Physical Chemistry II: Quantum Chemistry
Lecture 20: Introduction to Computational Quantum Chemistry

Yuan-Chung Cheng

yuanchung@ntu.edu.tw

5/14/2019

Tutorial Information

- https://ceiba.ntu.edu.tw/1063NCHUCompChem01

- Books:
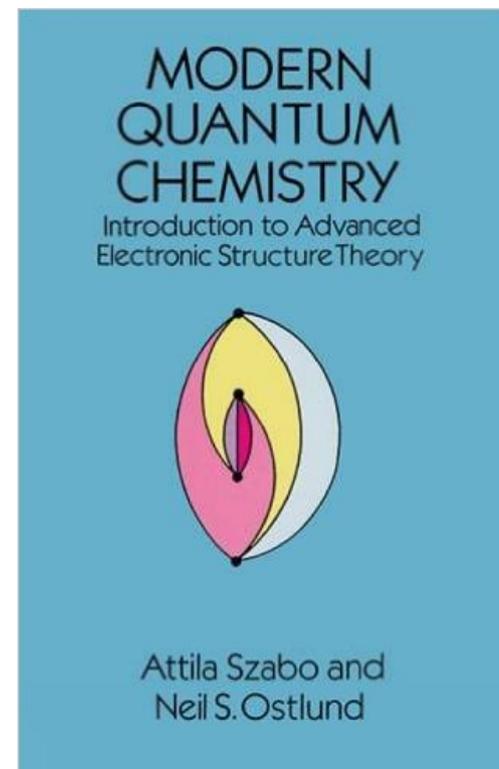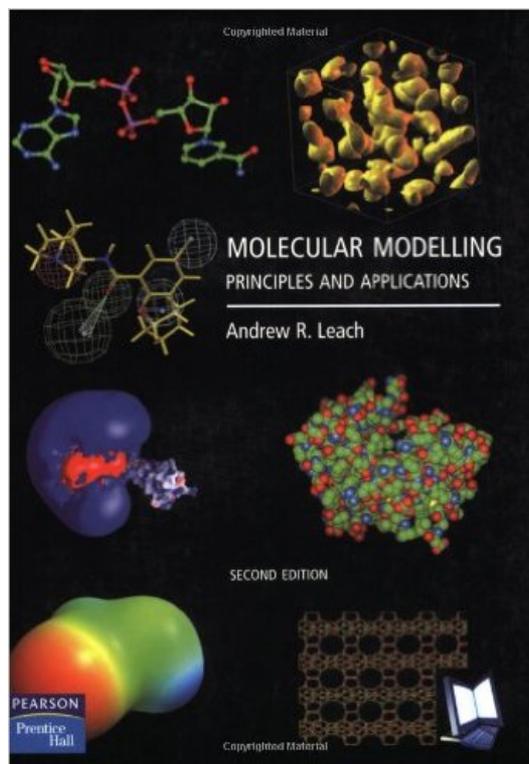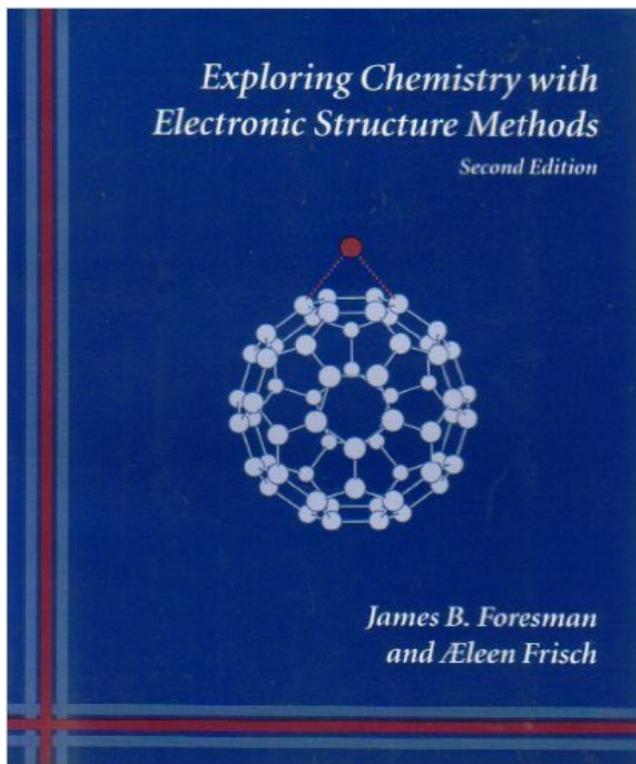
Computational Chemistry Overview

