

# Quantum Chemistry

Jan G. Korvink and Evgenii Rudnyi  
IMTEK  
Albert Ludwig University  
Freiburg, Germany



ALBERT-LUDWIGS-  
UNIVERSITÄT FREIBURG

## Learning Goals

- ◆ Where the potential function comes from: Adiabatic approximation
- ◆ Molecular orbitals and the Hartree-Fock equation
- ◆ Designing molecular orbitals - LCAO
- ◆ Electron correlation
- ◆ State of the art

## References

- ◆ Leach, A.R., *Molecular modelling: principles and applications*.

## On-line resources

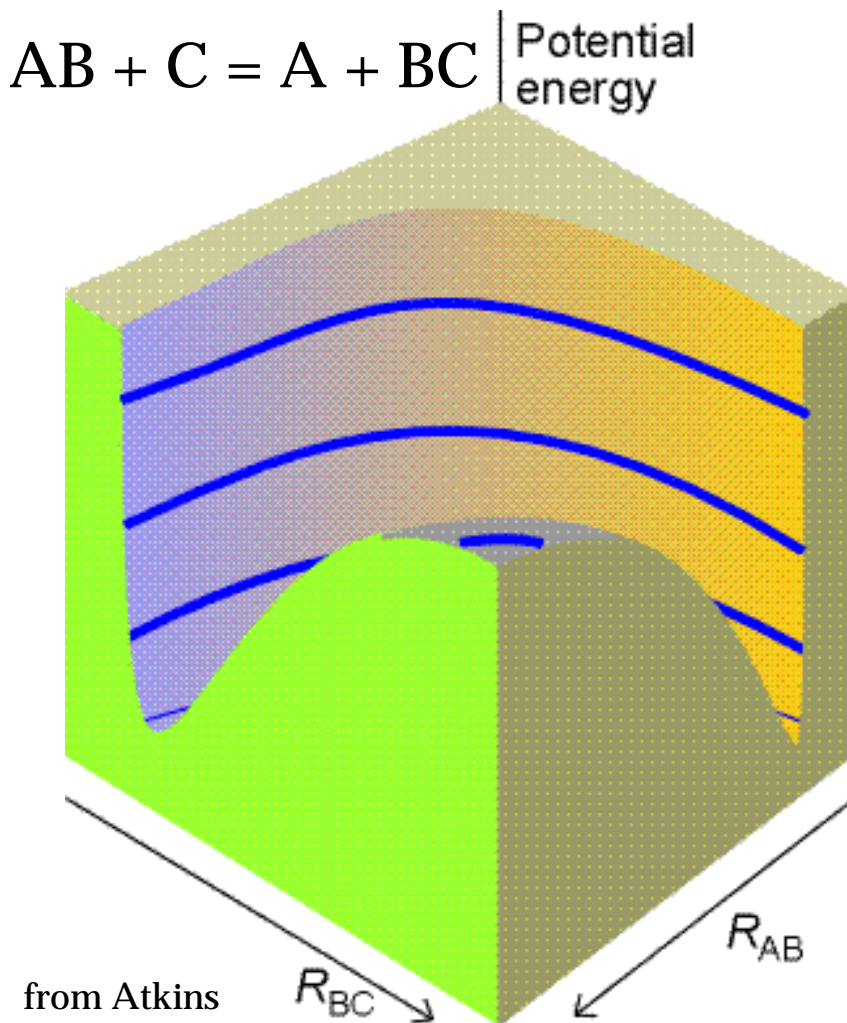
- ◆ **On-line book:** Jack Simons, *Quantum Mechanics in Chemistry*, [simons.hec.utah.edu/TheoryPage/index.html](http://simons.hec.utah.edu/TheoryPage/index.html)

## Tutorials

- ◆ Neal McDonald et al, *An Introduction to Quantum Mechanics* [www.chemistry.ohio-state.edu/betha/qm/](http://www.chemistry.ohio-state.edu/betha/qm/)
- ◆ C. David Sherrill, *Lectures in Quantum Chemistry*, [vergil.chemistry.gatech.edu/notes/index.html](http://vergil.chemistry.gatech.edu/notes/index.html)



- ◆ Time-dependent and stationary Schrödinger equation
- ◆ Molecular Hamiltonian
- ◆ Separating electronic and nuclear wavefunctions:  
Born-Oppenheimer approximation
- ◆ Example: Chemical Reaction Path



## Schrödinger Equation

- ◆ Time-dependent  $H\Psi = i\hbar\frac{d\Psi}{dt}$ 
  - ◆  $H$  - Hamiltonian operator,  
 $\hbar = h/2\pi$
  - ◆  $\Psi(\mathbf{r}, t)$  - wave function,  
 $|\Psi(\mathbf{r}, t)|^2$  - probability density
- ◆ Separation for time and space variation
  - ◆ Potential energy is independent of time.
  - ◆  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\theta(t)$
- ◆ Stationary equation  
 $H\psi = E\psi$
- ◆ Number of discrete states  
 $\{\psi_i, E_i\}$
- ◆ Ab initio - From the first principles - Based on a limited number of experimental results.
- ◆ All interatomic forces can be explained from the Coulomb law.
- ◆ We do not have potential surface yet.
- ◆ Energy does not depend on atom positions.

## Molecule Hamiltonian

Nuclei ( $R$ ) and electrons ( $r$ ):  
 $\Psi(R, r)$

$$H = T_{\text{nuc}} + T_{\text{elec}} + U_{\text{nuc-nuc}} + U_{\text{elec-elec}} + U_{\text{elec-nuc}}$$


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$$H = \sum_n \frac{-\hbar^2}{2m_n} \nabla_n^2 + \sum_i \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_{\text{Pairs of Nuclei}} \frac{Z_n Z_m e^2}{r_{nm}} + \sum_{\text{Pairs of Elec.}} \frac{e^2}{r_{ij}} - \sum_{n,i} \frac{Z_n e^2}{r_{in}}$$

del operator for nuclei  $\nabla_n^2$   
 del operator for electron  $\nabla_i^2$   
 mass of  $n^{\text{th}}$  nucleus  $m_n$   
 mass of electron  $m_e$   
 at. # of  $n^{\text{th}}$  nucleus  $Z_n$   
 distance between nuclei  $n$  and  $m$   $r_{nm}$   
 distance between electrons  $i$  &  $j$   $r_{ij}$   
 distance between electron  $i$  & nucleus  $n$   $r_{in}$

www-wilson.  
 ucsd.  
 edu/  
 educa-  
 tion/



## Born-Oppenheimer Approximation

- ◆ Proton is 1836 times heavier than electron.

