTIC QUANTUM MECHANICS (NRQM):

In the NRQM the particles are considered to be point-like and of infinite lifetime. The postulates mentioned below are redundant due to didactical reasons (see Postulate III). Also due to didactical reasons, not the most general form of the postulates is given, we will apply the coordinate representation in L_2 within the frame of the so-called Schrödinger picture. We use the interpretation of the Copenhagen School (CS) as the most generally accepted one.

I. Physical observables:

In the NRQM the parameters are interpreted as in the CM; however, each A dynamical variable is represented by a (linear and) self-adjoint operator whose form is chosen in a Cartesian coordinate system according to the fulfillment of the following substitutions in the expression of the corresponding dynamical variable used in CM:

$$\underline{r}_i \rightarrow \hat{\underline{r}}_i \equiv \hat{x}_i \underline{e}_1 + \hat{y}_i \underline{e}_2 + \hat{z}_i \underline{e}_3 \equiv \underline{r}_i \cdot, \text{ (i.e., } \hat{x}_i \equiv x_i \cdot \text{; etc.)}$$

$$\underline{p}_i \rightarrow \hat{\underline{p}}_i \equiv \hat{p}_{x_i} \underline{e}_1 + \hat{p}_{y_i} \underline{e}_2 + \hat{p}_{z_i} \underline{e}_3 \equiv -i\hbar \underline{\nabla}_i \cdot, \text{ (i.e., } \hat{p}_{x_i} \equiv -i\hbar \frac{\partial}{\partial x_i} \text{; etc.,}$$

$$\hbar = 1.0545887 \cdot 10^{-34} \text{ Js}$$

so we get:

$$\hat{\mathbf{A}} = \mathbf{A}(\hat{\underline{r}}_1, \hat{\underline{r}}_2, \dots, \hat{\underline{r}}_N, \hat{\underline{p}}_1, \hat{\underline{p}}_2, \dots, \hat{\underline{p}}_N; \mathbf{t}) .$$

Notes: 1. Here \hbar is the so-called Dirac-constant; its value is equal to the Planck-constant/ 2π . 2. In the aforementioned expression of the $\hat{\mathbf{A}}$ operator explicit depending of time can be thought only (so-called Schrödinger-picture). 3. By means of the Hamilton operator of the NRQM corresponding to the Hamiltonian function of CM, a relationship can be constructed between the analogs of a system described in the NRQM and CM, respectively: if the system's Hamilton-operator is time-independent, we call it to be conservative in the NRQM as well. All the operators of any important dynamical variables of a conservative system (e.g., atoms and molecules) are time-independent. 4. In case of the construction of the operators of dynamical variables not known in CM the aforementioned procedure can not be carried out (in these cases we have to use a trial-and-error method). In the NRQM such a dynamical variable is the spin (see Postulate IA below).

Examples (for simplicity, the $N = 1$ case is given):

Dynamical variable: Operator:

Angular momentum : $\hat{\underline{L}} = \hat{\underline{r}} \times \hat{\underline{p}} = \hat{L}_x \underline{e}_1 + \hat{L}_y \underline{e}_2 + \hat{L}_z \underline{e}_3 ,$

$$\text{where } \hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right),$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right),$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right).$$

$$\text{then } [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \text{ (and cyclically); } [\hat{\underline{L}}^2, \hat{L}_u] = \hat{0} \text{ (u = z, x, y).}$$

Kinetic energy : $\hat{\underline{T}} = \frac{\hat{\underline{p}}^2}{2m} = -\frac{\hbar^2}{2m} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \cdot \Delta$

Total mechanical energy : $\hat{\mathbf{H}} = \hat{\underline{T}} + \hat{\underline{V}} = -\frac{\hbar^2}{2m} \cdot \Delta + V(\underline{r})$

IA. The spin:

In the NRQM beyond its mass and charge, each particle is characterized by a new dynamical variable, the spin (inner angular momentum) that can not be deduced from the expression of position- and linear momentum vectors (evident that it is unknown in CM). For the characterization of the spin the \hat{s} vector operator is employed; for its components and square the same commutable conditions have to be valid as for the \hat{L} angular momentum operator were deduced (hereafter the latter will be called as orbital angular momentum):

$$[\hat{s}_x, \hat{s}_y] \equiv i\hbar\hat{s}_z \text{ (and cyclically); } [\hat{s}^2, \hat{s}_z] \equiv ([\hat{s}^2, \hat{s}_x] \equiv [\hat{s}^2, \hat{s}_y] \equiv) \equiv \hat{O}.$$

With the help of the aforementioned commutators the eigenvalues of the \hat{s}^2 and \hat{s}_z operators can be deduced:

$$\begin{aligned} \hat{s}^2 \text{ eigenvalue } s &\rightarrow \lambda\hbar^2 = s(s+1)\hbar^2; \\ \hat{s}_z \text{ eigenvalue } s &\rightarrow \xi\hbar = +s\hbar, (s-1)\hbar, (s-2)\hbar, \dots, -s\hbar, \end{aligned}$$

where the s spin quantum number is characteristic for the quality of the particle, whilst the ξ spincoordinate (or, spin-component quantum number) raises the particle's degrees of mechanical freedom from $f = 3$ to $f = 4$.

Notes: 1. In case of the electron the value of the spin quantum number is $s = 1/2$. 2. The raise of the degrees of mechanical freedom can be interpreted as the electron can be considered in a given (x,y,z) position of the space by $\xi = +1/2$ or $\xi = -1/2$ spincoordinate: (x,y,z, ξ). 3. Naturally, the aforementioned comments correspond to the case $N = 1$ particle. In a many-particle system, the corresponding resultant vectors have to be computed obviously whose eigenvalues are characteristic for the physical state of the system (see Postulate II). 4. According to the observations the electron spin has $g \approx 2,0023$ (so-called Landé-factor) times greater magnetic dipole moment as the orbital angular momentum does. This can be deduced from the Dirac-equation of the Relativistic Quantum Mechanics (RQM).

II. The physical state:

In the NRQM the physical state of a system can be unambiguously characterized by the normalized Ψ function of the L_2 space; the Ψ function is depending on the all coordinates of the all particles: $\Psi = \Psi(\underline{r}_1, \xi_1, \underline{r}_2, \xi_2, \dots, \underline{r}_N, \xi_N; t)$, where \underline{r}_i and ξ_i are the position vector and the spincoordinate of the i th particle, respectively.

Notes: 1. The possible values of the ξ spincoordinate are the eigenvalues of the \hat{s}_z spin-component operator (see Postulate IA). In case of an electron these are $+1/2$ and $-1/2$. 2. The name of the Ψ function is state vector/function or wave function. 3. The Ψ state vector does not mean "charge cloud" or "matter wave"; his meaning is nearer to "probability wave". The state vector has no direct meaning for fermions (see below) like, i.e., the electrons, so it is evident that it can not be measured either. However, the meaning of $|\Psi|^2$ is probability-density; the probability to find the 1. particle around the \underline{r}_1 point in a dV_1 volume with ξ_1 spincoordinate, the 2. particle around the \underline{r}_2 point in a dV_2 volume with ξ_2 spincoordinate, ..., and the N th particle around the \underline{r}_N point in a dV_N volume with ξ_N spincoordinate is given by:

$$|\Psi(\underline{r}_1, \xi_1, \underline{r}_2, \xi_2, \dots, \underline{r}_N, \xi_N; t)|^2 dV_1 d\xi_1 dV_2 d\xi_2 \dots dV_N d\xi_N,$$

where the role of $d\xi_i$ -s are symbolic only (in fact summation and not integration). 4. Used notations: $dx_i dy_i dz_i = dV_i$; $dV_i d\xi_i = d\tau_i$; $dV_1 dV_2 \dots dV_N = dV$; $d\tau_1 d\tau_2 \dots d\tau_N = d\tau$. 5. The Ψ state vector is not dimensionless: since $\langle \Psi | \Psi \rangle = 1$, e.g., for $N = 1$ particle the dimension of Ψ is $L^{-3/2}$, where L is the

dimension of the length. 6. The L_2 space mentioned before in the Postulate II differs from that of the 'L₂ linear vector space of the one-variable functions', rather being the space of functions with $3N$ (or, together with the spincoordinates $4N$) variables. The generalization is simple: an arbitrary m -variable function can always be written as the linear combination of products of one-variable functions:

$$\Psi(q_1, q_2, \dots, q_m) = \sum \sum \dots \sum C_{ij\dots s} \varphi_i(q_1) \varphi_j(q_2) \dots \varphi_s(q_m),$$

where the first summation goes along i , the 2nd one along j , ..., the m -th summation along s ; the $\varphi_k(q_l)$ functions ($k = 1, 2, \dots, \alpha_{q_l}$, where α_{q_l} is the dimension of the space of functions of q_l variable) form

the complete orthonormal (basis) set in the L_2 space of q_l variable, the $C_{ij\dots s}$ constants are the linear coefficients. Alternatively, we can use a much compact notation, as the L_2 space of many-variable functions is the direct product of the one-variable L_2 spaces: $L_2 \otimes L_2 \otimes L_2 \otimes \dots \otimes L_2$. 7. In case of NRQM it can be easily shown that the dimension of the phase space is only $3N$ (or, together with the spincoordinates is $4N$). However, due to the probability description of the quantum mechanics, the physical state of the system at a certain t point in time is represented by a function and not by a single point as in the CM.

III. The measurement:

In the NRQM the observation of an A dynamical variable on a system characterized by a state vector Ψ results any one of the eigenvalues of the \hat{A} operator representing the A dynamical variable (in case of idealistically accurate measurement), whilst the Ψ state function of the system goes 'instantaneously' to the eigenfunction of the \hat{A} operator (corresponding to the just measured eigenvalue). We distinguish two different cases:

1.) If the state vector of the system, preceded dt in time the point in time of the measurement, is equal to an eigenfunction of the \hat{A} operator, certainly we get the corresponding eigenvalue as the result of the measurement:

$$\hat{A}\Psi = a\Psi.$$

[In the 1.) case the value of A is 'sharply' defined (i.e., $\delta A = 0$, deviationless) on the system; with other words, being carried out 'very much' number of measurements (precisely, if the number of the measurements goes to infinity) the \bar{A} mean value of the measurements is $\bar{A} = a$, i.e., certainly an eigenvalue (the new concepts will be detailed below)].

2.) If the state vector of the system, preceded dt in time the point in time of the measurement, does not equal to any eigenfunction of the \hat{A} operator, we can not predict surely the result of a single measurement, only

α) the \bar{A} mean value (or, the quantum mechanical expectation value) in case where the number of the individual measurements goes to infinity:

$$\bar{A} \equiv \frac{\langle \Psi | \hat{A} \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (\text{this is not necessarily equal of any eigenvalue}), \text{ and the } \delta A$$

deviation:

$$\delta A \equiv \overline{(\hat{A} - \bar{A})^2}^{1/2}$$

β) or rather the $|c_i|^2$ probability of the measurement of an eigenvalue:

$$|c_i|^2 = |\langle \varphi_i | \Psi \rangle|^2, \text{ (where } \hat{A}\varphi_i = a_i\varphi_i, \text{ and } \Psi = \sum_i c_i \varphi_i \text{).}$$

[In the 2.) case the value of A is not sharply defined on the system (i.e., the value is not deviationless according to the interpretation of the CS].

Notes: 1. In the 2β) case we have supposed that Ψ is normalized, so, naturally, $\sum |c_i|^2 = 1$. 2. Note that according to the concept of CS in the 2.) case the “exact” value of the dynamical variable A is not “accurately” defined at all within the δA deviation. Thus, the δA deviation does not limit the recognition, because there no anything which can be understand better. 3. We have to note the so-called Heisenberg-type uncertainty relations as well. These, according to the CS, do not limit the recognition, and never will be a loophole against them. According to that, at the simultaneous measurement of two dynamical variable (let say A and B) on a system of Ψ state, their deviations are not always independent of each others one as follows:

$$\delta A \cdot \delta B \geq \frac{1}{2} \cdot \left| \frac{\langle \Psi | [\hat{A}, \hat{B}] \Psi \rangle}{\langle \Psi | \Psi \rangle} \right| .$$

According to this dynamical variables represented by non-commutable operators bother the measurement of each other (they have no common eigenvector-system), so they can be measured on the system only separately. In the opposite case there is no such bothering. In a special case when $A = x$ and $B = p_x$, we get $\delta x \cdot \delta p_x \geq \hbar/2$. Thus it is assorted with the theory that the electron can be particle-like ($\delta x \approx 0$) or wave-like ($\delta p_x \approx 0$) physical state, although the NRQM does not predicate any “duality”: between the aforementioned two extreme cases there are infinite number of intermediate *physical states* as well. The electron is a point-like particle in NRQM henceforward. It has to be emphasized that the $\delta E \cdot \Delta T \geq \hbar/2$ Heisenberg-Bohr-type energy-time “blurriness-relation” has no relation to the aforementioned uncertainty relations (within the frame of the NRQM). Here a formal similarity can be mentioned, because the time has no operator, thus it has not any deviation either. The $\delta E \cdot \Delta T \geq \hbar/2$ relationship can be deduced by the CSMCO (see below), together with the so-called quantum mechanical time-derivative within the frame of the NRQM. 4. The system could be brought into a “pure” (i.e., quantum mechanically unequivocally determined) physical state e.g., by observation. A system possessing f degree of freedom could be brought into such state by the *simultaneous* measurement of dynamical variables represented by $\hat{A}_1, \hat{A}_2, \dots, \hat{A}_f$ self-adjoint and mutually commutable operators (Complete Set of Mutually Commutable Operators, CSMCO): such a measurement is called as complete measurement. The CSMCO can be picked up (fixed) in many ways; for our gals the most profitable CSMCO contains always the Hamiltonian operator of the system. It is not always necessary to make a complete measurement in order to get a pure state of the system. In case of chemical systems (atom, molecules) the ground state is often non-degenerated. In such cases it is enough to measure the energy and this yield a pure state.

III. Equation of motion:

In the NRQM the time dependence of the Ψ state vector is determined by the so-called time-dependent Schrödinger-equation, as follows:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad ,$$

where \hat{H} is the Hamiltonian operator of the system.

Notes: 1. In the time-dependent Schrödinger equation the roles of the coordinates and the time is not “symmetrical”; this is not erroneous because our theory is non-relativistic. 2. In the possess of the initial physical state, the physical state of the system can be computed for any point in time later (causality), however, due to the probability description there is no determinism. 3. The aforementioned Schrödinger-equation is time-reversal as well, because the square of the absolute value of the Ψ state vector has only a physical meaning for fermions. 4. The measurement can not be described by the help of the time-dependent Schrödinger equation causally either: all the previous trials (among them those which included the interaction between the system and the measurement apparatus), had fault.

V. Antisymmetry and symmetry:

In the NRQM the particles characterized by identical inner state attributors (mass, charge, spin, etc.) have to be considered as *identical* particles. The state vector of the fermions (electron, proton, neutron, etc.) of half-spin ($s = 1/2, 3/2, \dots$) is antisymmetric for the exchange of the all (space and spin) coordinates of the identical particles:

$$\Psi(\underline{r}_1, \xi_1, \underline{r}_2, \xi_2, \dots, \underline{r}_i, \xi_i, \dots, \underline{r}_j, \xi_j, \dots, \underline{r}_N, \xi_N) = -\Psi(\underline{r}_1, \xi_1, \underline{r}_2, \xi_2, \dots, \underline{r}_j, \xi_j, \dots, \underline{r}_i, \xi_i, \dots, \underline{r}_N, \xi_N)$$

(i.e., the i th and j th particles are identical fermions).

The state vector of bosons (photon, π -meson, etc.) of integer-spin ($s = 0, 1, 2, \dots$) is symmetric for the exchange of the all coordinates of the identical particles:

$$\Psi(\underline{r}_1, \xi_1, \underline{r}_2, \xi_2, \dots, \underline{r}_i, \xi_i, \dots, \underline{r}_j, \xi_j, \dots, \underline{r}_N, \xi_N) =$$

$$\Psi(\underline{r}_1, \xi_1, \underline{r}_2, \xi_2, \dots, \underline{r}_j, \xi_j, \dots, \underline{r}_i, \xi_i, \dots, \underline{r}_N, \xi_N)$$

(i.e., the i th and j th particles are identical bosons).

Notes: 1. The resultant of the aforementioned antisymmetry postulate is the so-called Pauli-principle (within the one-particle approximation!). 2. Since the NRQM does not know trajectories, particles possessing the same set of inner state attributors can not be distinguished by their outer state attributions (trajectories) either. Even if we have isolated the identical particles at the start of the time by a non-permeable wall, after a small amount of time the probability function of the particles will overlap and can not be used as outer state attributors. 3. With the help of a simple rule we can decide whether a particle composed by elementary particles are fermions or bosons. In case of odd number of fermions the composite particle is fermion, on the other hand, composite particles containing even number of fermions play the role of bosons. In case of neutral atoms the sum of the atomic number and the atomic weight is crucial: even (boson), odd (fermion). 4. At the description of the ideal gases consisting of fermions or bosons we have to use different statistics. In the CM (Postulate V is not known) the Maxwell-Boltzmann statistics is used, in case of the NRQM the Fermi-Dirac statistics has to be applied for fermions, and the Bose-Einstein statistics is used for bosons. The Fermi-Dirac statistics is important in the metal and semiconductor physics, the Bose-Einstein statistics is important in case of atoms or molecules at low temperatures (rarely) only. In the chemistry the use of the Maxwell-Boltzmann statistics is convenient generally.

VI. Irreducibility:

The eigenfunctions of the \hat{H} operator are the basis functions of the irreducible representations of the symmetry group of the system (that is, all the eigenfunctions of the Hamiltonian operator lie in the subspaces belonging to various irreducible representations of the system's symmetry group.

Notes: 1. The spatial symmetry groups of the Hamiltonian operator of atoms and molecules are called as point groups (due to the fact that any of the symmetry operations allows invariantly at least one point (the center-of-mass of the nuclear frame) of the system). 2. The obligate degeneracy is caused always by the symmetry; however, we know the so-called accidental degeneracy as well: the latter usually occurs at special external circumstances, e.g., at certain value of special field strength), or at special choose of a structural parameter (e.g., bond length). 3. The Hamiltonian operator of molecules can be "decoupled" for the sum of electron structural, vibrational and rotational Hamiltonians in the adiabatic Born-approximation, the group theory can be applied in each topic separately at the quantum mechanical description. 4. At the use of the restricted Hartree-Fock (H-F) procedure the aforementioned Postulate is valid for the eigenfunctions of the Fock-operator (i.e., for the one-electron functions, or quantum mechanical "orbitals"). 5. With the help of the Postulate VI the Postulate V can be reformulated: the state vector of particles of integer-spin make a basis for the totally symmetrical irreducible representation of the $N!$ order S_N 'symmetrical group', whilst the state vector of half-spin particles transforms as the one-dimensional antisymmetric irreducible representation of the same group. 6. The character table of a point group does not say anything about the spin degeneracy (multiplicity) of a state: this has to be investigated separately.

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- [3] P. O'D. Offenhartz, *Atomic and Molecular Orbital Theory*, McGraw-Hill Book, New York, 1970.
- [4] E.C. Kemble, *The Fundamental Principles of Quantum Mechanics with Elementary Applications*, Dover Publications, New York, 1958.
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A

Compendium

of Modern

Quantum

Chemistry

G. Pongor

INTRODUCTION

...The number of the organic compounds (C,H,N,O,S) whose molecular weight is less than 750 g/mol, has been estimated to 10^{200} .

USA National Research Council, 1995.

...Chemistry: originally and traditionally an empirical science.

"Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry - an aberration which is happily almost impossible - it would occasion a rapid and widespread degeneration of that science."

A. Comte, 1830.

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

P.A.M. Dirac, 1929.

Appearance of the computers

"In the past quantum chemists believed that their foremost duty was to develop approximate methods with which one could reproduce physical quantities that can be measured accurately. Obviously, it will always be necessary to check new theoretical methods but the principal duty is becoming more and more the computation of (in principle measurable) physical quantities which are not or not easily amenable to experiments (e.g., properties of short-lived species). It is increasingly the cost which determines whether one computes a given physical quantity or decides to measure it..."

E. Kapuy, 1969.

In our days the theory started to play a commensurable role with the experiments in the chemistry. Computational results are often published even in preparative/experimental papers.

The advantages of the theory:

- 1.) There are NO qualitative problems (like identification);**
- 2.) Stable molecules as well as transient species can be treated equivalently;**
- 3.) The results are independent from any random noise.**
- 4.) "Easy", safe, rapid method.**

The disadvantages of the theory:

- 1.) To reach the experimental accuracy is very expensive and difficult;**
- 2.) For complex systems (many degrees of freedom) can not be applied (thermodynamical averages);**

3.) In many cases the calculations mean "numerical experiments", they do not help to understand the situation...

History of quantum chemistry (Q.C.):

I.) The ancient times of Q.C.: 1927-1950

The fundamental bases:

Quantum Mechanics:

A.) W. Heisenberg, *Zeitschrift für Physik*, 1925, 33, 879;

B.) E. Schrödinger, *Annalen der Physik*, 1926, 79, 361, 489.

First paper in Q.C.:

W. Heitler & F. London, *Zeitschrift für Physik*, 1927, 44, 455 (H₂);

The first three books on Q.C.:

1.) H. Hellmann: *Einführung für die Quantenchemie*, Franz Deuticke, Leipzig, 1937;

2.) Pál Gombás: *Bevezetés az atomfizikai többtestprobléma kvantummechanikai elméletébe*, Kolozsvár, 1943 (today: Cluj, Romania);

3.) H. Eyring, J. Walter & G.E. Kimball: *Quantum Chemistry*, John Wiley & Sons, 1944.

The computational speed: ~10⁻¹ Flops

II.) The middle age of Q.C.: 1950-1980

expensive "big" computers

The computational speed: ~100 MFlops

Computational efficiency: 10⁵ - 10⁶ \$/MFlops

NB: MFlops = Million Floating Point Operations per Second

III.) The modern times of Q.C.: 1980-today

"cheap", very effective workstations

Computational efficiency: <100 \$/MFlops

IV.) The future of Q.C.: (just started!)

parallel computational systems

The computational speed: > GFlops

have reached the TFlops, (T=tera= 10^{12})

Blue Gene Project (USA): 280 TFlops

(2005, LLNL, 2^{16} nodes)

The grow of the computational efficiency is quite even, by about a factor 2/year.

The key of the development of Q.C.:

The computers (which also stimulated the development of theoretical methods). Since 1970 the computational speed increased by 6 orders of magnitude, and, approximately, in this growing about 3-4 orders of magnitude is the developing of the computers, and 2-3 orders of magnitude is the perfecting of the procedures and programs.

Today:

treating of large molecules; molecular graphics is included into the big program systems. Not only the specialists but also the preparative chemists apply the computational results - a big break-through of the quantum chemistry.

ATOMIC UNITS:

Action	$\hbar = h/2\pi = 1.05457266(63) \cdot 10^{-34}$	J s
Mass	$m_e = 9.1093897(54) \cdot 10^{-31}$	kg
Charge	$ e = 1.60217733(49) \cdot 10^{-19}$	C
Length	$a_0 = 5.29177249(24) \cdot 10^{-11}$	m

("Quantities, Units and Symbols in Physical Chemistry", 2nd ed., IUPAC, Physical Chemistry Division, Blackwell Science, Oxford, 1993.)

energy $\epsilon_h = 4.3597482(26) \cdot 10^{-18}$ J

time $t_0 = 2.4188843341(29) \cdot 10^{-17}$ s

1. THE HARTREE-FOCK METHOD

n electrons are moving in the field of the fixed nuclei (Born-Oppenheimer approximation → see Appendix I)

The non-relativistic electronic Hamiltonian:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \Delta_i - \sum_{i=1}^n \sum_{a=1}^N \frac{Z_a}{r_{ia}} + \sum_{1=i < j}^n \sum \frac{1}{r_{ij}} + \sum_{1=a < b}^N \sum \frac{Z_a Z_b}{R_{ab}}$$



**this term
is constant
for fixed
nuclei**

The H-F method corresponds for the ground state (but can be generalized also for excited states...)

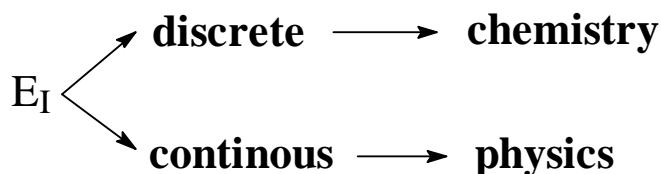
The electronic Schrödinger Equation:

$$\hat{H}\Psi_I(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_n) = E_I \Psi_I(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_n)$$

where $\underline{d}_i = x_i, y_i, z_i, \xi_i$

(spatial and spin coordinates:

$-\infty \leq x_i, y_i, z_i \leq \infty$; $\xi_i = \pm 1/2$).



naturally, $|\Psi_I|^2$ is the probability density:

$$\int_{\tau} |\Psi_I(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_n)|^2 d\tau_1 d\tau_2 \cdot \dots \cdot d\tau_n = 1 \text{ (normalization)}$$

In the absence of ext. magnetic field:

real Ψ functions.

Orbital-approximation:

A two-variable function $F(x_1, x_2)$ is usually more complicated than the product of two single-variable functions $[f(x_1)g(x_2)]$

It is evident that the expression of $\Psi_I(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_n)$ using one-electron functions (orbitals) is of essential importance, but it is only approximately true...

$$\hat{H} = \sum_{i=1}^n \left[-\frac{1}{2} \Delta_i - \sum_{a=1}^N \frac{Z_a}{r_{ia}} \right] + \sum_{1=i < j}^n \sum_{i < j}^n \frac{1}{r_{ij}} = \sum_{i=1}^n \hat{h}_i + \sum_{1=i < j}^n \sum_{i < j}^n \frac{1}{r_{ij}}$$

↑
 ...because of
 this term
 (repulsion)

Let it be

$$\hat{A}(x, y) = \hat{A}^{(1)}(x) + \hat{A}^{(2)}(y), \text{ and let them be}$$

$$\hat{A}^{(1)}(x) f_i^{(1)}(x) = a_i^{(1)} \cdot f_i^{(1)}(x)$$

$$\hat{A}^{(2)}(y) g_j^{(2)}(y) = a_j^{(2)} \cdot g_j^{(2)}(y)$$

[\hat{A} , $\hat{A}^{(1)}$ and $\hat{A}^{(2)}$ are self-adjoint operators!]

then the eigenproblem of $\hat{A}(x, y)$ can be exactly
 expressed as

$$\hat{A}(x, y) f_i^{(1)}(x) g_j^{(2)}(y) = [a_i^{(1)} + a_j^{(2)}] f_i^{(1)}(x) g_j^{(2)}(y)$$

(c.f. also size-consistency...)

Accordingly we suppose:

$$\Psi(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_n) \approx \phi_1(\underline{d}_1) \cdot \phi_2(\underline{d}_2) \cdot \dots \cdot \phi_n(\underline{d}_n)$$

"Hartree-product"

where the one-electron functions are the
 so-called spin-orbitals

$$\phi_k(\underline{d}_k) = \phi_k(x_k, y_k, z_k, \xi_k) = \phi_k(\underline{r}_k, \xi_k)$$

Unfortunately, the Hartree-product does NOT satisfy
 the Antisymmetry Postulate of the quantum
 mechanics, thus it is NOT a regular approximate
wave function (= trial function, "Ansatz", $\tilde{\Psi}$).

**Antisymmetry Postulate:
for electrons (identical fermions):**

$$\Psi(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_i, \dots, \underline{d}_j, \dots, \underline{d}_n) = -\Psi(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_j, \dots, \underline{d}_i, \dots, \underline{d}_n)$$

The Pauli-principle (exclusion principle) is a direct consequence of the Antisymmetry Principle for the case of the orbital approximation. The Antisymmetry Principle (or, the Pauli-principle) is essential for the description of the shell structure; without it we would not be able to give even a first-order approximation.

The simplest trial function is the Slater-determinant:

$$\tilde{\Psi} = \tilde{\Psi}(\underline{d}_1, \underline{d}_2, \dots, \underline{d}_n) = N \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_n(2) \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \phi_1(n) & \phi_2(n) & \dots & \phi_n(n) \end{vmatrix}$$

[where we have used the short notation

$$\phi_k(\underline{d}_k) \equiv \phi_k(x_k, y_k, z_k, \xi_k) \equiv \phi_k(k)]$$

The Hamiltonian is not separable for the electron coordinates, but we can average the repulsion.

How to find the spin-orbitals?

Variational Theorem → minimization:

$$W = \frac{\langle \tilde{\Psi} | \hat{H} \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \rightarrow \min$$

where W is the expectation value of the energy, \hat{H} is the exact non-relativistic Hamiltonian, and $\tilde{\Psi}$ is the trial function.

Many terms,... "It is only a book-keeping problem."
(Pulay)

We can use the following constraint (without loss of the generality):

$$\langle \phi_i | \phi_j \rangle = \int \phi_i^*(\underline{d}) \phi_j(\underline{d}) d\tau = \delta_{ij}$$

orthonormality (ON) of the spin - orbitals
(using, i.e., Schmidt-orthogonalization)

Nota bene: the spin-orbitals are not uniquely determined! The idea of "spin-orbital" exists rather in our mind than in the Nature. The "cut-up" of the many-electron wave function into spin-orbitals is not unambiguous.

Consequence: we can "mix" the spin-orbitals, and can get even "better" set than the "original" one...

After much manipulations ... we get:

$$W = \sum_{k=1}^n h_{kk} + \sum_k \sum_l J_{kl} - \sum_k \sum_l K_{kl}$$

(for ON spin-orbitals)

[where k,l are indices of the spin-orbitals,

$$h_{kk} = \langle \phi_k | \hat{h} \phi_k \rangle = \int \phi_k^*(\underline{d}) \hat{h} \phi_k(\underline{d}) d\tau$$

kinetic energy + skeleton (attract.)

(core integrals)

The electron coordinates are not distinguished because the value of the integral is the same for them.

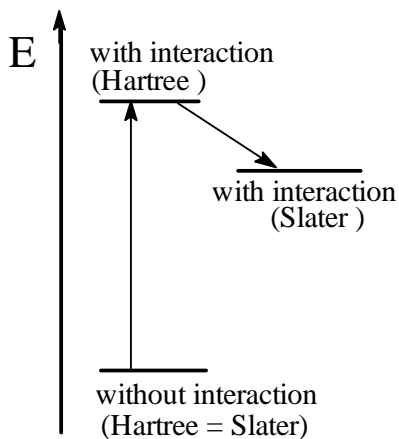
$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

$$J_{kl} = \left\langle \phi_k(\underline{d}_1)\phi_l(\underline{d}_2) \left| \frac{1}{r_{12}} \phi_k(\underline{d}_1)\phi_l(\underline{d}_2) \right. \right\rangle = \iint |\phi_k(\underline{d}_1)|^2 \frac{1}{r_{12}} |\phi_l(\underline{d}_2)|^2 d\tau_1 d\tau_2$$

(coulomb integrals: clear meaning, repulsion of the electron "clouds", always real and positive)

$$K_{kl} = \left\langle \phi_k(\underline{d}_1)\phi_l(\underline{d}_2) \left| \frac{1}{r_{12}} \phi_k(\underline{d}_2)\phi_l(\underline{d}_1) \right. \right\rangle = \iint \phi_k^*(\underline{d}_1)\phi_l^*(\underline{d}_2) \frac{1}{r_{12}} \phi_k(\underline{d}_2)\phi_l(\underline{d}_1) d\tau_1 d\tau_2$$

(exchange integrals: less clear, comes from the determinant directly since the electrons are keeping out of each other; always real and positive, thus reduces the energy comparing it to the Hartree-product...)]



Further approximation:

In d -s the spatial and spin coordinates are treated together.

Spin coordinates are much simpler than spatial ones:

→ only two possible values

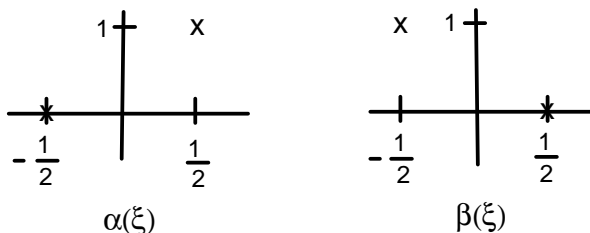
On the other hand, Hamiltonian does NOT contain the spin in the non-relativistic theory (spin-orbital coupling is more important for inner shells of heavy atoms)

→ **We can separate formally the spatial and spin parts of the spin-orbitals:**

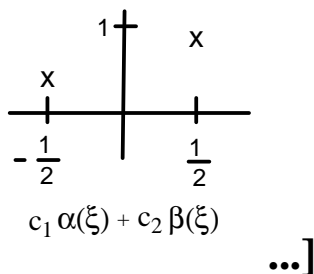
$$\phi(\underline{d}) = \phi(x, y, z, \xi) = u(\underline{r})\eta(\xi) \quad ,$$

where $u(\underline{r})$ **spatial function** (AO or MO)

and the **spin-function** $\eta(\xi) \begin{cases} \alpha(\xi) \\ \beta(\xi) \end{cases}$



[the most general $\eta(\xi)$ function $c_1 \cdot \alpha(\xi) + c_2 \cdot \beta(\xi)$ would be something like this



Unrestricted Hartree-Fock (UHF):

for the α and β cases different $u^\alpha(\underline{r})$ and $u^\beta(\underline{r})$ functions (determined by the Variational Principle)

Problem: \hat{S}_z , \hat{S}^2 and \hat{H} are commuting operators (because the Hamiltonian does not contain the spin!). Unfortunately, due to the Orbital-Approximation, the UHF $\tilde{\Psi}$ trial function is not an eigenfunction of \hat{S}^2 generally (excepting for singlet and high-spin multiplets, it is only that of \hat{S}_z and \hat{H}): $S(S+1)$ eigenvalues,

$$\begin{aligned} S &= 0 \quad \text{singlet,} \\ &= 1/2 \quad \text{doublet,} \\ &= 1 \quad \text{triplet, etc., ...} \end{aligned}$$

Restricted Hartree-Fock (RHF):

It is **NOT** appropriate for $S \neq 0$ cases.