Quantum Chemistry
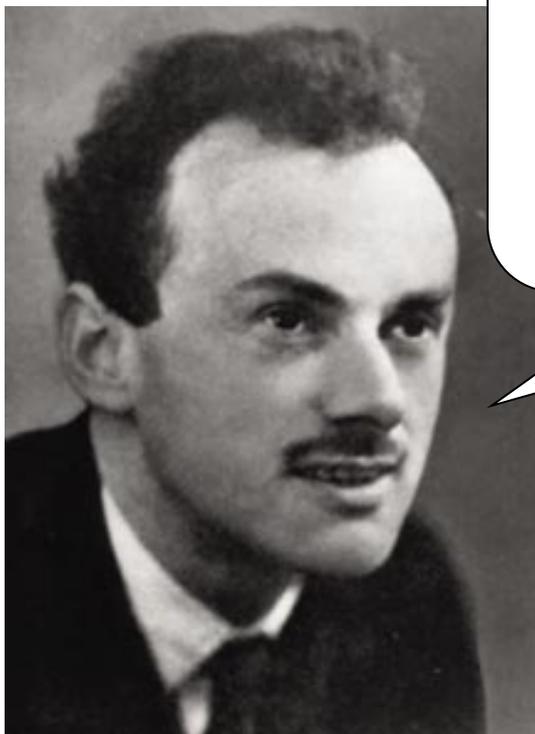
The general theory of quantum mechanics is now complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and **the whole of chemistry** are thus completely known – Paul Dirac, 1929.

Paul Dirac

Right: QM is the foundation
       of Chemistry
Wrong: Not so fast - complexities
          necessitate approximations

Nowadays we have powerful computers!!

The Nobel Prize in Chemistry 1998
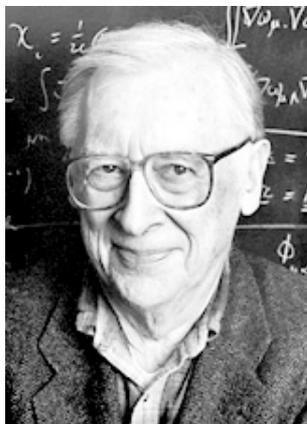
John A. Pople

"for his development of computational methods in quantum chemistry"

Walter Kohn

"for his development of the density-functional theory"

The Nobel Prize in Chemistry 2013

2013 Nobel Chemistry Prize jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.
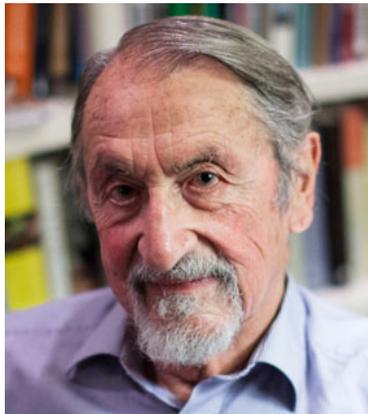
Martin Karplus   Michael Levitt   Arieh Warshel

Computational Chemistry Methods

- Molecular mechanics
- Semiempirical molecular orbital methods
- *Ab initio* molecular orbital methods
- Density functional method
- Quantum Monte Carlo method
- …

  Yields Energy, Structure, and Properties

Molecular Mechanics

- Simplest type of calculation
  - Used when systems are very large and approaches that are more accurate become to costly (in time and memory)

- Does not use any quantum mechanics instead uses parameters derived from experimental or *ab initio* data
 - Uses information like bond stretching, bond bending, torsions, electrostatic interactions, van der Waals forces and hydrogen bonding to predict the energetics of a system
  - The energy associated with a certain type of bond is applied throughout the molecule. This leads to a great simplification of the equation

- It should be clarified that the energies obtained from molecular mechanics do not have any physical meaning, but instead describe the difference between varying conformations (type of isomer). Molecular mechanics can supply results in heat of formation if the zero of energy is taken into account.

Courtesy of Shalayna Lair, University of Texas at El Paso

Semiempirical

- Semiempirical methods use experimental data to parameterize equations

- Like the *ab initio* methods, a Hamiltonian and wave function are used
  - □ much of the equation is approximated or eliminated

- Less accurate than *ab initio* methods but also much faster

- The equations are parameterized to reproduce specific results, usually the geometry and heat of formation, but these methods can be used to find other data.

Courtesy of Shalayna Lair, University of Texas at El Paso

Ab Initio Methods

- *"Ab initio"* – Latin, means *"from the beginning" or "from first principles."*

- No experimental input is used and calculations are based on fundamental laws of physics.

- Various levels of *ab initio* calculations (jargons):
  - ☐ Hartree-Fock Self-Consistent Field (HF-SCF)
    - simplest *ab initio* MO calculation
    - electron correlation is not taken into consideration.
  - ☐ Configuration Interaction (CI)
  - ☐ Coupled-Cluster (CC)
  - ☐ The Møller-Plesset Perturbation Theory (MP)
  - ☐ Density Functional Theory (DFT)

Include electron correlation

Main Group Thermochemistry

Transition Metal Chemistry

ΔE

D_e → 2

Noncovalent Interactions

Quantum Chemistry

Long-range Charge Transfer

Thermochemical Kinetics

Spectroscopy

σ (Mb)

600
500
400
300
200
100
0

Energy (eV)