- ◆ Factorize for nuclei part

$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi(\mathbf{R})\psi(\mathbf{r};\mathbf{R}).$$

- ◆ Schrödinger equation for electrons

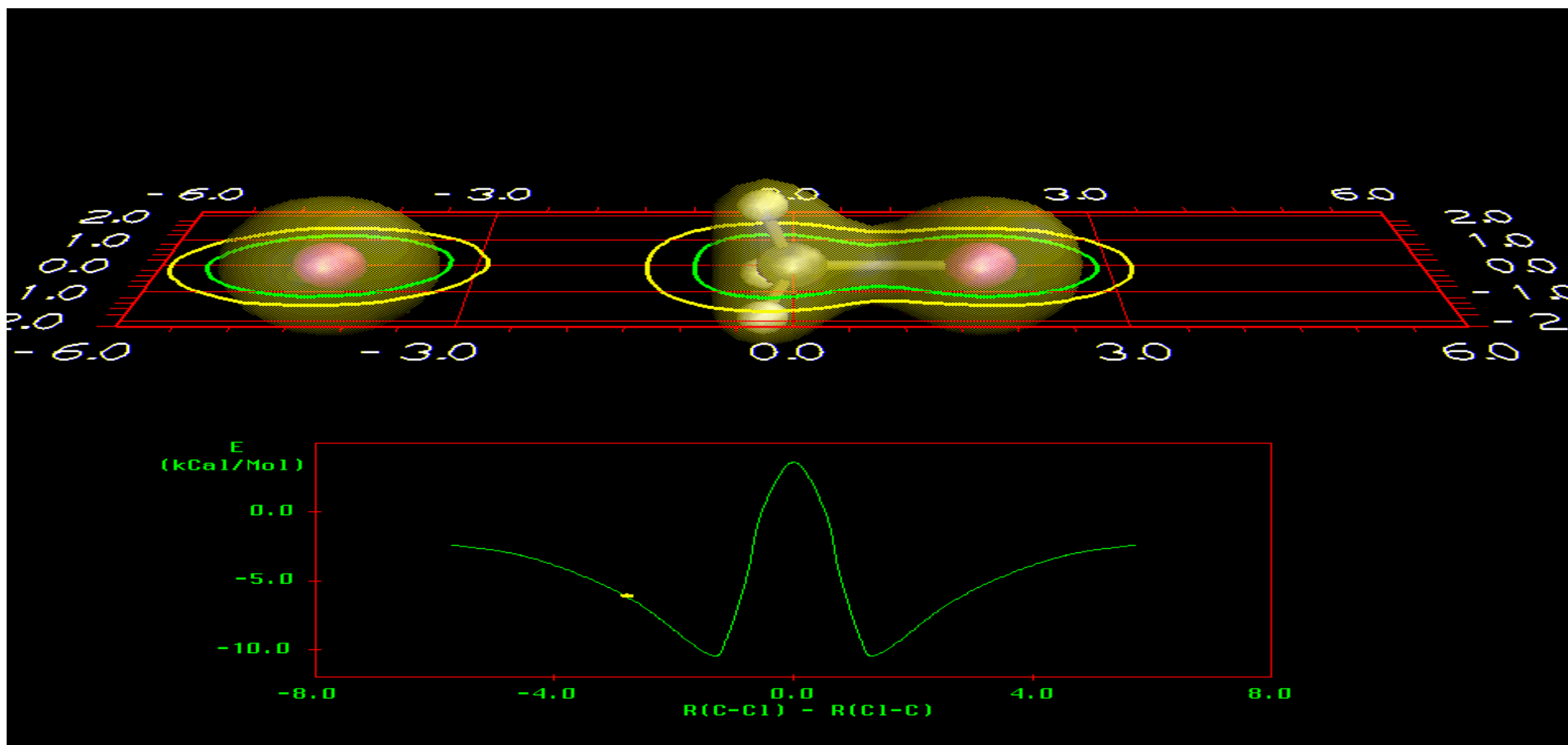
$$H_{el}\psi(\mathbf{r};\mathbf{R}) = E_{el}(\mathbf{R})\psi(\mathbf{r};\mathbf{R}).$$

- ◆ This is parametric equation over nuclei coordinates.
- ◆ Quantum chemistry solves the electronic equation.

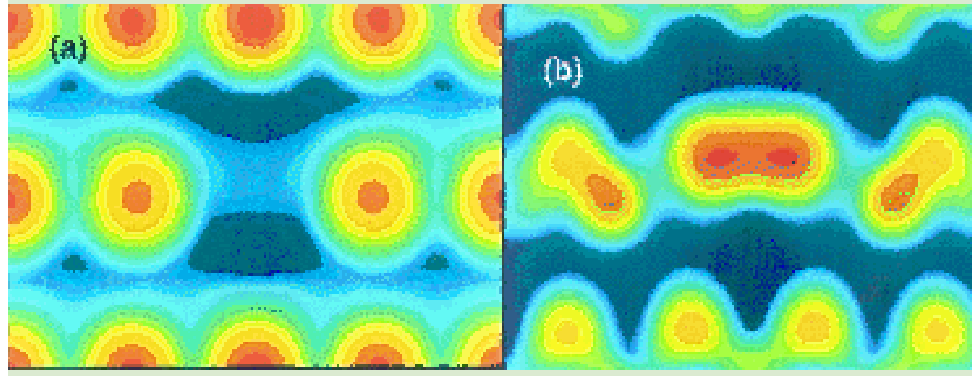
- ◆  $E_{el}(\mathbf{R})$  is the nuclei potential energy.
- ◆ Schrödinger equation for nuclei  $H_{nuc}(E_{el})\Psi(\mathbf{R}) = E_{nuc}\Psi(\mathbf{R})$ .
- ◆ Non-adiabatic coupling is neglected (typically this is a small term).
- ◆ Usually people solve the electronic equation only.
  - ◆ Nuclei movements is treated by the classical mechanics.