In the singlet case ($S = 0$) the solutions could be "coincided" for "usual" molecules (closed shell, e.g., H_2O)

Condition (not suff.): even number of the electrons

$$u^\alpha(\underline{r}) \equiv u^\beta(\underline{r})$$

The spin-functions are orthonormalized (ON):

$$\begin{aligned} \langle \alpha(\xi) | \alpha(\xi) \rangle &= \int \alpha^*(\xi) \alpha(\xi) d\xi = \\ &= \langle \beta(\xi) | \beta(\xi) \rangle = \int \beta^*(\xi) \beta(\xi) d\xi = 1 \end{aligned}$$

$$\begin{aligned} \langle \alpha(\xi) | \beta(\xi) \rangle &= \int \alpha^*(\xi) \beta(\xi) d\xi = \\ &= \langle \beta(\xi) | \alpha(\xi) \rangle = \int \beta^*(\xi) \alpha(\xi) d\xi = 0 \end{aligned}$$

Let the $u_k(\underline{r})$ functions also ON: $\langle u_k(\underline{r}_1) | u_l(\underline{r}_1) \rangle = \delta_{kl}$
(without loss of generality)

RHF, $^1\tilde{\Psi}$ singlet trial function (eigenfunction of \hat{S}^2 and \hat{S}_z), minimizing W according to the Variational Principle ...

$$h_{kk} = \left\langle \phi_k(\underline{d}_1) \left| \hat{h} \phi_k(\underline{d}_1) \right. \right\rangle = \int u_k^*(\underline{r}_1) \hat{h} u_k(\underline{r}_1) dV_1 \cdot \int |\eta_k(\xi_1)|^2 d\xi_1 = \int u_k^*(\underline{r}_1) \hat{h} u_k(\underline{r}_1) dV_1$$

$$J_{kl} = \left\langle \phi_k(\underline{d}_1) \phi_l(\underline{d}_2) \left| \frac{1}{r_{12}} \phi_k(\underline{d}_1) \phi_l(\underline{d}_2) \right. \right\rangle = \text{separable}$$

$$\int \int |u_k(\underline{r}_1)|^2 \frac{1}{r_{12}} |u_l(\underline{r}_2)|^2 dV_1 dV_2 \cdot \int |\eta_k(\xi_1)|^2 d\xi_1 \cdot \int |\eta_l(\xi_2)|^2 d\xi_2$$

$$K_{kl} = \left\langle \phi_k(\underline{d}_1) \phi_l(\underline{d}_2) \left| \frac{1}{r_{12}} \phi_k(\underline{d}_2) \phi_l(\underline{d}_1) \right. \right\rangle = \text{separable}$$

$$\int \int u_k^*(\underline{r}_1) u_l^*(\underline{r}_2) \frac{1}{r_{12}} u_k(\underline{r}_2) u_l(\underline{r}_1) dV_1 dV_2 \cdot \int \eta_k^*(\xi_1) \eta_l(\xi_1) d\xi_1 \cdot \int \eta_l^*(\xi_2) \eta_k(\xi_2) d\xi_2$$

using appropriate factors, utilizing $J_{kk} = K_{kk}$,
simple form:

$$W = 2 \sum_{k=1}^{n/2} h_{kk} + \sum_k \sum_l (2J_{kl} - K_{kl})$$

(for ON spatial orbitals)

[...Definition of one-electron orbital energies ϵ_k :

$$\epsilon_k \equiv h_{kk} + \sum_l (2J_{kl} - K_{kl})$$

$$\text{Total electronic energy: } \sum_k (\epsilon_k + h_{kk}) = 2 \sum_k \epsilon_k - \sum_k \sum_l (2J_{kl} - K_{kl})$$

A rule of thumb:

$$E_{\text{SCF}} \approx 0.67 \cdot \sum_i \epsilon_i$$

(wrote about it a lot, qualitatively it is good if the *Aufbau-principle* is valid, but not too interesting).

....]

Possibilities of solution:**1.) Numerical:**

Using a grid, numerically calculate the $u_k(\underline{r})$ functions, interpolation, fitting by a "smooth" function...

For **atoms**: $u_k(\underline{r}) = R(r)Y_l^m(\vartheta, \varphi)$

r, ϑ, φ : spherical polar-coordinates

$Y_l^m(\vartheta, \varphi)$ spherical harmonics

(polinoms on a spherical surface)

Charlotte Froese Fischer:

"The Hartree-Fock method for Atoms"

John Wiley & Sons, New York, 1977.

^2He - ... - ^{86}Rn ; (RHF and UHF)

For **molecules**: it seemed 20-25 years ago to be impossible. At present the situation is changeable; main problem: the atoms are spherical, the grids are quadratic ("quadrature of the circle" Pulay). The density is very uneven: at the nuclei large, at another places small... so we have to use:

2.) Basis set:

Using a finite basis set (**LCAO-approximation**):

$$u_k(\underline{r}) = \sum_{p=1}^m \chi_p(\underline{r}) C_{pk}$$



"atomic orbitals"

more correctly: basis functions

MOs are similar to atomic orbitals in the nearby of nuclei → centrally symmetrical → $\chi_p(\underline{r})$ centered on the nuclei.

The basis set is a crucial point of the calculations. It is necessary but not sufficient condition that at least for atoms they must give good results - in this case still possible that for molecules they give bad results...

Test for the basis set: augmenting the basis set by new functions...

Size of the basis set: $m \geq \frac{n}{2}$.

$m < \frac{n}{2}$ impossible (can not mix ON functions using less

b. functions); $m = \frac{n}{2}$ is not appropriate either, not

flexible). Good: $m \approx (1.5 - 15) \times \frac{n}{2}$.

Requirements for the basis set:

- 1.) $m \geq \frac{n}{2}$
- 2.) good description (comparison with other calculations)
- 3.) Make the calculations easier.
- 4.) Must give relatively "independent" description on different parts of the system ("floating" b.f. between atoms - not good)

Types of basis sets:

[Remember!

H-atom: $\Psi_{nlm}(r, \vartheta, \varphi) = R_{nl}(r)Y_l^m(\vartheta, \varphi)$

where $R_{nl}(r)$ contains exponential form

$Y_l^m(\vartheta, \varphi)$ the spherical harmonics]

Slater-type basis (STO):

$$\chi_p^{\text{STO}}(r, \vartheta, \varphi) = N r^{n-1} e(-\zeta r) Y_l^m(\vartheta, \varphi)$$

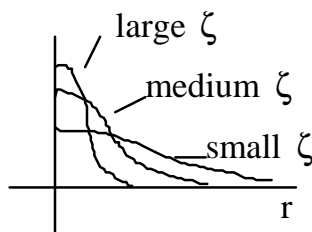
e^{-r} good description, cusp at the nuclei,
exponential decay at large r ...

Problematic: 3.) point (see above)- numerical difficulties...

Boys-type basis (Gaussian, GTO):

$$\chi_p^{\text{GTO}}(\underline{r}) = \begin{cases} N e(-\zeta r^2) Y_l^m(\vartheta, \varphi) \\ N x^u y^v z^w e(-\zeta r^2) \end{cases}$$

[here $x^u y^v z^w$ polinoms - "cubic harmonics"]
difficulties: has NO cusps, NOT exponential decay
cancel of these: lin. combination (e.g. 3 terms)



advantages: very easy to get integrals...

Contracted basis sets:

fixed lin. combination of several Gaussians;

idea: to approximate STOs

Pople's basis sets: most popular ones

For example:

STO-3G: 3 contracted Gaussian primitives
rather bad, but the "true" STO is
also...

Minimal basis set:

basis set size: occupied AOs in free atomic states.

STO-3G minimal basis:

H₂O: O_{1s}, O_{2s}, O_{2px}, O_{2py}, O_{2pz}, H_{1sA}, H_{1sB}
gives ~105° for the bond angle
qualitative mol. geometry
not used for publications anymore

4-31G:

H: $\underbrace{1s}_{3 \text{ Gauss}}$ $\underbrace{1s'}_{1 \text{ Gauss}}$

B – Ne: $\underbrace{1s}_{4 \text{ Gauss}}$ $\underbrace{2s, 2px, 2py, 2pz}_{3 \text{ Gauss}}$ $\underbrace{2s', 2px', 2py', 2pz'}_{1 \text{ Gauss}}$

Comments: H 1s: more compact, important for the description of the cusp;

H 1s': more diffuse, less important for the energy

heavy atoms: 1s core, practically does not change for formation of molecules [except hyperfine splitting]

heavy atoms: 2s, 2px, 2py, 2pz more compact

heavy atoms: 2s', 2px', 2py', 2pz' more diffuse

**effect: electron cloud can "breath",
 electrons can go to more diffuse part**

6-31G*:

1s-6 Gauss: Much better description for 1s core, but it is not so important → relative energies are essential.

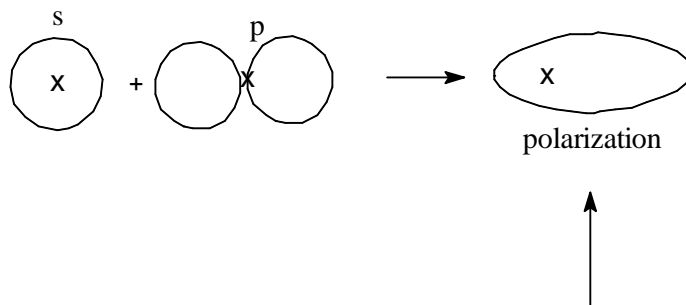
31: similar as above...

***: d-orbitals for the C atom (e.g.)**

6-31G: d-orbitals for the C atom,
 p-orbitals for the H atom**

In the ground state of free C and H, there are NOT occupied d (or p) orbitals.

However, makes the description of the polarization possible



**can NOT describe
using s-orbitals only
(but can by p, d, f, etc.)**

Nota bene: orbitals whose angular momentum higher than f ($l=3$) are not important from a chemical point of view. But f-orbitals can influent even the mol. geometry!!!

Determination of the C_{pk} LCAO-lin. coefficients:

(the shape of the MOs)

by the Variational Principle (minimization...)

for ON spatial orbitals we got:

$$W = 2 \sum_{k=1}^{n/2} h_{kk} + \sum_k \sum_l^{n/2} (2J_{kl} - K_{kl}) + \text{nucl. repulsion}$$

↑

**we can NOT abandon,
we add it finally**

Substituting $u_k(\underline{r}) = \sum_{p=1}^m \chi_p(\underline{r}) C_{pk}$ into W, we get

$$\begin{aligned}
 h_{kk} &= \langle u_k | \hat{h} u_k \rangle = \int u_k^*(\underline{r}) \hat{h} u_k(\underline{r}) dV = \\
 &= \sum_{p=1}^m \sum_{q=1}^m C_{pk}^* C_{qk} \langle \chi_p | \hat{h} \chi_q \rangle = \sum_{p=1}^m \sum_{q=1}^m C_{pk}^* C_{qk} h_{pq}
 \end{aligned}$$

↑

(one-electron integral)

can be calculated for known χ_{p-s} ;

$$\begin{aligned}
 J_{kl} &= \iint |u_k(\underline{r}_1)|^2 \frac{1}{r_{12}} |u_l(\underline{r}_2)|^2 dV_1 dV_2 = \\
 &= \sum_p^m \sum_q^m \sum_r^m \sum_s^m C_{pk}^* C_{qk} C_{rl}^* C_{sl} \left\langle \chi_p(\underline{r}_1) \chi_r(\underline{r}_2) \left| \frac{1}{r_{12}} \chi_q(\underline{r}_1) \chi_s(\underline{r}_2) \right. \right\rangle = \\
 &= \sum_p^m \sum_q^m \sum_r^m \sum_s^m C_{pk}^* C_{qk} C_{rl}^* C_{sl} (pq|rs)
 \end{aligned}$$

$K_{kl} = ?$ **Two possibilities: the same $(pq|rs)$ integral with different C coefficients, or the same coefficients with different integral ... We choose the second case:**

$$\begin{aligned}
 K_{kl} &= \iint u_k^*(\underline{r}_1) u_l^*(\underline{r}_2) \frac{1}{r_{12}} u_k(\underline{r}_2) u_l(\underline{r}_1) dV_1 dV_2 = \\
 &= \sum_p^m \sum_q^m \sum_r^m \sum_s^m C_{pk}^* C_{qk} C_{rl}^* C_{sl} (ps|rq)
 \end{aligned}$$

Here the $(pq|rs)$ integrals are two-electron integrals;

$$(pq|rs) = \left\langle \chi_p(\underline{r}_1) \chi_r(\underline{r}_2) \left| \frac{1}{r_{12}} \chi_q(\underline{r}_1) \chi_s(\underline{r}_2) \right. \right\rangle$$

Nota bene: the product of two Gaussian is also a Gaussian (similar to the center of mass - reduced mass problem...):

E.g., let two Gaussian primitives with exponents ζ_1 and ζ_2 at two centers

\mathbf{R}_1 and \mathbf{R}_2 , then:

$$e^{-\zeta_1(\mathbf{r}-\mathbf{R}_1)^2} \cdot e^{-\zeta_2(\mathbf{r}-\mathbf{R}_2)^2} = e^{-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(\mathbf{R}_1-\mathbf{R}_2)^2} \cdot e^{-(\zeta_1+\zeta_2)(\mathbf{r}-\mathbf{R})^2},$$

$$\text{where } \mathbf{R} = \frac{\zeta_1\mathbf{R}_1 + \zeta_2\mathbf{R}_2}{\zeta_1 + \zeta_2}$$

Pulay's proof?: no another function with this charact.

...It is reasonable to use the "density matrix":

$$D_{pq} \equiv 2 \sum_k^{n/2} C_{pk}^* C_{qk}$$

(obviously, $\underline{\underline{D}} = 2 \underline{\underline{C}} \underline{\underline{C}}^\dagger$, [here $\underline{\underline{D}}$ and $\underline{\underline{C}}$ matrices] the special case of the general density mx introduced by Wigner and others...). Thus

$W =$

$$\sum_p \sum_q h_{pq} D_{pq} + \frac{1}{4} \sum_p \sum_q \sum_r \sum_s D_{pq} D_{rs} [2(pq|rs) - (ps|rq)]$$

↑

(due to 2-s in $\underline{\underline{D}}$ matrix...)

Note that W is a quartic function of the lin. coeffs. → now these are the variables!!!

Minimization: deriv. = 0 (necessary but not suffic.)

Do Not Forget!!! W is valid ONLY for ON orbitals!!!

Conditional minimization by Lagrange-method

Method of the Lagrange-multipliers:

if we have to solve: $f(x, y, \dots, z) \rightarrow \min$

by the condition: $g(x, y, \dots, z) = 0$, we have to solve

$\mathcal{L} = f - \lambda g \rightarrow \min$ (according to x, y, \dots, z and λ).

Derivation by λ and $\dots = 0$, the g condition is satisfied.

How it works? Even the mathematicians are thinking...

Our condition(s): $\langle u_k(\underline{r}) | u_l(\underline{r}) \rangle = \int u_k^*(\underline{r}) u_l(\underline{r}) dV = \delta_{kl}$

for each k, l we have 1-1 condition, we introduce

for them 1-1 λ_{lk} multiplier, thus

$$-2 \sum_k \sum_l \lambda_{lk} (\langle u_k | u_l \rangle - \delta_{kl})$$

here -2 only for a convention...

[Introducing the S overlap matrix:

$$S_{pq} \equiv \langle \chi_p(\underline{r}) | \chi_q(\underline{r}) \rangle = \int \chi_p^*(\underline{r}) \chi_q(\underline{r}) dV]$$

$$\text{LCAO expans.: } \langle u_k | u_l \rangle = \sum_p \sum_q C_{pk}^* C_{ql} S_{pq} = (\underline{C}^\dagger \underline{S} \underline{C})_{kl}$$

Now:

$$\begin{aligned} \mathcal{L} &= W - 2 \sum_k \sum_l \lambda_{lk} (\langle u_k | u_l \rangle - \delta_{kl}) = \\ &= W - 2 \sum_k \sum_l \lambda_{lk} \left(\sum_p \sum_q C_{pk}^* C_{ql} S_{pq} - \delta_{kl} \right) \end{aligned}$$

Derivation of \mathcal{L} according to C_{ti} (we need a coeff. which does NOT take play above...)

Simplification: be all orbitals real!:

[Trick: for $C_{pk} C_{qk}$ enough for one of them to derive, then multiply by 2;

for $C_{pk}C_{qk}C_{rl}C_{sl}$ also, then multiply by 4 ...]

Thus:

$$0 = \frac{\partial \mathcal{L}}{\partial C_{ti}} = 4 \left\{ \sum_q^m h_{tq} C_{qi} + \sum_q^m \sum_r^m \sum_s^m C_{qi} \sum_l^{n/2} C_{rl} C_{sl} [2(tq|rs) - (ts|rq)] - \sum_q^m \sum_l^{n/2} S_{tq} C_{ql} \lambda_{li} \right\}$$

It is reasonable to write this in matrix notation:

$$G_{tq} \equiv \sum_r^m \sum_s^m [(tq|rs) - \frac{1}{2}(ts|rq)] D_{rs}$$

so we get:

$$\sum_q^m (\underline{h} + \underline{G})_{tq} C_{qi} = \sum_q^m \sum_l^{n/2} S_{tq} C_{ql} \lambda_{li}$$

Introducing the new (Fock) matrix $\underline{F} \equiv \underline{h} + \underline{G}$ we get the following matrix equation finally:

$$\underline{FC} = \underline{SC}\lambda$$

where ...

$$\begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ n/2 \end{array} = \begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ n/2 \end{array} \begin{array}{c} 1 \\ \square \\ n/2 \end{array}$$

$\begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ n/2 \end{array} = \begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ m \end{array} \begin{array}{c} 1 \\ \square \\ n/2 \end{array} \begin{array}{c} 1 \\ \square \\ n/2 \end{array}$

Comments:

1.) not a standard eigenvalue equation ($\underline{AX} = \underline{X}\underline{\Lambda}$, where $\underline{\Lambda}$ is diagonal)

2.) $\underline{\lambda}$ symmetrical matrix (comes from ON conditions), but it is not obvious that it is diagonal?

3.) The S matrix appears because the basis set is NOT ON!!!

4.) The definition of F contains G, and in G there is D, thus, obviously, F depends on C... How to solve?

We will manipulate with the equation, and change its form to an eigenvalue equation:

We know that the MOs are not uniquely defined (determinants, vide supra), we can mix them freely by unitary transformations...: $\underline{C} = \underline{C}'\underline{U}$

Unitary transformation

$$\text{e.g.: } \begin{pmatrix} u'_1 \\ u'_2 \end{pmatrix} = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \quad \text{rotation by } \alpha$$

For unitary transformations/operators: $\underline{U}^\dagger = \underline{U}^{-1}$

[Why unitary transformations? Because $\det(\underline{U}) = 1$, so $\det(\underline{C}) = \det(\underline{C}')\det(\underline{U})$, does not change $\tilde{\Psi}$ at all...]

Now:

$$\underline{F}\underline{C}'\underline{U} = \underline{S}\underline{C}'\underline{U}\underline{\lambda} \quad / \cdot \underline{U}^\dagger, \text{ right}$$

$$\underline{F}\underline{C}' = \underline{S}\underline{C}'\underline{U}\underline{\lambda}\underline{U}^\dagger$$

since U optional unitary (or orthogonal) matrix, can be chosen as

$$\underline{U}\underline{\lambda}\underline{U}^\dagger = \underline{\varepsilon} \quad (\text{where } \underline{\varepsilon} \text{ diagonal mx})$$

Let us define the self-adjoint matrices $\underline{S}^{-1/2}$ and $\underline{S}^{1/2}$

(where $(\underline{\underline{S}}^{-1/2})^2 \equiv \underline{\underline{S}}^{-1}$ and $(\underline{\underline{S}}^{1/2})^2 \equiv \underline{\underline{S}}$)

$$\underline{\underline{F}}\underline{\underline{C}}' = \underline{\underline{S}}\underline{\underline{C}}'\underline{\underline{U}}\underline{\underline{\lambda}}\underline{\underline{U}}^\dagger \quad / \cdot \underline{\underline{S}}^{-1/2} \text{ left}$$

$$\underline{\underline{S}}^{-1/2}\underline{\underline{F}}\underline{\underline{S}}^{-1/2}\underline{\underline{S}}^{1/2}\underline{\underline{C}}' = \underline{\underline{S}}^{-1/2}\underline{\underline{S}}\underline{\underline{C}}'\underline{\underline{\epsilon}}$$

$$\underline{\underline{S}}^{-1/2}\underline{\underline{F}}\underline{\underline{S}}^{-1/2}(\underline{\underline{S}}^{1/2}\underline{\underline{C}}') = (\underline{\underline{S}}^{1/2}\underline{\underline{C}}')\underline{\underline{\epsilon}}$$

denoted $\underline{\underline{V}} \equiv \underline{\underline{S}}^{1/2}\underline{\underline{C}}'$ we get

$$\underline{\underline{S}}^{-1/2}\underline{\underline{F}}\underline{\underline{S}}^{-1/2}\underline{\underline{V}} = \underline{\underline{V}}\underline{\underline{\epsilon}}$$

standard eigenvalue equation!

$\underline{\underline{C}}' = \underline{\underline{S}}^{-1/2}\underline{\underline{V}}$ the so-called "canonical orbitals"...

Above we have used a finite basis set. Can be also done generally, then \hat{F} Fock-operator ...

"Description of one electron in the field of the nuclei and in the averaged field of all the other orbitals occupied by electrons"

(kinetic + nucl. attraction + averaged electr. repulsion + exchange)

Solution of the $\underline{\underline{F}}\underline{\underline{C}} = \underline{\underline{S}}\underline{\underline{C}}\underline{\underline{\epsilon}}$ equation: SCF method (Hartree). Older method than the Hartree-Fock procedure itself.

$$\underline{\underline{C}}^{(0)} \rightarrow \underline{\underline{F}}^{(0)} \rightarrow \underline{\underline{C}}^{(1)} \rightarrow \underline{\underline{F}}^{(1)} \rightarrow \dots \rightarrow \text{convergence (?)}$$

in case of divergence it can be forced to converge (by, e.g., DIIS, Pulay)

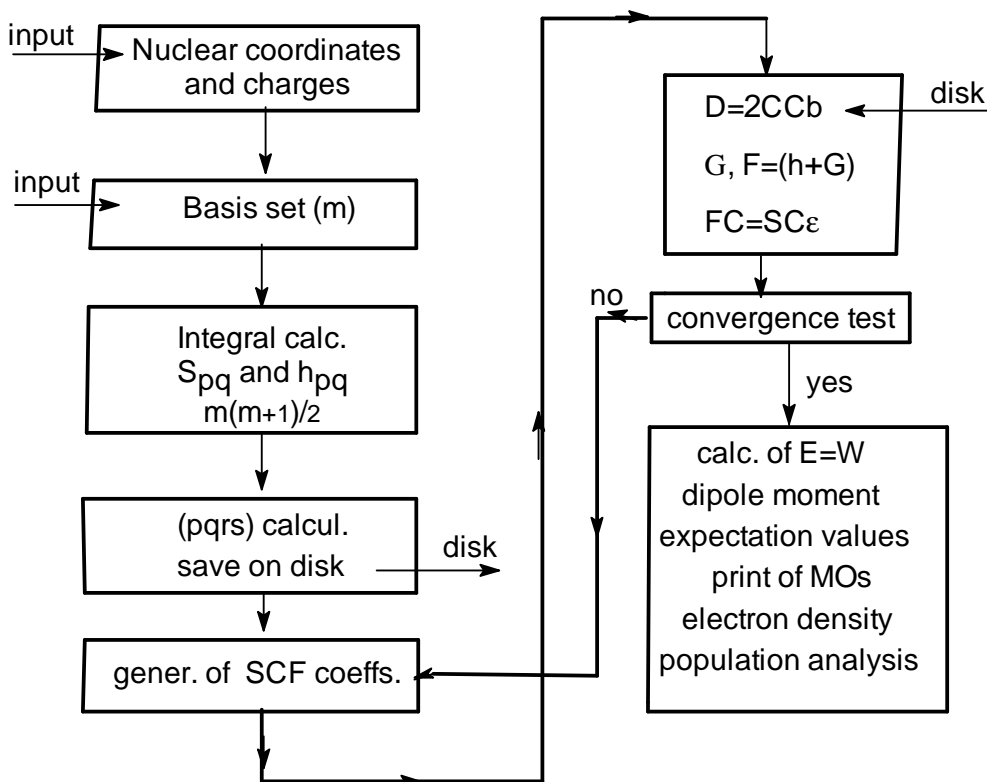
Test of convergence: better on $\underline{\underline{F}}$ than on $\underline{\underline{C}}$ (in the case of degeneration orbitals can mix freely...)

Remember!!! It is not sure that the result will be minimum (can be any stationary point, even maximum...).

**Method: C.C.J. Roothaan & G.G. Hall
(independently)**

**University of Chicago, Roothaan, memorial table:
"At this place mankind has activated the first self-sustaining molecular SCF calculation, initiating the uncontrolled release of marginal publications."**

Organization of a simple quantum chemical program:



Notes:

- nuclear coordinates - using mol. graphics**
- basis set "menus" (e.g., 6-31G**, or own...)**
- two-electron integrals (m^4 , external storage)**

d.)

$$(pq|rs) \times \begin{cases} D_{rs} \rightarrow G_{pq} \\ D_{pq} \rightarrow G_{rs} \\ \frac{1}{2} D_{pr} \rightarrow G_{qs} \\ \dots \rightarrow \dots \end{cases}, \text{ altogether 6 cases}$$

e.) the representative of the $\tilde{\Psi}$ is $\underline{\underline{C}}$.

Today the Hartree-Fock method has not too much future, still more than 90 % of the calcs. are made by it.

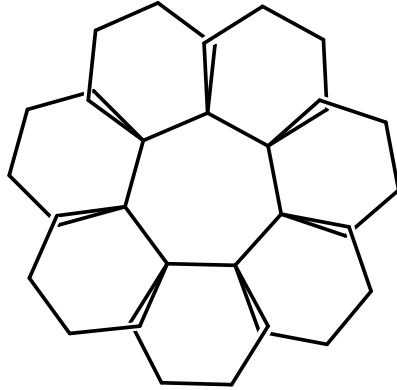
f.) First-order magnitudes (geometry, dipole moments) are good; second-order ones (force constants, polarizability) are quite good. But!!!: F_2 , NO, NO_2 , OF_2 , O_3 , and generally the explosive agents \rightarrow molecules of "jam-packed" electronic structure \rightarrow bad results by Hartree-Fock method.

g.) technical problems: calc. of $(pq|rs)$ integrals number of them roughly $\sim m^4$

for real functions, the interchange of $p \leftrightarrow q$ (or, $r \leftrightarrow s$) does not change its value \rightarrow divisor by 2×2 ; also, interchange of $pq \leftrightarrow rs \dots \rightarrow$ divisor by $2 \rightarrow$ finally, $m^4/8$ which is also quite large.

contraction of the basis set also does not diminish the integral calc.: the integrals between the Gaussian primitives have to be calculated, only the storage reduced (for contractions!!!)

**For example: 7-circulene ($C_{28}H_{14}$)
not planar, C_2 symmetry**



**4-31G basis set, 280 contracted functions,
12 million integrals (?)**

Method of shared exponents

**(Pople's group) the same ζ is used for s and p
orbitals: "shell" integral; $4 \times 4 \times 4 \times 4 = 256$ integral
can be calculated together**

h.) Basis sets and large molecules:

**small overlap if large
distance... the distance between pq and rs is not
interesting - slow decay ($1/r_{12}$)
but between p and q (and r and s) asymptotic...
 $m^2(\log m)^2$ above a small threshold value
(smaller than m^3)
works only for molecules large enough...**

HF: Possibilities today:

Molecs: ~ several 10^3 atoms, $n \times 10000$ basis functions

**Disks: earlier 100 MB was "big" for serious big
computers, now TB-s can be used for PCs !**

J. Almlöf: in the 80s years: "direct SCF" method
 the integrals are not stored at all; if necessary
 they will be calculated again. Much calc.s but
 the size is unlimited. (E.g., SCF converg. in 12
 cycles, thus 12× has to calc. again...gradient:
 equivalent to a few SCF cycles)

Since $\underline{\underline{F}} = \underline{\underline{h}} + \underline{\underline{G}}(\underline{\underline{D}})$, recursive generation of the
Fock matrix:

$$\underline{\underline{F}}^i = \underline{\underline{F}}^{i-1} + \underline{\underline{G}}(\underline{\underline{D}}^i - \underline{\underline{D}}^{i-1})$$

($\underline{\underline{F}}^i$: i index is the iteration step) up to 10 steps
 are good (due to the accumulation of the
 numerical errors).

If an integral is small, and the $\underline{\underline{\Delta D}} = \underline{\underline{D}}^i - \underline{\underline{D}}^{i-1}$ is
 also small, it can be abandoned: the magnitude
 of an integral can be estimated in advance, so if
 we estimate the biggest one of a shell-integral
 and the max. $\underline{\underline{\Delta D}}$ and if their product is $< 10^{-7}$
 the shell-integral will not be calculated.

Schlegel: up to a certain size the direct method is
 faster than the traditional one.

if G_{pq} we need with ε (e.g. = 10^{-8}) acc. and
 $|\underline{\underline{\Delta D}}_{rs}| < \eta$, the integral is important in F_{pq} only if

$$|(pq|rs)| > \frac{\varepsilon}{\eta}$$

Take care! The differences converge to 0 according to
 the SCF iteration, and the acceleration techniques can
 exaggerate the errors near the end...

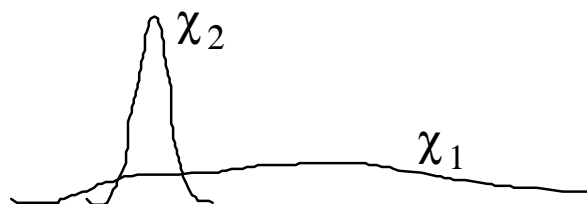
R. Ahlrichs: "semi-direct" method

"the 75 % of the computational work is caused by the 25 % of the integrals"

e.g. for a "long" contr. function (like 1s in 6-31G) the 1s-1s overlap is much more expensive than for a not-contracted ones → only the expensive integrals will be stored, others by direct method.

Van Alsenoy (started the work with Pulay in 1981):

"Multiplicative Integral Approximation (MIA)" in case of compact and diffuse functions:

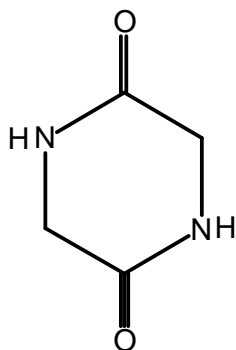


(diffuse functions are important e.g. in anions)

$$\chi_1(\underline{r})\chi_2(\underline{r}) \sim \underbrace{\chi_2(\underline{R}_1)}_{\substack{\text{at the centrum} \\ \text{(constant)}}} \cdot \chi_1(\underline{r})$$

Example:

diketo-piperazine (Van Alsenoy & Pulay)
 (1+12 = 13 moles, 186 atoms, 1012 basis f,
 crystal lattice was simulated by charges;
 without any symmetry;



geom. opt. for the crystal on a small personal computer...

2. DERIVATIVES

Energy: in the chemistry only the relative energy is important at the energy minimum. Thus, obviously, for the chemists it is not sufficient one energy value.

Potential surface (hypersurface) is only a model (not the reality): function of the molecular energy in terms of nuclear coordinates.

Variables	Function
1	curve
2	surface
3	hypersurface
...	...

Equilibrium geometry: can be determined effectively if we know the derivatives of the energy (at least the first derivative) according to the nucl. coordinates.

External perturbations (like \underline{F} , \underline{H}) are similar to the change of the nuclear coordinates. **Difference:** if the nuclei are moving, we have to move the basis functions, too (except if the space is "jam-packed" by functions...). In the case of external fields there is no such "moving": the electronic cloud will be deformed, but mostly the outer part. There is no need to move the basis set because the coulombic attraction has a deep minimum at the nuclei...

Used notations:

\underline{R} → nuclear coordinates (Cartesians or internals)
 of course, $3N$ Cartesians, $3N - 6$ intern. coords.

\underline{R}_0 → equilibrium geometry

ΔR → $R - \underline{R}_0$

R_a → the a -th nuclear coordinate

derivation → in superscript :

$$E^a = \left(\frac{\partial E}{\partial R_a} \right)_{\underline{R}_0}$$

\underline{F} and \underline{H} electric and magnetic fields ($\alpha = x, y, z$)

C_i the i -th parameter of the wave function

We are NOT able to describe the whole pot. energy hypersurface completely → we need its Taylor-expansion.

The Taylor-expansion of the mol. energy around the \underline{R}_0 equilibrium:

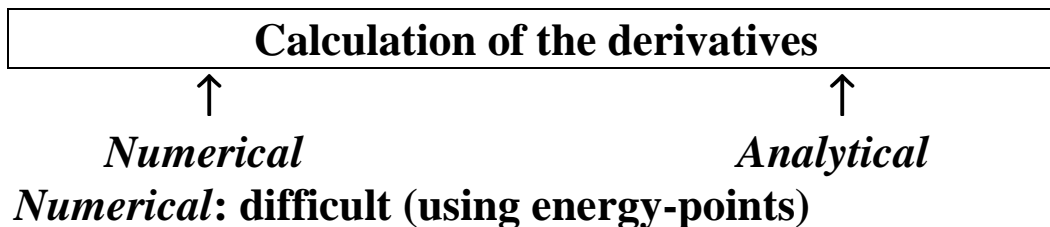
$$E(\underline{R}) = E(\underline{R}_0) + \sum_a E^a \Delta R_a + \frac{1}{2} \sum_a \sum_b E^{ab} \Delta R_a \Delta R_b + \dots$$

The expansion is useful in the vicinity of \underline{R}_0 . Here

$$E^{ab} = \left(\frac{\partial^2 E}{\partial R_a \partial R_b} \right)_{\underline{R}_0}$$

If we would knew E^a , E^{ab} , E^{abc} , ... (and not only E), we would have much more information. Of course, the number of the derivatives is very big: e.g., if the degree of freedom is 12, there are 12 first derivs., $12 \times 13 / 2$ second derivs., etc.

In the aforementioned case we could get a lot of information. The first derivs. give (with minus sign) the forces acting on the nuclei (geometry), the second derivs. are the force constants (vibrational freqs. in harmonic approximation, vibr. amplitudes), the third derivs. are the vibr. anharmonicities, the fourth derivs. have similar importance as the third ones...

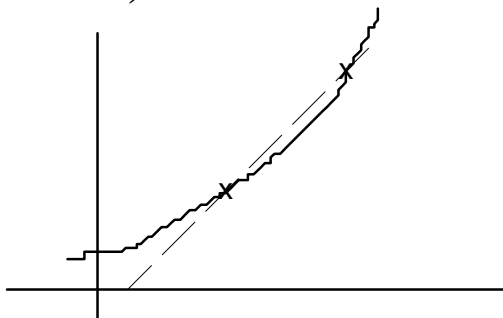


The advantages of the *analytical* method:

1.) More information from 1 calculation

Of course, this might require too much effort; fortunately, this is not so, the ratio of the *information/effort* is growing!!!

2.) Numerical derivation of a function is difficult:



two points → first derivative,

three points → second derivs.,...

The *formula error* can be negligible for neighboring points but the *numerical error* (due to the limited accuracy of the computer) will be larger in this case...
The analytical calc. is more accurate.

The bigger the molecule, the larger the importance of the argument outlined above.

The drawbacks of the *analytical* method:

1.) complicated programs

2.) larger comp. time

(10×1 hour is easier than 1×10...Today this is decreasingly...)

Perturbations:

Topics:

$$\partial E / \partial R_a$$

forces on nuclei; equilibrium geometry; geom. of transition states

$$\partial^2 E / \partial R_a \partial R_b$$

force constants; fundamental freqs., shapes, vibr. amplit.

$$\partial^3 E / \partial R_a \partial R_b \partial R_c$$

anharm. of mol. vibr. (cubic

$$\partial^4 E / \partial R_a \partial R_b \partial R_c \partial R_d$$

and quartic constants are ~ equiv. important)

$$\partial E / \partial F_\alpha$$

dip.mom.

$$\partial^2 E / \partial F_\alpha \partial F_\beta$$

polarizability

$$\partial^3 E / \partial F_\alpha \partial F_\beta \partial F_\gamma$$

hyperpolarizabilities [today

$$\partial^4 E / \dots$$

have great importance: "non-linear optical matters": matters of non-linear polarizability → conversion of the freq. of the light (2×, 3×) by optical converters...]

Mixed terms

$$\partial^2 E / \partial R_a \partial F_\alpha$$

dip.mom. derivs (IR intensity, dominant term)

$$\partial^2 E / \partial R_a \partial F_\alpha \partial F_\beta$$

polariz. derivs (Raman int.s)

mixed terms of higher order

intensities of non-fundamental freqs

$$\partial E / \partial H_\alpha$$

magnetic dip.mom. (zero for most molecules)

$$\partial^2 E / \partial H_\alpha \partial H_\beta$$

magnetic susceptibility (determinates para- or diamagnetic character)

$$\partial^3 E / \partial F_\alpha \partial H_\beta \partial R_a$$

important in IR circular dichroism & optical rotational dispersion [peptide-structure]

Calculation of the derivatives: (general treatment)

W is the energy

nuclear coordinates/the comps. of electric or magnetic fields



$$W(\underline{C}, \underline{R})$$



parameters of the wave function

[at a certain \underline{R} at any \underline{C} the W can be calculated]

I.§. Variational deduction without constraints:

Variational energy and wave function:

$$\left. \frac{\partial W}{\partial C_i} \right| = W^i = 0$$

necessary but not sufficient conditions

+ side-conditions for orthonormality

(not important: even H-F can be formulated without side-conditions ...)