Courtesy of Donald G Truhlar
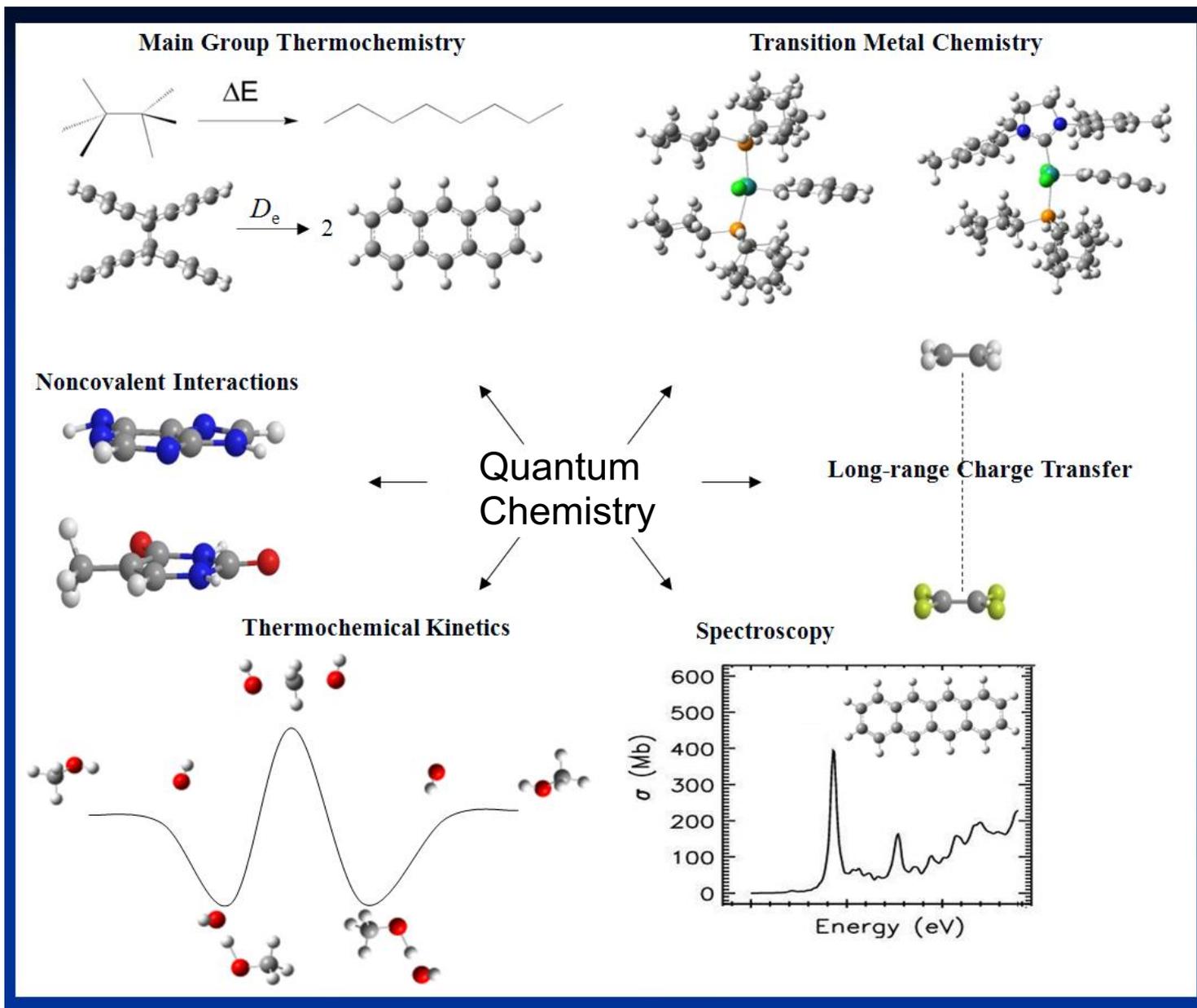
Hartree-Fock SCF Review

Slides from Hai Lin

Schrödinger Equation

$$H\Psi = E\Psi$$

$$\mathbf{H} = \mathbf{T}_n + \mathbf{T}_e + \mathbf{V}_{nn} + \mathbf{V}_{ee} + \mathbf{V}_{ne}$$

$$\mathbf{T}_n = -\sum_a^{N_n} \frac{1}{2M_a} \nabla_a^2 \qquad \text{Kinetic energy of nuclei}$$

$$\mathbf{T}_e = -\sum_i^{N_e} \frac{1}{2m_e} \nabla_i^2 \qquad \text{Kinetic energy of electrons}$$

$$\mathbf{V}_{nn} = \sum_a^{N_n} \sum_{b>a}^{N_n} \frac{Z_a Z_b}{r_{ab}} \qquad \text{Coulombic energy between nuclei}$$

$$\mathbf{V}_{ee} = \sum_i^{N_e} \sum_{i>j}^{N_e} \frac{1}{r_{ij}} \qquad \text{Coulombic energy between electrons}$$

$$\mathbf{V}_{ne} = \sum_a^{N_n} \sum_i^{N_e} \frac{Z_a}{r_{ai}} \qquad \text{Coulombic energy between nuclei and electrons}$$

The "electronic structure problem"
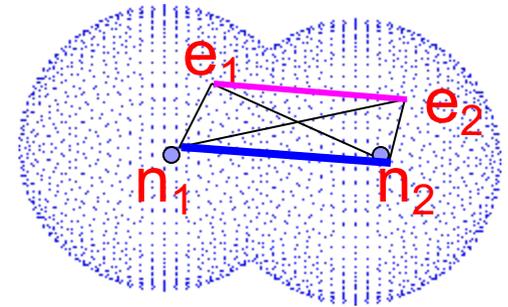
Approximations

To solve the Schrödinger equation approximately, assumptions are made to simplify the equation:

- **Born-Oppenheimer approximation** allows separate treatment of nuclei and electrons. ($m_a \gg m_e$)

- **Hartree-Fock independent electron approximation** allows each electron to be considered as being affected by the sum (field) of all other electrons.