## Example - Chemical Reaction Path

- ◆ Demonstration from [scsg9.unige.ch/fln/eng/toc.html](http://scsg9.unige.ch/fln/eng/toc.html)



- ◆ Atomic units
- ◆ Variation Principle
- ◆ Molecular orbitals
- ◆ Hartree-Fock Self Consistent Field (HF SCF)
- ◆ Language For Chemists



Simulated STM images for an arsenic vacancy on the (110) surface of GaAs.

[www-users.cs.umn.edu/~saad/projects/DMR/page4\\_rt.htm](http://www-users.cs.umn.edu/~saad/projects/DMR/page4_rt.htm)



## Atomic Units

◆ 1 unit of charge is the electron charge  $|e| = 1.60219 \times 10^{-19}$  C.

◆ 1 unit of mass is the electron mass  $m_e = 9.10593 \times 10^{-31}$  kg.

◆ 1 unit of length (1 Bohr) is

$$a_o = h^2 / 4\pi^2 m_e e^2 = 5.29177 \times 10^{-11} \text{ m}$$

◆  $h = 2\pi, \hbar = 1$

◆ 1 unit of energy (1 Hartree) is

$$E_a = e^2 / 4\pi\epsilon_o a_o = 4.35981 \times 10^{-18} \text{ J}$$

◆ 1 Hartree = 2.63 MJ/mol = 27.3 eV

- ◆ Zero energy is nuclei and electrons separated at infinity.
- ◆ Dissociation energy is a small difference of huge numbers.
  - ◆ Example (GAMESS + simple HF):
  - ◆ Cl<sub>2</sub>:  $E_{el} = -918.9371$
  - ◆ Cl:  $E_{el} = -459.4734$
  - ◆ 2Cl:  $E_{el} = -918.9468$
  - ◆ Cl<sub>2</sub> = 2Cl  $\Delta E = 0.0097 = 25$  kJ/mol.
  - ◆ Experimental: 240 kJ/mol.



## Variation Principle

### Electronic Hamiltonian

$$\diamond -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_I^N \frac{Z_I}{r_{Ii}} + \frac{1}{2} \sum_{i,j}^n \frac{1}{r_{ij}}$$

without nucleus-nucleus repulsion

### Variational theorem

- ◆ Choose a trial wavefunction,  $\Psi_{trial}$  with unknown parameters
- ◆ Minimize Rayleigh ratio

$$\varepsilon = \frac{\int \Psi_{trial}^* H \Psi_{trial} dx}{\int \Psi_{trial}^* \Psi_{trial} dx} \text{ over}$$

unknowns

- ◆ For any  $\Psi_{trial}$   $\varepsilon \geq E_0$



## Molecular Orbitals

$$\Psi(1, 2, \dots, N) = \chi_1(1)\chi_2(2)\dots\chi_N(N)$$

- ◆ Does not work - breaks indistinguishability criterion

## Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{bmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_N(2) \\ \dots & \dots & \dots & \dots \\ \chi_1(N) & \chi_2(N) & \dots & \chi_N(N) \end{bmatrix}$$

- ◆ Satisfies antisymmetry principle

## Electron has spin: +1/2 or -1/2

- ◆ Closed shells: Restricted Hartree-Fock (RHF) - Each space MO holds two electrons.
- ◆ Open shells (odd number of electrons)
  - ◆ Restricted Open Shell HF (ROHF) - Just few space MOs holds one electron.
  - ◆ Unrestricted HF (UHF) - Each space MO holds one electron.



## Hartree-Fock Self Consistent Field

- ◆ Substitute the Slater determinant into Rayleigh ratio. The minimum is given by

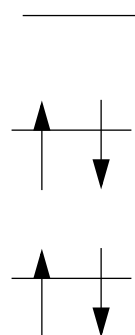
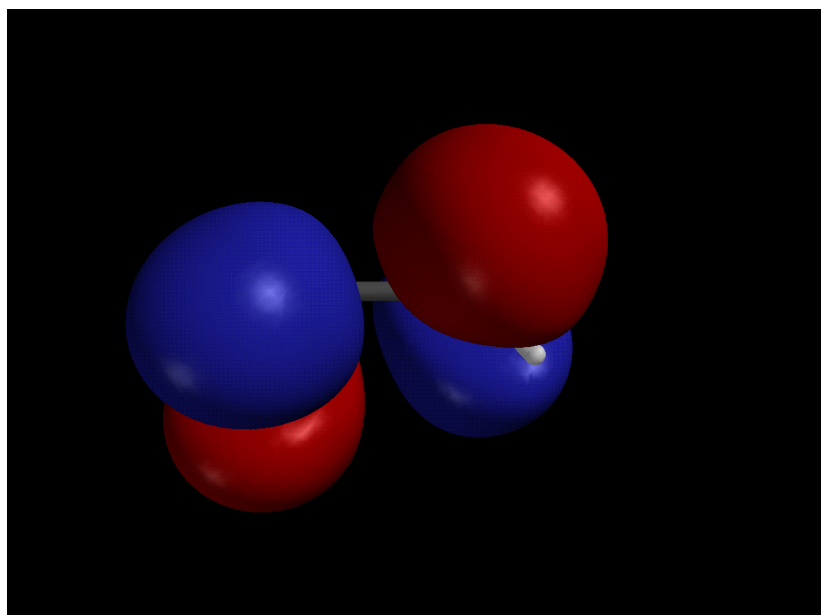
## Hartree-Fock Equations

- ◆  $f_i \chi_i = \varepsilon_i \chi_i$ 
  - ◆  $f_i$  - Fock operator (depends on all the molecular orbitals)
  - ◆  $\varepsilon_i$  - Molecular orbital energy

- ◆ A system of coupled non-linear integral-differential equations
- ◆ Iterative solution: start with some  $\chi_i$ , compute  $f_i$ , solve for new  $\chi_i$ , and so on.
- ◆ Introduces a language for chemists.
  - ◆ But this is just an approximation.