...→resulted $\underline{C}_{\min} = \underline{C}(\underline{R})$

Thus

$$E = E(\underline{R}) = W(\underline{C}(\underline{R}), \underline{R})$$

(The same observable considering in terms of different variables, is not the same function!)

Be careful!!! From here \underline{R} can be nucl. coords., comps. of electric/magnetic field... Nucl. coords. are the most difficult ones: in this case the basis functions also have to "move"...

$$\frac{\partial E}{\partial R_a} = E^a = \sum_i \frac{\partial W}{\partial C_i} \cdot \frac{\partial C_i}{\partial R_a} + \frac{\partial W}{\partial R_a} = W^a + \underbrace{\sum_i W^i C_i^a}_{\text{at the minimum } W^i=0 \rightarrow \text{zero}}$$

It is a very important facility that we do not need C_i^a -s. The C-s are coming from the SCF procedure, at first it is not obvious how to derive them...

Thus:
$$\frac{\partial E}{\partial R_a} = W^a$$

$$\frac{\partial^2 E}{\partial R_a \partial R_b} = \frac{\partial W^a(\underline{C}(\underline{R}), \underline{R})}{\partial R_b} = \sum_i \underbrace{W^{ai} C_i^b}_{\text{cannot be neglected}} + W^{ab}$$

it is not sure that $W^{ai} = 0$, thus we need $C_i^b \dots$

The use of the second derivative is useful but does not give as big increase of information as the first derivative, and it needs much more work!!! The third, and, generally, the odd derivatives have more importance; there are fourth-derivative programs (M. Handy), too.

Calculation of C_i^b :

Since $W^i = 0$ / $\frac{\partial}{\partial R_b}$, and $W^i = W^i(\underline{C}(\underline{R}), \underline{R})$

$$\frac{\partial}{\partial R_b} W^i(\underline{C}(\underline{R}), \underline{R}) = \sum_j W^{ij} C_j^b + W^{ib} = 0$$

For a given point W and also \underline{C} is given (minimization). W^{ij} and W^{ib} is known (i.e., can be calculated easily), C_i^b are unknown, so can be determined from a very big system of lin. equations (Pople):

$$\sum_j W^{ij} C_j^b = -W^{ib}$$

For example, naphthalene, 4-31G basis set, $m = 106$; no. of electrons = 68; occupied orbs. = $n/2 = 34$. Coefficient matrix: 106×34 but these are not independent (!); we have to subtract the ON conditions: virtual orbs. = $106 - 34 = 72$.

Now $\text{occ} \times \text{virt} = 34 \times 72 \approx 2500$, that is

$W^{ij} 2500 \times 2500$.

Solution: traditional (by inversion) here is not possible!

Now: iterative solution of the syst. of lin. equations (...DIIS, Pulay).

"In principle, near the end of an SCF iteration such equations are solved, also iteratively. For a long time I did not understand this..." (Pulay)

First deriv. needs more time than SCF but it is commensurable. Moreover, in case of direct methods need less computer time.

For example: 100 nuclear coordinates;

Numerical gradient: 100 points \rightarrow 100 SCF calculations.

**Analytical gradient: about 3 SCF calculations
about 30 \times factor of acceleration.**

Second analytical derivative: not such big increase of information \rightarrow for each b we have to determine the C_j^b -s, approximately it is equivalent by the multiple (repeated) solution of the SCF equations; this gives for bigger molecules only (2-3) \times acceleration comparing to the first analytical, second numerical derivation (Pulay's "force" method, *Mol. Phys.*, 1969.).

$\sum_j W^{ij} C_j^b = -W^{ib}$ "response" equations: the "answer" of the wave function to the perturbation...

In case of dipole moment derivatives [both nuclear coordinates (R_a) and electric field (R_b)], naturally, b will be the field (only 3 components).

Alternative expression:

$$E^{ab} = W^{ab} + \underbrace{\sum_i \sum_j W^{ij} C_i^a C_j^b + \sum_i W^{ib} C_i^a + \sum_j W^{aj} C_j^b}_{\sum_i C_i^a [\sum_j W^{ij} C_j^b + W^{ib}]}$$

If we minimize this (stationary point), we get the "response" equation.

2.§. Variational deduction with constraints:

Modification in case of side-conditions:

$$g_k(\underline{C}, \underline{R}) = 0 \quad (\text{constraints}),$$

$$\mathcal{L} = W - \sum_k \lambda_k g_k \rightarrow \min$$

In this case:

$$E = \mathcal{L}(\underline{C}(\underline{R}), \lambda(\underline{R}), \underline{R})$$

$$E^a = \mathcal{L}^a + \underbrace{\sum_i \mathcal{L}^i C_i^a + \sum_k \mathcal{L}^k \lambda_k^a}_{\text{both are zero}} = \mathcal{L}^a$$

second derivative:

$$E^{ab} = \mathcal{L}^{ab} + \sum_i \mathcal{L}^{ai} C_i^b - \sum_k \lambda_k^b g_k^a$$

$$\sum_j \mathcal{L}^{ij} C_j^b - \sum_k g_k^i \lambda_k^b + \mathcal{L}^{ib} = 0$$

$$\sum_i g_k^i C_i^b + g_k^b = 0$$

3.§. Non-variational deduction:

In case of non-variational energy formula:

$$E^a = W^a + \sum_i \underbrace{W^i}_{\text{now it is not zero}} C_i^a$$

The C-s (the parameters of the wave function) are usually determined in the following manner:

$$f_i(\underline{C}, \underline{R}) = 0 \rightarrow C_i(\underline{R})$$

$$\frac{\partial}{\partial R_a} /: \sum_j f_i^j C_j^a + f_i^a = 0$$

we would have to solve this for each perturbation, thus we could loose the "profit"...

The trick of Handy (& Schaefer): let us note

$$f_i^j = (\underline{h})_{ij} \quad \text{and} \quad f_i^a = \underline{b}^a \quad \text{then :}$$

$$\underline{h} \underline{C}^a = -\underline{b}^a, \quad \text{and} \quad \underline{C}^a = -\underline{h}^{-1} \underline{b}^a$$

But the inverse of \underline{h} is can not be treated (too large...),

so

$$E^a = W^a - \sum_i W^i \sum_j (\underline{h}^{-1})_{ij} b_j^a =$$

$$W^a - \sum_j (\sum_i (\underline{h}^{-1})_{ij} W^i) b_j^a$$

let us note $\sum_i (\underline{h}^{-1})_{ij} W^i = Z_j$, i.e., $(\underline{h}^{-1})^T \underline{W}' = \underline{Z}$,

thus $\underline{h}^T \underline{Z} = \underline{W}'$ (only once has to solve!!!)

4.§. First derivative of the Hartree-Fock energy:

(See also 2.§.)

Presently an important amount of the computer time in quantum chemistry is due to the first deriv. of the SCF energy.

Specially, the derivative of the SCF energy:

$$\mathcal{L} = W - \underbrace{2\text{tr}[\underline{\epsilon}(\underline{C}^\dagger \underline{S} \underline{C} - \underline{I})]}_{\text{the constrains in some-what modified form}}$$

$$\mathcal{L}^a = \sum_p \sum_q D_{pq} h_{pq}^a + \frac{1}{4} \sum_p \sum_q \sum_r \sum_s D_{pq} D_{rs} [2(pq|rs)^a - (ps|rq)^a] - 2\text{tr}[\underline{\epsilon}(\underline{C}^\dagger \underline{S}^a \underline{C} - \underline{I})] + \frac{\partial}{\partial R_a} [\sum_k \sum_l \frac{Z_k Z_l}{R_{kl}}]$$

Since \underline{D} density matrix is known, we have to calculate the derivatives of the integrals:

$$h_{pq}^a = \langle \chi_p | \hat{h} \chi_q \rangle^a = \langle \chi_p^a | \hat{h} \chi_q \rangle + \langle \chi_p | \hat{h} \chi_q^a \rangle + \langle \chi_p | \hat{h}^a \chi_q \rangle$$

$$(pq|rs)^a = (p^a q|rs) + (pq^a|rs) + (pq|r^a s) + (pq|rs^a)$$

Due to "orbital-following", the terms are not zero only if the appropriate χ function is on the given nucleus a .

The derivative of an s-type function is a p-type function, and so on..., thus, functions with higher quantum numbers of the angular momentum appear...

In the practical calcs. the aforementioned expression is not effective enough: we are not going through the nuclei, rather we consider one given integral, take into consideration on which nuclear coordinates it depends altogether and calculate its contribution to many derivatives...

Although $(p^a q|rs)$ 4×3 coordinates \rightarrow 12 derivatives, the comput. work is not 12 times as much, many common terms \rightarrow (2-3) \times SCF time (less than direct SCF if it is well programmed).

Popular/notable ab initio program systems:

Gaussian, Inc. (originally J.A. Pople, Pittsburgh)

more than 90% of the calcs. made by it...

"Quantum Chemistry Software Uproar -

-Gaussian says license policies are needed to protect code, but some chemists say restrictions go too far", Chemical & Engineering News, July 12, 1999, pp. 27-30;

PQS	(TEXAS, TX90) <u>P. Pulay</u>, Fayetteville;
CADPAC	<u>Handy</u>, Cambridge;
TurboMol	<u>Ahlrichs</u>, Karlsruhe;
Spartan	<u>Hehre</u> (it is connected with a modeling program).
AcesII	Bartlett & Stanton, Gainesville.

Of course, the mentioned programs can calculate not only the SCF gradient... All of them have advantages and disadvantages.

Determination of the geometry:

The use of the first derivative (gradient).

Let us suppose that molecular energy is a smooth function of the nuclear coordinates (not always, e.g. the crossing of excited states is funnel-shaped, but this is rare, we will not discuss this...):

$$E(\underline{R}) = E(\underline{R}_0) + \sum_a E^a \Delta R_a + \frac{1}{2} \sum_a \sum_b E^{ab} \Delta R_a \Delta R_b + \dots$$

- (i) the linear function is an incline, it has no minimum;
- (ii) the function which has minimum, is at least quadratic, so we need the E^{ab} term;
- (iii) neglect of the cubic, quartic, etc. terms is not always justified but in the vicinity of the minimum.

$$E(\underline{R}) = E_0 - \underline{f}^\dagger \underline{\Delta R} + \frac{1}{2} \underline{\Delta R}^\dagger \underline{\underline{F}} \underline{\Delta R} + \underbrace{\dots \text{higher terms}}_{\text{neglected}}$$

where

$$\left(\underline{\underline{f}} \right)_a = -E^a \quad ; \quad \left(\underline{\underline{F}} \right)_{ab} = E^{ab}$$

force vector force constant (or
Hessian) matrix

All the minimization procedures go back to this quadratic expression. If we use the mentioned quadratic approximation (not exact!), we can get the minimum in a closed expression.

Truncated expression of the energy, deriv.:

$$E_{\text{trunc}}^a = -f_a + (\underline{\underline{F}} \underline{\Delta R})_a = 0 \quad (\text{at the minimum})$$

**that is $\underline{\underline{F}} \underline{\Delta R} = \underline{f} \rightarrow$ from this we get: $\underline{\Delta R} = \underline{\underline{F}}^{-1} \underline{f}$
only if the surface is quadratic indeed (we are quite near to the minimum...**

For example, along one coordinate $\Delta R = \frac{1}{F} \cdot f$, it is necessary to step into the direction of the force, but "how far" ← it depends on the force constant.

**We do not need the force constant matrix accurately.
The hypersurface is not accurately quadratic either.
One step is never the solution: iteration.
Our hope: the quadratic model goes to the minimum
closer and closer.**

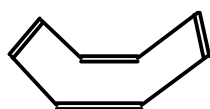
Calculation of $\underline{\underline{F}}$: quite big work, questionable, it is worthwhile or not... If yes, usually even in that case are not able to get the solution in one step.

All the mentioned program systems have analytical first derivative for the wave functions at many different level of the approximation, but, usually, F can be calculated only for the simpler wave functions.

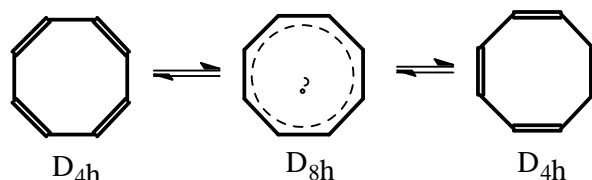
Example: *cyclo-octatetraene* (COT, antiaromat. mol.)

[Wenthold et al., Science, 1996, 272, 1456-1459.]

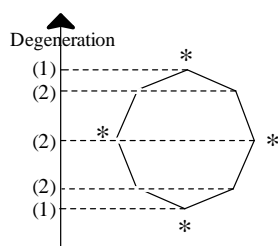
$^1A_{1g}$ ground state:



minimum; tub-form; D_{2d}
transition ($^1A_{1g}$ and $^1B_{1g}$) / excited ($^3A_{2u}$)
state(s):



In planar conformation the double bonds can be rearranged easily ($\sim 3-4$ kcal/mol), whilst the ring inversion has an activation energy of 10-11 kcal/mol (dynamic NMR measurements on COT-derivatives). The planar structure of antiaromatic character (Hückel $4n+2$ rule) has high symmetry (D_{8h}). Since the molecule belongs to the Alternant Hydrocarbons (AH), the simple geometrical generation of the $p\pi$ -MOs is valid:



Obviously, the 8π electrons will occupy the lower five MOs, of which the degenerate e_{2u} HOMOs are partially occupied. In principle, there are 6 independent states:

$\{(\uparrow\downarrow)_a\}$, $\{(\uparrow\downarrow)_b\}$, $\{(\uparrow_a\uparrow_b)\}$, $\{(\downarrow_a\downarrow_b)\}$, $\{\uparrow_a\downarrow_b\}$, $\{\downarrow_a\uparrow_b\}$.
 From these we can construct 3 singlet and one triplet eigenstates of the \hat{H} , \hat{S}^2 and \hat{S}_z operators. From the D_{8h} character table [G. Herzberg: "Molecular spectra and molecular structure", D. Van Nostrand, Princeton, 1966.] we know that $E_{2u} \otimes E_{2u} = A_{1g} \oplus A_{2u} \oplus B_{1g} \oplus B_{2g}$. Using the Pauli-principle, we can determine the possible state functions: ${}^3A_{2u}$, ${}^1B_{1g}$, ${}^1A_{1g}$, ${}^1B_{2g}$. According to the Hund's rule the ${}^3A_{2u}$ triplet state has to be the lowest, but (according to qualitative theory of biradicals with disjoint NBMOs, where the two degenerate NBMOs can be chosen so that they have no atoms in common) here the Hund's rule is violated: one of the singlets (${}^1B_{1g}$) is below the triplet state (verifications: calculations & PES experiment).

According to the Jahn-Teller principle [Jahn & Teller, *Proc. Roy. Soc. (London)* 1937, *A161*, 220] in the case of spatial degeneration of a non-linear molecule of higher symmetry the nuclei move spontaneously into a structure of lower symmetry so as to remove the degeneracy (first-order Jahn-Teller instability: acting force). The effect can be understood by the perturbation theory, using an unusual partition (q means small change of some distortion coordinate):

$$\hat{H}(q) = \hat{H}^{(0)} + \eta \hat{H}^{(1)} + \eta^2 \hat{H}^{(2)} + \dots =$$

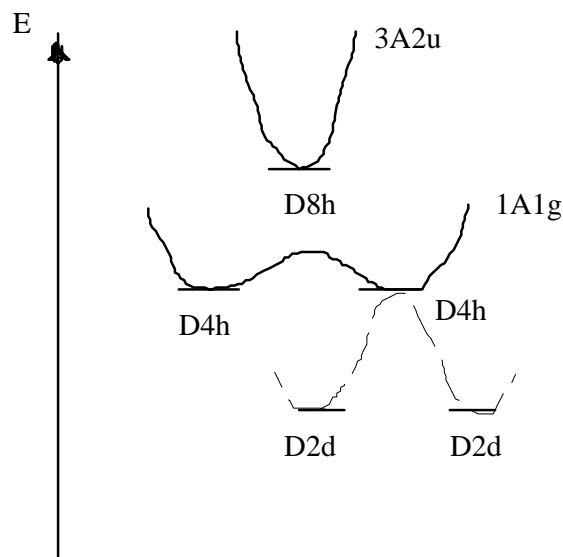
$$\hat{H}^{(0)}(0) + \left(\frac{\partial \hat{H}}{\partial q} \right)_0 q + \left(\frac{\partial^2 \hat{H}}{\partial q^2} \right)_0 q^2 + \dots$$

(Herzberg-Teller expansion)

Thus the E_0 electronic energy for the $|0\rangle$ ground state:

$$\begin{aligned}
 E_0(q) &= E_0^{(0)}(0) + E_0^{(1)}(q) + E_0^{(2)}(q) + \dots = \\
 &= E_0^{(0)}(0) + \left\langle 0 \left| \frac{\partial \hat{H}}{\partial q} \right| 0 \right\rangle q + \\
 &\left[\left\langle 0 \left| \frac{\partial^2 \hat{H}}{\partial q^2} \right| 0 \right\rangle - \sum_{j(\neq 0)} \frac{\left| \left\langle 0 \left| \frac{\partial \hat{H}}{\partial q} \right| j \right\rangle \right|^2}{E_j(0) - E_0(0)} \right] q^2 + \dots
 \end{aligned}$$

The first-order term is the (Hellmann-Feynman) gradient, the second-order one is the force constant. If none of the ground and excited states belong to two-dimensional irr. reps., they will not show the first-order, but can show the second-order Jahn-Teller effect (saddle-point). The ${}^1A_{1g}$ (D_{4h}) structure results from second-order Jahn-Teller distortion in COT (starting at the ${}^1B_{1g}$ (D_{8h}) ground state = saddle-point) which splits the e_{2u} orbitals into b_{1u} and b_{2u} orbitals. Both of these structures D_{4h} are also saddle points: along the ring torsion coordinate we can get the D_{2d} minima. The schematic potential energy surface:



(x: bond-alternation coordinate; z: ring inversion coordinate, dashed line) Obviously, the potential surface can not be described by a single quadratic function (which

has only one minimum).

Standard examples for the Jahn-Teller effect:

A.) first-order torsion: $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}\text{SO}_4$: blue, salted by NaCl : green. $\text{Cu}^0 : 3d^{10}4s^1 \rightarrow \text{Cu}^{2+} : 3d^9$ in an octahedral (O_h) case the electr.conf. is e_g^3 (2E_g state) \rightarrow torsion: four short and two long Cu-O bonds \rightarrow unstable complex, the ligands can be substituted by four Cl-ions, maximally.

B.) second-order instability: NO degenerate states!!!
E.g., NH_3 is pyramidal: simple orbital mixing of the HOMO and LUMO orbitals in planar ammonia (i.e., an out-of-plane bending motion from the 1A_1 electronic ground state to the ${}^1A''$ first excited state).

The procedure outlined above is planned for continuous functions. The finer details are in that,

1.) how we can estimate the $\underline{\underline{F}}$ matrix...

problematic case, not quadratic surface at all: if we step into the direction of the force, and it grows (!). Fletcher's book is a good guide to the minimization...

2.) the use of suitable set of coordinates:

Cartesian: simple, but estimate of $\underline{\underline{F}}$ is difficult.

internal: it is easy to estimate the $\underline{\underline{F}}$ matrix. (It would be also possible to calculate it by semiempirical methods, but it is not so important...)

If the forces acting on the nuclei vanish, the point can be saddle point or maximum beyond minimum.

The character of a stationary point:

$$E^a = 0 \quad , \text{ or } \underline{f} = \underline{0}$$

if we choose E_0 as the zero energy,

$$E = \frac{1}{2} \underline{\Delta R}^\dagger \underline{F} \underline{\Delta R}$$

Let the eigenequation of \underline{F} be: $\underline{F}\underline{U} = \underline{U}\underline{\Lambda} \quad / \underline{U}^\dagger$

$$\underline{F} = \underline{U}\underline{\Lambda}\underline{U}^\dagger$$

$$E = \frac{1}{2} \underline{\Delta R}^\dagger \underline{U}\underline{\Lambda}\underline{U}^\dagger \underline{\Delta R}$$

if we rotate the system of coordinates into the direction

of the eigenvectors of \underline{F} : $\underline{\Delta R}' \equiv \underline{U}^\dagger \underline{\Delta R}$, then

$$E = \frac{1}{2} (\underline{\Delta R}')^\dagger \underline{\Lambda} \underline{\Delta R}' = \frac{1}{2} \sum_a \lambda_a (\underline{\Delta R}')_a^2$$

if all the λ_a are positive \rightarrow minimum;

if t of the λ_a -s are negative \rightarrow (t-order) saddle point;

if all the λ_a are negative \rightarrow maximum.

First-order saddle points: If the average energy of the molecules reaches the energy of the saddle point, the reaction goes quickly into the direction with negative eigenvalue.

Higher-order saddle points: their chemical importance is relatively small; usually the reaction coordinate has only one of the directions with negative eigenvalue, along the other one(s) (which is/are orthogonal to the former one) the reaction will be avoided...

Global minimum: there is NO method to find it. In case of N degree of freedom, it is an Nth-order wandering-problem: this is exponentially scaled by N.

5.§. Second derivatives of the Hartree-Fock energy:

$$E^{ab} = \mathcal{L}^{ab} + \sum_i \mathcal{L}^{ia} C_i^b - \sum_k g_k^a \lambda_k^b$$

Here \uparrow the integrals have to be substituted with their second derivatives. E.g., two-electron integral - 12 nuclear coordinates - : 3 can be left (the "center-of-mass" of the coordinate: if all go into one direction, the value of the integral does not change; the "rotation" of the integral would be similar in this context but nobody could solve it). The second deriv. of an s-function is a d-type function, at least it also has such a component. The saving is not problematic here.

\mathcal{L}^{ia} simple, only third-order (cubic) function (of the C_{ij} -s). The term of constraints (last term) is simple, not problematic either. The C_i^b -s (param.s of the SCF wave function) mean the main problem, they can be determined from the HF-equations:

with the derivation of $\underline{\underline{FC}} = \underline{\underline{SC}}\underline{\underline{\varepsilon}}$

$$\underline{\underline{F}}^a \underline{\underline{C}} + \underline{\underline{FC}}^a = \underline{\underline{S}}^a \underline{\underline{C}}\underline{\underline{\varepsilon}} + \underline{\underline{SC}}^a \underline{\underline{\varepsilon}} + \underline{\underline{SC}}\underline{\underline{\varepsilon}}^a$$

this equation has to be solved for each nuclear coordinate: how it is scaled with the mol. size?

HF-method roughly by m^4 (where m is the size of the basis set; for large moles will be less than m^3)

The last equation (iterative solution; N is the number of the nucl. coords): $m^4 N \sim o(m^5)$ formally; for large moles will be less than m^4). Conclusively, the calc. of

the second derivative can be much more expensive than that of the first one.

Second deriv. can be calculated by post-HF methods, too.

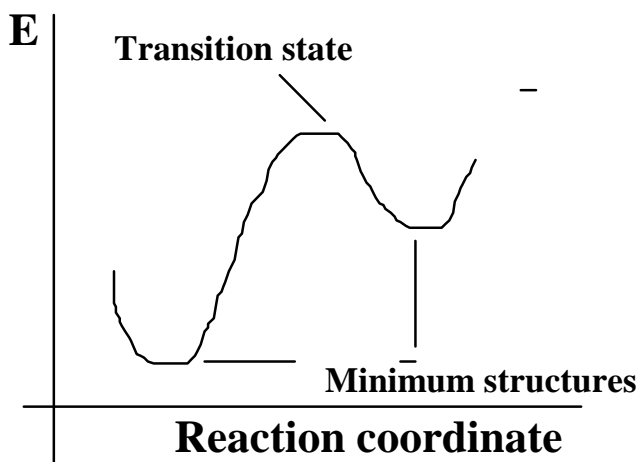
3rd and 4th derivatives: only Handy calculates them, the program is overcomplicated. The calc. of the 3rd deriv. is not more expensive than the 2nd one. The importance of the odd derivatives is larger.

(The CC third derivative is in progress in 2006).

Molecular anharmonicities: calc. in Cartesians, but in this system the estimate of the small terms is more difficult. E.g., for benzene more 10000 4th derivatives, but due to the high symmetry, in internal coords only 1400 independent, non-zero element.

Reaction paths:

It is often required to fix the values of some coordinate(s) during a geometry optimization. This is called constrained geometry optimization. It can be performed by using an infinitely large diagonal force constant for the fixed coordinate(s) [or, alternatively, we have to use zeros in the appropriate rows and columns (corresponding to the constrained coordinates) of the $\underline{\underline{F}}^{-1}$ matrix]. The method of the constrained geometry optimization is often used at the generation of adiabatic reaction paths: in these cases the value of a single coordinate (the so-called reaction-coordinate) is fixed at several selected values, and all the other coordinates are optimized at these points:



The nomenclature of the Pople's group is used for the notation of the chosen level of the quantum mechanical approximation:

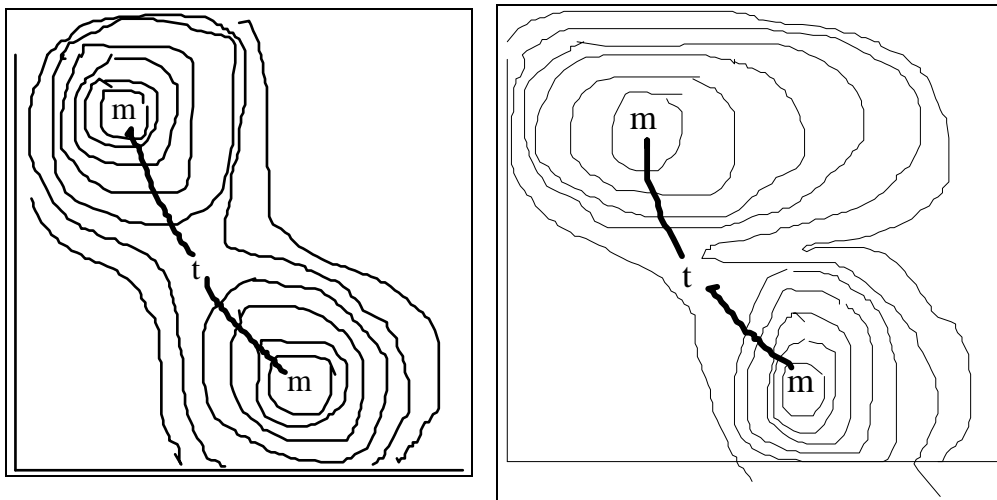
level of energy points // level of constr. geometry opt.
(e.g., MP2/6-31G* // RHF/6-31G*)

A reaction path usually connects two energy minima. **It must be emphasized that the reaction paths are NOT physically defined!** Consequently, they are NOT invariant with respect to the choice of the reaction coordinate. If we change the definition of the reaction coordinate, we may get a discontinuity of the reaction path (or, alternatively, if the change was made at a saddle point, of its derivative). The analogy between a mountain and a potential energy hypersurface is erroneous because the mountain exists in the physical reality and the hypersurface is only a mathematical construction. This construction depends upon the coordinate system used.

Only the stationary points of a hypersurface are invariant with respect to the coordinate system.

The most general coordinate transformations are nonorthogonal (nonunitary; e.g., Cartesians to internal coordinates). The figures below show the hypothetical potential energy surface of a simple nonlinear ABC system at a special value of the bond

angle using two different sets of coordinate systems (let say \underline{x} and \underline{y}) connected by a nonorthogonal transformation \underline{S} (the ordinate and the abscissa are the AB and BC bond lengths):



The figure on the left shows a "steepest descent" reaction path. Although the figure on the right shows the same path (at least wants to show the same path; !!!this is a joke!!!) obtained by a nonorthogonal transformation, it is NOT a steepest descent path anymore.

The mathematical treatment is the following: let us start at the point P_0 , and in the \underline{x} coordinate system let us denote its coordinate vector by \underline{x}_0 , the value of the potential energy at P_0 by $V_x(\underline{x}_0)$, and the gradient vector at P_0 by \underline{g}_x . Let us make a small step along the gradient to a point P whose coordinate vector is \underline{x} , and the value of the potential energy is $V_x(\underline{x})$. In this case: $\underline{x} - \underline{x}_0 = \varepsilon \underline{g}_x$ where ε is a small scalar, and, naturally,

$V_x(\underline{x}) - V_x(\underline{x}_0) = \underline{g}_x^\dagger (\underline{x} - \underline{x}_0) + \dots$ In another \underline{y} coordinate system the analogous symbols will be \underline{y}_0 ,

$V_y(\underline{y}_0)$, \underline{g}_y , \underline{y} , and $V_y(\underline{y})$. Obviously, the potential energy can NOT be changed if we use the y system instead of the original x system, i.e., the relation $V_x(\underline{x}) - V_x(\underline{x}_0) = V_y(\underline{y}) - V_y(\underline{y}_0)$ is valid. We will show, however, that the analogous expression $\underline{y} - \underline{y}_0 = \varepsilon \underline{g}_y$ is NOT always valid. Indeed, let the transformation be between the two systems be $\underline{y} = \underline{S}\underline{x}$ where \underline{S} is nonsingular. In this case

$$\begin{aligned} V_x(\underline{x}) - V_x(\underline{x}_0) &= \underline{g}_x^\dagger (\underline{x} - \underline{x}_0) + \dots = \underline{g}_y^\dagger (\underline{y} - \underline{y}_0) + \dots = \\ &= \underline{g}_y^\dagger \underline{S}(\underline{x} - \underline{x}_0) + \dots = (\underline{S}^\dagger \underline{g}_y)^\dagger (\underline{x} - \underline{x}_0) + \dots \end{aligned}$$

this means that $\underline{g}_x = \underline{S}^\dagger \underline{g}_y$

Thus we get:

$$\underline{y} - \underline{y}_0 = \underline{S}(\underline{x} - \underline{x}_0) = \underline{S}\varepsilon \underline{g}_x = \varepsilon(\underline{S}\underline{S}^\dagger) \underline{g}_y$$

In the y coordinate system the point P will be steepest descent (i.e., along the \underline{g}_y gradient) if and only if \underline{S} is an orthogonal (unitary) transformation. Q.E.D.

Solutions for the lack of uniqueness of reaction path:

- (i) use of a "standard" coordinate system: mass-weighted Cartesian coordinates $\sqrt{m_i} \underline{r}_i$;
- (ii) dynamic way: to choose the classical mechanical trajectory of lowest possible energy which passes through the transition state (bob-sleigh effect).
- (iii) however, the choice of the reaction coordinate is often quite unambiguous due to chemical intuition. In the molecules frequently exists a much less rigid direction comparing to the others (the natural way of selection of a reaction coordinate). If this is true, the reaction path is almost invariant with respect to the selection of the reaction coordinate (e.g., most of the

internal rotations). In this case we can make a Born-type separation of the "slow motion" along the reaction coordinate from the "fast motions". This slow motion will occur on an effective potential energy curve and this curve can be approximated by the adiabatic reaction path. In case when the second derivatives of the surface (around the rigid directions) are changing significantly along the soft direction (i.e., along the reaction coordinate), we can get a better result adding the Zero Point Energy (ZPE) of the rigid modes to the potential energy of the reaction path.

Example: The HF-based SQM Force Field method:
P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, *JACS*, 1983, 105, 7037.

(SQM = Scaled Quantum Mechanical)

Harmonic force fields are important:
vibrational fundamentals
IR/Raman intensities
finer details of UV/VIS and PES spectra
start for an anharmonic analysis

Yeljasevich-Wilson vibrational equation:

$$\underline{\underline{G}}\underline{\underline{F}}\underline{\underline{L}} = \underline{\underline{L}}\underline{\underline{\Lambda}}$$

where $\underline{\underline{G}}$ is the inverse kinetic energy matrix, $\underline{\underline{F}}$ is the quadratic force constant matrix, $\underline{\underline{L}}$ the matrix of the eigenvectors, and the diagonal $\underline{\underline{\Lambda}}$ matrix contains the frequencies.

The SQM procedure means the reliable combination of the theoretical (ab initio Q.C.) and experimental information:

A.) Theoretical (ab initio Q. Chemical information):

$$F_{ij} = \left(\frac{\partial^2 E}{\partial q_i \partial q_j} \right)_0 = \left(\frac{\partial}{\partial q_i} \left(\frac{\partial E}{\partial q_j} \right) \right)_0$$

where E is the total molecular energy (electronic + nuclear repulsion energy) and q_i is the nuclear coordinate.

Level of the Q.M. approximation:

Hartree-Fock, 4-21G basis set (Pulay et al.);

Reference geometry: empirically corrected theoretical;

Earlier: Pulay's force (or, gradient) method;

nuclear coordinates: "natural internal coordinates" (NICs).

B.) Experimental information:

Fitting the calculated force field to the experimental fundamentals by empirical parameters ("standard" scale factors)

$$\underline{\underline{F}}^{scaled} = \underline{\underline{T}}^\dagger \cdot \underline{\underline{F}} \cdot \underline{\underline{T}} \quad , \text{ where } \underline{\underline{T}} \rightarrow \text{diag}(x_i^{1/2})$$

x_i scale factors : 0.7 - 0.9 usually

Fitting: SCALE,...,SCALE3 program (G.P.)

$$\mathcal{L} = \sum_i w_i (v_i^{calc} - v_i^{exp})^2 \rightarrow \min \quad (\text{Gauss - Newton})$$

where w_i are the weighting factors (usually $1/v$)

Input:

theoretical force constant matrix/ces

experimental fundamentals

start values of the scale factors

definition of the internal coordinates

dipole moment derivatives

Output:

scaled force constant matrix/ces
 optimized scale factors
 scaled vibrational fundamentals
 absolute IR intensities
 mean-square vibrational amplitudes

Scale factors: standard and/or "extra"

"Extra" scaling (for aromatic or polyene systems):

$$F_{ij}^{\text{scaled}} = x_A^{\text{extra}} \cdot F_{ij}$$

where x_A^{extra} -s are the extra scale factors (due to the strong effect of correlation).

Values: fixed or optimized

**Glyoxal, acrolein, butadiene, ethylene, formaldehyde
light and perdeuterated isomers**

mean deviation: 12.3 cm⁻¹ in-plane
 6.7 cm⁻¹ out-of-plane
 max. individual deviation: < 20 cm⁻¹

A priori SQM Force Fields:

transferring scale factors from one system to another

First example: from benzene to pyridine...

G. Pongor, P. Pulay, G. Fogarasi, J.E. Boggs, *JACS*, 1984, 106, 2765.

G. Pongor, G. Fogarasi, J.E. Boggs, P. Pulay, *J. Molec. Spectroscopy*, 1985, 114, 445.

**Benzene, Hartree-Fock/4-21G (from P. Pulay, G. Fogarasi, J.E. Boggs, *J. Chem. Phys.* 1981, 74, 3999.)
Table VIII., Set II.**

<u>Description</u>	<u>Scale factor</u>
CH stretch	0.863
CC stretch	0.911
CH in-plane bend	0.797
ring planar deform.	0.808
CH wagg	0.739
ring tors	0.768
	<u>Extra scale factors</u>
CC stretch/CC stretch	0.774
ortho	0.645
meta/para	
CC stretch/E _{2g} ring def	0.72

benzene:

mean deviation: 6.0 cm⁻¹

max. individual deviation: 13.0 cm⁻¹

transferring these to pyridine:

pyridine:

mean deviation: 5.7 cm⁻¹

max. individual deviation: 15.0 cm⁻¹

Natural Internal Coordinates (NIC):

G. Fogarasi, X. Zhou, W. Taylor, P. Pulay,
JACS, 1992, 114, 8191.

Optimization:

BFGS (Broyden-Fletcher-Goldfarb-Shanno),

Berny (Schlegel),

GDIIS (Pulay & P. Császár)→see Appendix II.