- **LCAO Approximation** represents molecular orbitals as linear combinations of atomic orbitals (basis functions).

Born-Oppenheimer Approximation

- Nuclei are much heavier than electrons ($m_a / m_e > 1836$) and move much slower.
- Effectively, electrons adjust themselves instantaneously to nuclear configurations.
- Electron and nuclear motions are uncoupled, thus the energies of the two are separable.

1. For a given nuclear configuration, one calculates electronic energy.
2. As nuclei move continuously, the points of electronic energy joint to form a potential energy surface on which nuclei move.
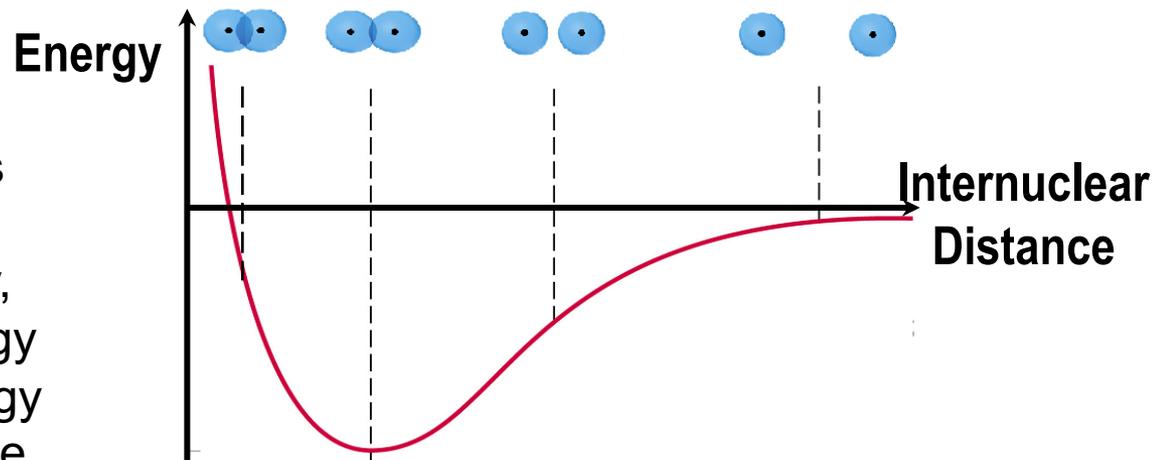
Elec. Schrodinger equation: $H(R)\Psi(R) = E(R)\Psi(R)$

Basic Quantum Mechanics

Schrodinger equation: $H\Psi = E\Psi$

Variational principle: $E = \left\langle \Psi \left| \hat{\mathbf{H}} \right| \Psi \right\rangle \geq E_{\text{exact}}$

$$\Psi = \Psi(x_1, x_2 ..., x_N)$$

The N-electron wave function is a function with 3N dimensions, this is too complicated to even "think about" practically for systems with > 3 electrons → must simplify the functional form of the wave function.

Many-electron Wave function

Hartree product: All electrons are independent, each in its own orbital.

$$\psi^{HP}(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) = f_1(\mathbf{x}_1)f_2(\mathbf{x}_2)\cdots f_N(\mathbf{x}_N)$$

Pauli principle: Two electrons can not have all quantum number equal.

This requires that the total (many-electron) wave function is anti-symmetric whenever one exchanges two electrons' coordinates.

$$\psi(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) = -\psi(\mathbf{x}_2,\mathbf{x}_1,...,\mathbf{x}_N)$$

Slater determinant satisfies the Pauli exclusion principle.

$$\psi(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} f_1(\mathbf{x}_1) & f_2(\mathbf{x}_1) & \cdots & f_N(\mathbf{x}_1) \\ f_1(\mathbf{x}_2) & f_2(\mathbf{x}_2) & \cdots & f_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ f_1(\mathbf{x}_N) & f_2(\mathbf{x}_N) & \cdots & f_N(\mathbf{x}_N) \end{vmatrix}$$

e_1 e_2 e_i $\cdots$ e_N
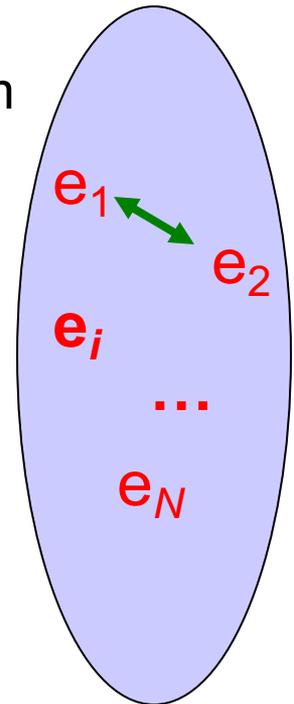
Many-electron Wave function (2)

Example: A two-electron system.