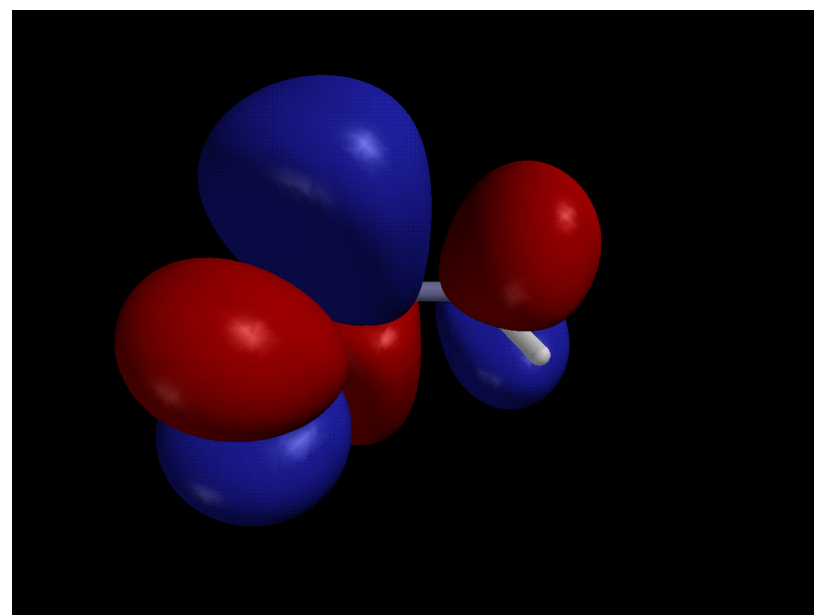
## Language For Chemists

- ◆ HOMO - Highest Occupied

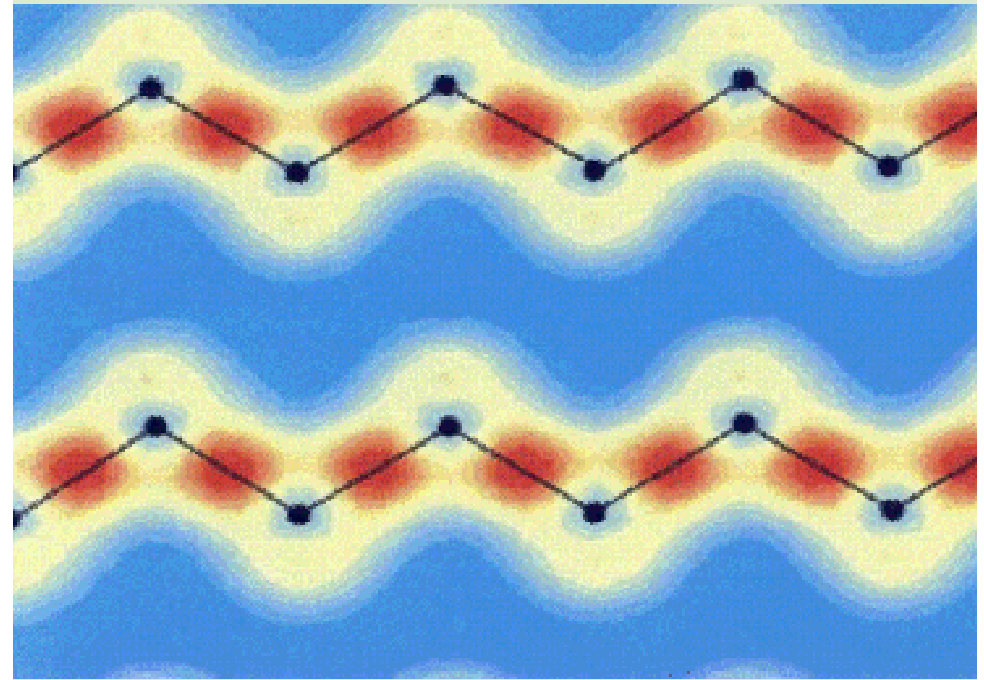


- ◆ HOMO and LUMO of formamide from Leach's book

- ◆ Molecular Orbital
- ◆ LUMO - Lowest Unoccupied Molecular Orbital



- ◆ Linear Combination of Atomic Orbitals (LCAO)
- ◆ Visualizing 3d atomic orbital
- ◆ Roothan-Hall Equations
- ◆ Basis set
- ◆ Semi-empirical methods



Electronic charge density of silicon in the diamond structure.

[www-users.cs.umn.edu/~saad/projects/DMR/page4\\_rt.htm](http://www-users.cs.umn.edu/~saad/projects/DMR/page4_rt.htm)

## Molecular Orbitals

### Closed shells

- ◆ For each pair of two spin orbitals  $\chi_i = \phi_j\alpha$  and  $\chi_{i+1} = \phi_j\beta$ .
- ◆ For open shells there are more problems, see textbooks.

### Linear Combination of Atomic Orbitals

- ◆  $\phi_j = \sum_m^K c_{mj}\phi_m$  unknowns are

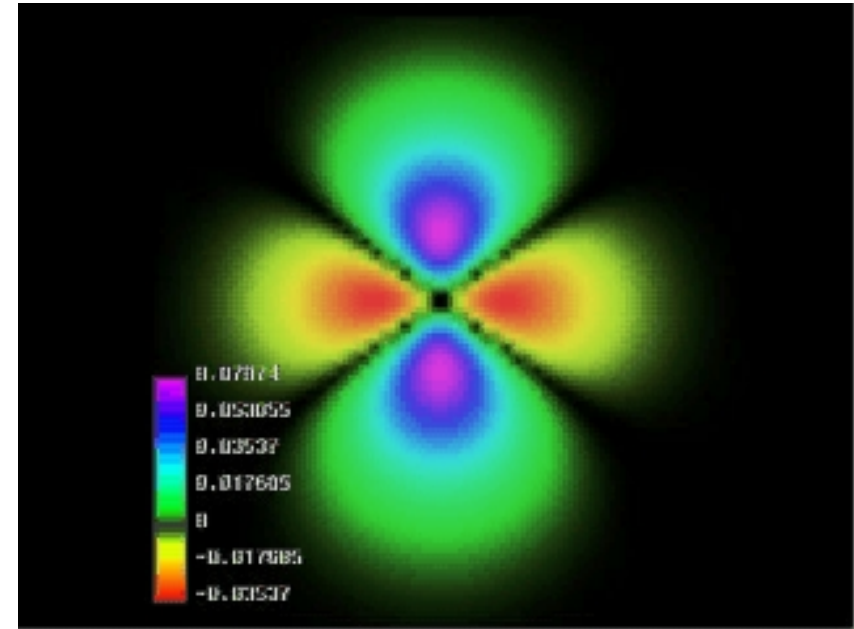
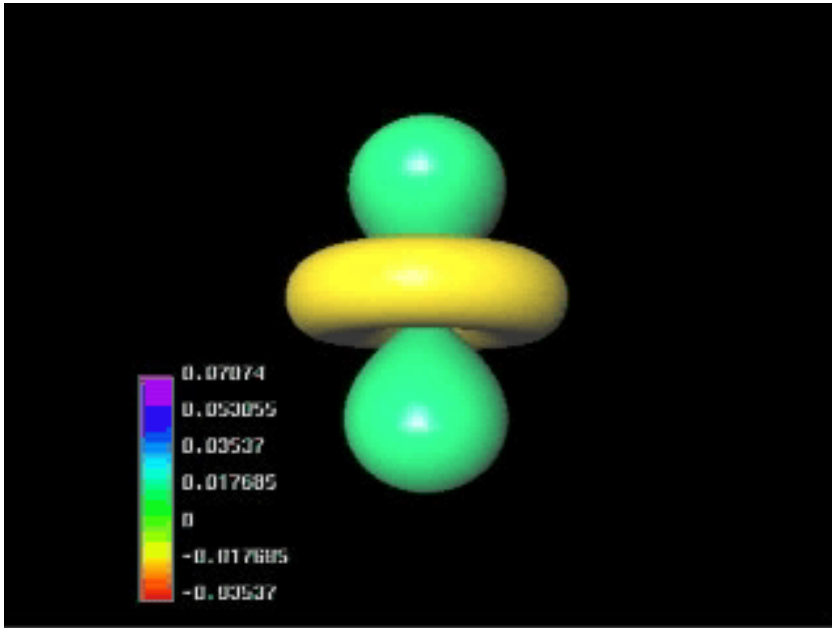
$c_{mj}$ .