Because of the high cost of Q. Chemical calculations, it is reasonable to develop optimization algorithms which need as few steps as possible. However, analytic second derivatives seem to be too expensive than to be worthwhile to implement them into the procedure. If one uses only the gradient information, the convergence of the geom. optimization can be significantly accelerated by the use of a carefully selected set of internal coordinates.

Improvement of optimization:

use lower level force constant matrix
"clever" choice of internal coordinates

Two sets of proper (complete and nonredundant) coordinates, connected by a linear transformation, are naturally equivalent. Thus the only difference can be in that an approximate Hessian can be easier given in one set of valence-type internal coordinates

Cartesians: less effective (even with a good estimate of the "start" Hessian) because of the anharmonic couplings. Far from the equilibrium these couplings are very important.

Curvilinear internals: came from the theory of molecular vibrations; also were used in geom. optimizations by the first gradient program of Pulay.

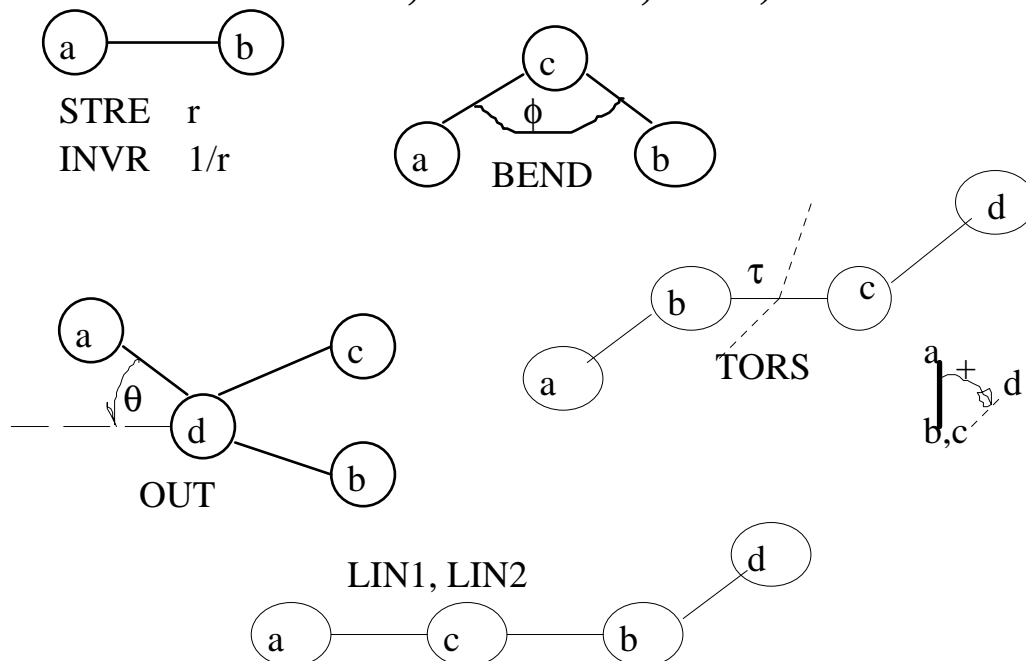
Two types: (a) Z-matrix, (b) spectroscopic

↑unsatisfactory for ring systems

System of NICs:

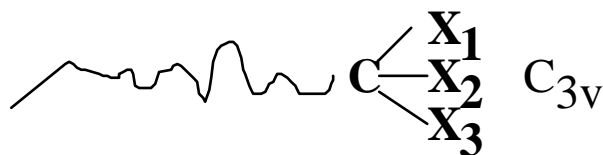
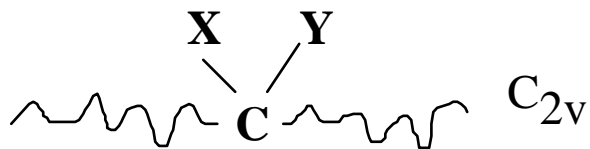
They minimize the couplings, on both harmonic and anharmonic levels. They are fixed lin. combinations

of primitive valence-coordinates (stretchings, bendings, torsions, see e.g., E.B. Wilson, J.C. Decius, P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955. New edition: Dover, New York, 1980):



Complete and nonredundant set of internal coords.:
 (coming from vibrational spectroscopy)

- (i) **Individual stretching coordinates (even for rings)**
 low couplings on quadratic level, compact description of anharmonicity...
- (ii) **Local pseudo-symmetry coordinates for angle deformations:** easy to treat the redundancy, also good for couplings

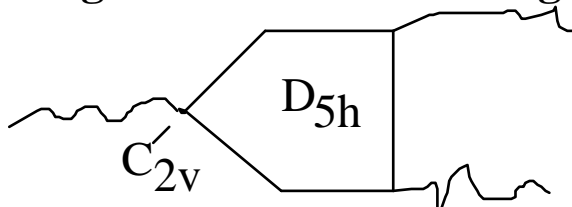


...etc.

Normalization for composite bending

coordinates (AND ring-torsions): $(\sum_i c_i^2)^{-1/2}$

(iii) Ring deform.: idealized highest symmetry



n-membered ring: idealized symmetry D_{nh}

$3n-6$ degrees of freedom: n individual stretchings, $n-3$ symmetrized bendings, $n-3$ symmetrized torsions.

(iv) Torsions $\sum_i \tau_i$ (with special $1/n$ normalization for NON-ring coordinates only!!!)

(v) Polycyclic systems: special treatment for the relative motion of the rings

INTC program (Fogarasi, Pulay): automated search for the NICs. It has been included into the TX90 and PQS programs, later into the AcesII, too; independently, a similar program has been written to TURBOMOLE.

On the next pages:

A.) Recommended Internal Coordinates (pre-NICs)

B.) example output of the INTC program.

Table III. Recommended Internal Coordinate System^a

1. bond stretchings:	individual coordinates rather than combinations. possible exceptions: methyl and methylene groups where symmetrized combinations of the CH stretchings may be used
2. $X_m A - BY_n$ and $X_m A = BY_n$	torsions and twistings: the sum of all possible dihedral angles $X_i A B Y_j$
3. methyl:	sym def = $\alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3$ asym def = $2\alpha_1 - \alpha_2 + \alpha_3$ asym def' = $\alpha_2 - \alpha_3$ rocking = $2\beta_1 - \beta_2 - \beta_3$ rocking' = $\beta_2 - \beta_3$
4. methylene (sp^3):	CH ₂ scissoring = $5\alpha + \gamma$ CXY scissoring = $\alpha + 5\gamma$ CH ₂ rocking = $\beta_1 - \beta_2 + \beta_3 - \beta_4$ CH ₂ wagging = $\beta_1 + \beta_2 - \beta_3 - \beta_4$ CH ₂ twisting = $\beta_1 - \beta_2 - \beta_3 + \beta_4$
5. methylene (sp^2):	sym def = $2\alpha - \beta_1 - \beta_2$ rocking = $\beta_1 - \beta_2$ wagging = X out of CH ₂ plane
6. methine (sp^2):	CH rocking = $\beta_1 - \beta_2$ XCY def = $2\alpha - \beta_1 - \beta_2$ CH wagging = H out of XCY plane
7. methine (sp^3):	CH rocking = $2\beta_1 - \beta_2 - \beta_3$ CH rocking' = $\beta_2 - \beta_3$ XCY def = $4\alpha_{XCY} + \alpha_{XCZ} + \alpha_{YCZ}$ XCZ and YCZ deformations are analogously defined
8. amino:	scissoring = $2\alpha - \beta_1 - \beta_2$ rocking = $\beta_1 - \beta_2$ wagging = X out of NH ₂ plane
9. imino (sp^3):	NH rocking = $\beta_1 - \beta_2$ XNY def = $2\alpha - \beta_1 - \beta_2$ wagging = H out of XNY plane
10. four-ring:	ring def = $\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4$ puckering = $\tau_1 - \tau_2 + \tau_3 - \tau_4$
11. five-ring:	ring def = $\alpha_1 + a(\alpha_2 + \alpha_5) + b(\alpha_3 + \alpha_4)$ ring def' = $(a - b)(\alpha_2 - \alpha_5) + (1 - a)(\alpha_3 - \alpha_4)$ torsion = $b(\tau_1 + \tau_5) + a(\tau_2 + \tau_4) + \tau_3$ torsion' = $(a - b)(\tau_4 - \tau_2) + (1 - a)(\tau_5 - \tau_1)$ where $a = \cos 144^\circ$, $b = \cos 72^\circ$
12. six-ring:	trigonal def = $\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$ asym def = $2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$ asym def' = $\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$ puckering = $\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$ asym torsion = $\tau_1 - \tau_3 + \tau_4 - \tau_6$ asym torsion' = $-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6$

^a See Figure 1 for the definition of bond angles. In the rings, α_2 is, e.g., the angle 1-2-3 and τ_2 is the dihedral angle 1-2-3-4. Note that the coordinates are still subject to some arbitrariness owing to the freedom in the numbering of the atoms for degenerate coordinates. Also, the sign of the out-of-plane coordinates must be specified in each case. Normalization constants are not given here. For definiteness, they are chosen as $N = (\sum c_i^2)^{-1/2}$, where the c_i are the coefficients of the individual valence coordinates. In some cases, e.g., for compounds containing divalent oxygen, the definition of coordinates is obvious and is not given. Note the possibility of using nonstandard valence coordinates: the inverse bond length coordinate, or the coordinate replacing the out-of-plane angle, $(e_1) \times (e_2 \cdot e_3)$, where e_1 , e_2 , and e_3 are unit vectors directed along the bonds.

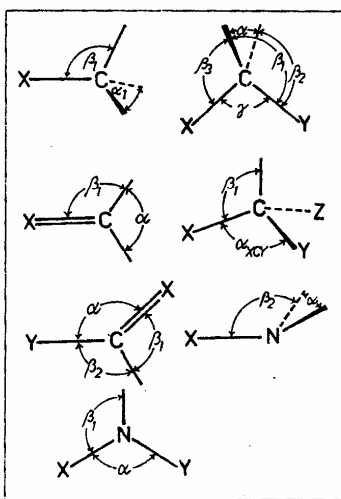
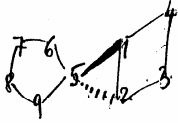


Figure 1. Definition of internal coordinates in methyl, methylene (sp^3), methylene (sp^2), methine (sp^2), methine (sp^3), amino, and imino groups.

q1 - q18: individual bond stretchings



Descr.	Coeff.	Type	Atoms	Descr.	Coeff.	Type	Atoms
q19	1.	bend	2, 4, 3	q24	.5877853	tors	8, 9, 5, 6
4-ring	-1.		3, 1, 4	5-ring	-.9510565		9, 5, 6, 7
in-pl.	1.		4, 2, 1	out-pl.	.9510565		5, 6, 7, 8
def.	-1.		1, 3, 2	def.	-.5877853		6, 7, 8, 9
q20	1.	tors	2, 3, 4, 1	q25	1.	tors	4, 1, 2, 5
4-ring	-1.		3, 4, 1, 2	butterfly	-1.		5, 1, 2, 3
out-pl.	1.		4, 1, 2, 3	q26	1.	bend	1, 6, 5
def.	-1.		1, 2, 3, 4	ring-ring	1.		2, 6, 5
q21	1.0000000	bend	5, 7, 6	wagg.	-1.		1, 9, 5
5-ring	-.8090170		6, 8, 7		-1.		2, 9, 5
in-pl.	.3090170		7, 9, 8	q27	1.	bend	1, 6, 5
def..	.3090170		8, 5, 9	ring-ring	-1.		2, 6, 5
	-.8090170		9, 6, 5	rock.	1.		1, 9, 5
q22	.5877853	bend	6, 8, 7		-1.		2, 9, 5
5-ring	-.9510565		7, 9, 8	q28	1.	bend	1, 6, 5
in-pl.	.9510565		8, 5, 9	ring-ring	-1.		2, 6, 5
def.	-.5877853		9, 6, 5	twist.	-1.		1, 9, 5
q23	1.0000000	tors	7, 8, 9, 5		1.		2, 9, 5
5-ring	-.8090170		8, 9, 5, 6				
out-pl.	.3090170		9, 5, 6, 7				
def.	.3090170		5, 6, 7, 8				
	-.8090170		6, 7, 8, 9				

Internal coordinates and orthonormality:

Instead of the usual Cartesians we can also apply a complete and nonredundant set of the internal coordinates.

In order to understand the use of them, let us consider a molecular system consisting of N nuclei; in its equilibrium geometry let the position vectors of the nuclei be $\underline{R}_1^0, \underline{R}_2^0, \dots, \underline{R}_N^0$ in the usual 3-dimensional manifold \mathcal{E}_3 . Equivalently, we can use instead of this a single point \underline{R}^0 of a hypothetical $3N$ -dimensional manifold \mathcal{R}_{3N} , that is, $\underline{R}^0 \in \mathcal{R}_{3N}$. Let us denote an orthonormal (Cartesian) basis set of the \mathcal{R}_{3N} manifold by $\{\underline{e}_k\}_1^{3N}$, for which the well-known equations hold:

$$\langle \underline{e}_k | \underline{e}_l \rangle = \delta_{kl} \quad , \quad (k, l = 1, 2, \dots, 3N)$$

(that is, the Gram-matrix of the \underline{e}_k unit vectors is the unit matrix.) Naturally,

$$\underline{R}^0 = \sum_k^{3N} R_k \underline{e}_k \quad .$$

Let us construct another manifold in order to determine the *nuclear configuration* of the molecule (without the center-of-mass and the rotations). This manifold will be denoted by \mathcal{R}_{3N-6} and its basis set by $\{\underline{\sigma}_i\}_1^{3N-6}$. Let us denote the vector of the given nuclear configuration at the equilibrium geometry by \underline{S}^0 , i.e., $\underline{S}^0 \in \mathcal{R}_{3N-6}$ and we can write

$$\underline{S}^0 = \sum_i^{3N-6} S_i \underline{\sigma}_i \quad (\text{here the } S_i\text{-s are the so-called internal coordinates). The } \underline{\sigma}_i \text{ unit vectors of } \mathcal{R}_{3N-6} \text{ are}$$

constructed as fixed linear combinations of the primitive curvilinear valence coordinates (bond lengths, bond angles, out-of-plane and dihedral angles), similarly to the contracted Gaussian basis sets in Quantum Chemistry. [Of course, there is a significant difference between the unit vectors of the "internal manifold" \mathcal{R}_{3N-6} and the Cartesian unit vectors (or the Gaussian primitives): each of the latter corresponds to (is centered on) a single nucleus.] Let us express the $\underline{\sigma}_i$ unit vectors of \mathcal{R}_{3N-6} by a simple linear transformation around the molecular equilibrium (linear approximation, see later):

$$\underline{\sigma}_i = \sum_k^{3N} e_k A_{ki} \quad . \quad (\text{Here the role of the } A_{ki} \text{ linear}$$

coefficients is not known yet. Let us collect the $\underline{\sigma}_i$ unit vectors of \mathcal{R}_{3N-6} and the e_k unit vectors of \mathcal{R}_{3N} into the super-row vectors $(\underline{\sigma})$ and (\underline{e}) , respectively. Now we can write the following expression, obviously:

$$(\underline{\sigma}) = (\underline{e})\underline{A} \quad .$$

Also, let us consider the following equation:

$$(\underline{e})\underline{R} = (\underline{e})\underline{A}\underline{B}\underline{R} = (\underline{\sigma})\underline{B}\underline{R} = (\underline{\sigma})\underline{S} \quad ,$$

from where it is obvious that $\underline{A}\underline{B} = \underline{E}$, and on the other hand $\underline{S} = \underline{B}\underline{R}$, where the B matrix is the well-known one of Wilson and Yelyasevich. Thus, the matrix A is the generalized inverse of the matrix B as follows:

$$\underline{\underline{A}} = \underline{\underline{B}}^+ (\underline{\underline{B}} \underline{\underline{B}}^+)^{-1} .)$$

Moreover, one can write $\underline{\sigma}_j = \sum_l^{3N} \underline{e}_l A_{lj}$ (*vide supra*), so we get for a typical $\langle \underline{\sigma}_i | \underline{\sigma}_j \rangle$ element of the Gram-matrix of the $\underline{\sigma}_i$ unit vectors:

$$\begin{aligned} \langle \underline{\sigma}_i | \underline{\sigma}_j \rangle &= \left\langle \sum_k^{3N} \underline{e}_k A_{ki} \left| \sum_l^{3N} \underline{e}_l A_{lj} \right. \right\rangle = \sum_k^{3N} \sum_l^{3N} A_{ki} A_{lj} \langle \underline{e}_k | \underline{e}_l \rangle = \\ &= \sum_k^{3N} \sum_l^{3N} A_{ki} A_{lj} \delta_{kl} = \sum_k^{3N} A_{ki} A_{kj} \end{aligned} ;$$

as can be seen the $\{\underline{\sigma}_i\}_1^{3N-6}$ basis set is NOT orthonormal in the \mathcal{R}_{3N-6} manifold. However, there are such applications when one can postulate the unit vectors of \mathcal{R}_{3N-6} as orthonormal vectors. Indeed, this is usually not very far from the real case considering the fact that the $\underline{\underline{B}}$ matrix is frequently a "sparse matrix" (as, for example, in case of the choice of the Natural Internal Coordinates).

Note that $\underline{S} = \underline{\underline{B}} \underline{R}$ is valid only in linear approximation, thus the $(\underline{\sigma}) = (\underline{e}) \underline{\underline{A}}$ equation is true in the same approximation as well.

3. POST-HF METHODS

The disadvantages of the Hartree-Fock method:

(1) electron correlation: this error can not be eliminated within the HF method because it comes from the simple determinantal approximation of the trial function.

(2) error of MOs: due to the finite basis set - we can reduce this using larger and larger basis sets...

Generally, the Slater-determinant is not a bad trial function, let us start with that:

CI-expansion: Not normalized!!! (intermediate...)

$$\Psi = \Phi_0 + \sum_i \sum_a C_i^a \Phi_i^a + \sum_i \sum_j \sum_a \sum_b C_{ij}^{ab} \Phi_{ij}^{ab} + \dots =$$

$$= (\hat{I} + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \dots) \Phi_0$$

where Φ_0 is the HF-determinant, and **BE CAREFUL**, C_i^a and C_{ij}^{ab} are **NOT** derivatives anymore, rather the coefficients of the "excited" (substituted) determinants (Φ_i^a : the i-th occupied spinorbital is substituted by the a-th virtual one, etc.), \hat{I} is the identity operator, and \hat{C}_p produces the p-fold "excited" configurations.

no = number of the occupied orbitals;

nv = number of the virtual orbitals.

Singly subst. configurations: $i \rightarrow a$: $no \times nv$;

Doubly subst. configurations: $ij \rightarrow ab$: $(no \times nv)^2$ roughly

.....

Finite number of substitutions, at most n electrons can be "excited"! Using a finite basis set the expansion is also finite!!!

Perturbation Theory:

In a physical sense there are 2 kinds of perturbations (mathematically only one case):

↓	↓
"changeable"	"non-changeable"
e.g., ext. magnetic field,...	the strength of the pert. is not changeable

Let it \hat{H}_0 the (non-physical) operator whose exact eigenfunction would be the HF (SCF) solution:

$$\hat{H}_0 = \sum_i \hat{F}(i) = \sum_i [\underbrace{\hat{h}(i)}_{\text{core}} + \underbrace{\hat{G}(i)}_{\text{aver. repulsion of the other electrons + exchange}}]$$

(i for each electrons; \hat{F} op. would be different for each orbitals; \hat{F} contains also the non-physical repulsion with its own charge density but the "self-exchange" term cancel it... Without the el-el. repulsion the electronic structure of the molecule would be more compact - the shell structure would be characteristic in this case too, because of the Pauli-principle...)

It is not necessary, but let us use the canonical spin-orbitals in the following expressions:

$$\hat{H}_0 \Phi_0 = (\varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_n) \Phi_0 = E_0 \Phi_0$$

Take care!!! The Φ_0 is the exact eigenfunction of \hat{H}_0 , but $E_0 \neq E_{\text{SCF}}$ (\hat{F} contains the twice of the el-el. interaction).

$$\hat{H}_0 \Phi_i^a = (\varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_a + \dots + \varepsilon_n) \Phi_i^a = (E_0 + \varepsilon_a - \varepsilon_i) \Phi_i^a$$

$$\hat{H}_0 \Phi_{ij}^{ab} = (E_0 + \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j) \Phi_{ij}^{ab}$$

... ..

As can be seen, the eigenfunctions of \hat{H}_0 are the HF-determinant and its substituted configurations.

Obviously,

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad , \quad \text{where } \hat{H}' = \hat{H} - \hat{H}_0 \text{ is "small"}$$

"Møller-Plesset (MP) partition of the Hamiltonian"

(we can use hypothetically a λ parameter, changing continuously from 0 to 1, and put $\lambda = 1$.)

Using a power expansion in λ , the

first-order energy correction:

$$E^{(1)} = \langle \Phi_0 | \hat{H}' \Phi_0 \rangle = \langle \Phi_0 | \hat{H} \Phi_0 \rangle - \langle \Phi_0 | \hat{H}_0 \Phi_0 \rangle$$

$$\begin{array}{ccc} & \uparrow & \uparrow \\ & E_{\text{SCF}} & E_0 \end{array}$$

The total energy with the first-order correction:

$$E_0 + E^{(1)} = E_0 + E_{\text{SCF}} - E_0 = E_{\text{SCF}}$$

The energy up to first order is the SCF energy.

The

second-order energy correction:

$$E^{(2)} = -\sum_I \frac{|\langle \Phi_0 | \hat{H}' \Phi_I \rangle|^2}{E_I - E_0}$$

where the summation goes over the all eigenfunctions of \hat{H}_0 , the I is not orbital, but configurational index!!!

All the Φ_I -s are the eigenfunctions of \hat{H}_0 (in form of N-electronic determinants, e.g., Φ_0 , Φ_i^a , Φ_{ij}^{ab}) which can be constructed by the canonical spinorbitals according to the all possible ways...

(It is more convenient to think about spinorbitals than closed-shell spatial MOs here...)

When $\langle \Phi_0 | \hat{H}' | \Phi_I \rangle$ is not zero?

Two components of \hat{H}' : \hat{H} and \hat{H}_0 ;

\hat{H}_0 is the sum of one - electronic operators,

\hat{H} is the sum of one - and two - electronic operators

Using orthogonal orbitals, due to the ‘Slater-rules’:

(a) Zero-electronic operators (nuclear repulsion) can have non-zero matrix elements between Slater-determinants which do not differ even in one spin-orbital.

(b) One-electronic operators can only have non-zero matrix elements between Slater-determinants which differ at most in one spin-orbital.

(c) Two-electronic operators can only have non-zero matrix elements between Slater-determinants which differ at most in two spin-orbitals.

Conclusively, using the exact non-relativistic Hamiltonian, the Φ_I -s will contain singly and doubly substitutions only, the summations have to make for these dominant terms only.

Moreover: the singly substitutions are not too important either because of the...

Brillouin-theorem:

the matrix elements between the HF-determinant Φ_0 and the single substitutions Φ_i^a will be zero:

$$\langle \Phi_0 | \hat{H}' \Phi_i^a \rangle = 0$$

Proof: if it would not have been zero, we could construct a determinant with *lower* energy than the HF-determinant ('reductio ad absurdum'):

$$\begin{aligned} \hat{H}' &= \hat{H} - \hat{H}_0 \\ \langle \Phi_0 | \hat{H}_0 \Phi_i^a \rangle &= \langle \hat{H}_0 \Phi_0 | \Phi_i^a \rangle = E_0 \langle \Phi_0 | \Phi_i^a \rangle = 0 \\ &\text{zero!!!} \end{aligned}$$

Let us suppose that $\langle \Phi_0 | \hat{H} \Phi_i^a \rangle \neq 0$,

and let pay attention to the following (not normalized) lin. combination:

$$\Phi = \Phi_0 + \eta \Phi_i^a$$

We have to keep in mind that the sum of two determinants (differing in one row/column) can be written as a single determinant. Indeed, Φ can be written as a single determinant if we substitute the i-th spinorbital in Φ_0 by $\phi_i \rightarrow \phi_i + \eta \phi_a$.

Obviously, this change can not improve the HF-orbitals since they were optimized previously... Now:

$$\begin{aligned} E(\Phi) &= \frac{\langle \Phi | \hat{H} \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \Phi_0 | \hat{H} \Phi_0 \rangle + 2\eta \langle \Phi_0 | \hat{H} \Phi_i^a \rangle + \eta^2 \langle \Phi_i^a | \hat{H} \Phi_i^a \rangle}{\langle \Phi_0 | \Phi_0 \rangle + 2\eta \langle \Phi_0 | \Phi_i^a \rangle + \eta^2 \langle \Phi_i^a | \Phi_i^a \rangle} = \\ &= \frac{E_{\text{SCF}} + 2\eta \langle \Phi_0 | \hat{H} \Phi_i^a \rangle + \eta^2 \langle \Phi_i^a | \hat{H} \Phi_i^a \rangle}{1 + \eta^2} \approx E_{\text{SCF}} + 2\eta \langle \Phi_0 | \hat{H} \Phi_i^a \rangle \end{aligned}$$

If η is small enough, η^2 can be neglected (see above). If the sign of η is the opposite to that of $\langle \Phi_0 | \hat{H} \Phi_i^a \rangle$, we

would have energy lowering comparing to the HF case for a one-determinantal trial function ...

"Credo quia absurdum", Tertullianus, St. Augustinus?

Thus, the most important terms in the second order of the CI expansion are the Φ_{ij}^{ab} doubly substituted configurations of the SCF determinant. Physically Φ_{ij}^{ab} express the "collision of two electrons which go to higher orbitals..."

Many Body Perturbation Theory (MBPT):

In higher order the terms are more and more complicated. Up to the 4th order it is possible to treat the formulas algebraically, over this order the perturbation theory is not too important from a chemical point of view.

In QED (= quantum electrodynamics) the higher orders (> 4) are important. Here the diagram techniques (originate from Feynman) can help.

MBPT: it is not well defined by itself, the partition of the Hamiltonian is important.

Problematic cases: open-shell species, or, if the HF is not a good approximation it is not a unique method for the selection of \hat{H}_0 .

Usual cases: closed shell species, where HF is a good approximation (many times...):

$$\hat{H}_0 \equiv \sum_i \hat{F}(i)$$

MBPT with the Møller-Plesset (MP) partition (1934).

MP2 (Pople, Gaussian[®]): second order MP, the simplest correlation method based on the configurational expansion. Gives very good results if the correlation is not too strong: 85-95 % of the correlation energy obtainable in a given basis set.

We could think MP3 or MP4 is even better, but this is not the case generally. MP3 is worse, and MP4 improves roughly to the same level as MP2 gave. The final convergence of the MBPT is not as good as it was hoped. Generally, if MP3 and MP4 give about the same result, the MP2 results are reliable.

Coupled Cluster (CC) methods: similar to MBPT but some substitutions are treated at infinite order.

Cížek & Paldus (1966-1971): "exponential Ansatz"

$$\tilde{\Psi}^{\text{CC}} = e^{\hat{T}} \Phi_0 = \left(\hat{I} + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \dots \right) \Phi_0 \quad \text{breaks down at } n$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_n$$

where Φ_0 is the Hartree-Fock determinant and the \hat{T} "cluster operator" (previously used in nuclear physics) produces the p-fold "excited" configurations.

Appearance of "disconnected terms" in the expansion: even CCD introduces quadruple excitations Φ_{ijkl}^{abcd} and

hextuples excitations Φ_{ijklmv}^{abcdef} ..., up to all n-tuples as

can be easily seen:

$$\tilde{\Psi}^{\text{CCD}} = (\hat{I} + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \dots)\Phi_0 =$$

$$\Phi_0 + \sum_{\substack{i < j \\ a < b}} t_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{\substack{i < j < k < l \\ a < b < c < d}} t_{ij}^{ab} t_{kl}^{cd} \Phi_{ijkl}^{abcd} + \dots$$

naturally, in this case the coefficients of the higher excitations are simple products of the same t_{ij}^{ab}

coefficients...

Main features: (i) determination of the wave function coefficients are more complicated (exponential!!!); (ii) converges more rapidly than CI; (iii) size-consistent (see below), contrary to the CI method; (iv) very accurate: with a large one-electron basis set CC results sometimes are considered more accurate than experimental data, [e.g., features of CCSD(T) (see below): bond lengths $\sim (2-3) \times 0.001 \text{ \AA}$, fundamental frequencies $\sim \text{few cm}^{-1}$, dipole moments $< 0.1 \text{ D}$]; (v) EOM-CC method is capable for determination of the excited states (excitation energies correct to within ca. 0.2 eV), by diagonalization of the effective $e^{-\hat{T}} \hat{H}_e \hat{T}$ Hamiltonian within a specified determinantal space; (vi) It is NOT variational method.

Variational CI method:

In the config. expansion we can stop at the important doubly substituted configurations, and the values of the coefficients will be determined by the variational method. The singly substituted configs. are also important, even if we would not hope this on the basis of the perturbation theory (see above). Although their contribution to the energy is not considerable, but it is very important for the calc. of the other properties.

For the excited states the variational CI method still has advantages which can not reach with the perturbation theory. Interestingly, the early hopes for the calculations of the ground states are not fulfilled with the variational CI method: it is **NOT** size-consistent (this means that the energy is **NOT** extensive accurately, contrary to the thermodynamics; only the full-CI is consistent, the truncated one is **NOT**).

Size consistency: e.g., 2 He atoms at a large distance; their energy must be accurately twice as big as that of one of the atoms (c.f., the separation of the eigenvalue problem in \mathcal{L}_2 space...):

$$\begin{aligned}\hat{H}(AB) &= \hat{H}(A) + \hat{H}(B) \quad ; \quad (\text{A and B are very far...}) \\ \Psi(AB) &= \Psi(A) \cdot \Psi(B) \\ E(AB) &= E(A) + E(B)\end{aligned}$$

The Hartree-Fock level is size-consistent, so the Møller-Plesset perturbation theory (at any order) is... **But NOT** the variational CI method: if, e.g., doubly "excited" configurations are taken into consideration maximally for each of the He atoms, the product wave function contains quadruply "excited" configurations, too:

$$\begin{aligned}\tilde{\Psi}^{\text{CID}}(A)\tilde{\Psi}^{\text{CID}}(B) &= \\ &= [\hat{I}(A) + \hat{C}_2(A)]\Phi_0(A) \cdot [\hat{I}(B) + \hat{C}_2(B)]\Phi_0(B) = \\ &= [\hat{I}(A) + \hat{C}_2(A)][\hat{I}(B) + \hat{C}_2(B)]\Phi_0(AB) = \\ &= [\hat{I}(A)\hat{I}(B) + \dots + \hat{C}_2(A)\hat{C}_2(B)]\Phi_0(AB) \neq \\ &\neq [\hat{I}(AB) + \hat{C}_2(AB)]\Phi_0(AB) = \tilde{\Psi}^{\text{CID}}(AB)\end{aligned}$$

The CC method (at any \hat{T}) gives:

$$\begin{aligned}\tilde{\Psi}^{\text{CC}}(A)\tilde{\Psi}^{\text{CC}}(B) &= e^{\hat{T}(A)}\Phi_0(A)e^{\hat{T}(B)}\Phi_0(B) = \\ &= e^{\hat{T}(A)+\hat{T}(B)}\Phi_0(AB) = e^{\hat{T}(AB)}\Phi_0(AB)\end{aligned}$$

thus the CC method is size-consistent.

The CCSD(T) method is also size-consistent (CCSD+perturbative T...).

Computational requirements:

$$E_{MP}^{(2)} = -\frac{1}{4} \sum_i \sum_j \sum_a \sum_b \frac{\left| \langle \Phi_0 | \hat{H}' \Phi_{ij}^{ab} \rangle \right|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

↑ if the summation is without constraints.

(With a computer not in this way, the sum of the contributions will be calcd. ... Moreover,

$$E_I = E_{ij}^{ab} = E_0 + \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j .)$$

Thus we get:
$$E_{MP}^{(2)} = -\frac{1}{4} \sum_i \sum_j \sum_a \sum_b \frac{|(ia||jb)|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

where $(ia||jb) \equiv (ia|jb) - (ib|ja)$ and $(ia|jb)$ are defined for the spinorbitals similarly as earlier for the χ_p basis

functions:

$$(ia | jb) \equiv \iint \phi_i(1)\phi_a(1) \frac{1}{r_{12}} \phi_j(2)\phi_b(2) d\tau_1 d\tau_2$$

real

(can not be calculated itself directly, may be on a grid...???, but using an LCAO-expansion:

$$\phi_i = \sum_p C_{pi} \chi_p \quad , \quad \text{etc., we get}$$

$$(ia|jb) = \sum_p \sum_q \sum_r \sum_s C_{pi} C_{qa} C_{rj} C_{sb} (pq|rs)$$

{transformation performed in the following way:

like the DO loops at matrix multiplication in Fortran

$$(ia|jb) = \sum_p C_{pi} [\sum_q C_{qa} [\sum_r C_{rj} [\sum_s C_{sb} (pq|rs)]]] \quad \}$$

m = number of the basis functions;

n = number of the electrons

For basis functions: $\circ(m^4)$ integrals (SCF)

MP2: $\circ(m^4n)$, formally 5th order

(N = the size of the molecule, in any units...)	
HF (SCF):	$\circ(N^4)$
MP2:	$\circ(N^5)$
MP3, CISD, CC-SD:	$\circ(N^6)$
MP4, CC-SD(T):	$\circ(N^7)$
MP5, CISDT, CCSDT	$\circ(N^8)$
MP6	$\circ(N^9)$
MP7, CISDTQ	$\circ(N^{10})$

Nota bene: $\circ(N^x)$ shows the increase only but not in an absolute sense (they can be multiplied by a small number...).

In terms of accuracy with a medium sized basis set the following order is often observed for single-reference methods:

HF << MP2 < CISD < MP4(SDQ) ~ CC-SD < MP4 < CC-SD(T)

Categories of the electron correlation (Sinanoğlu):

1.) dynamic correlation: weak; accounts for the instantaneous repulsion of the electrons; means a quite significant correction (to HF) which is typically the sum of many small contributions; less depending on the geometry, but strongly depends on spin (for bigger S states it is lowering: it is reasonable because the electrons with parallel spin keep out of each other).

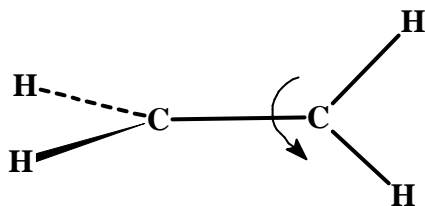
"Single-reference" case, $C_I < 0.1$;

2.) nondynamic (also: static = symmetry required, quasi-degenerated) correlation: accounts for the existence of near-degeneracy of low-lying electronic configurations; here the HF is not good even qualitatively; significant correction that is the sum of a few, large contributions. It strongly depends on geometry (due to low-lying virtual orbitals).

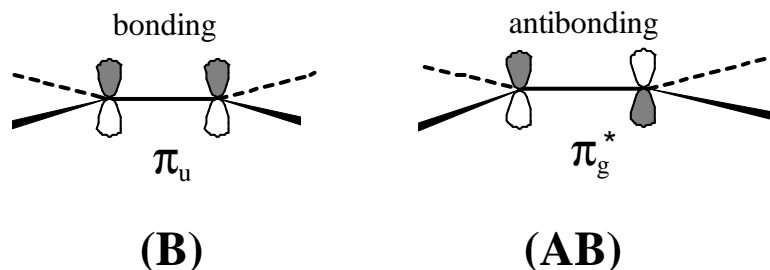
"Multi-reference case, $C_{0J} > 0.2$ ".

In the limit when all possible configurations are included in the CI expansion then dynamical correlation completely describes the nondynamic component. However, when we use truncated expansions, proper description of nondynamic effects becomes important.