Hartree product: Both electrons are independent.

$$\psi^{HP}(\mathbf{x}_1, \mathbf{x}_2) = f_1(\mathbf{x}_1) f_2(\mathbf{x}_2)$$

Slater determinant satisfies the Pauli principle.

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} f_1(\mathbf{x}_1) & f_2(\mathbf{x}_1) \\ f_1(\mathbf{x}_2) & f_2(\mathbf{x}_2) \end{vmatrix}$$

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = (1/2)^{1/2} \left[f_1(\mathbf{x}_1) f_2(\mathbf{x}_2) - f_2(\mathbf{x}_1) f_1(\mathbf{x}_2) \right]$$

$$\psi(\mathbf{x}_2, \mathbf{x}_1) = (1/2)^{1/2} \left[f_1(\mathbf{x}_2) f_2(\mathbf{x}_1) - f_2(\mathbf{x}_2) f_1(\mathbf{x}_1) \right] = -\psi(\mathbf{x}_1, \mathbf{x}_2)$$

The total (many-electron) wavefuntion is anti-symmetric when one exchanges two electrons' coordinates x_1 and x_2.
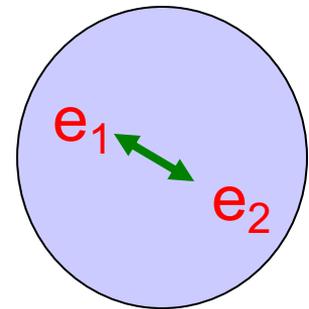
Hartree-Fock Approximation

- Assume the wave function is a single Slater determinant.
- Each electron "feels" all other electrons as a whole (field of charge), .i.e., an electron moves in a mean-field generated by all other electrons. → variational ground state composed of "optimal" single electron wavefunctions (orbitals)
- A Fock operator $\mathbf{F}$ is introduced for a given electron in the i-th orbital:

$$\mathbf{F}_i \, \phi_i = \varepsilon_i \, \phi_i$$

$\mathbf{F}_i =$ kinetic energy term of the given electron $+$ potential energy term due to fixed nuclei

$+$ averaged potential energy term due to the other electrons
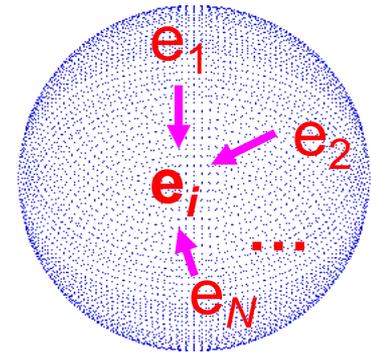
ϕ_i is the i-th molecular orbital, and ε_i is the corresponding orbital energy.

Note: The total energy is NOT the sum of orbital energies. If you sum them up, you count the electron-electron interactions twice.

The Fock Operator

$$\mathbf{F}_i = \mathbf{h}_i + \sum_{j}^{N} (\mathbf{J}_j - \mathbf{K}_j)$$

Core-Hamiltonian operator

Coulomb operator

Exchange operator

Kinetic energy term and nuclear attraction for the given electron

Coulombic energy term for the given electron due to another electron

Exchange energy due to another electron (A pure quantum mechanical term due to the Pauli principle, no classical interpretation)

Self-consistency

- Each electron "feels" all the other electrons as a whole (field of charge), .i.e., an electron moves in a mean-field generated by all the other electrons.

- The Fock equation for an electron in the i-th orbital contains information of all the other electrons (in an averaged fashion), i.e., the Fock equations for all electrons are coupled with each other.

- All equations must be solved together (iteratively until self-consistency is obtained).
  — Self-consistent field (SCF) method.
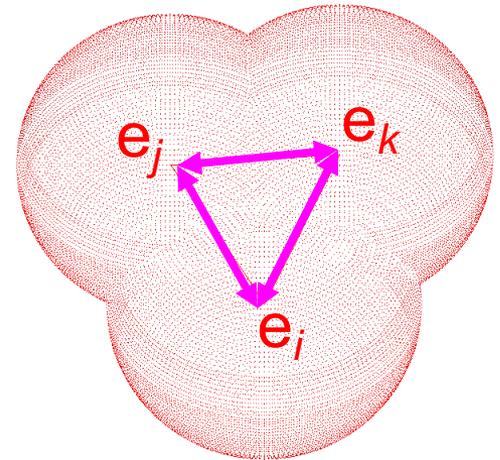
Molecular Orbital & Slater Determinant
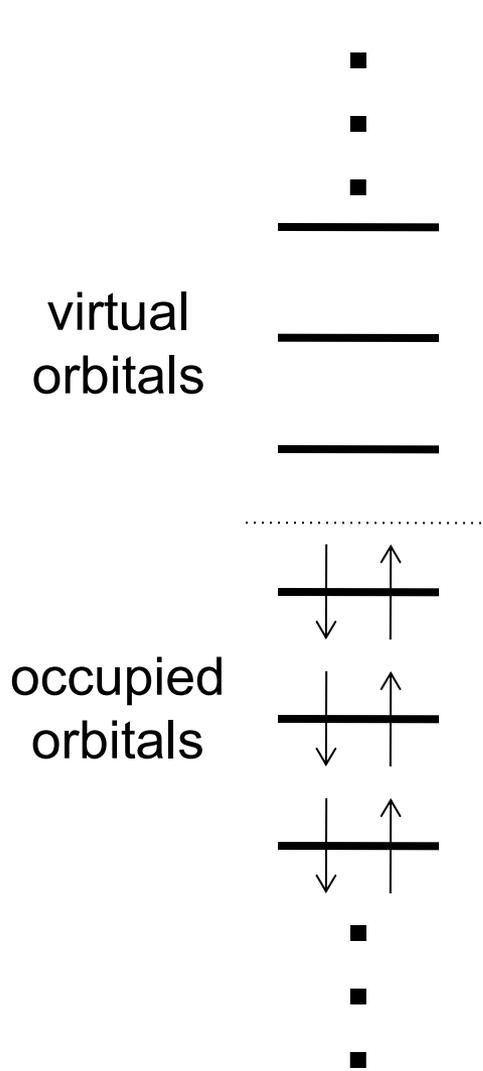
Single-electron wavefunction (orbital!!):