### Atomic orbitals

- ◆ Solving Schrödinger equation for the atom (1s, 2s, 2p, 3s, 3p, 3d, ...).
- ◆ K atomic basis functions produces 2K spin orbitals.
- ◆ N electrons, then there are 2K-N unoccupied orbitals.
- ◆ Typically for large molecular systems  $K \gg N$ .



## Visualizing 3d Orbital ♦ Isosurfaces and slices



(<http://www-wilson.ucsd.edu/education/>)



# Roothan-Hall Equations

- ◆ Substitute LCAO for molecular orbitals in the Hartree-Fock equations - for the closed shell the solution is given by a matrix equation
- ◆  $FC = SCE$ 
  - ◆ F - Fock matrix: obtained from the different integrals over basis functions, number of integrals  $(K^4 + 2K^3 + 3K^2 + 2K) / 8$
- ◆ S - overlap matrix: to make molecular orbitals orthogonal
- ◆ C - matrix with unknowns in LCAO
- ◆ E - diagonal matrix with molecular orbital energies
- ◆ F and S depends on C. The solution is again iterative: start with some C, compute F and S, then compute new C and E, and so on.
- ◆ Fortunately non-linearity is rather weak.

## Basis Set

- ◆ Slater Type Orbital (STO)

- ◆ Radial part

$$\psi(r) = Ar^{n-1}e^{-ar} \text{ (already some approximation)}$$

- ◆ Still, computing integrals takes too much time

- ◆ Gaussian Type Orbitals (GTO)

- ◆  $\psi(r) = Ax^jy^jz^k e^{-ar^2}$  (very fast to compute integrals)

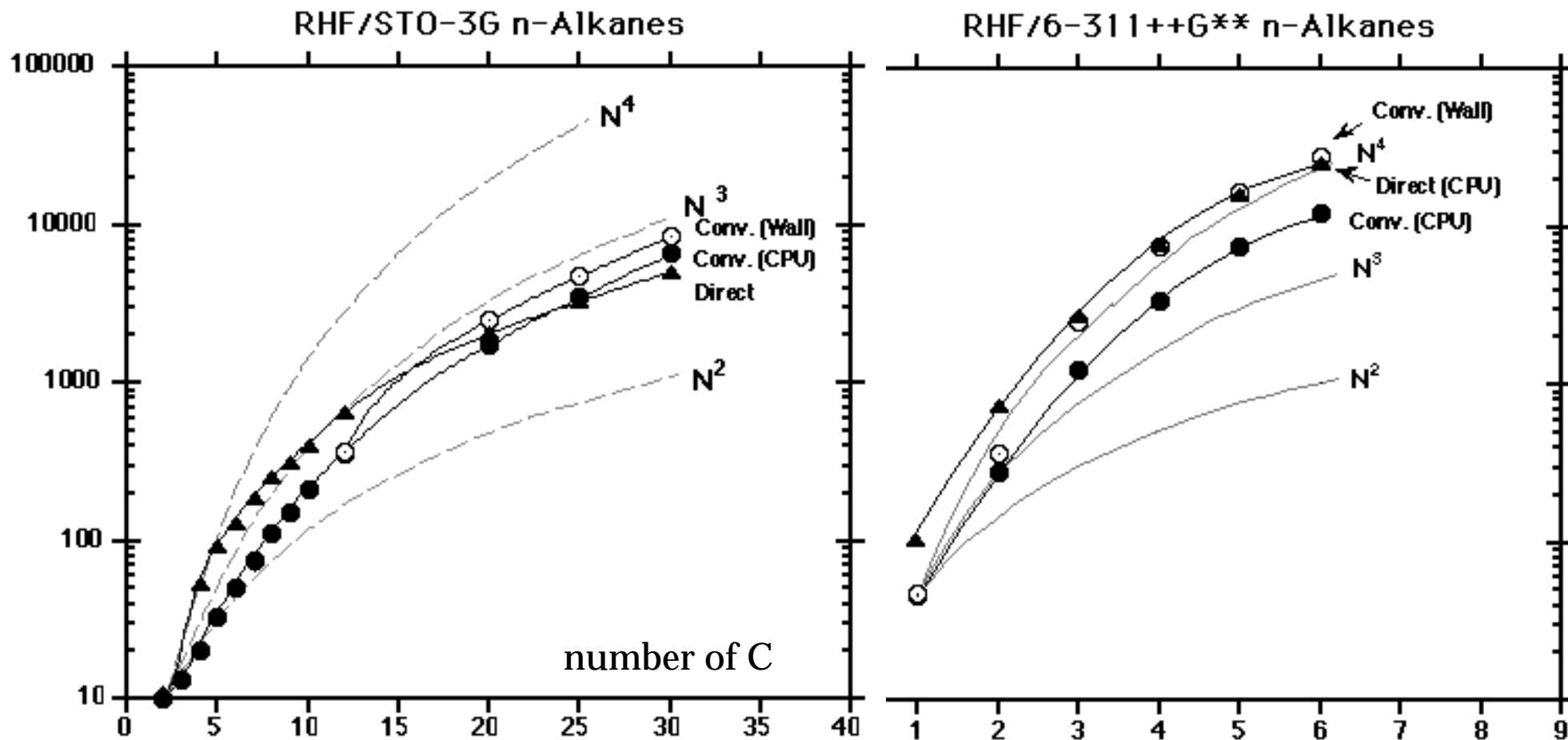
- ◆ Equilibrium bond length of H<sub>2</sub>