Example: ethene (ethylene):

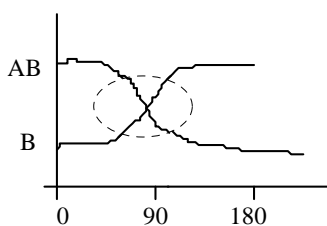


rotation of the methylene groups comparing to each other. During the rotation the bonding orbital will have less bonding character, the antibonding orbital will have less antibonding character:



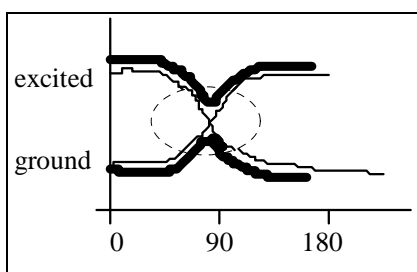
The kinetic energy will be larger (due to the nodal plane) so the bonding character of the BO lowers...

The orbital energies (ϵ):



The difference between the orbital energies will be small: here the HF method is not good, it is not enough one determinant even in the zeroth order.

The total energies (E) of the states:



using more than one determinant, the unrealistic cusp disappears and the lines will be continuous (c.f., Appendix III, pp.163-171).

When the nondynamic correlation is important?

always if the MOs around the Fermi-level (HOMO, LUMO) are not fully occupied (see ethene around 90° (above)→can be 4 electrons but there are only 2).

That is, important

A.) in transition states (chemical reactions), at the formation or cleavages of covalent bonds, [especially, in reactions which are forbidden by the Woodward-Hoffmann rules].

Nota bene: the rotation of the methyl group is NOT such a case: in that there are not forming or rupturing bonds...

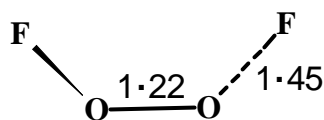
B.) in compounds of highly electronegative elements: e.g., F_2 , O_3 , NO , NO_2 , N_2O_4 , F_2O_2 etc.

Example 1: F_2 : dissociation energy is very low, the structure is pushed from F-F into the direction of $F\cdot F$ biradical. There is a bond but the antibonding levels are

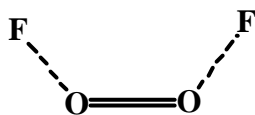
also occupied. Due to the large electronegativity the antibonding levels fall down (near to the bonding MOs).
Example 2: O_3 : biradical character. Acyclic, it is NOT similar to *cyclo*-propane (cyclic structure also exists but it is rather unstable).

Example 3: NO , NO_2 , N_2O_4 , F_2O_2 :

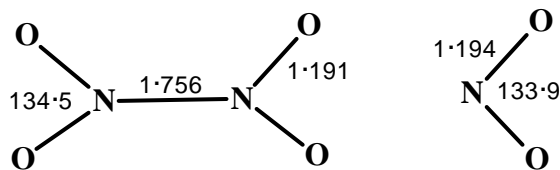
e.g., F_2O_2 the SCF fails completely (not stable):
 the accurate structure is (in Angstroms units)



, contrary to the usual chemical viewpoint. The O-O bond length is so small that it is similar to the O=O bond:



The structure of N_2O_4 :



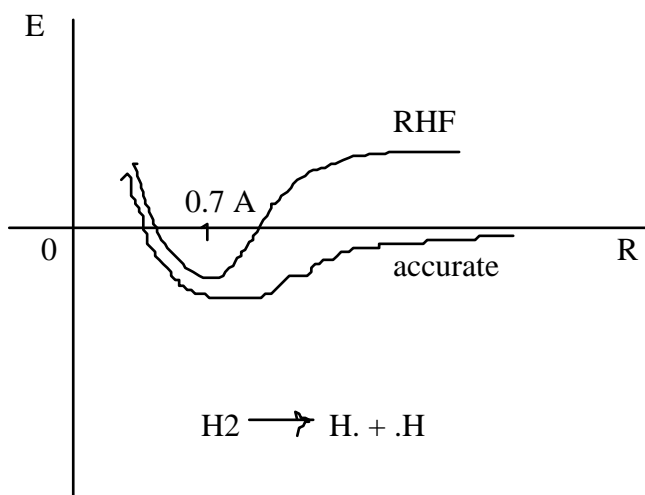
weakly bound character of a dimer!

(comparison: N-N bond length in hydrazine 1.447 Å.)

Example 4: compounds of transition metals. There are not enough electrons for the complete occupancy either. Interestingly the first row (Cr, Mn, Fe, Co, Ni) is more difficult to treat theoretically than the second one (Mo, ..., Pd) which are heavier...

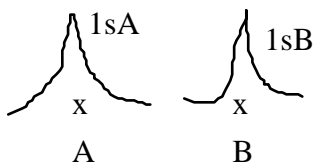
Example 5: Dissociation of H_2 :

Here the transition state is actually at the infinity. The rupture of the chemical bond → important the nondynamic correlation.



The RHF bond length is only slightly smaller, the main problem is the incorrect dissociation: the RHF overestimates the barrier at the rupture of a covalent bond.

The strange behavior of the RHF is (using a minimal basis of two s-functions):



now the bonding and antibonding MOs:

$$u_b = \frac{1}{\sqrt{2 + 2S}} (1s_A + 1s_B) \quad \text{bonding}$$

$$u_a = \frac{1}{\sqrt{2 - 2S}} (1s_A - 1s_B) \quad \text{antibonding}$$

(where S is the overlap integral)

The RHF-determinant:

$$\begin{aligned}
\Phi_{\text{SCF}} &= |u_b \alpha u_b \beta| = |u_b \bar{u}_b| = \\
&= \frac{1}{\sqrt{2}} \begin{vmatrix} u_b(1)\alpha(1) & u_b(1)\beta(1) \\ u_b(2)\alpha(2) & u_b(2)\beta(2) \end{vmatrix} = \\
&= \underbrace{u_b(\underline{r}_1)u_b(\underline{r}_2)}_{\text{spatial part}} \frac{1}{\sqrt{2}} \underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin part } \Theta(1,2)} = \\
&= \frac{1}{2 + 2S} \left[\underbrace{1s_A(\underline{r}_1)1s_B(\underline{r}_2)}_{\text{H+H}} + \underbrace{1s_A(\underline{r}_2)1s_B(\underline{r}_1)}_{\text{H+H}} + \right. \\
&\left. \underbrace{1s_A(\underline{r}_1)1s_A(\underline{r}_2)}_{\text{H}^- + \text{H}^+} + \underbrace{1s_B(\underline{r}_1)1s_B(\underline{r}_2)}_{\text{H}^+ + \text{H}^-} \right] \cdot \underbrace{\Theta(1,2)}_{\text{spin}}
\end{aligned}$$

At large R distances the result is two H-atom in the reality (can be H⁺ and H⁻ also at a much higher energy), so the relative weights of the ionic forms are too large in the RHF wave function!!! Obviously, the RHF wave function is physically bad; the reason is that if R → ∞, the orbital energies of the bonding and antibonding orbitals will be close to each other, the occupancy around the Fermi-level is not complete...

Heitler & London (1927): First Paper in Quantum Chemistry : Good dissociation !!!

Valence Bond (VB) trial function: the last two ionic terms are omitted in the expression given above.

[Generalization of the VB method (GVB; N! of determinants made of N non-orthogonal orbitals; of course, this is only 2 at H₂) is very difficult for polyatomic moles. It is NOT equivalent in a strict sense with the MO method, see later.]

Multiconfigurational Hartree-Fock (MC-SCF):

(alternative solution for the H_2 dissociation problem...)

We put 2 electrons from the bonding (b) to antibonding (a)

MO:

$$\Phi_{bb}^{\bar{a}a} = |\underline{u}_a \alpha \underline{u}_a \beta| = \frac{-1}{2 - 2S} [1s_A(\underline{r}_1)1s_B(\underline{r}_2) + 1s_A(\underline{r}_2)1s_B(\underline{r}_1) - 1s_A(\underline{r}_1)1s_A(\underline{r}_2) - 1s_B(\underline{r}_1)1s_B(\underline{r}_2)] \cdot \text{spin part}$$

(the covalent and ionic structures have opposite signs)

Now the sum

$$\tilde{\Psi} = A_1 \Phi_{SCF} + A_2 \Phi_{bb}^{\bar{a}a}$$

electron configuration
 b^2
 a^2

(where $A_1^2 + A_2^2 = 1$; $A_2 < 0$)

if $R \rightarrow \infty$ then $S \rightarrow 0$ and ionic terms will be fallen out
right dissociation !!!

also, if $R = R_e$ then $A_2 \ll A_1$ the weight of $\Phi_{bb}^{\bar{a}a}$ is small
and here the RHF is good.

Obviously, the MC-SCF trial function can be regarded as an interpolation between the RHF and VB trial functions.

This was only a very simple case (using only two b^2 and a^2 configurations for H_2). In the case of more complex systems: other configs. (singly, doubly, triply, etc. "excited" configurations) are also involved in the expansion.

Two trends can be distinguished:

A.) full CI	B.) MC-SCF
<p>the "complete" correlation has to be calculated (that is very difficult for large systems)</p>	<p>the correlation must be calculated for the important orbitals only</p>

MC-SCF: typically a linear combination of MANY determinants (can be several 10^6) which are made of a common, orthogonal set of the MOs.

Both the C_{ij} -s (lin. coeffs within the MOs) and the A_i -s (lin. coeffs within the CI-expansion) will be optimized variationally.

Nota bene: (i) If we would take all the orbitals, their optimization is NOT important (CI-method)

(ii) If only a small set of the orbitals is considered, their optimization IS important (MC-SCF method).

MC-SCF is not as well-defined procedure as Hartree-Fock. Due to many technical/definitional problems it did not become to a black-box method like RHF...

Goal: one could find a method which is comparable in accuracy with the HF method but for strongly-correlated systems.

Difficulties:

(i) **technical:** convergence problems (it is solved now);

(ii) **definition (MAIN!!!):** a.) which MOs will be partially occupied?; b.) which configurations will be used?

a.) **Three classes of the MOs:**

I. MOs (with large negative ϵ orbital energies) which are occupied in each substitutions: **doubly occupied orbitals;**

II. MOs (with intermediate ϵ orbital energies) playing an *active* role in the substitutions (i.e., in one are occupied, and in another are unoccupied): **fractionally occupied "active" orbitals;**

III. MOs (with high ϵ orbital energies) which are unoccupied in any of the substitutions: **unoccupied orbitals.**

b.) **Configurations:**

because it is impossible to predict which config. will be important (this would influence the resulted hypersurface...),

Ruedenberg, Roos and Taylor suggested that ALL the configurations (=complete) must apply which originate from the arrangements of the electrons on the active orbitals (with correct spatial and spin symmetry!):

CAS-SCF (Complete Active Space) = essentially a "full-CI" limited to a special part (n_1) of the active electrons and to a special part (n_2) of the active orbitals with variational optimization of both the MOs and the lin.coeffs of the configurations. $n_1 \times n_2$ CAS (typically $n_1 = n_2$ but not always).

E.g., 4×4 CAS - half-occupied active space.

E.g., 120 half-occupied active orbitals \Rightarrow 1/2 million configs.

In the optimization \Rightarrow not always unambiguous results \Rightarrow we have to estimate the orbitals at the beginning...

CAS-SCF is the most frequently used MC-SCF method. Another popular MC-SCF method is the...→

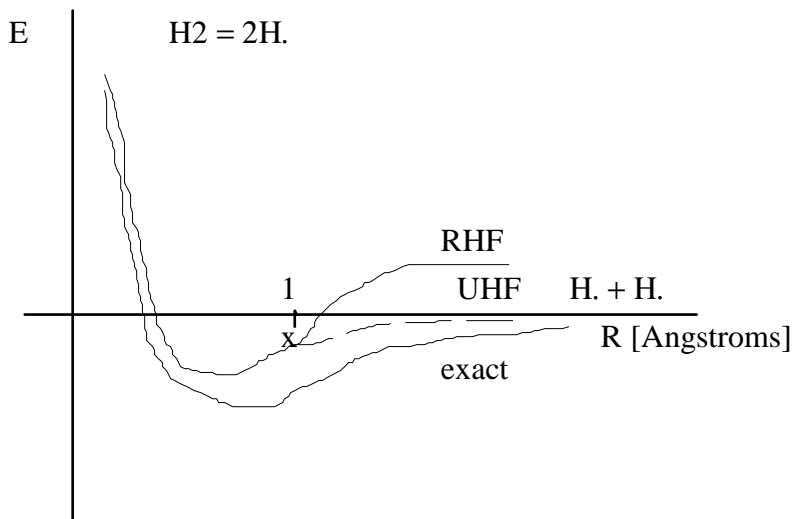
Generalized Valence Bond (GVB) method:

(W. Goddard) VB-type determinants are considered only in a rationally selected subspace of the CAS. (c.f., the aforementioned description of the dissociation of H_2 where the subspace had two configs. only, these do expand the whole CAS space, naturally).

Sometimes gives quite good results like in the case of a bond rupture/formation.

Transforming the occupied orbitals to localized orbitals, the corresponding antibonding orbitals can be guessed/invented. Still the GVB is a "manual-method", and the choice of the CAS can not be automated.

Pulay's procedure ("...our own method...", P.P.) is based on the UHF (Unrestricted Hartree-Fock) method: "different orbitals for different spins" ($u^\alpha \neq u^\beta$)...



approximately at 1 Å the RHF becomes triplet-unstable, from here the electrons go into different two orbitals. It is difficult to understand: why there is no separation of the alpha-beta orbitals at shorter R distances???

Independently from the electron-electron repulsion, both electrons would prefer the "optimal" MO. If there are TWO orbitals, none of them is "optimum". Which is the stronger effect: interaction or optimum?

Starting from singlet H₂ the problem is that in case of the UHF method the wave function will not be a "pure" eigenfunction of the \hat{S}^2 operator (i.e., will not be a pure singlet state):

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 =$$

$$(\hat{s}_{x_1} + \hat{s}_{x_2})^2 + (\hat{s}_{y_1} + \hat{s}_{y_2})^2 + (\hat{s}_{z_1} + \hat{s}_{z_2})^2$$

that is, the \hat{S}_x , \hat{S}_y , \hat{S}_z operators are not one-electron operators due to the mixed ($\hat{s}_{x_1}\hat{s}_{x_2}$ -type) terms (!!!).

As it is well-known, the eigenvalues of \hat{S}^2 are $S(S+1)$ in atomic units. Starting from the singlet ground state of H₂, at larger distances the UHF solutions are: $\uparrow+\downarrow$, or, alternatively, $\downarrow+\uparrow$ (the correct $\tilde{\Psi}$ would be the mixture of these). Indeed, none of them are good completely, each of them is constructed by a lin. combination of a singlet and a triplet states. Energetically they ($\uparrow+\downarrow$ and $\downarrow+\uparrow$) have the same energy (during the observation they are not able to "go through", tunneling is also slow, conclusively they can be considered as stationary

states). The involvement of the excited triplet state at the problematic distances ($> 1 \text{ \AA}$ which is still not ∞) resulted in higher energy than the exact value...

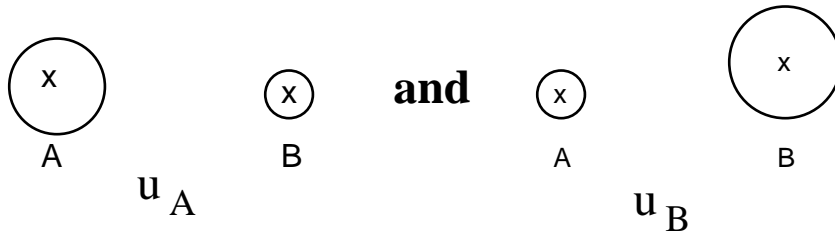
$$\tilde{\Psi}_{\text{UHF}} = |u_A \bar{u}_B|$$

at large R distances: u_A and u_B are AOs, at smaller R distances not the AOs (but also one electron is on A, the other is on B).

Projected UHF: the re-establishment of the pure spin state:

$$\tilde{\Psi}_{\text{PUHF}} = N(|u_A \bar{u}_B| - |\bar{u}_A u_B|)$$

(actually $\uparrow+\downarrow$ and $\downarrow+\uparrow$ are the lin. combinations of two states). It gave a good idea that u_A and u_B are not orthogonal orbitals spatially, at intermediate R distances:



Evident that spinorbitals are orthogonal to each other due to spin but (as we have seen) their spatial part is **NOT** orthogonal. However, we can introduce spatially orthogonalized orbitals (these correspond roughly to the bonding and antibonding orbitals):

$$u_{1,2} = (2 \pm 2\lambda)^{-1/2} [u_A \pm u_B]$$

\uparrow due to symmetry, and λ is the spatial overlap ($\lambda = \langle u_A | u_B \rangle$) here ($\lambda \leq 1$).

If $\lambda = 1$ then $u_A = u_B$ (**RHF**): in this case there is no u_2 solution. Substituting this into $\tilde{\Psi}_{\text{PUHF}}$ we get

$$\tilde{\Psi}_{\text{PUHF}} = A_1 |u_1 \bar{u}_1| - A_2 |u_2 \bar{u}_2|$$

(where $A_{1,2} = (1 \pm \lambda)(2 + 2\lambda^2)^{-1/2}$).

This trial function is built of two configurations, its form is similar to the MC-SCF trial function, but here neither the $u_{1,2}$ orbitals, nor the $A_{1,2}$ coefficients are fully optimized, these originate from the UHF method. The PUHF method gives two orbitals \Rightarrow logical that these give good starting orbitals to the MC-SCF method. Generalization for n electrons...

First a few new ideas... More general density matrix (whose special case is the one met at the HF method)...

First-order reduced (spatial-spin) density matrix:

$$\rho(1,1') = \int \Psi^*(1',2,\dots,n) \Psi(1,2,\dots,n) d\tau_2 d\tau_3 \dots d\tau_n$$

where $1'$ and 1 mean four-four coordinates of an electron (e.g., $1 = x_1, y_1, z_1, \xi_1$). Actually it is a function that is similar to a matrix (with continuous indices). Its diagonal elements are $1' = 1$:

$$\rho(1,1) = \rho(x, y, z, \xi) = \rho(\underline{r}, \xi)$$

this gives the probability (density) that we can find an electron with a given spin in a volume of 1 bohr^3 around a given \underline{r} point.

Now the density can be expressed in terms of the basis functions:

$$\rho(1',1) = \sum_p \sum_q D_{pq} \chi_p^*(1') \chi_q(1)$$

(where the \underline{D} is our "old friend", it is the matrix representation of ρ first-order reduced density matrix).

Second-order reduced density matrix: has 4 variables $(1',1,2',2)$. It can be show that ALL we can calculate in the nonrelativistic quantum mechanics from the wave function, is determined by the second-order reduced

density matrix (i.e., contains all the information) \Leftrightarrow two-electron operators only in the Hamiltonian!!!

Many efforts have been wasted for the direct derivation of the second-order reduced density matrix, for nothing ...

The first-order reduced density matrix prescribes the values of all the one-electron quantities, among others the electron density.

Löwdin: how ρ can be represented in the most simple form? \Rightarrow diagonalization of the infinite, continuous matrix:

$$\rho(1',1) = \sum_i \sigma_i \varphi_i^*(1') \varphi_i(1)$$

where $\underline{\underline{\sigma}}$ is the diagonalized form of the $\underline{\underline{D}}$ matrix on the basis of the φ_i "natural spinorbitals" (NSOs). The σ_i -s are the spatial-spin occupation numbers.

First-order reduced *spatial* (or, charge-, or spinless) density matrix (it is even more important than the spatial-spin density matrix mentioned before):

$$\rho(\underline{r}_{1'}, \underline{r}_1) = \int \rho(1',1) d\xi_{1'} d\xi_1 = \text{sum of 4 terms for all the}$$

$$\text{alpha - beta spins} = \sum_i \sigma_i u_i^*(\underline{r}_{1'}) u_i(\underline{r}_1) \quad (\text{Löwdin})$$

↑ another σ_i : spatial occupation number of the u_i natural (spatial) orbitals (NOs).

Aforementioned diagonal representations: ϕ_i natural spinorbitals (NSOs): spatial+spin u_i natural orbitals (NOs): spatial**E.g.,****HF (SCF):** the spatial-spin occupation numbers of all the NSOs are 1 and 0;**RHF:** at any orthogonal set the spatial occupation numbers of the NOs are 2 and 0;**UHF:** the spatial occ. numbers are $0 \leq \sigma_i \leq 2$. For a two-electron model (i.e., in case of two electron) just the $u_{1,2}$ bonding/antibonding orthogonal orbitals (vide supra) will be the NOs, their spatial occ. numbers are

$$\sigma_1 = A_1^2 \quad \text{and} \quad \sigma_2 = A_2^2 ; \text{ (because}$$

$$\tilde{\Psi}_{\text{PUHF}} = A_1 |u_1 \bar{u}_1| - A_2 |u_2 \bar{u}_2| \text{). Conclusively,}$$

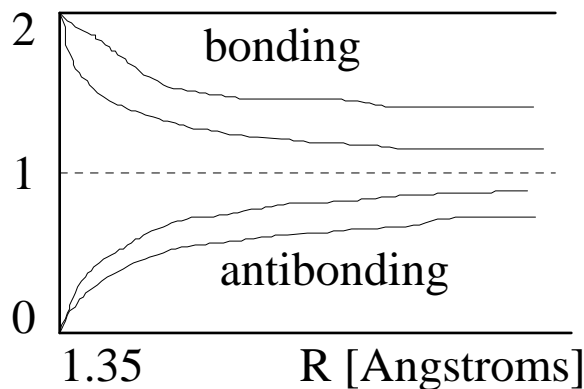
the NOs of UHF and PUHF are the SAME!!!**It is NOT *natural*, quite strange, Harriman proved it (Harriman theorem).****Thus the PUHF can be written in the form of MC-SCF. From here came Pulay's idea that the active orbitals of the CAS-SCF have to be deduced from the UHF NOs, regarding to the occ. numbers.****If spatial $\sigma_i \sim 2$, big force keeps the electrons on the same spatial orbital, they can not separate. If spatial $\sigma_i \sim 0$, the electrons do not want to go to those orbitals. If $\sigma_i \sim 1$, these orbitals are the active ones.**

In the first approximation the ~ 2 occ. orbitals are the doubly occupied CAS-SCF orbitals; the fractionally $0 < \sigma_i < 2$. occupied UHF orbitals are the active CAS-SCF orbitals, and finally, the vacant UHF orbitals do NOT play any role in the CAS-SCF configurations (unoccupied orbitals).

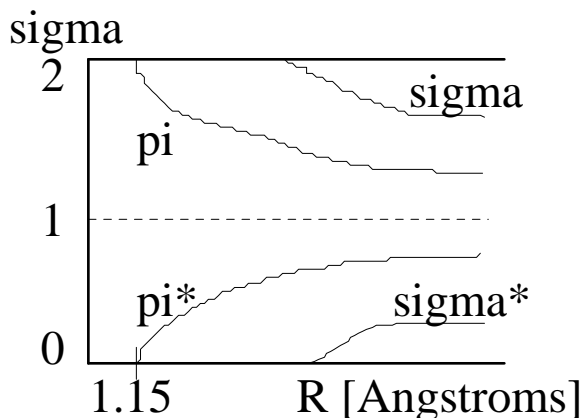
Fortunately, the UHF has quite unambiguous solution, and these natural orbitals give a very good first approximation for the CAS-SCF method.

Example 1: H₂O spatial occ. numbers versus symmetric stretching (R), i.e., the two bonds will be stretched simultaneously. Physically it is not too interesting but it IS from a theoretical point of view: bond rupture!!!

sigma



They tend to unity... To about ~ 1.35 Å, the RHF is suitable for the description of the process. Only four orbitals have been drawn, but the others are zero or 2.

Example 2: •NO radical:

If the UHF and RHF starts to differ (at any intermediate values of R) here appear the fractionally occupied orbitals:

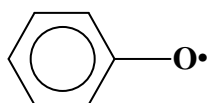
$$0.02 < \sigma < 1.98 \quad (\text{Pulay})$$

Strict proof exists for the 2-electron case only: when the UHF starts to differ from the RHF ("triplet instability"), the 2 electron \times 2 orbital CAS-SCF trial function will be determined:

$$\tilde{\Psi} = A_1 |u_1 \bar{u}_1| - A_2 |u_2 \bar{u}_2|$$

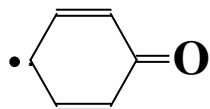
if $|A_2| > 0.23$, that is $A_2^2 > 0.05$, then

the RHF solution is triplet unstable, and E_{UHF} will be lower than E_{RHF} . Here appears the strong correlation in the wave function.

Example 1: phenoxy-radical

3B_1 ground state (on the π orbital there is one unpaired electron).

If an unpaired electron is near to an unsaturated bond, there is a large resonance, the result will be a chinoidal structure:



Orbitals 1-21: $\sigma_i > 1.998$ occupied

Orbitals 22-28: $\sigma_i : 1.97, 1.87, 1.86$

1.0,

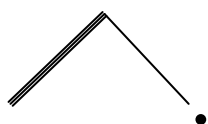
0.14, 0.13, 0.03 active

symmetry can be observed; it is not necessary since the electrons go from one orbital to another

Orbitals 29-...: $\sigma_i \leq 0.002$

If the system is not planar, it is not possible to assign the π orbital; still the method retains that 7 orbitals form the CAS...

Example 2: allyl-radical ("propene - H")



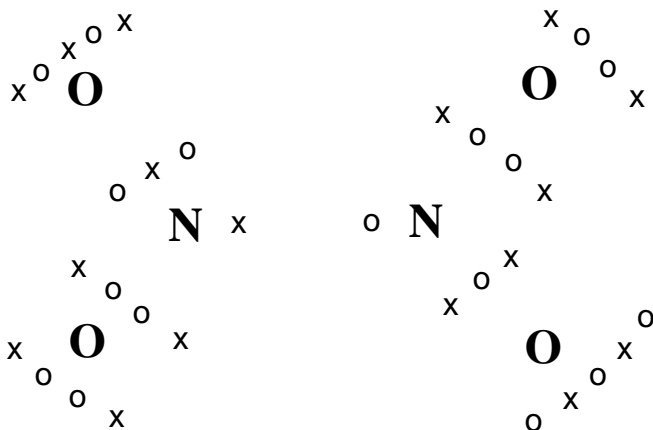
in the reality:



3 active orbitals

Example 3: N₂O₄ : 6 orbitals in CAS

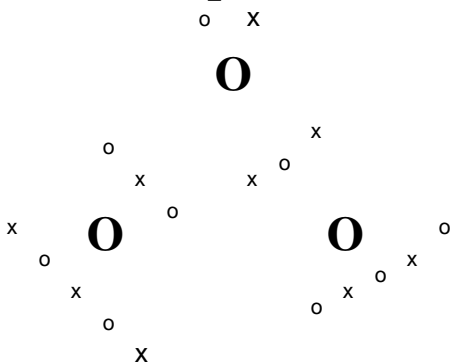
The "functioning"(working) of the UHF trial function is difficult to understand but if we localize them it is possible. Denoted by + and o the maxima of the alpha and the beta electron densities, respectively:



UHF does not show the symmetry (its pair an UHF in which the NO₂ group is rotated), this error disappears in CAS-SCF.

Linnett's theory: octet-principle is incorrect, in the reality is double quartet.

Example 4: O₃ : it is a very strongly correlated system, it is NOT possible to describe without correlation.



Linnett's quartets are actually localized UHF MOs. If the UHF and RHF does NOT differ, results in the octet-rule. But the theory of Linnett is more than the octet-principle. Its main problem was that Linnett did NOT give any theoretical explanation to his theory.

The CAS-SCF is quite expensive, needs approximately as many times more computational time than RHF as the number of the active orbitals. Also, its convergence is worse (it can be repaired by quadratically converging methods but it causes even larger comp. time).

Hitherto: from the UHF NOs we have got the active space of MC-SCF, the starting orbitals were determined only.

Now: one more step:

The UHF NOs (= UNOs) are so good approximations to the MC-SCF orbitals that there is no need to optimize them, it is enough to optimize the coeffs. of the determinants = UNO-CAS method (Pulay).
I.e., it is enough to perform CI in CAS!!!

This modification lowers the computational time by one order of magnitude comparing to the MC-SCF.

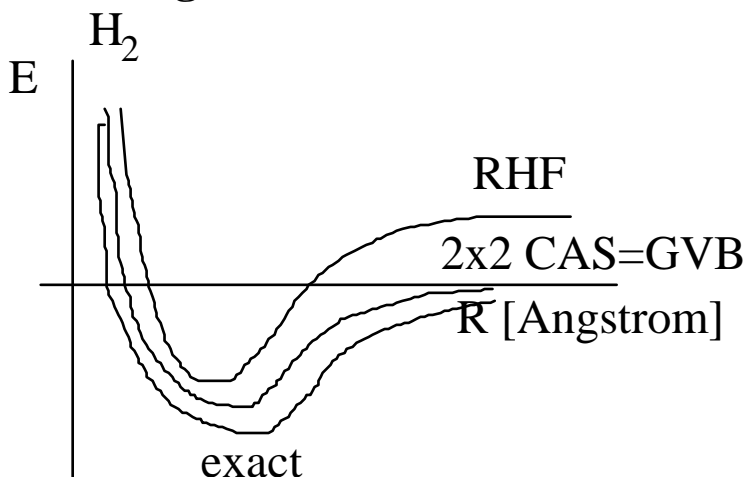
Example 5: O₃ geometry calculation (DZP basis set)

Method	R(O-O) [Å]	α [deg.]
SCF	1.207	119
2×2 CAS=GVB	1.257	115
UHF	1.301	110
UNO-CAS	1.259	115
+GMP2 (Dynamic corr.)*	1.279*	117*
Exp.	1.271	117

* The perturbation is added to the UNO-CAS result (Pulay's GMP2 method).

The problematic features of the MC-SCF method:

(I) it is still not quantitative method. Its error often contrary to the RHF method (for the barrier) due to the following:



As can be seen the GVB method describes the dissociation well (at infinite R describes well the correlation because there is NO dynamic correlation). But at smaller Rs the dynamic corr. exists and it is not described, thus the barrier will be too small (contrary to the RHF theory that exaggerates it). Dynamic correlation changes strongly with the multiplicity (reverse ratio, see above...). Fragments (H. + .H) are dublets, the H₂ is singlet. Evident that the fragments are better described than the molecule with the CAS-SCF method. Of course, the dynamic correlation is not considered here, so we make an error that changes during the dissociation ⇒ the barrier will be too small. If we add the dynamic correlation to the CAS-SCF result, the situation will be better (but never will be smooth enough due to the two parts). Different possibilities:

(IA) Correlation calculated for the all orbitals. It can NOT be done for large systems.

(IB) Correlation calculated for a few, strongly correlated orbitals only. Problematic if (during the change of the geometry) one orbital "changes its character" and goes into another class of MOs (e.g., active \Rightarrow virtual).

(IC) CI method: MC-CI. This means for us the sum of MC-SCF + MC-CI methods. Size consistency problem. Very expensive. If we neglect some configs. the surface will be uneven, gradients will be BAD...

(ID) Perturbation theory: second-order PT for MC-SCF: would be very good model for chemical reactions (e.g., for orbital crossing etc.) but these methods are still not quantitative. The partition is difficult, Pulay's procedure is the GMP2 (Generalized 2nd order Møller-Plesset method). Roos made the CAS-PT2 procedure...

The geometry optimization is VERY DIFFICULT for reactions due to avoided crossing problems...

If the multiplicity changes slowly, the hypersurface will be good. In the opposite case can be very bad!!!

Extreme example: Cr₂ . Efremov (Soviet) experimental $r_e = 1.66 \text{ \AA}$ (spectroscopy). Extreme short!!! Efremov stated that there is a 6-times bond between the Cr atoms. Goddard (based on his GVB calculation) did not believed this fact, he said that the experiment had an error. But the observation was good: Cr el.config. 3d⁵4s (Hund-rule) resulted state ⁷S

(spherical septet). But at the forming of Cr_2 the state is $^1\Sigma_g$. The system has 12 active orbitals, has to describe with a 12×12 UNO-CAS which shows a very shallow minimum \Rightarrow the proper description can be done by dynamic correlation methods only.

(II) A big question is the definition. There is NO sharp limit between the dynamic and nondynamic correlation. In order to describe the smooth potential surface a difficult question has to be solved... The problem of the definition was solved by Pulay et al. Earlier MC-SCF was not used in the Gaussian package at all. Later UNO-CAS has been implemented (without mention Pulay's name... after a letter they started to cite him).

(III) If the number of the active orbitals is too big (limit around ≥ 12) the UNO-CAS method can NOT be used. E.g., the porphin has 18 active orbs., some configs. have to be avoided.

4. DENSITY FUNCTIONAL METHODS

In principle, DFT (Density Functional Theory) is a simple, semiempirical method for the dynamic correlation. Its origin is very old, from the early quantum mechanics, Thomas-Fermi atomic model starting from electron density.

Hungarian scientists (Prof. Gombás, Prof. Gáspár) also worked on this topic (Prof. Gombás was the head of the department where Prof. Kapuy† worked earlier...).

From the 60-ies: physicists used it for solid body's energy gaps, very simple model, $X\alpha$ Scattered Wave.

They became very slowly popular because they were too simple but very good methods. They work on the pattern of the Hartree-Fock method. The physicists say that the DFT methods are "exact" but only if we take into consideration the Universal Constant (i.e., the difference between the exact and the calculated values!!!).

Foundation:

Hohenberg-Kohn theorems:

("It is interesting but without too much meaning" N.N.; "These proofs are ... existence proofs rather than constructive proofs so that the task of developing methods which rely on these proofs is still largely a matter of experience and trial and error" Cook; Also it is worthwhile to note that Kohn never was at any chemical conference BEFORE he got the Nobel Prize.)

In the Born-Oppenheimer non-relativistic approximation the Hamiltonian → new partition:

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_G$$

where the first and the last terms are general (universal) at ANY system of n electrons, and the second term (the "external potential") which characterizes the system (or, alternatively, n and $\hat{V}(\underline{r}_i) = \hat{V}(\underline{r})$ vide infra) is:

$$\hat{V}_{\text{ext}} = - \sum_{i=1}^n \sum_{a=1}^N \frac{Z_a}{r_{ai}} = \sum_{i=1}^n \hat{V}(\underline{r}_i) = n\hat{V}(\underline{r})$$

i.e., as the sum of the external potential of the individual electrons.

It is obvious that the external potential fixes the Hamiltonian, so n and $\hat{V}(\underline{r})$ determine all properties of the ground state:

(for normalised wavefunction)

$$\begin{aligned} E &= \langle \Psi | \hat{H} \Psi \rangle = \langle \Psi | \hat{T} \Psi \rangle + \langle \Psi | \hat{V}_{ext} \Psi \rangle + \langle \Psi | \hat{V}_G \Psi \rangle = \\ &= \langle \Psi | \hat{T} \Psi \rangle + \langle \Psi | \hat{V}_G \Psi \rangle + \sum_{i=1}^n \langle \Psi | \hat{V}(\underline{r}_i) \Psi \rangle = \\ &= \langle \Psi | \hat{T} \Psi \rangle + \langle \Psi | \hat{V}_G \Psi \rangle + n \langle \Psi | \hat{V}(\underline{r}) \Psi \rangle = \\ &= \langle \Psi | \hat{T} \Psi \rangle + \langle \Psi | \hat{V}_G \Psi \rangle + n \int \hat{V}(\underline{r}) \rho(\underline{r}) d\underline{r} \end{aligned}$$

The first Hohenberg-Kohn theorem (1964) states: The external potential $\hat{V}(\underline{r})$ is determined, within a trivial additive constant, by the electron density $\rho(\underline{r})$.