$$\chi_i(x_1): \text{ spin orbital}$$

$$x_1: \text{ electron variable}$$

N-electron wavefunction: Slater determinants

virtual
orbitals

occupied
orbitals

$$\Psi(x_1,...,x_N) = (N!)^{1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_N) \\ \vdots & \vdots & & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix}$$

Given a basis, Hartree-Fock theory provides a variational groundstate & molecular orbitals within the single determinant approximation ➔ mean-field, no electron correlations

Molecular Orbital & Slater Determinant
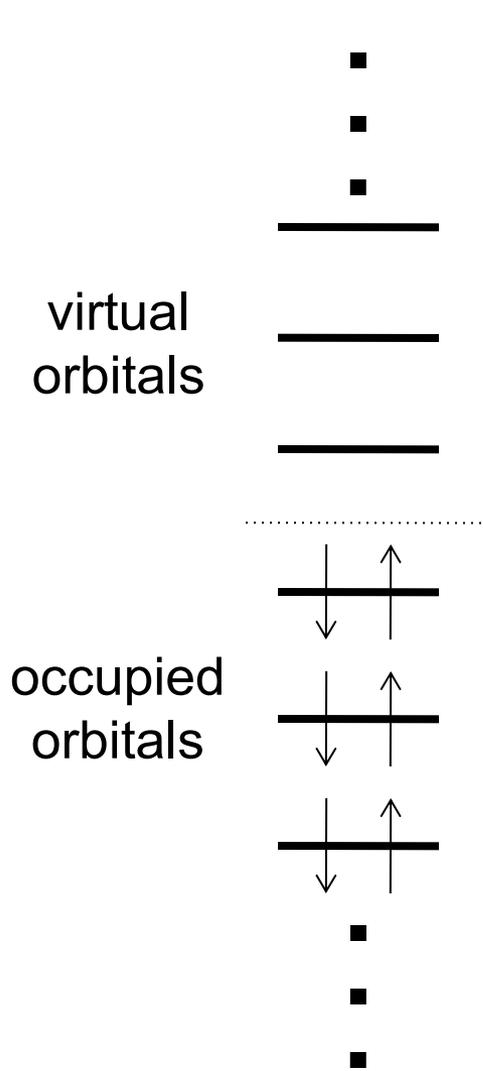
Single-electron wavefunction (orbital!!):

$$\chi_i(\mathrm{x}_1): \text{ spin orbital}$$

$$\mathrm{x}_1: \text{ electron variable}$$

N-electron wavefunction: Slater determinants

virtual orbitals

occupied orbitals

$$\Psi(\mathrm{x}_1,...,\mathrm{x}_N) = (N!)^{1/2} \begin{vmatrix} \chi_i(\mathrm{x}_1) & \chi_j(\mathrm{x}_1) & \cdots & \chi_k(\mathrm{x}_1) \\ \chi_i(\mathrm{x}_2) & \chi_j(\mathrm{x}_2) & \cdots & \chi_k(\mathrm{x}_N) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathrm{x}_N) & \chi_j(\mathrm{x}_N) & \cdots & \chi_k(\mathrm{x}_N) \end{vmatrix}$$

Electron configuration: a many-electron wave function constructed from a single slater determinant