STO-3G	4-31G	6-31G*	6-31G**	Expr.
1.346	1.380	1.380	1.385	1.401

(atomic units)

## Comparison of Basis Sets

◆ 1997, [www.emsl.pnl.gov:2080/docs/tms/abinitio/cover.html](http://www.emsl.pnl.gov:2080/docs/tms/abinitio/cover.html)



## Semi-Empirical Methods

### Simplifying computing

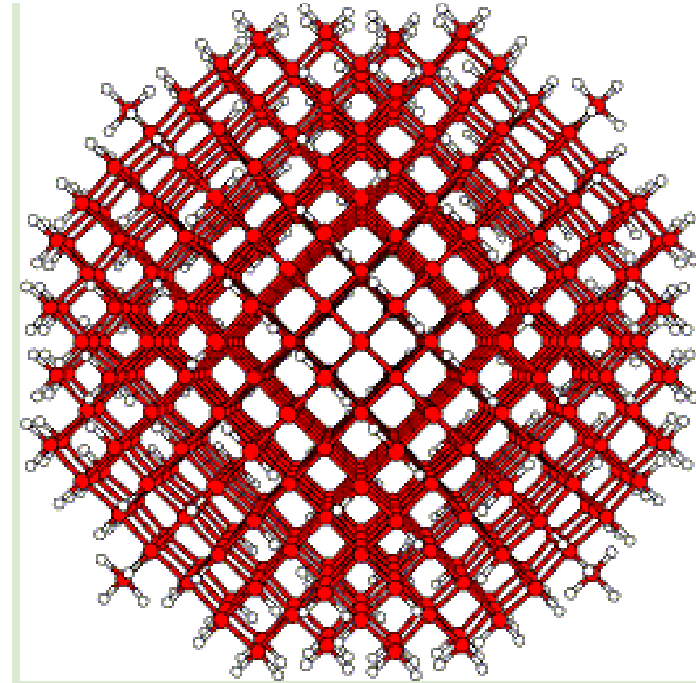
- ◆ Leave Roothan-Hall equations
- ◆ Take into account valence electrons only, ignore core electrons
- ◆ Neglect some integrals
- ◆ Parametrize the other integrals from experimental values

### Neglect of differential overlap

- ◆ CNDO - complete neglect, INDO - intermediate neglect, MINDO - modified intermediate neglect, MNDO - modified neglect
- ◆ AM1 - Austin model 1
- ◆ PM3 - Parametrization 3

**The zero energy is different.**

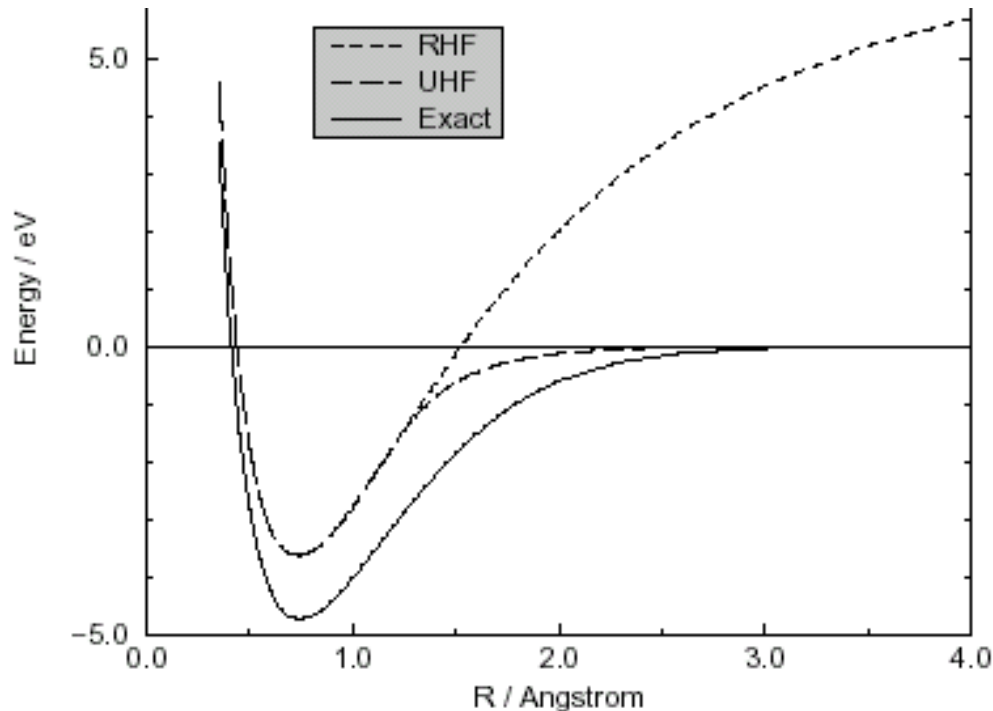
- ◆ Electron correlation
- ◆ Configuration Interaction
- ◆ Density Functional Theorem
- ◆ Summary
- ◆ Relativistic corrections



Quantum Dot calculation (more than 1000 atoms)