Proof:

Let us assume the opposite: there are two possible one-particle external potentials ($\hat{V}(\underline{r})$ and $\hat{V}'(\underline{r})$) which correspond to the same $\rho(\underline{r})$ density: In this case:

$$\hat{H} \Psi = E \Psi, \text{ where } \hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_G$$

$$\hat{H}' \Psi' = E' \Psi', \text{ where } \hat{H}' = \hat{T} + \hat{V}'_{ext} + \hat{V}_G$$

(where $\hat{V}_{ext} \neq \hat{V}'_{ext}$)

$$\rho(\underline{r}) = \int |\Psi(\underline{r}, \xi, 2, 3, \dots, n)|^2 d\xi d\tau_2 d\tau_3 \cdot \dots \cdot d\tau_n =$$

$$= \int |\Psi'(\underline{r}, \xi, 2, 3, \dots, n)|^2 d\xi d\tau_2 d\tau_3 \cdot \dots \cdot d\tau_n$$

(except for the trivial case when the external potentials differ by a constant, Ψ and Ψ' will be different).

But for the expectation values of the energy (variation theorem) we get (for normalised wave functions):

$$W = \langle \Psi' | \hat{H} \Psi' \rangle > E$$

$$W' = \langle \Psi | \hat{H}' \Psi \rangle > E'$$

Thus:

$$E < \langle \Psi' | \hat{H} \Psi' \rangle = \langle \Psi' | \hat{H}' \Psi' \rangle + \langle \Psi' | (\hat{H} - \hat{H}') \Psi' \rangle =$$

$$= E' + n \int [\hat{V}(\underline{r}) - \hat{V}'(\underline{r})] \rho(\underline{r}) d\underline{r}$$

$$E' < \langle \Psi | \hat{H}' \Psi \rangle = \langle \Psi | \hat{H} \Psi \rangle + \langle \Psi | (\hat{H}' - \hat{H}) \Psi \rangle =$$

$$= E - n \int [\hat{V}(\underline{r}) - \hat{V}'(\underline{r})] \rho(\underline{r}) d\underline{r}$$

which mean that $E + E' < E' + E$, i.e., "reductio ad absurdum". (Q.E.D.)

Consequences:

Since $\rho(\underline{r}) \leftrightarrow$ external potential uniquely \leftrightarrow

Hamiltonian uniquely \leftrightarrow ground-state wave function uniquely, thus the ground-state wave function and the ground-state total energy must be a functional of the ground-state density:

$$\Psi(1, 2, \dots, n) = f[\rho(\underline{r})]$$

$$E = E[\rho(\underline{r})]$$

This means (since $\langle \Psi | \hat{V}_{ext} \Psi \rangle = n \int \hat{V}(\underline{r}) \rho(\underline{r}) d\underline{r}$) that a similar functional must exist for the expectation value of the "general" terms of the Hamiltonian:

$$\langle \Psi | (\hat{T} + \hat{V}_G) \Psi \rangle = F[\rho(\underline{r})]$$

The problem is the $F[\rho(\underline{r})]$ functional: it is NOT only not known but very probably can NOT be known (P.P.; justification of second kind..., G.P.; if it is true, I. Mayer proved this...).

Holographic electron density theorem (P. Mezey):
(Extension of Hohenberg-Kohn I. theorem)

Mol. Phys. 1999, 96, 169.

States that any electron density fragment of a nonzero volume of a molecular electron density contains all information about the complete, boundaryless molecular electron density.

The second Hohenberg-Kohn theorem (1964) states:
For an n-representable trial density $\tilde{\rho}(\underline{r})$, such that $\tilde{\rho}(\underline{r}) \geq 0$ and integrates to the number of electrons in the system ($\int \tilde{\rho}(\underline{r}) d\underline{r} = n$),
the equation $E[\tilde{\rho}(\underline{r})] \geq E_0$ is valid,
where E_0 is the exact nonrelativistic energy of the ground state ($\tilde{\rho}(\underline{r})$ is the trial-density function).

Proof:

According to Hohenberg-Kohn I., a given $\tilde{\rho}(\underline{r})$ density uniquely corresponds to an external potential $\hat{V}(\underline{r})$, so exists a Hamiltonian \hat{H} whose Schrödinger-equation is:

$$\hat{H}\tilde{\Psi} = \tilde{E}\tilde{\Psi} \quad (\tilde{\Psi} \text{ is normalized})$$

Let us use the $\tilde{\rho}(\underline{r})$ density function to evaluate the energy of a system with a different, known external potential $\hat{V}(\underline{r})$ which corresponds to the known Hamiltonian $\hat{H} : \tilde{E} = \langle \tilde{\Psi} | \hat{H} \tilde{\Psi} \rangle = E[\tilde{\rho}(\underline{r})]$ (corollary of Hohenberg-Kohn I.). Since

$$\tilde{E} \geq E_0 = \langle \Psi | \hat{H} \Psi \rangle$$

(where $\hat{H}\Psi = E_0\Psi$)

and by the corollary mentioned above:

$E_0 = E[\rho(\underline{r})]$, we get:

$$E[\tilde{\rho}(\underline{r})] \geq E_0 \quad (\text{Q.E.D.})$$

that is:

If we would have the energy of the system as a functional of the $\rho(\underline{r})$ electron density

$$E[\rho(\underline{r})] = \int V(\underline{r})\rho(\underline{r})d\underline{r} + F[\rho(\underline{r})]$$

where $F[\rho(\underline{r})]$ is a functional that contains the kinetic energy + the electron-electron repulsion, **we could determine the minimum of the $E(\rho)$ functional and we could have the accurate energy.**

*"...If I could,
I surely would..."*

(Simon & Garfunkel, "Bridge over troubled water")

Though, this would be very good because the Ψ wave function is very complicated, whilst the density is a simple 3-variables function.

The situation can be explained **within the HF theory**: with $\varphi_i(\underline{r})$ spinorbitals we can write the complete one-electron density as

$$\rho(\underline{r}) = \sum_i^n |\varphi_i(\underline{r})|^2$$

The expectation value of the (external) potential energy is then (hereafter $\hat{V}_{\text{ext}} \equiv \hat{V}$)

$$\langle \hat{V} \rangle = \sum_i^n \int \varphi_i^*(\underline{r}) \hat{V}(\underline{r}) \varphi_i(\underline{r}) d\underline{r}$$

↑ *local* operator (has a value at any \underline{r}).

(A local operator is **NOT** the most general one...) Now

$$\langle \hat{V} \rangle = \int \hat{V}(\underline{r}) [\sum_i \varphi_i^*(\underline{r}) \varphi_i(\underline{r})] d\underline{r} = \int \hat{V}(\underline{r}) \rho(\underline{r}) d\underline{r}$$

It is valid not only for HF, but also for the complete CI wave function (it is proved).

"Nobody understands accurately why the DFT methods work" (P.P.)

$$\text{Thus } E[\rho] = \langle \hat{V} \rangle + F[\rho]$$

where the last term contains the kinetic energy + the repulsion of the electrons.

The kinetic energy can be written (Thomas-Fermi model) as a crude estimate (plane waves in a box):

$$T \sim \int \rho^{5/3} d\underline{r}$$

Kohn & Sham method:

(Slater called it as Gáspár-Kohn-Sham ...)

they said that the kinetic energy has to be calculated much more accurately. Let us think that there is **NO** electron repulsion then the $\Phi = \det|\varphi_1 \varphi_2 \dots \varphi_n|$ Slater-determinant would give the same energy as the **true nonrelativistic wave function**

$$\text{kinetic energy } T_S = -\sum_i \int \varphi_i^*(\underline{r}) \left[\frac{1}{2} \nabla^2 \right] \varphi_i(\underline{r}) d\underline{r}$$

(the S index means 'single particle': without repulsion!) Naturally, this is not expressed by the density, it contains the second derivatives (NON-local). With elementary modification we get

$$T_S = -\frac{1}{2} \sum_i \int |\nabla \varphi_i(\underline{r})|^2 d\underline{r}$$

where only the first derivatives play a role (error in the Atkins' book: "the second deriv. is needed"). Let it be

$$W = T_S + \int V(\underline{r}) \rho(\underline{r}) d\underline{r} + \frac{1}{2} \iint \rho(\underline{r}_1) \frac{1}{r_{12}} \rho(\underline{r}_2) d\underline{r}_1 d\underline{r}_2 + \\ + E_{XC}[\rho(\underline{r})] + V_{NN}$$

The first term is the single particle kinetic energy (strongly non-local!!!), the second one is the expectation value of the external \hat{V} (local), the third term is the Coulomb-repulsion of the electrons and the fourth term is the exchange (X)-correlation(C) functional, the last term is trivial (nuclear repulsion).

In E_{XC} are the following: the terms of the kinetic energy which are NOT involved in T_S , (correlation functional) + the exchange functional. The E_{XC} is "smaller" functional than $F[\rho]$, we will approximate it by a local function.

Now comes the 'variational principle' (as in the HF theory):

$$\mathcal{L} = W - \sum_k \sum_l \varepsilon_{lk} (\langle \varphi_k | \varphi_l \rangle - \delta_{kl}) \rightarrow \min$$

(Nota bene : for spinorbitals the factor 2 is not needed)

The variation of the i-th spinorbital:

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$

If in the expression of $\delta\mathcal{L}$ the $\delta\varphi_i$ would take part multiplied by a, let say, positive constant c , and if we would have chosen the $\delta\varphi_i$ negative (or vice versa), then the \mathcal{L} would lower, starting from the minimum. This is absurdum, so the first variation of \mathcal{L} according to $\delta\varphi_i$ has to vanish:

$$\delta T_S = 2 \left[\left\langle \delta\varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_i \right\rangle \right]$$

$$\delta\rho = 2\delta\varphi_i\varphi_i \quad (\text{real}) \quad (\text{because } \rho(\underline{r}) = \sum_{\mathbf{k}} \varphi_{\mathbf{k}}^*(\underline{r})\varphi_{\mathbf{k}}(\underline{r}))$$

$$\delta V = 2 \int \delta\varphi_i V(\underline{r}) \varphi_i d\underline{r} = 2 \langle \delta\varphi_i | V | \varphi_i \rangle$$

$$\begin{aligned} \delta E_{Coulomb} &= 4 \cdot \frac{1}{2} \iint \delta\varphi_i(\underline{r}_1) \varphi_i(\underline{r}_1) \frac{1}{r_{12}} \rho(\underline{r}_2) d\underline{r}_1 d\underline{r}_2 = \\ &= 2 \langle \delta\varphi_i | \hat{J} | \varphi_i \rangle \end{aligned}$$

where the $\hat{J} \equiv J(\underline{r}_1)$ local Coulomb operator is the operator of the multiplication by the function $J(\underline{r}_1)$:

$$\hat{J} \equiv J(\underline{r}_1) \cdot = \int \frac{\rho(\underline{r}_2)}{r_{12}} d\underline{r}_2 \cdot$$

which describes the complete repulsion of the electron cloud at the \underline{r}_1 point.

Let us suppose that a local E_{XC} exists:

$$E_{XC}(\text{local}) = \int \varepsilon_{XC}[\rho(\underline{r})] d\underline{r} \approx \text{const} \cdot \rho^{4/3}$$

completely local function

$$\delta E_{XC} = \delta \int \varepsilon_{XC}[\rho] d\underline{r} = \int \frac{\partial \varepsilon_{XC}[\rho]}{\partial \rho} \delta \rho d\underline{r} =$$

$$= 2 \int \delta\varphi_i \frac{\partial \varepsilon_{XC}[\rho]}{\partial \rho} \varphi_i d\underline{r} = 2 \langle \delta\varphi_i | V_{XC}[\rho] | \varphi_i \rangle$$

where ε_{XC} is the density of the exchange-correlation energy, and we substituted $\delta\rho$ with the expression given above...

Nota bene: V_{XC} is the potential corresponding to the exchange energy, it is proportional about $\text{const} \cdot \rho^{1/3}$ being the derivative of ε_{XC} .

$$\delta[-\sum_k \sum_l \varepsilon_{lk} (\langle \varphi_k | \varphi_l \rangle - \delta_{kl})] = -2 \sum_k \varepsilon_{ik} \langle \delta\varphi_i | \varphi_k \rangle$$

summing up:

$$\frac{1}{2} \delta\mathcal{L} = \left\langle \delta\varphi_i \left| -\frac{1}{2} \nabla^2 + \hat{V}(\underline{r}) + \hat{J}(\underline{r}) + \hat{V}_{XC} \right| \varphi_i \right\rangle - \sum_k \varepsilon_{ik} \langle \delta\varphi_i | \varphi_k \rangle = 0$$

[Nota bene: the last term can be written as $\varepsilon_{ii} \langle \delta\varphi_i | \varphi_i \rangle = \varepsilon_i \langle \delta\varphi_i | \varphi_i \rangle$ similarly to the Hartree-Fock theory, canonical form...]

If this expression is not zero, and negative, there has to be such a $\delta\varphi_i$ which lowers the energy. If this expression is not zero, and positive, then using $\delta\varphi_i$ with the opposite sign the energy will lower also... \Rightarrow has to be zero.

This can be true for each φ_i only if

$$\left[-\frac{1}{2} \nabla^2 + \hat{V}(\underline{r}) + \hat{J}(\underline{r}) + V_{XC} \right] \varphi_i = \varepsilon_i \varphi_i$$

similar to Hartree-Fock: the difference is V_{XC} which is dominated by the X exchange (over the C correlation). This new function can be derived from the homogenous electron-gas as a local function, with the jellium-model: electrons in the field of uniformly distributed positive charges (the whole is neutral)...

Nota bene: Solution: SCF technique. The Kohn-Sham orbitals do NOT have similar meaning as the HF-orbitals; the determinant built by them can NOT be considered as an approximation to the exact nonrelativistic Ψ .

Nota bene: programming is very similar to HF, too:

$$E = \sum_r \sum_s P_{rs} H_{rs} + \frac{1}{2} \sum_p \sum_q \sum_r \sum_s P_{pq} P_{rs} (pq|rs) + V_{XC}$$

General case: non-local V_{XC} function.

Theory of metals: Wigner, later Slater.

Slater: homogenous electron-gas (jellium), the Hartree-Fock functions are sin functions (simply from symmetry, translation), Born-Kármán conditions, on the surface of the cubes the sin functions are vanish:

$$V_X = -3 \left(\frac{3}{8\pi} \right)^{1/3} \rho^{1/3}$$

Slater derived the average of the exchange energy, this is NOT completely correct.

Gáspár (Acta Physica Hungarica, 1954): the exact derivate is given...

Kohn and Sham 1965): newly derived the same as Gáspár, wanted to publish, but Slater noticed, ...

$$V_X = -3\alpha \left(\frac{3}{8\pi} \right)^{1/3} \rho^{1/3}$$

where $\alpha = \frac{2}{3}$ in the exact deduction.

X_α method (Slater):

empirically 0.7 is a bit better: if the alpha is somewhat larger (instead of 0.667), the exchange will be larger

also, so the correlation (considered similar to exchange) is involved.

Scattered Wave X_α method (K. Johnson): using the "muffin-tin" potential: around the atoms is spherical, between them is homogenous potential... Very bad for geometry: e.g., water is linear.

After these problems the X_α density functional methods discredited themselves, Slater did not get Nobel Prize ... Today the method is not used. The orbitals were quite good...

Valuation:

Generally, it can use approximate formulas much rather in Ψ than in \hat{H} or in any operator. Indeed, in Ψ we can be quite "liberal", because its error appears in the energy in a larger order of magnitude:

let Ψ be the exact (normalised and real) wavefunction, let its error be $\delta\Psi$ (where $\langle \delta\Psi | \Psi \rangle = 0$, naturally), then we get:

$$E[\Psi + \delta\Psi] = \langle \Psi + \delta\Psi | \hat{H}(\Psi + \delta\Psi) \rangle = \langle \Psi | \hat{H}\Psi \rangle + 2\langle \delta\Psi | \hat{H}\Psi \rangle + 2E\langle \delta\Psi | \Psi \rangle + \langle \delta\Psi | \hat{H}\delta\Psi \rangle = \langle \Psi | \hat{H}\Psi \rangle + \langle \delta\Psi | \hat{H}\delta\Psi \rangle$$

conclusion: the first-order error in Ψ means a second-order error in E . Any intervention in \hat{H} causes changes immediately in first-order. thus, it is a very big daring to approximate the terms within the Fock-operator, it is a crude intervention. However, it works very well, this is a *miracle*. Very INTERESTING: the local V_{XC} potential works even BETTER than the exact Hartree-

Fock exchange!!! T. Ziegler (Canada) explained this, he compared the HF and the local V_{XC} in a very simple model (2 H atoms at a very big distance):

$$u = \frac{1}{\sqrt{2}}(u_A + u_B), \text{ so}$$

$$E = 2\langle u | \hat{h}u \rangle + 2(uu|uu) - (uu|uu)$$

where $\langle | \rangle$, $(..|..)$ and $(..|..)$ terms correspond to one atom (the second one is the Coulomb interaction, the third one is the exchange term. As can be seen, at large R the Coulomb and the exchange term does not cancel each other, whilst in the DFT this compensation is more accurate (still not exact...).

E. Clementi (and others) tried to improve the method: he used the exact HF exchange augmented by the local approximation of the correlation - it is interesting that the result was worse. Conclusively, we have to approximate/treat the exchange AND the correlation together as a local potential.

<u>Hartree-Fock-Slater method (HFS):</u> $\rho^{1/3}$; $\alpha = 0.7$

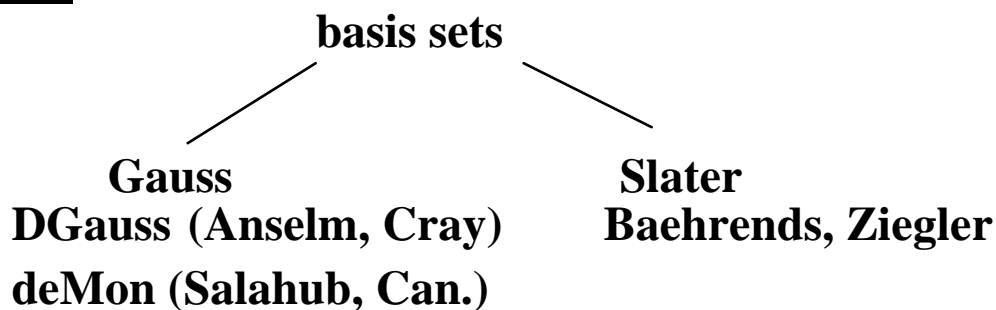
Ziegler results for bond distances in *JCP*, 1991, 94, 6057 ... HF slightly longer, F_2 is very good, LiH slightly longer, CO almost perfect, SF_6 good. The NL (non-local) values are slightly over-corrected. For frequencies in *JCP*, 1992, ...

Numerical details:

The Handy's HFS method (without neglecting terms, the "clear formulas" were used with a high numerical accuracy differently from the physicists) was slower than Hartree-Fock, the results were also similar, but

contrary, if the HF method gave very bad results (like CO, F₂) their DFT values were better.

There is NO standard DFT method (like Hartree-Fock), we have to use also a basis set for the description of the orbitals:



The MOs are calculated numerically (e.g., 1 orbital in 100 points means 10⁶ data) in DMol program: molecule in a box, basis set: plane waves [disadvantages: very big basis has to use e.g. ~40000; the atomic cores have to be described by pseudo-potentials (Gombás, Hellmann started, Corning Glass glass-factory made...); advantages: it is very easy to calculate with them].

"Augmented Plane Waves": plane waves + atomic basis set (Gaussian orbitals are also the best ones here). The completely numerical procedure is NOT pretty good. Even the Gaussian[®] calculates the Coulomb-terms (naturally, the Coulomb-term is much simpler than the exchange, physically) like in case of the Hartree-Fock method, i.e., without approximations (first we have to check the method without too much approximations...). Evident that if the Coulomb-terms are NOT approximated, the HFS procedure is more expensive than the Hartree-Fock method, but it is much cheaper than the MP2 (disregarding the most modern "fast MP2" programs which are as speedy as the DFT methods...).

The use of approximate ρ density: it is very promising since the density is a much simpler function than the orbitals (the individual orbitals are complicated, have many nodes, their resultant is more smooth, spherical):

$$\rho \approx \tilde{\rho} = \sum_r R_r \eta_r \quad \text{"fitted density"}$$

where η_r -s are the basis functions for the density [note the simplicity: we have used single summation instead of the usual double one $\rho = \sum_r \sum_s D_{rs} \chi_r(\underline{r}) \chi_s(\underline{r})$. The double summation is accurate using a finite number of terms, the "fitted density" is accurate, in principle, using infinite number of terms only: first has a good convergence, later slower... However, the fitted density will be the "future". Still has a big problem: the derivatives need more accurate description.] The result of the fitted density for the matrix elements of the Coulomb-operator:

$$\begin{aligned} \text{fitted density: } \sum_r R_r (\chi_p \chi_q | \eta_r) &\sim o(N^3) \\ \langle \chi_p | \hat{J} \chi_q \rangle = & \\ \text{accurate: } \sum_r \sum_s D_{rs} (pq | rs) &\sim o(N^4) \end{aligned}$$

Determination of the coefficients in fitted density:

Trick: the error of the complete Coulomb-energy has to be of second-order in $(\rho - \tilde{\rho})$. Dunlop minimized the expression

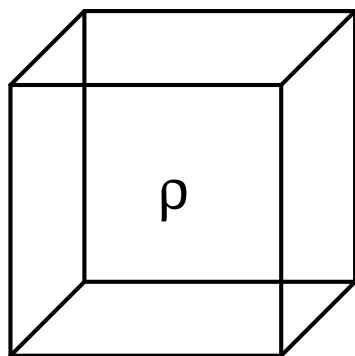
$$(\rho - \tilde{\rho} | \frac{1}{r_{12}} | \rho - \tilde{\rho}) = (\rho | \frac{1}{r_{12}} | \rho) - 2(\tilde{\rho} | \frac{1}{r_{12}} | \rho) + (\tilde{\rho} | \frac{1}{r_{12}} | \tilde{\rho})$$

where the first term disappears at the derivation, does not depend on the fitting...

Exchange-correlation (XC) energy: accurately is NOT computable (even for $\rho^{1/3}$ either, since the cubic root of

a sum is not the sum of the cubic roots of the terms).
 Two possibilities: numerical integration or fitting in each SCF cycle.

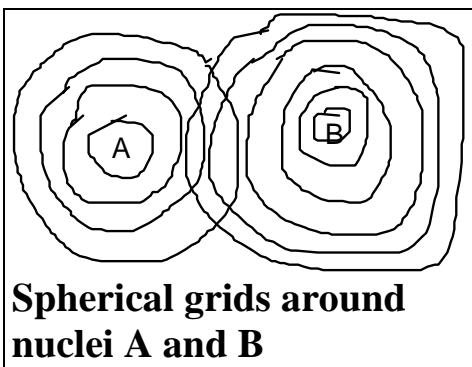
Handy: everything accurately, XC by a very accurate numerical integration. Numerical integration:



grid, using, e.g., $\Delta = 0.01 \text{ \AA}$, in an elementary cube by length of 0.01 \AA the ρ density can be considered as constant, multiplied by the volume, make the sum... This is NOT possible for the atomic cores: there is an inherent contradiction between a

grid and a sphere. The greatest error occurs around the nuclei where the density is very big and changes rapidly - this effect can be described by grid of constant length rather poorly.

Axel Becke (Canada): (*JCP*, 1988, 88, 2547) the numerical integration will be performed by Voronoi-polyhedrals: the space of the molecule will be decomposed by planes for atomic and interstitial parts. Around the nuclei uses spherical grids, the points



Spherical grids around nuclei A and B

are uniformly distributed by Lebedeff's method (e.g., 14 points,...); uses weights in order to avoid the 2 times integration because the integration is independently goes around the nuclei: the weight is 1 around

the "own" nucleus (according to the Voronoi-polyhedrals), in the interstitial places it is lower, at another nucleus is zero... It is well-known that the

numerical integration of a smooth function is very easy, but the same for a cusp is VERY difficult. Becke's mixed method seems to be quite good.

Handy uses several 10000 gridpoints/atom - it is many but it is still scaled by $o(N^3)$ only...

Non-local functional approximations:

V_{XC} : Slater-Gáspar-Kohn-Sham; it contains only the exchange, in principle. It is possible to make more accurate if we deduce a local function for the electron-gas and fitting it numerically (by Monte-Carlo method, with plane waves): Perdew-Zunger, von Barth, Vosko (the best).

We get a non-local potential if we use the gradient-correction (electron-gas in which the density changes, how influence this the exchange correlation?):

Becke (B; fitted for atoms!!!):

$$V_X^{NL} = -b\rho^{1/3} \frac{x^2}{1 + 6bx \cdot \operatorname{ar sinh} x}$$

where $x = \frac{|\nabla\rho|}{\rho^{4/3}}$, $b = 0.0042$

(naturally, $\nabla\rho$ is the gradient of the density).

Lee-Yang-Parr correlation functional: another...

$$V_C^{LYP} = -a \frac{\gamma}{(1 + d\rho^{-1/3})} - ab \frac{\gamma e^{-c\rho^{-1/3}}}{9(1 + d\rho^{-1/3})\rho^{8/3}} \left\{ 18(2^{2/3})C_F(\rho_\alpha^{8/3} + \rho_\beta^{8/3}) - 18\rho t_w + \rho_\alpha(2t_w^\alpha + \nabla^2 \rho_\alpha) + \rho_\beta(2t_w^\beta + \nabla^2 \rho_\beta) \right\} ,$$

where $\gamma = 2\left[1 - \frac{\rho_\alpha^2 + \rho_\beta^2}{\rho^2}\right]$ and $t_w^\sigma = \frac{1}{8} \left(\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} - \nabla^2 \rho_\sigma \right)$

the a, b, c , and d parameters are determined by fitting to data for the helium atom.

B-LYP: works very well. It is better than MP2, scaling is approximately Hartree-Fock or smaller, computational time more than HF. **B3LYP**:

Models which include the exact exchange (given by the Hartree-Fock theory for a Slater-determinant composed of Kohn-Sham orbitals) are often called hybrid methods. Becke's 3 parameter hybrid functional with the LYP correlation functional:

$$V_{XC}^{B3LYP} = aV_X^{DS} + (1-a)V_X^{HF} + bV_X^{B88} + cV_C^{LYP} + (1-c)V_C^{VWN}$$

where the superscripts DS, HF, LYP, and VWN refer to the Dirac-Slater, Hartree-Fock, Lee-Yang-Parr, and Vosko-Wilk-Nusair exchange/correlation functionals. The values of the a, b , and c parameters were determined by fitting to atomization energies, ionization potentials, proton affinities of model compounds. Very popular method...

Problems of DFT methods:

- (i) excited states, negative ions. It is difficult to manage the orthogonality;
- (ii) states which can NOT be described by one-determinant due to spatial symmetry (e.g., in atoms like 1S and 1D states in C atom);
- (iii) states which can NOT be described by one-determinant due to spin-symmetry (Local Spin Density LSD ~ RHF) - UHF analogue: e.g., open shell singlet $|(closed\ shell)\ \uparrow i\ \downarrow \bar{j}| - |(closed\ shell)\ \downarrow \bar{i}\ \uparrow j|$

it is impossible to describe with the present methods.

(iv) Long-range dispersion forces: typically correlation effect (adhesive tapes!!!) - weak attraction

(v) Can NOT be improved systematically.

Example: DFT-based SQM Force Field Method

"An application of the DFT-based scaled quantum mechanical force field method to a weakly bonded system: N₂O₄"

A. Kovács, K.B. Borisenko, G. Pongor: *Chem. Phys. Lett.* 1997, 280, 451.

SQM Force Field: combination of theoretical and experimental information

[P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs and A. Vargha,

J. Am. Chem. Soc. 1983, 105, 7037.]

Theoretical information

$$F_{ij} = \left(\frac{\partial^2 E}{\partial q_i \partial q_j} \right)_0 = \left(\frac{\partial}{\partial q_i} \left(\frac{\partial E}{\partial q_j} \right)_0 \right)_0$$

***E*: total energy (electronic + nuclear repulsion)**

***q_i, q_j*: nuclear coordinates**

• **level of QM approximation (method + basis)**

- choice of reference geometry
- appropriate internal coordinates (NIC)

Experimental information

$$F^{scaled} = \tilde{T} \cdot F \cdot T, \text{ where } T \rightarrow \text{diag}(x_i^{1/2})$$

x_i : scale factors
(congruent transformation)

$$GF^{scaled}L = LA^{calc}$$

G: inverse kinetic energy matrix

F: force constant matrix ("force field")

A^{calc}: eigenvalues (diagonal) (~frequencies²)

L: eigenvectors (normal vibration)

$$\sum_i w_i \cdot (v_i^{calc} - v_i^{exp})^2 \rightarrow \min$$

result: scale factors in a least-square sense

Earlier:

Hartree-Fock method / split-valence basis sets

Rauhut and Pulay: [*J. Phys. Chem.* 1995, 99, 3093]

DFT, B3-LYP functional / 6-31G* basis set

natural internal coordinates

11 transferable scale factors

mean deviation = 13 cm⁻¹

(31 molecules, 644 fundamentals)

training set: 20 organic compounds
(common structural motifs)

Non-common compounds ???

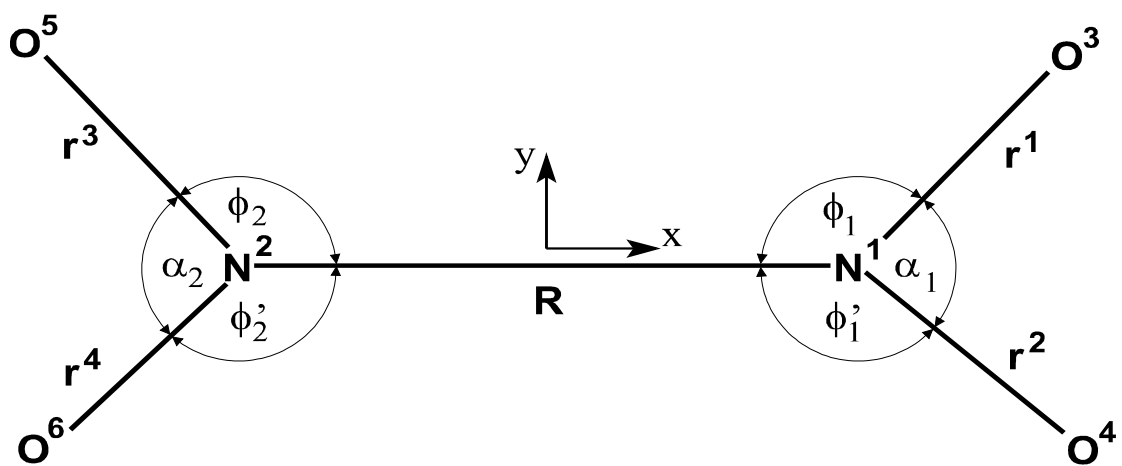
weakly bonded dimer of nitrogen dioxide: N₂O₄

**(none of the molecules in the "training set" of
 Rauhut and Pulay contained any N-O bonds !!!)**

Natural Internal Coordinates and Scale Factors for N₂O₄

no.	coordinate	description	scale factor
1	R	NN stre	0.922
2-5	r ₁ , ..., r ₄	NO stre	0.922
6-7	$\beta_1 = 2^{-1/2}(\phi_1 - \phi_1')$, $\beta_2 = 2^{-1/2}(\phi_2 - \phi_2')$	NO ₂ rock	0.990
8-9	$\gamma_1 = 6^{-1/2}(2\alpha_1 - \phi_1 - \phi_1')$, $\gamma_2 = 6^{-1/2}(2\alpha_2 - \phi_2 - \phi_2')$	NO ₂ scis	0.990
10-11	$\delta_1 = \delta_{1243}$, $\delta_2 = \delta_{2156}$	NO ₂ wag	0.976
12	$\tau = 4^{-1}(\tau_{2513} +$ $+ \tau_{2613} +$ $+ \tau_{2614} + \tau_{2514})$	ONNO torsion	0.831

Note: for coordinates 10-11 Califano's definition was used.



Theoretical and Experimental Structural Parameters of N₂O₄ (in Ångstroms and degrees)
--

Gaussian '94, IBM SP2 Model 203

method	N-N	N-O	O-N-O
Theoretical:			
B3-LYP/6-31G*	1.782	1.196	134.7
B3-LYP/cc-pVTZ	1.796	1.186	134.7
B3-LYP/cc-pVQZ	1.797	1.185	134.6
B3-LYP/aug-cc-pVQZ	1.799	1.185	134.7
B3-LYP/6-311+G(2d,2p)	1.795	1.188	134.6
CASPT2/Q/T	1.7940	1.1906	134.90
MP2/6-311G*(f _N)	1.794	1.198	135.1
MP2/6-31G(d,f _N)	1.786	1.208	135.2
VWN/TZP	1.774	1.194	134.8
CCSD(T)/TZ2P+f _N	1.752	1.195	134.7
Experimental:			
ED	1.777(6)	1.192(3)	134.6(4)
ND	1.756	1.191	134.4
IR	1.756	1.196	133.8

Calculated and Experimental Vibrational Spectra of N₂O₄
--

Species	Exp (cm ⁻¹)	IR Int (km/mole)	SQMDFT (cm ⁻¹)	Calc. int.
A_g	1380		1407	6.1 R
	806		828	9.6 R
	254		289	100.0 R
A_u	79		87	(-)
B_{1g}	1724		1762	1.8 R
	498		497	17.9 R
B_{1u}	436	-	428	16.6 IR
B_{2g}	677		673	0.4 R
B_{2u}	1757	718.9	1784	584.4 IR
	?	-	228	0.2 IR
B_{3u}	1261	440.9	1278	455.6 IR
	751	270.0	752	227.3 IR

mean deviation: 20.7 cm⁻¹
 maximal individual deviation: 38 cm⁻¹

Consequently, the DFT-derived SQM force field method of Rauhut and Pulay may give reliable results for non-common compounds as well.

5. MAGNETIC PROPERTIES; NMR CHEMICAL SHIFTS

Quite new chapter of the Q.C., in the books rarely written. It is "mysterious" for many chemists

The magnetic field is caused ALWAYS by moving electric charges (magnetic monopole is NOT known). Basically different from the electricity: it depends on the velocity and NOT on the positions!!!

Good description:

H.F. Hamaker: *Advanced Quantum Chemistry (Theory of Interaction between Molecules and Electromagnetic Fields)*, Addison-Wesley, ?, 1965.

"The modern physics has not changed from the old times of Newton, only augmented it with not too small amount of knowledge..." P.P.

$$\underline{\nabla} = \frac{\partial}{\partial x} \underline{i} + \frac{\partial}{\partial y} \underline{j} + \frac{\partial}{\partial z} \underline{k} \quad \text{Nabla-vector (...St. David's harp)}$$

$$\underline{B} = B_x \underline{i} + B_y \underline{j} + B_z \underline{k} \quad \text{magnetic induction vector}$$

BE CAREFUL!!!

Hereafter $V=V(\underline{r})$ means the electric potential (and NOT the potential energy function/operator as it is usual in the Quantum Mechanics/Chemistry.

Electric field: $\underline{F} = \text{grad}V(\underline{r}) = \underline{\nabla}V$ can be expressed as the gradient of a (scalar) electric potential function.

Magnetic field (induction): analogously a (directly NOT observable) $\underline{A}(\underline{r})$ vector-potential can be deduced:

$$\underline{B} = \text{curl}\underline{A} = \underline{\nabla} \times \underline{A}(\underline{r}) = \begin{vmatrix} \underline{i} & \underline{j} & \underline{k} \\ \partial / \partial x & \partial / \partial y & \partial / \partial z \\ A_x & A_y & A_z \end{vmatrix} =$$

$$\left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right)\underline{i} + \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\underline{j} + \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)\underline{k}$$

Nota bene: curl is also called rot.

External fields:

["External" means external for an atom or molecule.]

In the case of an external field, into the Hamiltonian "comes" $V(\underline{r})$ (and NOT \underline{F}), and $\underline{A}(\underline{r})$ (and NOT \underline{B}) (...Bohm's paradox).