Molecular Orbital & Slater Determinant
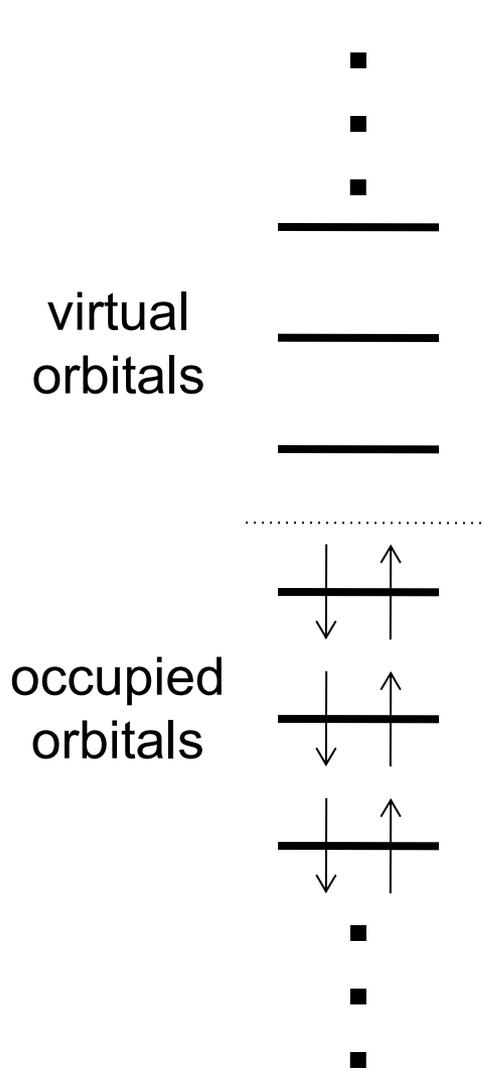
Single-electron wavefunction (orbital!!):

$$\chi_i(x_1): \text{ spin orbital}$$

$$x_1: \text{ electron variable}$$

N-electron wavefunction: Slater determinants

virtual orbitals

occupied orbitals

$$\Psi(x_1,...,x_N) = (N!)^{1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_N) \\ \vdots & \vdots & & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix}$$

$\chi_i(x_1)$ written as linear combination of atomic orbitals → basis functions!

LCAO ➜ Basis Functions

- ## Use a form that describes hydrogenic orbitals well

  - ☐ Slater functions (STO): physical, but difficult to calculate two-electron integrals

  - ☐ Gaussians (GTO): analytical two-electron integrals, but wrong behavior at nucleus and decays too fast with r

$$\phi_{1s}(\vec{r};\zeta_1) = \sqrt{\frac{\zeta_1^3}{\pi}} \exp(-\zeta_1 \vec{r})$$

$$g_s(\vec{r};\alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha \vec{r}^2)$$

Slater function   Gaussian

Distance/a_0
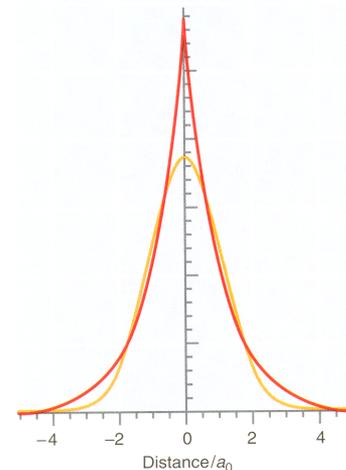
Gaussian Basis Functions

- GTOs have many advantages, most importantly, product of two Gaussians remains a Gaussian – analytical integrals

$$e^{-a_m r_m^2} e^{-a_n r_n^2} = e^{-\frac{a_m a_n}{a_m + a_n} r_{mn}^2} e^{-a r_c^2}$$
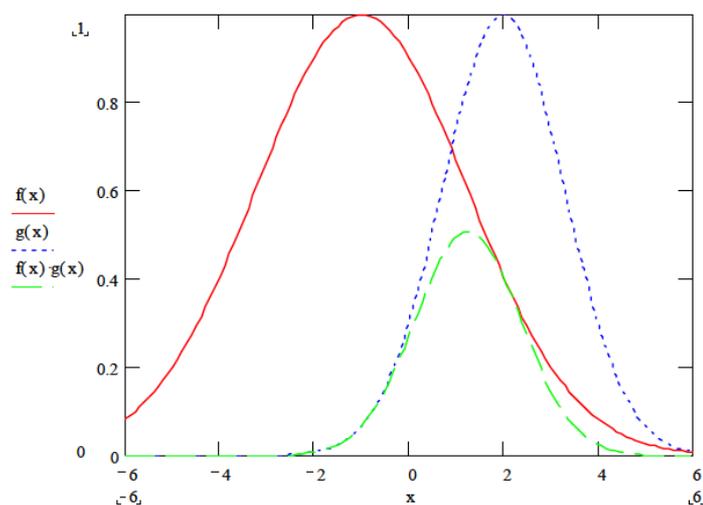
Basis Functions