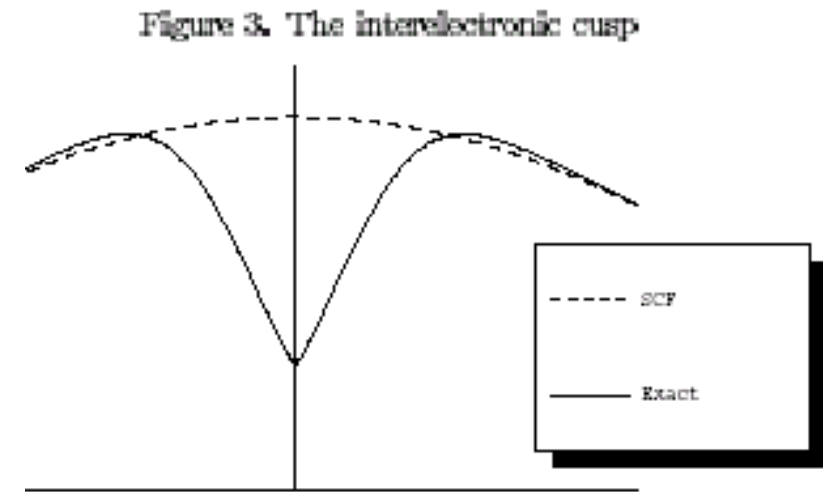
[http://www-users.cs.umn.edu/~saad/projects/DMR/page2\\_rt.htm](http://www-users.cs.umn.edu/~saad/projects/DMR/page2_rt.htm)

- ◆ Hartree-Fock is a mean field theory



- ◆ Overestimate ionic states at long distances and the probability to

- ◆ As a result, for two electrons  $P(r_1, r_2) = P(r_1)P(r_2)$



Peter Knowles

<http://www.fz-juelich.de/nic-series/Volume3/Volume3.html>

find two electrons close together

## Configuration Interaction (CI)

- ◆ K basis functions produces 2K spin orbitals.
- ◆ N electrons, then there are 2K-N unoccupied orbitals.
- ◆ CI:  
$$\Psi = c_0 \Psi_0 + c_1 \Psi_1 + c_2 \Psi_2 + \dots$$
- ◆ Number of configurations is  $(2K!) / [N!(2K-N)!]$ .
- ◆ CIS, CID, CISD, however they are not size consistent.

## Moller and Plesset perturbation theory

- ◆  $H = H_0 + \lambda V$
- ◆ MP2, MP3, MP4, for example, MP2/6-31G\*

## Density Functional Theory

- ◆ Hohenberg & Kohn, 1964.
- ◆ Ground-state energy is uniquely defined by the electron density

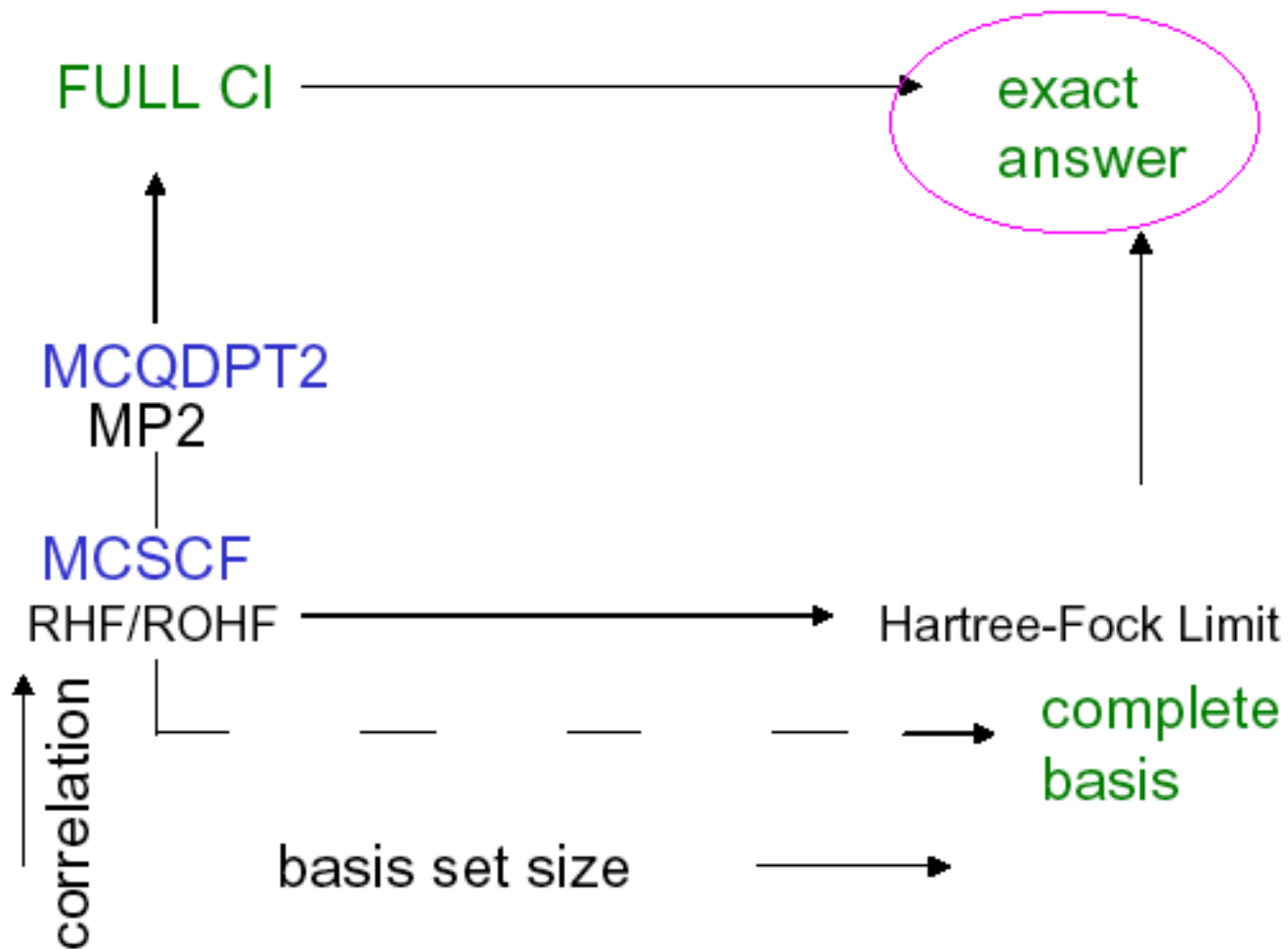
$$E[\rho(r)] = \int V_{ext}(r)\rho(r)dr + F[\rho(r)].$$

- ◆  $\rho$  is the electron density.
- ◆  $V$  is the external potential (Coulomb interaction with nuclei).

- ◆  $F$  is some functional (unfortunately not known).
- ◆ Kohn & Sham (1965) suggested some empiric approximation for  $F$ .
- ◆ LDA - local density approximation.
- ◆ BLYP - Becke-Lee-Yang-Par gradient-corrected functional.
- ◆ Roughly speaking: to take into account the electron correlation for for a single HF computation.