Problem: $\underline{A}(\underline{r}) \rightarrow \underline{A}(\underline{r}) + \text{grad}(\text{any scalar function})$:

\underline{B} is the same (it is NOT affected!!!).

For the NMR effect it is NOT needed the most general $\underline{A}(\underline{r})$, it is enough the **homogeneous magnetic field:**

$$\underline{A}(\underline{r}) = \frac{1}{2}\underline{B} \times \underline{r} = \frac{1}{2} \begin{vmatrix} \underline{i} & \underline{j} & \underline{k} \\ B_x & B_y & B_z \\ x & y & z \end{vmatrix}$$

If we push the origin of the coordinate system by a constant vector, it does NOT change the magnetic field (the derivative does NOT change).

The nucleus can be considered as a magnetic dipole (due to its nuclear spin). The vector-potential of the $\underline{\mu}_N$ nuclear magnetic dipole moment is

$$\underline{A}_N = \frac{\underline{\mu}_N \times (\underline{r} - \underline{R}_N)}{|\underline{r} - \underline{R}_N|^3}$$

where \underline{R}_N is the coordinate vector of the nucleus N. (It is analogous to the potential of the electric charge or to the force which decrease by $1/r$ and $1/r^2$, respectively).

From the Hamilton-function can be deduced:

electrostatics + fixed nuclei: does NOT generate a magnetic field, a very weak effect comes from their vibration only:

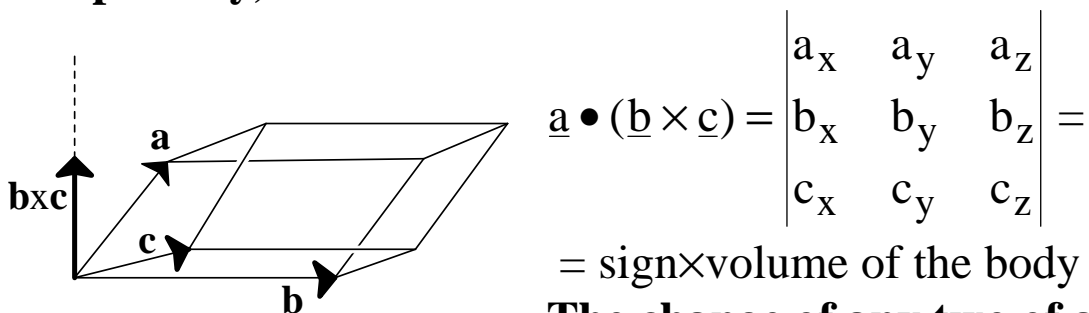
$$\hat{H} = \frac{1}{2} \sum_{i=1}^n [\hat{p}_i + \frac{1}{c} \underline{A}(\underline{r}_i)]^2 + ne_{\text{attr}} + ee_{\text{rep}} + nn_{\text{rep}}$$

(where c is the velocity of the light; the last three terms of the expression are the usual potential terms, e.g., nuclear-electronic attraction, etc.) that is, the kinetic energy term changes (c.f., magnetism & velocity!!!). The perturbation originating from the nuclear magnetic moment is very WEAK: practically does NOT perturb the electronic structure.

Let us assume that only one nucleus has $\underline{\mu}_N$ magnetic dipole moment. [In the reality many nuclei have $\underline{\mu}_N$ -s, and there exists a VERY important spin-spin coupling between them, but this is not interesting now due to the chemical shift. Even the spin-spin couplings have different types, too: one of them can be observed in solid state only, another works through the electronic system...(The derivative of the electronic density at the nucleus can be expressed by the nuclear charge Z: this is a theorem.)] In this case we get:

$$\hat{H} = \hat{H}_0 + \frac{1}{2c} \sum_{i=1}^n \left\{ \hat{\underline{p}}_i \cdot (\underline{B} \times \underline{r}_i) + 2 \hat{\underline{p}}_i \cdot \frac{[\underline{\mu}_N \times (\underline{r}_i - \underline{R}_N)]}{|\underline{r}_i - \underline{R}_N|^3} \right\}$$

(where \hat{H}_0 is the Hamiltonian of the system without magnetic field, and \bullet means scalar product). In the last equation we retained the first-order terms only (the second-order terms are very important for the magnetic susceptibility).



$$\underline{a} \cdot (\underline{b} \times \underline{c}) = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} =$$

= sign \times volume of the body

The change of any two of a,

b, and c will change the sign but, naturally, it is invariant cyclically:

$$\hat{\underline{p}}_i \cdot (\underline{B} \times \underline{r}_i) = \underline{B} \cdot (\underline{r}_i \times \hat{\underline{p}}_i) = \underline{B} \cdot \hat{\underline{l}}_i$$

thus this perturbation brings the angular momentum, naturally: the external B field rotates (curl = rot) the

molecule around the direction of the $\underline{\mathbf{B}}$ vector in the complex space... The second term:

$$2\hat{\underline{\mathbf{p}}}_i \cdot \frac{\underline{\mu}_N \times (\underline{\mathbf{r}}_i - \underline{\mathbf{R}}_N)}{|\underline{\mathbf{r}}_i - \underline{\mathbf{R}}_N|^3} = 2\underline{\mu}_N \cdot \frac{(\underline{\mathbf{r}}_i - \underline{\mathbf{R}}_N) \times \hat{\underline{\mathbf{p}}}_i}{|\underline{\mathbf{r}}_i - \underline{\mathbf{R}}_N|^3} = 2\underline{\mu}_N \cdot \hat{\underline{\mathbf{l}}}_{iN}$$

of course, the angular momentum is independent from the space if the system does NOT move (in the opposite case depending...). Here $\hat{\underline{\mathbf{l}}}_{iN}$ is the angular momentum of the i -th electron corresponding to a coordinate system possessing the origin at the N -th nucleus.

The chemical shift is a second-order tensor:

$$\sigma_{\alpha\beta} = \frac{\partial^2 E}{\partial B_\alpha \partial \mu_\beta}$$

where $\alpha, \beta = \text{spatial } x, y, z$

the observation of the non-symmetrical part is very difficult... The NMR is a "slow method", the molecule can move freely in liquid state, thus, only the isotropic part can be observed:

$$\sigma_{\text{isotropic}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

In solid states the anisotropic part is important and can be observed (e.g., if the molecule is adsorbed on the surface of zeolith, the orientation can be determined): e.g., at the HF (SCF) level for the second-order perturbations the calculation of the second derivatives can be applied (Pulay).

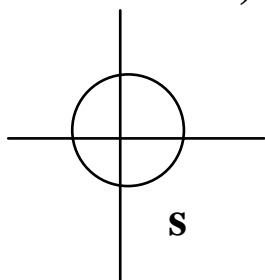
Gauge-invariance: in the simplest case means that the origin can be moved and in this case we have to add to

$\underline{A}(\underline{r})$ a constant vector: this can not change the electrodynamics of the system

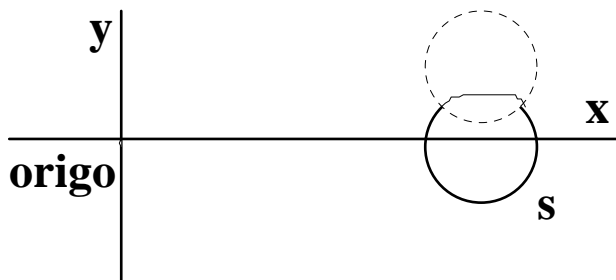
$$\underline{A} = \frac{1}{2} \underline{B} \times \underline{r} \quad ; \quad \underline{A}' = \frac{1}{2} \underline{B} \times (\underline{r} - \underline{R}_0)$$

so we must have the same result also in the second case, i.e., the calculated values can NOT be depending on the location of the molecule in the coordinate system.

Problem: (i) in case of the H atom (or any other atom of closed-shell) there is NO problem:



the rotation does NOT change the s-orbital. The three p-orbitals individually rotate, but can be described uniformly with/without the perturbation; (ii) In case, e.g., a B_z homog. magnetic field and IF the atom is NOT at the origo



the B_z field tries to rotate the orbital around the z-axis, will be multiplied with an imaginary factor. If the atom is at the origin, can be uniformly described with/without \underline{B} . If the atom is very far from the origo, it can be described without \underline{B} . But with \underline{B} the orbitals will be slightly moved and if the B_z operator acts on a moved orbital the rotation can NOT be well described by the basis functions (more accurately, the basis functions can

not describe well the perturbed wavefunction). For atoms the result can be good, but for MOLECULES **NOT: it is NOT possible to place all the atoms into the origin, thus the results will depend on the basis set used and on the choice of the origin and the orientation. At a very large basis set the problem will disappear.**

For a small molecule, if we use a moderate basis set and if only one nucleus is interesting, we have to put it into the origin and the problem is solved... But for a larger molecule...

F. London, 1937: first-order perturbation for an AO

$$\chi_p(\underline{r}, \underline{B}) = \chi_p(\underline{r}, 0) \cdot \exp\left[\frac{i}{2c} (\underline{B} \times \underline{R}_p) \bullet \underline{r}\right]$$

where $\chi_p(\underline{r}, 0)$ is the original AO, \underline{R}_p is the centre of the AO, and i is the imaginary unit.

That is, if the change of the basis set is allowed in a magnetic field, we will NOT get different results depending on where we put the atoms...

Gauge Independent Atomic Orbitals (GIAO) (as it was named by R. Ditchfield in 1974): In case of GIAO, the orbitals ARE depending on the field ("orbital following") but the results ARE independent.

Derivative methods: Pulay, 1987, Advanced Chem.

Phys.: he noticed that the effect of the magnetic perturbation (caused by a homogenous magnetic field) is the same as the calculation of the second derivatives at the Hartree-Fock level. For Gaussian basis sets:

$$\chi_p(\underline{r}, \underline{B}) = e^{-a(\underline{r}-\underline{R}_p)^2} \cdot e^{\frac{i}{2c} (\underline{B} \times \underline{R}_p) \bullet \underline{r}}$$

"All the physics can be described by a few mathematical formulas: the completion for a complete quadrate, the sine/cosine of the sum of two angles, and the sum of a geometric series ..." P.P.

with an elementary modification we get:

$$(\underline{r} - \underline{R}_p)^2 + A_x \rightarrow (\underline{r} - \underline{R}_p')^2 + \text{const.}$$

Nota bene: The \underline{R}_p' center will be complex but this will NOT cause any difficulties...

[Alternative methods:

Individual Gauge for Localised Orbitals (IGLO):

Kutzelnigg, 1980: localizes the MOs, and introduces for these a gauge-factor. The localised orbitals can be considered roughly spherical. We have to move the origin of the coordinate system into the "center-of-mass" of the localised orbital...

Localised Orbital Local Origin (LORG):

Hansen, von Bouman, 1985, ...]

"The future: the GIAO method..." (P.P.)

The NMR shift (shielding) calculation at the SCF level takes $2-3 \times$ Time of the energy calculation.

^{13}C shieldings can be easily(well) calculated at this level.

Nuclei with lone pairs (like N) cause much more problem: correlation... These need correlation methods like MP2-NMR shifts, DFT-NMR shifts. Mentioned

methods are implemented into the most modern program systems (ACES II, PQS, Gaussian).

Examples: 7-circulene: 300 basis functions, energy 3 hours, SCF-NMR shieldings 2.5×3 hours (1 hour computer time is about 1 \$).

Hexa-radiallene: people thought it is planar; Calculations showed that NOT: 40 mhartree (25 kcal/mol) lower energy if it is out of the plane. In THIS case we get the experimental NMR shifts.

Silicon compounds: ipse feci...

Fluorinated triptophane: it is build up into the peptide. It can be located within the peptide by NMR.

Gramicidine: Pulay.

EPILOGUE

Problems in the future:

- 1.) Effective correlation methods for large molecules, excited states.
- 2.) Relativistic effects, heavy atoms.
- 3.) Global geometry optimization methods for large/floppy molecules.
- 4.) Solvent effects.
- 5.) Effective parallel softwares.

Suggested reading:

T.D. Crawford, S.S. Wesolowski, E.F. Valeev, R.A. King, M.L. Leininger, H.F. Schaefer III: *"The Past, Present, and Future of Quantum Chemistry"*, in *Science at the Turn of the Millennium* (E. Keinan, ed.) Wolff Foundation, ?, ?, 2000.

F. Jensen: *Introduction to Computational Chemistry*, John Wiley & Sons, Chichester, 1999.

D.B. Cook: *Handbook of Computational Quantum Chemistry*, Oxford Univ. Press, Oxford, 1998.

R.G. Parr & W. Yang: *Density-Functional Theory of Atoms and Molecules*, Oxford Univ. Press, Oxford, 1989.

W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople: *Ab Initio Molecular Orbital Theory*, J. Wiley & Sons, New York, 1986.

A. Szabo & N.S. Ostlund: *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, Macmillan, New York, 1982.

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###

APPENDIX I

The Born–Oppenheimer approximation and beyond

1. Goal:

The separation of the electronic and nuclear motion. Anyway, this is not absolutely needed: there is a way to solve the Schrödinger equation of the “complete” (electrons + nuclei) Hamiltonian for small systems, see, e.g.: M. Cafiero, S. Bubin, L. Adamowicz, “Non-Born–Oppenheimer Calculations of Atoms and Molecules”, *Phys. Chem. Chem. Phys.* 5, 1491 (2003).

2. History:

Originally it was called as Born–Oppenheimer (B–O) [1] approximation. It has to be emphasized that Heitler and London [2] used the B–O approximation ‘implicitly’, even before the publication of the B–O paper [1]. The problem related to the B–O approximation was/is the rather clumsy (perturbational) description. Later Born developed another, more elegant method [3] that is not based on the perturbation theory (apparently, Slater [4] was the first who discovered the so-called ‘Born method’). Today everybody speaks about the B–O approximation but uses the (Slater–)Born method [Kapuy’s comment]. (After the World War II Oppenheimer and Teller had a strong conflict (see, e.g., [5]) which is well-known for the international scientific community. Anyway,

Oppenheimer has a grand portrait in the KGB museum, Moscow [6].) Both the B–O- and the (simpler) Slater–Born-methods are called as *adiabatic approximations* (Born and Fock, [7]) although the resulted equations are not the same (!). Later Sellers and Pulay [8] introduced the diagonal correction of the adiabatic (also cited as B–O) approximation. A brief and brilliant summary of the topic is written by Kutzelnigg [9].

3. The B–O theory: (the first step of Born-hierarchy of approximations [3a])

It is a perturbative treatment of the problem. The perturbation parameter is

$$\eta = \bar{m}^{-4}$$

(here \bar{m} is the average of the mass of the nuclei building up the molecule). Born and Oppenheimer, neglecting the corrections higher than quartic order, showed that the molecular energy is

$$E = \eta^0 E_K + \eta^2 E_{KV} + \eta^4 E_{KVR}$$

where E_K is the energy of the *electronic* system, E_{KV} is the *vibrational* energy, and last, E_{KVR} is the *rotational* energy (the first- and third-order corrections vanish).

Appreciation and problems:

1. Valid only for small molecules ($N = 2$) [13] and for vibrations of small amplitudes; 2. It is difficult to estimate the role of the neglected higher terms; 3. Divergent (!); 4. Valid only if the electronic states are well-separated; 5. Confirmed the already *accepted* chemical concept of the shape and sterical structure of the molecules [15].

According to the B–O approximation the electrons can adapt immediately to the relatively slow movement of the nuclei, and the nuclei “see” the averaged distribution of the electrons only.

The nonrelativistic total Hamiltonian of a molecule (n electrons, N nuclei) in *atomic units* is:

$$\hat{H} = -\frac{1}{2} \sum_{a=1}^N M_a^{-1} \nabla_a^2 - \frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_a \sum_i Z_a r_{ai}^{-1} + \sum_{i < j}^n r_{ij}^{-1} + \sum_{a < b}^N Z_a Z_b r_{ab}^{-1}$$

where r_{kl} is the distance between particles k and l , Z_a and M_a are the nuclear charge and mass of the a -th nucleus, resp. (naturally, the M_a nuclear masses are measured in units of the electronic mass m_e). The Schrödinger equation (Sch.E.) of the aforementioned Hamiltonian is as follows:

$$\hat{H}\Psi(\underline{d}_i, \underline{D}_a) = \mathcal{E}\Psi(\underline{d}_i, \underline{D}_a)$$

(here \underline{d}_i and \underline{D}_a are the space- *and* spin-coordinates of the electrons and nuclei, resp.) The mass of the nuclei is much larger than that of the electrons (see above)... Thus, the Schr.E. of the aforementioned Hamiltonian can be separated into two parts: the Sch.E.s of the electronic (I) and the nuclear (II) Hamiltonians. In order to derive them, let us define the electronic Hamiltonian as

$$\hat{H}^{el} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_a \sum_i Z_a r_{ai}^{-1} + \sum_{i < j}^n r_{ij}^{-1} + \sum_{a < b}^N r_{ab}^{-1}$$

The Sch.E. (I) of the electrons, in the field of the *fixed* nuclei is

$$\hat{H}^{el} \Psi_{\kappa}(\underline{d}_i; \underline{R}_a) = E_{\kappa}(\underline{R}_a) \Psi_{\kappa}(\underline{d}_i; \underline{R}_a)$$

(I)

where the character “;” means that there is *parametric* dependence only on the \underline{R}_a ($a = 1, 2, \dots, N$) nuclear configuration (i.e., here $M_a^{-1} \nabla_a^2 \rightarrow 0$ if $M_a \rightarrow \infty$).

The Sch.E. of the nuclei (II) can be derived, if we consider the terms corresponding to the electrons in the *total* Hamiltonian as expectation values (averaged on the electronic coordinates already)

$$\hat{H}^{nucl} = -\frac{1}{2} \sum_{a=1}^N M_a^{-1} \nabla_a^2 + -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_a \sum_i Z_a r_{ai}^{-1} + \sum_{i < j} r_{ij}^{-1} + \sum_{a < b} Z_a Z_b r_{ab}^{-1} =$$

$$= \left[-\frac{1}{2} \sum_{a=1}^N M_a^{-1} \nabla_a^2 + E_{\kappa}(\cdot; \underline{R}_a) \right]$$

thus the Sch.E. (II) is as follows

$$\hat{H}^{nucl} \Psi_{\kappa\mu}(\underline{D}_a) = E_{\kappa\mu} \Psi_{\kappa\mu}(\underline{D}_a) \quad (\text{II})$$

The crucial point is the potential (energy hyper-) surface

$$\hat{V}^{nucl} = E_{\kappa}(\cdot; \underline{R}_a) \quad ,$$

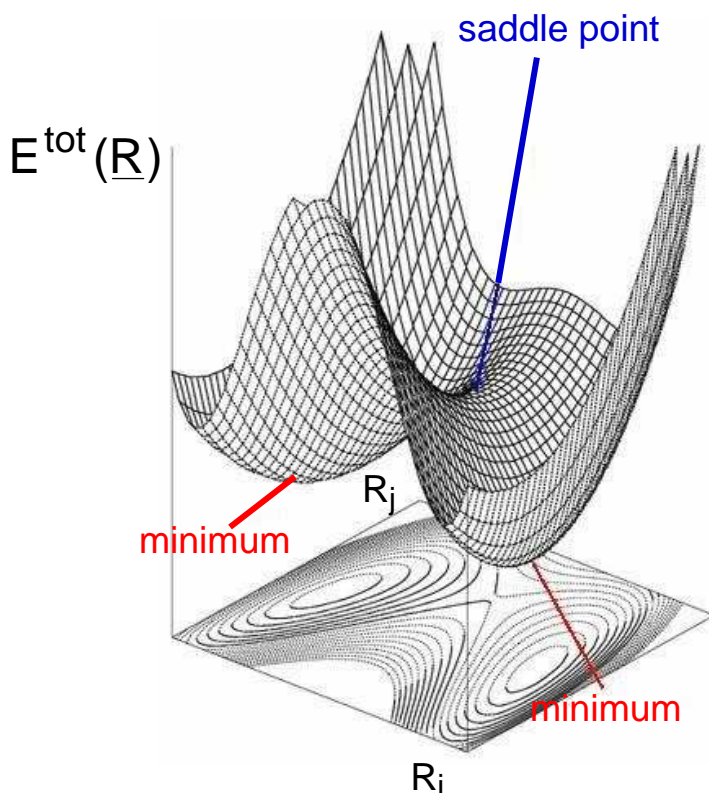
where the motion of the nuclei takes place.

(According to the *adiabatic theorem* (or, *adiabatic approximation* [7]) the κ electronic state does not change during the motion of the nuclei.)

The B–O approximation is of great importance in (quantum) chemistry. Its use gives the possibility for the definition of the potential energy curves, surfaces and hypersurfaces, allows us to visualize the chemical reactions, reaction coordinates, and validates the idea of the molecular equilibrium geometry. It must be emphasized that some of these concepts were used in chemistry earlier as the B–O approximation has been

discovered, so the B–O approximation only confirmed these ideas.

Precisely, only the *stationary points* of the effective potential energy surface are definite (i.e., the reaction coordinate can not be determined uniquely) [10]. Stationary points are: the *minima* (starting materials and end products), the *saddle points* (transition states), and the ‘*local minima*’ (reactive intermediates).



The ‘reaction coordinates’ are *not* observables. However, their definition can be given in statical or dynamical sense [10]. 1. Statical: not unambiguous (see later); 2. Dynamical: the classical trajectory could be determined on an *effective* potential surface (calculated

via quantum chemistry) for a ball (semiclassical approximation). “Bob-slay effect”: thus the actual activation energy can be higher than the gap itself (e.g., reaction of molecular hydrogen and iodine).

Note: In the B–O approximation the total wave function is approximated in the form as follows:

$$\Psi(\underline{r}, \underline{R}) = \chi(\underline{R}) \Psi_{\kappa}(\underline{r}; \underline{R})$$

(here the spin coordinates are ignored). This expression is not an approximation *itself*; the approximation is that the Ψ_{κ} and χ functions *are* the eigenfunctions of the separated Sch.E.s I (electronic) and II (nuclear). Indeed, let’s assume that there exists a $\Psi(\underline{r}, \underline{R})$ function with the feature $\langle \Psi | \Psi \rangle_{\underline{r}, \underline{R}} = 1$; in this case the function Ψ is *always* can be presented in the form of $\Psi = \chi(\underline{R}) \Psi_{\kappa}(\underline{r}; \underline{R})$, where $\langle \chi | \chi \rangle_{\underline{R}} = \langle \Psi_{\kappa} | \Psi_{\kappa} \rangle_{\underline{r}} = 1$. In order to prove this let us start with $\left(\langle \Psi | \Psi \rangle_{\underline{r}} \right)^{1/2} = \chi(\underline{R})$ (obviously, the integration of Ψ over the electronic coordinates is some χ function of the nuclear ones). Now

$\langle \chi | \chi \rangle_{\underline{R}} = \langle \Psi | \Psi \rangle_{\underline{r}, \underline{R}} = 1$. On the other hand, we can write

$$\Psi_{\kappa}(\underline{r}; \underline{R}) = \Psi(\underline{r}, \underline{R}) / \chi(\underline{R}) , \text{ from where we get}$$

$$\langle \Psi_{\kappa} | \Psi_{\kappa} \rangle_{\underline{r}} = \langle \Psi | \Psi \rangle_{\underline{r}} / \chi^2(\underline{R}) = \chi^2(\underline{R}) / \chi^2(\underline{R}) = 1$$

(QED).

Here we have followed the argument of Stepanov and Pupyshev [12]. The $\chi(\underline{R})\Psi_{\kappa}(\underline{r};\underline{R})$ expression means a specific way of a strong (or, ‘autocratic’) correlation [9b], in which one motion leads to the other (i.e., it is only seemingly similar to the case of separated, independent coordinates of ‘democratic’ correlation [9b], see the box in p. 8).

4. The Slater–Born method:

The $\Psi_{\kappa}(\underline{d}_i; \underline{R}_a)$ eigenfunctions of the *electronic* Hamiltonian constitute a complete orthonormal (von Neumann-) set at each \underline{R}_a ($a = 1, 2, \dots, N$) configuration. With the help of them the eigenfunctions of the total nonrelativistic Hamiltonian can be expressed in the form of a power series:

$$\Psi(\underline{d}_i, \underline{D}_a) = \sum_{\lambda} \chi_{\lambda}(\underline{R}_a, \underline{\Xi}_a) \Psi_{\lambda}(\underline{d}_i; \underline{R}_a) \quad \text{(III)}$$

(here the χ_{λ} coefficients describe the movement of the nuclei, and $\underline{\Xi}_a$ is the vector of the nuclear spins). Substituting the Eq. (III) into the Sch.E. of the *total* nonrelativistic Hamiltonian, then multiplying both sides of the equation by $\Psi_{\kappa}^*(\underline{d}_i; \underline{R}_a)$ and finally, integrating them over the *electronic* coordinates, we get the

following *coupled* system of equations for the χ_λ coefficients:

$$\left\{ \hat{T}^{nucl} + E_\kappa(\underline{R}_a) + \hat{B}_{\kappa\kappa}(\underline{R}_a) \right\} \chi_\kappa(\underline{R}_a, \underline{\Xi}_a) + \sum_{\lambda \neq \kappa} \hat{B}_{\kappa\lambda}(\underline{R}_a) \chi_\lambda(\underline{R}_a, \underline{\Xi}_a) = \mathcal{E} \chi_\kappa(\underline{R}_a, \underline{\Xi}_a) \quad (\text{IV})$$

where the matrix elements of the *coupling operator* \hat{B} are as follows

$$\hat{B}_{\kappa\lambda}(\underline{R}_a) = -\frac{1}{2} \sum_a M_a^{-1} \left\{ \langle \kappa | \Delta_a \lambda \rangle + 2 \langle \kappa | \nabla_a \lambda \rangle \nabla_a \right\}$$

(Here the crucial point was the following: \hat{T}^{nucl} contains double derivation according to the nuclear coordinates, and we have to derivate the function $\chi_\lambda(\underline{R}_a, \underline{\Xi}_a) \Psi_\lambda(\underline{d}_i; \underline{R}_a)$ in a *lege artis* manner, i.e., $\chi \Psi + \chi \Psi', \dots!$)

[It is easy to show the different levels of the Born-hierarchy of approximations using Eq. IV. If *all* the matrix elements of the coupling operator \hat{B} are neglected, this is the B–O approximation. If all the *off-diagonal* terms are neglected, this is the adiabatic approximation (in a strict sense). If *all the coupling matrix elements* were taken into consideration, this is the non-adiabatic (or, diabatic) approximation.]

Up to this point the procedure is completely correct (apropos, we have to summarize in Eq. (III) over both the discrete *and* continuous spectra of eigenvalues!). If we neglect the *off-diagonal* coupling elements, Eq. (IV) disintegrates into independent eigenvalue equations:

$$\begin{aligned} \left\{ \hat{T}^{nucl} + E_{\kappa}(\cdot; \underline{R}_a) + \hat{B}_{\kappa\kappa}(\underline{R}_a) \right\} \chi_{\kappa\mu}(\underline{R}_a, \underline{\Xi}_a) = \\ = \mathcal{E}_{\kappa\mu} \chi_{\kappa\mu}(\underline{R}_a, \underline{\Xi}_a) \quad (\kappa, \mu = 0, 1, 2, \dots) \end{aligned} \quad (\text{V})$$

In a specific, stricter sense, this is the (Slater–Born-type) ‘adiabatic’ approximation. This is the second step of the Born-hierarchy of approximations. Let us write the $\hat{B}_{\kappa\kappa}$ term as follows:

$$\begin{aligned} \hat{B}_{\kappa\kappa} &= -\frac{1}{2} \sum_a M_a^{-1} \left\{ \langle \kappa | \Delta_a \kappa \rangle + 2 \langle \kappa | \nabla_a \kappa \rangle \nabla_a \right\} = \\ &= \left\langle \kappa \left| \hat{T}^{nucl} \right| \kappa \right\rangle, \end{aligned}$$

(because $\langle \Psi_{\kappa} | \nabla_a \Psi_{\kappa} \rangle = 0$, as it can easily be shown by differentiating the normalization condition $\langle \Psi_{\kappa} | \Psi_{\kappa} \rangle = 1$).

The $\hat{B}_{\kappa\kappa}$ term of the nuclear Hamiltonian is called as *adiabatic correction* (of the B–O potential surface) which is sometimes also called ‘diagonal B–O correction’, DBOC. At first, the DBOC was computed for the special case of the Hartree–Fock theory by Sellers and Pulay [8]. Note that an effective potential energy surface is still exists within the frame of the

‘adiabatic approximation’, although it slightly differs for isotopologues [through masses (\hat{T}^{nucl}) in $\hat{B}_{\kappa\kappa}$]. The Ansatz for the adiabatic approximation is as follows:

$$\Psi(\underline{d}_i, \underline{D}_a) = \chi_{\kappa}(\underline{R}_a, \underline{\Xi}_a) \psi_{\kappa}(\underline{d}_i; \underline{R}_a) \quad .$$

The highest level of the Born-hierarchy of approximations is the non-adiabatic [sometimes also called diabatic (!)] approximation. In that case the Ansatz has the general form as is given in Eq. (III). The linear combination could have smaller or larger number of terms, for the first-order and second-order non-adiabatic effects, respectively. *First-order non-adiabatic effects* arise if the electronic states close to, or they are (avoided) crossing each other. In this case a small number of the terms in Eq. (III) is needed. *Second-order non-adiabatic effects* arise if an electronic state is well separated from other ones but a higher accuracy is required. In that case a large number of terms have to be used in Eq. (III).

Example: the DBOC of the H-atom [9a,9b]:

Here we can treat exactly the center of mass (COM) and relative coordinates, and can compare the result with the B–O (or adiabatic) approximation.

Let \underline{r} and \underline{R} the coordinates of the electron and the nucleus, resp. The full Hamiltonian \mathcal{H} (in terms of \underline{r} and \underline{R}) can be transformed into a new form using the $\underline{\mathcal{R}}$ COM and the $\underline{\rho}$ relative (internal) coordinates as follows:

$$\underline{\mathcal{R}} = \frac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 + m_2} = \frac{\underline{r} + M \underline{R}}{M + 1} ; \mathcal{M} = M + 1$$

$$\underline{\rho} = \underline{r} - \underline{R} ; \mu = \frac{m_1 m_2}{m_1 + m_2} = \left(1 + \frac{1}{M}\right)^{-1} = 1 - \frac{1}{M} + O\left(\frac{1}{M^2}\right)$$

$$\mathcal{H} = H_{\underline{\mathcal{R}}} + H_{\underline{\rho}} ; H_{\underline{\mathcal{R}}} = T_{\underline{\mathcal{R}}} = -\frac{1}{2\mathcal{M}} \nabla_{\underline{\mathcal{R}}}^2 ; H_{\underline{\rho}} = -\frac{1}{2\mu} \nabla_{\underline{\rho}}^2 - \frac{1}{\rho}$$

(where \mathcal{M} and μ are the respective total and reduced masses, and ρ is the norm of $\underline{\rho}$). The exact nonrelativistic energy and wave function for the electronic ground state moving with total momentum \underline{K} are

$$\mathcal{E} = -\frac{\mu}{2} + \frac{K^2}{2(M + 1)} ; \Psi = \psi(\mu \underline{\rho}) \exp(i \underline{K} \cdot \underline{\mathcal{R}}) ;$$

$$\psi(\mu \underline{\rho}) = \frac{\mu^{3/2}}{\sqrt{\pi}} \exp(-\mu \rho) .$$

In the B–O approximation, starting from the nonseparated Hamiltonian of fixed nucleus:

$$\mathcal{H} = H_{fixed} + T_{nucl} ; H_{fixed} = T_{el} - \frac{1}{r} ; T_{el} = -\frac{1}{2} \nabla_{\underline{r}}^2 ;$$

$$T_{nucl} = -\frac{1}{2M} \nabla_{\underline{R}}^2$$

(here r is the norm of \underline{r}), the energy of the H atom in its ground state traveling with momentum \underline{K} is

$$\mathcal{E}_{\text{B-O}} = -\frac{1}{2} + \frac{K^2}{2M} \quad ; \quad \Psi = \psi(\underline{\rho}) \exp(i\underline{K} \cdot \underline{R}) \quad ; \quad \psi(\underline{\rho}) = \frac{1}{\sqrt{\pi}} \exp(-\rho) \quad .$$

Obviously, the B–O approximation causes two errors: (a) uses the electronic mass instead of the reduced mass, i.e., neglects the motion of the nucleus in the relative motion; (b) replaces $K^2 / 2(M+1)$ by $K^2 / 2M$, i.e., neglects the participation of the electron in the translational motion. From these two errors only the first one is cancelled in the adiabatic approximation, since the DBOC is as follows:

$$\begin{aligned} \text{DBOC} &= \langle \psi(\underline{\rho}) | T_{\text{nucl}} \psi(\underline{\rho}) \rangle = \frac{1}{M} \langle \psi(\underline{\rho}) | T_{\text{el}} \psi(\underline{\rho}) \rangle = \\ &= \frac{1}{2M} \quad . \end{aligned}$$

(In the last Eq. a simple trick was used:

$$\left\langle \frac{\partial \psi(\underline{\rho})}{\partial \underline{\rho}} \cdot \frac{\partial \underline{\rho}}{\partial \underline{R}} \middle| \frac{\partial \psi(\underline{\rho})}{\partial \underline{\rho}} \cdot \frac{\partial \underline{\rho}}{\partial \underline{R}} \right\rangle = \left\langle \frac{\partial \psi(\underline{\rho})}{\partial \underline{\rho}} \cdot \frac{\partial \underline{\rho}}{\partial \underline{r}} \middle| \frac{\partial \psi(\underline{\rho})}{\partial \underline{\rho}} \cdot \frac{\partial \underline{\rho}}{\partial \underline{r}} \right\rangle$$

•

The $1/2$ comes from the virial theorem.)

The sum of the electronic B–O energy and the DBOC is:

$$-\frac{1}{2} + \frac{1}{2M} = -\frac{1}{2} \left(1 - \frac{1}{M} \right) = -\frac{\mu}{2} + O(M^{-2})$$

This sum agrees with the electronic part of the exact energy to $O(M^{-1})$.

Note that there is no adiabatic correction to the translational motion. Only the non-adiabatic Ansatz can describe the translation correctly within the Born-hierarchy.