## Summary

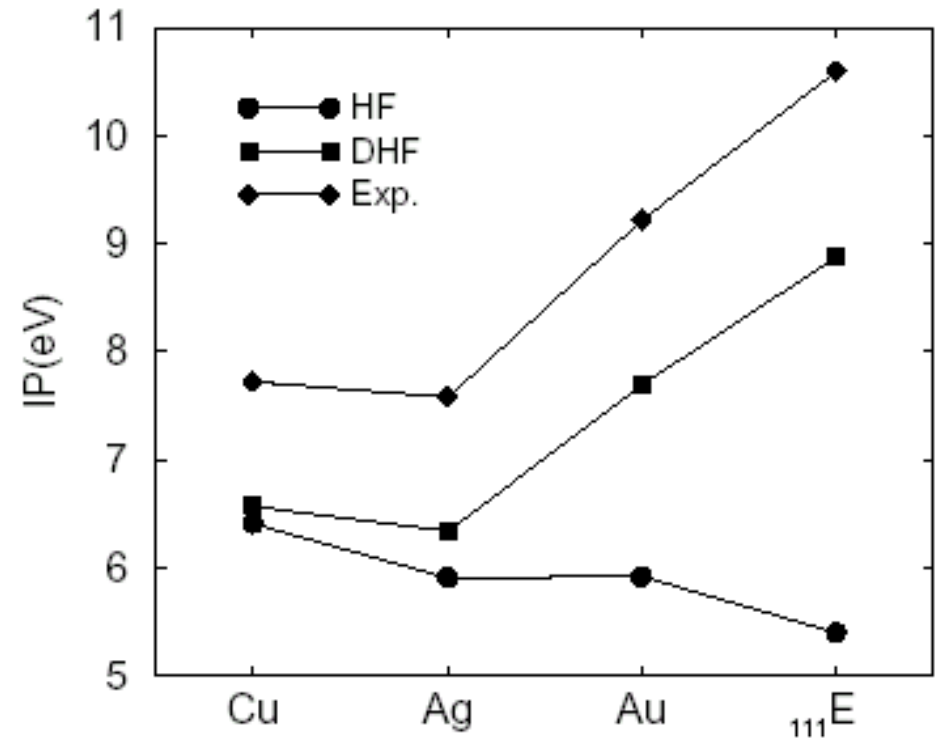
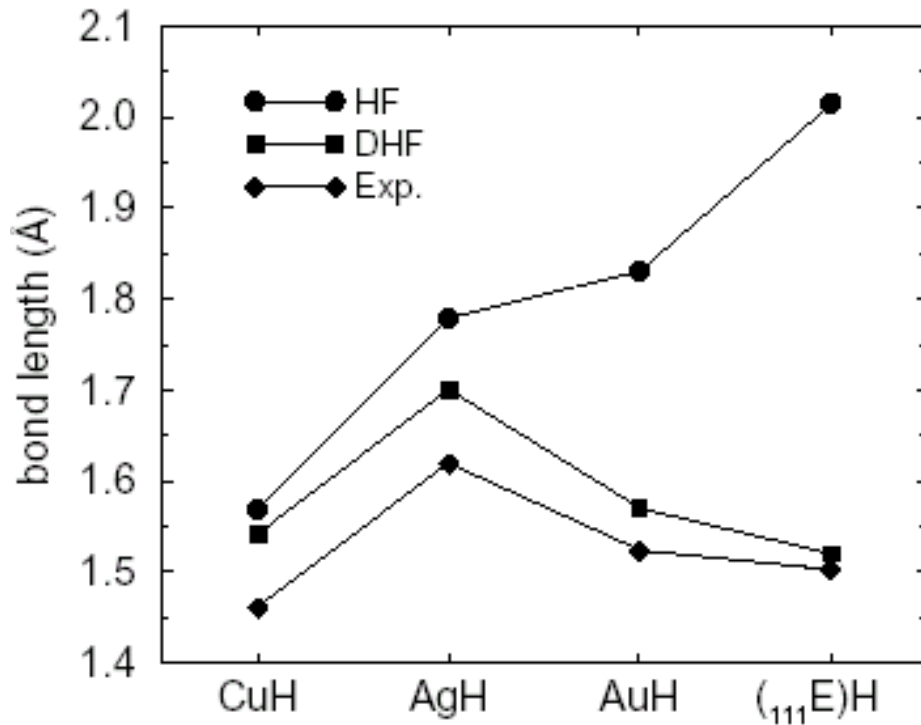


Mark S. Gordon  
Tutorial for GAMESS

[www.msg.ameslab.gov/Group/GroupTutor.html](http://www.msg.ameslab.gov/Group/GroupTutor.html)

- ◆ In principle, it is necessary to solve not Schrödinger but rather

Dirac equation - a set of four coupled differential equations



M. Dolg, [www.fz-juelich.de/nic-series/Volume3/Volume3.html](http://www.fz-juelich.de/nic-series/Volume3/Volume3.html)

- ◆ A - Ethylene, 16 electrons, Basis Set = 6-311++G\*\* (74 functions)
- ◆ B - Ethylene, 16 electrons, 6-311++G(3df,3pd) (150 functions)
- ◆ C -18-crown-6, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>, 144 electrons - 606 functions

	A	B	C
RHF	8	45	90197
RHF-gradient	14	133	
RHF-gaussian	56	789	
MP2	11	481	
MP4	83		
CISD	46		

## Commercial

- ◆ GAUSSIAN:  
[www.gaussian.com/](http://www.gaussian.com/)
- ◆ CACHE:  
[www.cachesoftware.com](http://www.cachesoftware.com)
- ◆ Materials Studio:  
[www.accelrys.com](http://www.accelrys.com)

## Free

- ◆ General Atomic and Molecular Electronic Structure System (GAMESS)  
[www.msg.ameslab.gov/GAMESS/](http://www.msg.ameslab.gov/GAMESS/)

## Lists

- ◆ [www.ch.ic.ac.uk/local/organic/mod/software.html](http://www.ch.ic.ac.uk/local/organic/mod/software.html)

- ◆ Where the potential function comes from: Adiabatic approximation
- ◆ Atomic and molecular orbitals
- ◆ Multi-electron systems: Hartree-Fock equation
- ◆ Electron correlation: Configuration Interaction
- ◆ Current state of the art