To check the effect of the non-adiabatic Ansatz, we transform the exact wave function Ψ to terms of $\underline{\rho}$ and $\underline{\mathcal{R}}$ (rather than \underline{r} and $\underline{\mathcal{R}}$):

$$\underline{\mathcal{R}} = \frac{M \underline{R} + \underline{r}}{M + 1} = \frac{(M + 1) \underline{R} + \underline{\rho}}{M + 1} = \underline{R} + \frac{\underline{\rho}}{M + 1};$$

and

$$\begin{aligned} \Psi &= \psi(\mu \underline{\rho}) \exp(i \underline{K} \cdot \underline{\mathcal{R}}) = \psi(\mu \underline{\rho}) \exp(i \underline{K} \underline{R}) \exp\left(i \frac{\underline{K} \underline{\rho}}{M + 1}\right) = \\ &= \tilde{\psi}(\underline{\rho}) \exp(i \underline{K} \underline{R}) , \end{aligned}$$

where $\tilde{\psi}$ is the electronic and $\exp(i \underline{K} \underline{R})$ is the nuclear wave function component, resp.. The energy of the nuclear motion is

$$\mathcal{E}_{nucl} = \langle \chi | T_{nucl} \chi \rangle = \langle \exp(i \underline{K} \underline{R}) | T_{nucl} \exp(i \underline{K} \underline{R}) \rangle = \frac{K^2}{2M};$$

and the electronic energy is

$$\begin{aligned}\tilde{\mathcal{E}} &= \langle \tilde{\psi} | (H_{fixed} + T_{nucl}) \tilde{\psi} \rangle = \left\langle \psi \left| \left(\exp\left(-i \frac{K\rho}{M+1}\right) \right) \mathcal{H} \left(\exp\left(i \frac{K\rho}{M+1}\right) \right) \psi \right. \right\rangle = \\ &= \langle \psi | H_{fixed} \psi \rangle + \left\langle \psi \left| \left[T_{el,i} \frac{K\rho}{M+1} \right] + \frac{1}{2} \left[\left[T_{el,i} \frac{K\rho}{M+1} \right], i \frac{K\rho}{M+1} \right] \right. \right. \psi \left. \right\rangle + O(M^{-3})\end{aligned}$$

(here the so-called Baker-Campbell-Hausdorff expansion was used, see, e.g. [16], as follows

$$e^{-\hat{B}} \hat{A} e^{\hat{B}} = \hat{A} + [\hat{A}, \hat{B}] + \frac{1}{2} [[\hat{A}, \hat{B}], \hat{B}] + \frac{1}{3!} [[[\hat{A}, \hat{B}], \hat{B}], \hat{B}] + \dots).$$

Note that the single commutator is imaginary (does not contribute), since the double commutator gives a term of

$$[[T_{el,i} \underline{K\rho}], i \underline{K\rho}] = -K^2 \quad . \quad (\text{Error!!! See p. 179, G.P.})$$

(the term with T_{nucl} was ignored in the double commutator because its value is less than $O(M^2)$). Thus we get:

$$\tilde{\mathcal{E}} = \langle \psi | H_{fixed} \psi \rangle - \frac{K^2}{2(M+1)^2} + O(M^{-3}) \quad .$$

The sum of the K -dependent terms is

$$E_{COM} = \frac{K^2}{2M} - \frac{K^2}{2(M+1)^2} = \frac{K^2}{2(M+1)} + O(M^{-3}) \quad ,$$

so we have got the energy of the COM motion with $O(M^{-2})$ accuracy. Summing up, the participation of the nucleus in the relative motion is an *adiabatic* effect, whereas the participation of the electron in translation is a *non-adiabatic* effect.

Discussion:

1. Sutcliff [13]: For neutral or positive atoms there are an infinite number of bound states. For negative atoms there is at most a finite number of bound states. For molecules with fixed nuclei the situation is similar. If the nuclei are allowed to move, the problem becomes very difficult. In neutral or weakly positive systems there are some bound states (dissociation to atoms) but not necessarily of an infinite number. For too negative or too positive molecules there are not any bound states at all. These are according to the Hunzicker's theorem [14]. (Ipsa feci: anyway, we have to use the discrete (bound) *and* continuous spectra in Eq. III.)
2. Inevitably, the electronic energy surfaces touch and cross somewhere: here the coupling matrix elements are likely to be divergent [13]. In such cases one can ignore the matrix element and the coupling has taken into consideration in the potential.
3. Adiabatic *versus* non-adiabatic corrections:

Leading contributions in energy terms:

electronic: $O(M^0)$

(harmonic) vibration: $O(M^{1/2})$

(rigid) rotation: $O(M^{-1})$

translation: $O(M^{-1})$

In calculation of the electronic energy, the $O(M^{-1})$ adiabatic correction is important, the $O(M^2)$ non-adiabatic correction can be neglected if the question are connected to the potential energy surface (dissociation energy, reaction barriers, etc.).

Adiabatic and non-adiabatic corrections are of equally important to vibration and rotation. This can be seen in a numerical study of H_2 [17], as follows:

Adiabatic and non-adiabatic corrections to the vibrational frequencies of H_2 (in cm^{-1}) [17]

N	B–O	$\Delta_{ad.}$	$\Delta_{non-ad.}$	Exp.
0→1	4163.40	-1.40	-0.83	4161.14
1→2	8091.15	-2.55	-1.59	8087.93
2→3	11788.14	-3.47	-2.27	11782.36

4. It is possible to define a Born-hierarchy with/without first separating the COM motion. It is non-trivial that the adiabatic energy is independent of whether or not the COM motion has been separated off. It must be emphasized that the adiabatic *corrections* differ in the two options (the electronic energy after separation of COM motion contains contribution of $O(M^{-1})$ that can be considered as adiabatic correction).

In spite of the equivalence, it is an interesting question of which of the two Born hierarchies is internally more consistent. An argument to first eliminating the COM motion is that the Hamiltonian has bound states only after this elimination (Sutcliffe, [13]). On the other hand, without this separation, one

starts from the electronic energy of fixed nuclei (it is strictly of $O(M^0)$), whereas it (after the separation of the COM motion) contains terms of $O(M^{-1})$ as the adiabatic correction does. This makes the Born hierarchy without separation of the COM motion more internally consistent.

5. Kutzelnigg [9a,9b]: The electrons play two, not really compatible, roles: i.) The quant.mech.-al interference (exchange) of the electrons is responsible for the existence of an attraction between nuclei; ii.) Can electrons at the same time join to the nuclei in vibrational or rotational movement (in slow classical motions)? It looks plausible that inner-shell electrons do not contribute to the binding energy, but participate to a large extent in the nuclear motion.

A good compromise effective masses for vibration are the *atomic* masses, but for rotation the *nuclear* masses.

6. Spectroscopic/diffraction methods:
In order to make groups of different spectroscopic methods, we can use the electronic and nuclear wave function components.

Electronic		Nuclear
<i>Electronspectr.</i>		<i>Rotational spectr.</i>
(ultraviolet, visible)		(microwave, far IR)
<i>PES spectr.</i>	<i>Equilibrium geometry</i>	<i>Vibrational spectr.</i>
(ultraviolet, X-ray)	(electron-; X-ray; neutron diffraction)	(infrared; IR/Raman)
<i>ESR</i>		<i>NMR</i>
(microwave)		(radiowave)

The molecular structure is depending on the electronic state. Ethylene: ground state (closed-shell singlet): D_{2h} (planar); first excited state (open-shell triplet [11]): S_4 (twisted).

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APPENDIX II

GDIIS

Geometry Optimization by Direct Inversion in the Iterative Subspace

Pál Császár[†], Péter Pulay

J. Mol. Struct. **114**, 31-34 (1984).

Geometry optimization is one of the most frequently encountered problems in QC. All modern methods are based on gradient (force) technique:

1. Force relaxation method (P. Pulay, *Mol. Phys.* **17**, 197 (1969): needs fair guess of Hessian
2. Variable metric techniques: automatic modifying of Hessian during iteration (e.g., R. Fletcher, *Comput. J.*, **13**, 317 (1970)).
3. GDIIS: the best method.

The goal of GDIIS: the location of stationary points (usually minima) on a (nearly quadratic or rather non-quadratic) potential energy surface:

$$E = E(\underline{q}) = E(q_1, q_2, \dots, q_n)$$

(here n is 3N-6, typically large). The essence of DIIS: the parameter vectors generated in previous iterations,

$$\underline{q}_1, \underline{q}_2, \dots, \underline{q}_m$$

are linearly combined to find the *best* parameter vector in the m-dim. subspace (here m is not large). Let us denote the sought-for solution \underline{q}_0 , and express the \underline{e}_i error vectors as follows:

$$\underline{q}_i = \underline{q}_0 + \underline{e}_i \quad (i = 1, 2, \dots, m)$$

Let us suppose that

$$\sum_i c_i \underline{q}_i \approx \underline{q}_0$$

is valid in a least-square sense (usually $n > m$). Thus:

$$\sum_i c_i (\underline{q}_0 + \underline{e}_i) = \sum_i c_i \underline{q}_0 + \underbrace{\sum_i c_i \underline{e}_i}_{\approx 0} = \underline{q}_0$$

i.e., the following method can be formulated:

$$\|\sum_i c_i \underline{e}_i\| \rightarrow \min$$

$$\sum_i c_i = 1$$

which means a Lagrange-type constrained minimization. However, it is easier to minimize the square of the norm of the residual vector

$$F = \|\sum_i c_i \underline{e}_i\|^2 = \langle \sum_i c_i \underline{e}_i | \sum_j c_j \underline{e}_j \rangle = \sum_i \sum_j c_i c_j \langle \underline{e}_i | \underline{e}_j \rangle = \sum_i \sum_j c_i c_j D_{ij} \rightarrow \min$$

Using the method of the undetermined multipliers (Lagrange), the following functional has to be minimized:

$$\mathcal{F} = \sum_i \sum_j c_i c_j D_{ij} - 2\lambda(\sum_i c_i - 1) \rightarrow \min$$

(here 2 stands for convention). Derivation of \mathcal{F} according to c_k and λ we get:

$$\sum_i c_i D_{ki} - \lambda = 0$$

$$\sum_i c_i - 1 = 0$$

that is,

$$\begin{bmatrix} D_{11} & D_{12} & \dots & D_{1m} & 1 \\ D_{21} & D_{22} & \dots & D_{2m} & 1 \\ \dots & \dots & \dots & \dots & \dots \\ D_{m1} & D_{m2} & \dots & D_{mm} & 1 \\ 1 & 1 & \dots & 1 & 0 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \dots \\ c_m \\ -\lambda \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \dots \\ 0 \\ 1 \end{bmatrix}$$

The true error vectors are not known, naturally. However, in the (nearly quadratic) vicinity of the stationary point they can be approximated as

$$\underline{e}_i = -\underline{H}^{-1} \underline{g}_i$$

where \underline{g}_i is the gradient vector corresponding to the geometry \underline{q}_i , and \underline{H} is an approximation to the Hessian.

In case of linearly (almost) dependent parameter vectors the aforementioned matrix (GDIIS) equation is ill-conditioned. In order to treat this problem, the simplest technique is the omission of the error vector with the largest norm (see also below).

The solution of the GDIIS equation yields an interpolated parameter and gradient vector:

$$\underline{q}'_{m+1} = \sum_i c_i \underline{q}_i$$

$$\underline{g}'_{m+1} = \sum_i c_i \underline{g}_i$$

The new, independent geometry step will be generated as follows:

$$\underline{q}_{m+1} = \underline{q}'_{m+1} - \underline{H}^{-1} \underline{g}'_{m+1}$$

(the gradient vector is not explicitly evaluated for the parameter vector \underline{q}'_{m+1} !!!). Convergence checking can be done, e.g., on the norm of the approximated error vector...

Results:

Molecule	N	GDIIS	Fletcher
Ethylene	3	4	3
formamide	9	4	17
Thymine	32	4	11

Note that GDIIS significantly outperforms the variable metric methods for larger molecules.

The Calculation of ab Initio Molecular Geometries: Efficient Optimization by Natural Internal Coordinates and Empirical Correction by Offset Forces

G. Fogarasi, X. Zhou, P.W. Taylor, P. Pulay,
J. Am. Chem. Soc. 114, 8191 (1992).

Convergence of GDIIS can be significantly accelerated by the appropriate choice of nuclear coordinates. These

coordinates are the Natural Internal Coordinates (NICs) originated from vibrational spectroscopy. (Note that the „Z-matrix method” implemented, e.g., in Gaussian, is designed for input specification rather than for geometry optimization. Even Cartesians are better choice for ring molecules.) The NICs minimize the coupling terms between the coordinates so their use gives the „most quasi-quadratic” potential surface.

The INTC program has been written for generation the NICs automatically. Pulay’s programs (TX90, PQS) and TurboMole (independently) can use this automatic generation of NICs.

The use of NICs, simple diagonal guess of Hessian (!!!), in conjunction with the GDIIS method yields very good results at geometry optimization. Convergence of organic molecules is typically achieved in 8 - 15 steps even for systems with over 100 degrees of freedom.

Constrained optimizations can be introduced for several purposes. Extremely „weak” coordinates causes a very anharmonic surface: the minimum can be found only by fixing the floppy coordinate at several values and reoptimizing the remaining coordinates at each of them. A more important application is the search for transition states (TSs). GDIIS can be used to find TSs. Constrained optimization is usually very successful to locate the transition region.

Geometry optimization can easily be generalized to handle redundant coordinates.

DIRECT INVERSION IN ITERATIVE SUBSPACES (DIIS)

Recollection by Peter Pulay

in: "Molecular Quantum Mechanics: Analytic Gradients and Beyond" (eds.: A.G. Császár, G. Fogarasi, H.F. Schaefer III, P.G. Szalay), ELTE Institute of Chemistry, Budapest, Hungary, 2007, pp. 71 – 73.

Several modifications of the original DIIS method have been suggested over the years yielding slight improvement only. It is worthwhile to mention one modification of Peter Pulay which went unpublished, although it is used in all of his/theirs programs. In order to make the DIIS method more robust numerically, he adds a small positive number b to the diagonal elements of the DIIS matrix. Its effect is equivalent to adding (with a small multiplicative factor) the squared norm of the DIIS coefficients to the original object functional \mathcal{F} :

$$\mathcal{F}' = \sum_i \sum_j c_i c_j D_{ij} + b \sum_i c_i^2 - 2\lambda (\sum_i c_i - 1) \rightarrow \min$$

This is an application of Levenberg's (or Levenberg–Marquardt's) "damped least square method" (c.f., the orthonormality of the basis set is supposed).

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APPENDIX III

Avoided crossing, conical intersection

The electronic wavefunction of the \hat{H}_e Hamiltonian operator (in which we have omitted the term of the nuclear repulsion) is solved [5]

$$\hat{H}_e \Phi(r, Q) = E_e(Q) \Phi(r, Q)$$

(where r means all the electronic coordinates, Q stands for the spatial nuclear coordinates, respectively) in the basis of two functions (Φ_1 and Φ_2) by the variational method, that is:

$$\tilde{\Phi} = C_1(Q) \Phi_1 + C_2(Q) \Phi_2 \quad .$$

This yields two potential surfaces $E_{e1}(Q)$ and $E_{e2}(Q)$ which mean upper limits for the energies of the two states. We have to solve the

$$\underline{H} \underline{C}_i = \varepsilon_i \underline{C}_i$$

eigenvalue equation (here $\varepsilon_i = E_{ei}(Q)$, $i = 1, 2$, respectively). Let us denote by

$$H_{kl}(Q) = \langle \Phi_k | \hat{H}_e | \Phi_l \rangle \quad (\text{where } k, l = 1, 2)$$

the matrix elements of the Hamiltonian, then it is clear that

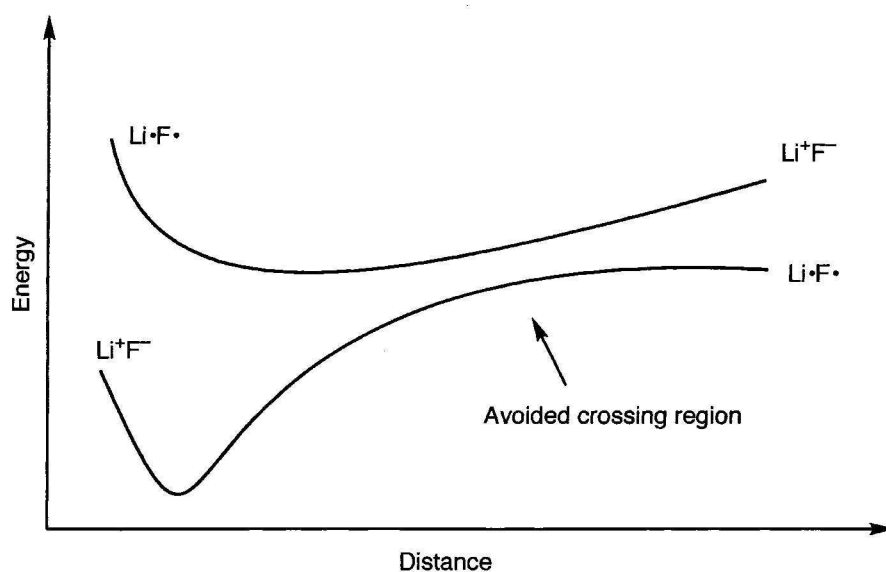
$$\varepsilon_{1,2}(Q) = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}H_{21}}}{2} .$$

These eigenvalues depend on Q , thus their behavior can be different. **Question:** can they cross each other, i.e., $\varepsilon_1 = \varepsilon_2$ at any special value of Q ? Obviously, such an equivalence can be exist at the simultaneous fulfillment of the following two conditions:

$$H_{11}(Q) = H_{22}(Q) \quad \text{and} \quad |H_{12}(Q)|^2 = 0$$

For a diatomic molecule there is only one variable which determines the nuclear configuration (the R nuclear distance). In this case there is no way to satisfy the system of the aforementioned conditions generally (there are two conditions and a sole parameter), so we conclude to the statement of the avoided crossing. The crossing is possible if and only if anyone of the two conditions will be satisfied automatically. This can be the situation if the Φ_1 and Φ_2 functions belong to different symmetry (and/or multiplicity). For such a case the rule states that only states of different symmetry types (or multiplicity) could cross each other. Another situation is also possible, in which the Φ_1 and Φ_2 functions are the exact eigenfunctions of the \hat{H}_e operator: in this case we can not state that the $\varepsilon_1 = H_{11}(Q)$ and the $\varepsilon_2 = H_{22}(Q)$ potential curves could cross or not because no another condition

appears. (Note that there is a mathematical theorem corresponding for the orthogonality of eigenfunctions corresponding to non-degenerate eigenvalues, as well as the general non-orthogonality of eigenfunctions belonging to degenerate eigenvalues which can not be applied here...) Summing up, for approximate functions it can be stated that they *generally* do not cross each other, for exact potential curves there is no definite answer. This is a bit paradox situation: nevertheless, it can be expected that even the exact potential curves do not cross each other usually.



The correlation diagram of LiF

For polyatomic molecules the validity of the avoided crossing rule is even less understandable. It can only be stated that the crossing of different potential hypersurfaces at which $Q_i = c_i$ for all the i -s but one selected Q_k variable, the situation is very likely similar to the avoided crossing rule of diatomics formally. If we

write the Ansatz as linear combination of many Φ_i functions:

$$\tilde{\Phi} = \sum_i^n C_i \Phi_i \quad ,$$

the crossing rule means (at special values of the Q_k) that there exists *at least* two eigenvectors (\underline{a} and \underline{b}) with the same eigenvalue ε . (Of course, any linear combination of these vectors, let's say $\underline{a} + \lambda \underline{b}$, will also satisfy the eigenequation with the same eigenvalue.) This means that – generally speaking – there are two such conditions which satisfy the secular equation

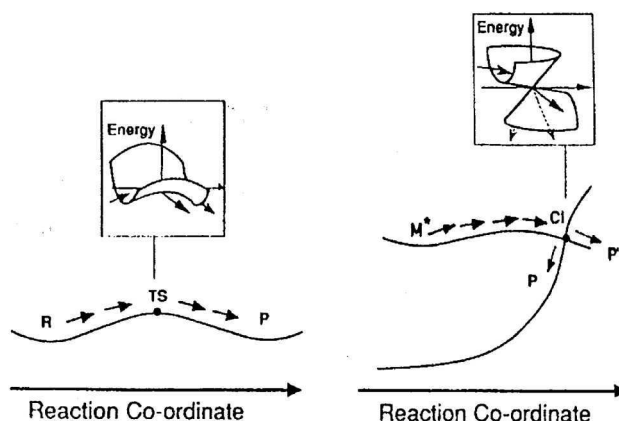
$$\left| H_{ij} - \varepsilon \delta_{ij} \right| = 0$$

with such an ε which is equal to the degenerate eigenvalue. For example, in case of $n = 3$ these conditions are:

$$(H_{11} - \varepsilon)(H_{22} - \varepsilon) - H_{12}H_{21} = 0$$

$$H_{12}H_{23} - H_{13}(H_{22} - \varepsilon) = 0$$

Conclusively, in case of $n > 2$ intersections are possible but the hypersurface (whose dimension is less by 2 than that of the starting potential hypersurfaces due to the two conditions) can be described as “conical intersection”, that is such an intersection which seemingly matches a peak of a conical surface.



The graphic representation of a transition state (left) and a conical intersection (right)

The rule of avoided crossing, ignoring its relativity, is very popular at the change of the nuclear configuration, at the qualitative analysis of the behavior of molecular states. For example, such a case appears if we investigate the change of the electronic energy of diatomic molecules' various states, starting from very small atom-atom distances ($R \rightarrow 0$) to very large distances ($R \rightarrow \infty$, isolated atoms). An analogous view can be applied at the change of a reaction coordinate, starting from certain initial value (that corresponds to the reactants) up to a value describing the products. For such transitions the graphic representation of the energy change is called as correlation diagrams.

Some finer details on the conical intersection [6-11]:

The ICS (Intersection Coordinate Subspace) is a $n-2$ dimensional hypersurface, on which the two potential hypersurfaces intersect (cross) each other

(here n is the number of the internal degrees of freedom).

The conical intersection is of great importance in photochemical reactions: in these processes the absorption of a photon with a certain frequency/energy puts the system into an excited state; from here it could get into the conical intersection by vibrational relaxation where two ways are opened: i.) going back to the minimum of the initial/ground state; ii.) or, remaining in the excited state and getting into a new minimum. According to a semiclassical model, symbolizing the nuclei by a ball of classical way of motion, the ball starts to turn round and round circularly in the cone of the conical intersection, thus it could get back to the initial state as well.

The modern description of the conical intersection is the following:

Two adiabatic states Ψ_1 and Ψ_2 which have an intersection, can be described by the linear combination of two arbitrary and orthogonal, non-adiabatic (or, diabatic) functions Φ_1 and Φ_2 . The latter span the Hilbert space together with the other electronic wavefunctions Ψ_κ (where $\kappa \geq 3$) supposing that their E_3, E_4, \dots eigenvalues are not degenerate by E_1 and E_2 :

$$\Psi_1 = \Phi_1 C_{11} + \Phi_2 C_{21} \quad ; \quad \Psi_2 = \Phi_1 C_{12} + \Phi_2 C_{22}$$

where the C_{ij} linear coefficients and the corresponding E_1 and E_2 energies could be determined from the eigenvalue problem of the Hamiltonian matrix:

$$H_{ij} = \langle \Phi_i | H \Phi_j \rangle$$

In the practically important cases the matrix elements are real. Naturally, the Hamiltonian matrix (and its elements) depend on the n nuclear/internal coordinates $q = (q_1, q_2, \dots, q_n)$, that is $H_{ij} = H_{ij}(q)$. Now write the Hamiltonian matrix into the following form:

$$H = \bar{H}E + RU \quad ,$$

where E is the unit matrix, U , \bar{H} , R and α are defined as follows:

$$U = \begin{pmatrix} \cos \alpha & \sin \alpha \\ \sin \alpha & -\cos \alpha \end{pmatrix}$$

$$\bar{H} = (H_{11} + H_{22})/2$$

$$\Delta H = (H_{11} - H_{22})/2 \quad .$$

$$R = \left(\Delta H^2 + H_{12}^2 \right)^{1/2}$$

$$\cos \alpha = \Delta H / R \quad ; \quad \sin \alpha = H_{12} / R$$

Substituting the equation of the H matrix and an arbitrary linear combination $\tilde{\Psi} = \Phi_1 \cos \gamma + \Phi_2 \sin \gamma$ into the expectation value equation we get:

$$\langle \tilde{\Psi} | H \tilde{\Psi} \rangle = \bar{H} + R \cos(2\gamma - \alpha) \quad .$$

The extrema of this function yield the two electronic eigenstates and the corresponding energies:

$$\begin{aligned} \Psi_1 &= \Phi_1 \cos \alpha / 2 + \Phi_2 \sin \alpha / 2 ; E_1 = \bar{H} + R \\ \Psi_2 &= \Phi_1 \cos(\alpha + \pi) / 2 + \Phi_2 \sin(\alpha + \pi) / 2 = \quad . \\ &\quad - \Phi_1 \sin \alpha / 2 + \Phi_2 \cos \alpha / 2 ; E_2 = \bar{H} - R \end{aligned}$$

It can be seen that the degeneracy occurs when R disappears: the latter needs the simultaneous fulfillment of the two conditions:

$$\Delta H = 0 ; H_{12} = 0 \quad .$$

Thus the intersection of the two states requires two conditions: the offdiagonal matrix elements of the Hamiltonian matrix have to disappear, and the diagonal values have to be equal. The form of the electronic wavefunctions are so that the change of the angle α from 0 to 2π causes the change of the sign of the wavefunction. If the number of the internal degrees of freedom is 4, the hypersurfaces of the two states could be equal on a two-dimensional surface. Its deepest point is the minimum of the ICS, and the reaction occurs

through this point. This is not a trivial problem since the conditions for the intersection need non-adiabatic coupling terms H_{ij} .

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APPENDIX IV
A brief description of the independent particle
 (Hartree-Fock) model

Let us start with the electronic Hamiltonian operator

$$\hat{H}^{el} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_a \sum_i \frac{Z_a}{r_{ai}} + \sum_{i<j}^n \sum r_{ij}^{-1} + \sum_{a<b}^N \sum r_{ab}^{-1} \quad (1)$$

(it is the exact, non-relativistic operator in atomic units, see the Appendix I for the notation). It is worthy to rewrite Eq. (1) in the following form:

$$\hat{H}^{el} = \sum_i h(i) + \sum_{i<j} \sum r_{ij}^{-1} \quad (2)$$

where the one-electron parts of Eq. (1) are collected in $h(i)$ (the last term is a constant).

If the Hamiltonian is approximated by its one-electron part ($\hat{H}^{el} \approx \sum_i h(i) = h_0$), we can exactly solve the

Schrödinger equation since an eigenfunction of a sum of one-electron operators can be constructed as a product of one-particle functions $\varphi_j(r_j)$ as follows:

$$\Phi_0(\underline{r}; \underline{R}) = \varphi_1(r_1) \varphi_2(r_2) \cdots \varphi_n(r_n)$$

(here the dependence of the eigenfunction on the electronic spin-coordinates is eliminated and its dependence on the nuclear coordinates is parametrical only). Now

$$\left[\sum_i h(i) \right] \varphi_1(\underline{r}_1) \varphi_2(\underline{r}_2) \cdots \varphi_n(\underline{r}_n) = [h(\underline{r}_1) \varphi_1(\underline{r}_1)] \varphi_2(\underline{r}_2) \cdots \varphi_n(\underline{r}_n) + \varphi_1(\underline{r}_1) [h(\underline{r}_2) \varphi_2(\underline{r}_2)] \varphi_3(\underline{r}_3) \cdots \varphi_n(\underline{r}_n) + \varphi_1(\underline{r}_1) \varphi_2(\underline{r}_2) \cdots [h(\underline{r}_n) \varphi_n(\underline{r}_n)] .$$

Since each one-particle function is an eigenfunction to $h(\underline{r}_i)$ with energy ε_i we can write

$$h_0 \Phi_0 = E_0 \Phi_0 \quad , \quad \text{with} \quad E_0 = \sum_i \varepsilon_i \quad .$$

We can open an even better way approximating the two-particle term of Eq. (2) as an effective one-particle operator $v(\underline{r}_i)$ (here we considered the average repulsion of all other electrons in the system to electron i):

$$\hat{H}^{el} = \sum_i^n [h(\underline{r}_i) + v(\underline{r}_i)] + \sum_{i < j} \sum r_{ij}^{-1} - \sum_i^n v(\underline{r}_i) =$$

$$\sum_i^n \hat{F}(\underline{r}_i) + V = H_0 + V \quad .$$

V is small (it is surely smaller than the two-particle term), so we can assume that the replacement of H^{el} by

H_0 is a good approximation. But H_0 is also separable, thus

$$\hat{F}(\underline{r}_i)u_i(\underline{r}_i) = \varepsilon_i u_i(\underline{r}_i)$$

(here F is the Fock-operator, an effective one-particle Hamiltonian).

First to specify the procedure we must take into consideration the electron spin. Each one-particle function will be either $u_i(\underline{r}_i)\alpha(\zeta_i)$ or $u_i(\underline{r}_i)\beta(\zeta_i)$, or, using a simpler notation, $u_i(\underline{r}_i)\alpha(\zeta_i) = \varphi_i(\underline{d}_i)$. It is valid that

$$\hat{F}(\underline{d}_i)\varphi_i(\underline{d}_i) = \varepsilon_i \varphi_i(\underline{d}_i) \quad .$$

Second, the eigenfunctions of H^{el} must satisfy the antisymmetry postulate of the quantum mechanics (the electrons are fermions). This circumstance will cause the simplest form of the trial function (Ansatz):

$$\Phi_0 = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(\underline{d}_1) & \varphi_2(\underline{d}_1) & \dots & \varphi_n(\underline{d}_1) \\ \varphi_1(\underline{d}_2) & \varphi_2(\underline{d}_2) & \dots & \varphi_n(\underline{d}_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(\underline{d}_n) & \varphi_2(\underline{d}_n) & \dots & \varphi_n(\underline{d}_n) \end{vmatrix} = \hat{\mathcal{A}}(\varphi_1(\underline{d}_1) \cdots \varphi_n(\underline{d}_n))$$

where $\hat{\mathcal{A}}$ is the antisymmetrizer operator ($\hat{\mathcal{A}} = (1/\sqrt{n!})\sum_P (-1)^P \hat{P}$ where P is the permutation operator and $(-1)^P$ is the parity factor). It is easy to

prove that H_0 and \hat{A} are commutable operators, thus we get the same one-particle equations (using a new notation):

$$\hat{F}(1)\varphi_i(1) = \varepsilon_i\varphi_i(1) \quad ,$$

moreover,

$$H_0\hat{A}(\varphi_1(1)\cdots\varphi_n(n)) = E_0\hat{A}(\varphi_1(1)\cdots\varphi_n(n))$$

$$H_0\Phi_0 = E_0\Phi_0 \quad .$$

(Other eigenstates of H_0 are Φ_i^a in which the occupied orbital $\varphi_i(i)$ is replaced by the virtual orbital $\varphi_a(i)$ being as well an eigenfunction of $F(i)$:

$$\begin{aligned} H_0\Phi_i^a &= H_0\hat{A}(\varphi_1(1)\cdots\varphi_a(i)\cdots\varphi_n(n)) \\ &= E_i^a\hat{A}(\varphi_1(1)\cdots\varphi_a(i)\cdots\varphi_n(n)) \\ &= E_i^a\Phi_i^a \quad , \end{aligned}$$

where the eigenvalue is as follows:

$$E_i^a = \left(\sum_{k(\neq i)} \varepsilon_k \right) + \varepsilon_a = E_0 + \varepsilon_a - \varepsilon_i \quad .$$

Up to here the outline of the general independent particle model was given. It becomes the Hartree-Fock (or, SCF) approximation if Φ_0 is the “best” single-

determinant approximation to Ψ_0 energetically. This means that we use the variational principle $E_{SCF} = \langle \Phi_0 | \hat{H} \Phi_0 \rangle \geq E_{exact0}$. Via the deduction of the energy variation we obtain:

$$\hat{F}(1) = h(1) + v(1) = h(1) + \sum_j^n \int \varphi_j^*(2) r_{12}^{-1} (1 - \hat{P}_{12}) \varphi_j(2) d\tau_2$$

It is evident that the Fock operator is dependent on the form of all the spin orbitals φ_j . That is why the Fock operator is a one-electron operator only formally, so we need a self-consistent solution of its pseudo-eigenvalue equation. Moreover,

$$\begin{aligned} E_{SCF} &= \langle \Phi_0 | \hat{H} \Phi_0 \rangle = \sum_i \langle \varphi_i | h(1) \varphi_i \rangle + \frac{1}{2} \sum_i \sum_j \langle \varphi_i \varphi_j | \varphi_i \varphi_j \rangle \\ &= \sum_i \langle i | h | i \rangle + \sum_{i < j} \sum \langle ij | ij \rangle = \sum_i \varepsilon_i - \sum_{i < j} \sum \langle ij | ij \rangle \\ &= E_0 + \langle \Phi_0 | V \Phi_0 \rangle . \end{aligned}$$

Obviously, E_{SCF} is not a simple sum of the ε_i orbital energies. Above the double bar means

$$\langle ij | ij \rangle = \langle ij | ij \rangle - \langle ij | ji \rangle , \text{ where}$$

$$\langle ij | ij \rangle = \int \varphi_i^*(1) \varphi_j^*(2) r_{12}^{-1} \varphi_i(1) \varphi_j(2) d\tau_1 d\tau_2 = \langle ii | jj \rangle .$$

The aforementioned SCF equations are called as the Unrestricted Hartree-Fock (UHF) equations (it is not assumed that the spatial orbitals are doubly occupied). This means that $\varphi_i = u_i\alpha$ and $\varphi_{i+1} = u_i'\beta$ where $u_i \neq u_i'$. In closed shell systems (at usual molecular geometries) we get the best energy while having $u_i = u_i'$ which means the Restricted Hartree-Fock (RHF) equations. The Restricted Open-Shell Hartree-Fock (ROHF) equations have maximum double occupancy as possible.

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ERRATUM

To the Born-Oppenheimer approximation

To
 Prof. Dr. Werner Kutzelnigg,
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Budapest, March 5, 2010.

Dear Prof. Dr. Kutzelnigg,

I read your papers ((a) W. Kutzelnigg, in *Molecular Quantum Mechanics: Analytic Gradients and Beyond*, eds. A.G. Császár, G. Fogarasi, H.F. Schaefer III, P.G. Szalay, ELTE Institute of Chemistry, Budapest, Hungary, 2007, pp. 184-192; (b) W. Kutzelnigg, *Mol. Phys.* 105, 2627 (2007)) with much interest. However, in the detailed version of the study (*Mol. Phys.* 105, 2627 (2007)) I found a mistake when I prepared the text for my classes. In page 2633, Eq. (31) is as follows (hereafter the atomic units are used as in your paper):

$$[[T_e, i\mathbf{K}r_{rel}], i\mathbf{K}r_{rel}] = -\mathbf{K}^2$$

(the letters K and r are bold-faced letters in the paper). I think the expression is positive, since

$$[[T_e, i\mathbf{K}r_{rel}], i\mathbf{K}r_{rel}] = -i^2 \left[\left[\frac{1}{2} \frac{\partial^2}{\partial r_e^2}, \mathbf{K}r_{rel} \right], \mathbf{K}r_{rel} \right] = \mathbf{K}^2 .$$

If we would like to avoid the use of the Baker-Campbell-Hausdorff formula, this can be seen also using the scalar product

$$\left\langle \exp\left(i \frac{\mathbf{K}r}{M+1}\right) \middle| T_e \exp\left(i \frac{\mathbf{K}r}{M+1}\right) \right\rangle = \frac{1}{2} \left\langle \nabla_e \exp\left(i \frac{\mathbf{K}r}{M+1}\right) \middle| \nabla_e \exp\left(i \frac{\mathbf{K}r}{M+1}\right) \right\rangle > 0 ,$$

obviously. The positive value (instead of the negative one) changes somewhat the final Eq. (32) as well:

$$E_{com} = \frac{K^2}{2M} + \frac{K^2}{2M(M+1)^2} = \frac{K^2}{2(M+1)} + O(M^{-2}) ,$$

that is, we got the kinetic energy of the COM motion to $O(M^1)$ only, and not to $O(M^2)$ as in the paper.

Another reason of this letter is the following. My former teacher (and later my fatherly friend) was Prof. Dr. Ede Kapuy. He was an excellent scientist and an extremely learned person. Also, he was altruistic on a bit exaggerated level. Earlier, in the seventies happened that Ede worked out a theorem which was a new, original work that time in the quantum chemistry. He said to his colleagues the theorem at his university, he discussed it with his colleagues, made repeated deductions, but he never published it. If I know properly a few years later he opened a journal in the library and noticed that a (young American ?) scientist found the same result and published it. Under these circumstances almost all the people would have been either disappointed or sad but not Ede: he run along the department and said happily to everybody: see this, I was right. Let the Lord give him peace in the eternal home (he has died 10 years ago)! Unfortunately, we do not remember which was the theorem mentioned above. I think that you, Prof. Kutzelnigg, knew him, and may be you have heard this old story as a funny and very characteristic story for Ede. Could you let me know which theorem was the aforementioned one? It would be very interesting for us, also for Prof. Dr. Péter Pulay who forgot the name of the theorem as well.

Thank you very much for your kind efforts in advance.

Your faithfully,

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