Hydroden-like atomic orbitals
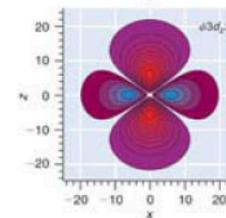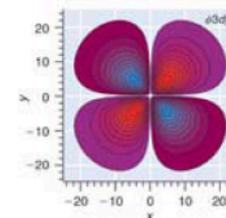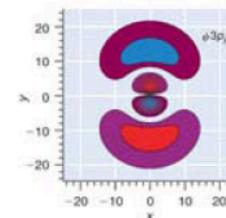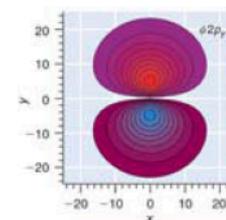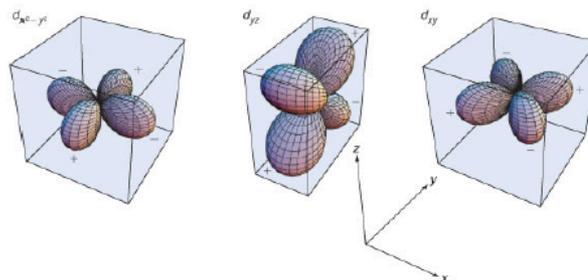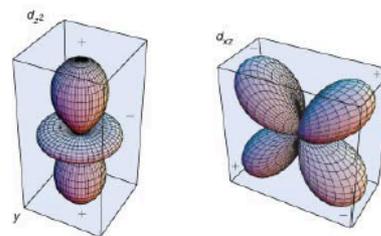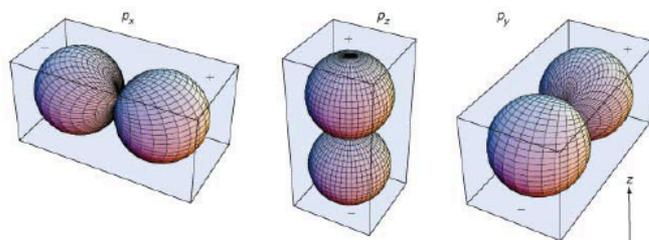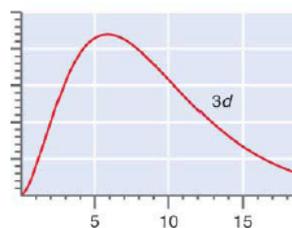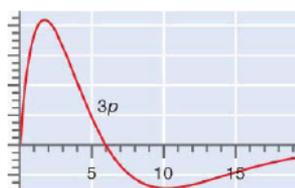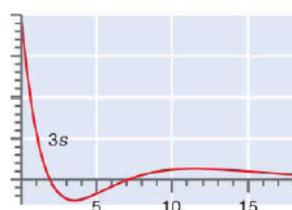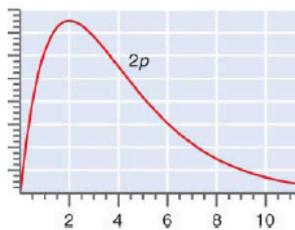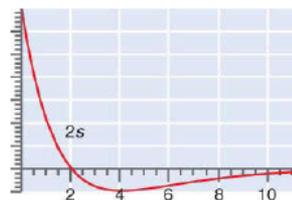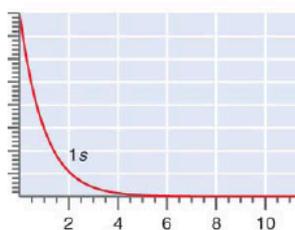
Ab initio Jargons: Basis Set

- STO-nG: use n Gaussians to approach a Slater-type orbital

- Many basis sets with different sizes and characteristics: STO-nG, 3-21G, 4-31G, 6-31G*, 6-311G**, cc-pVDZ, cc-pVTZ, aug-cc-pVDZ…

- Choose wisely according to the problem at hand

STO-3G for 1s

Amplitude

Distance/a_0

1   2   3   4   5
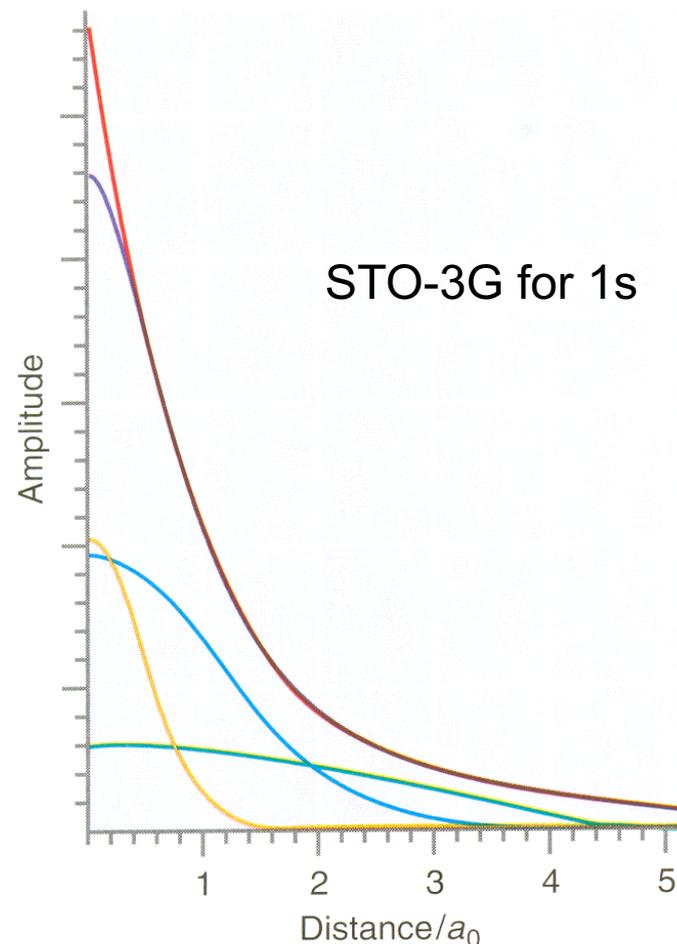
Basis Set Size Effects
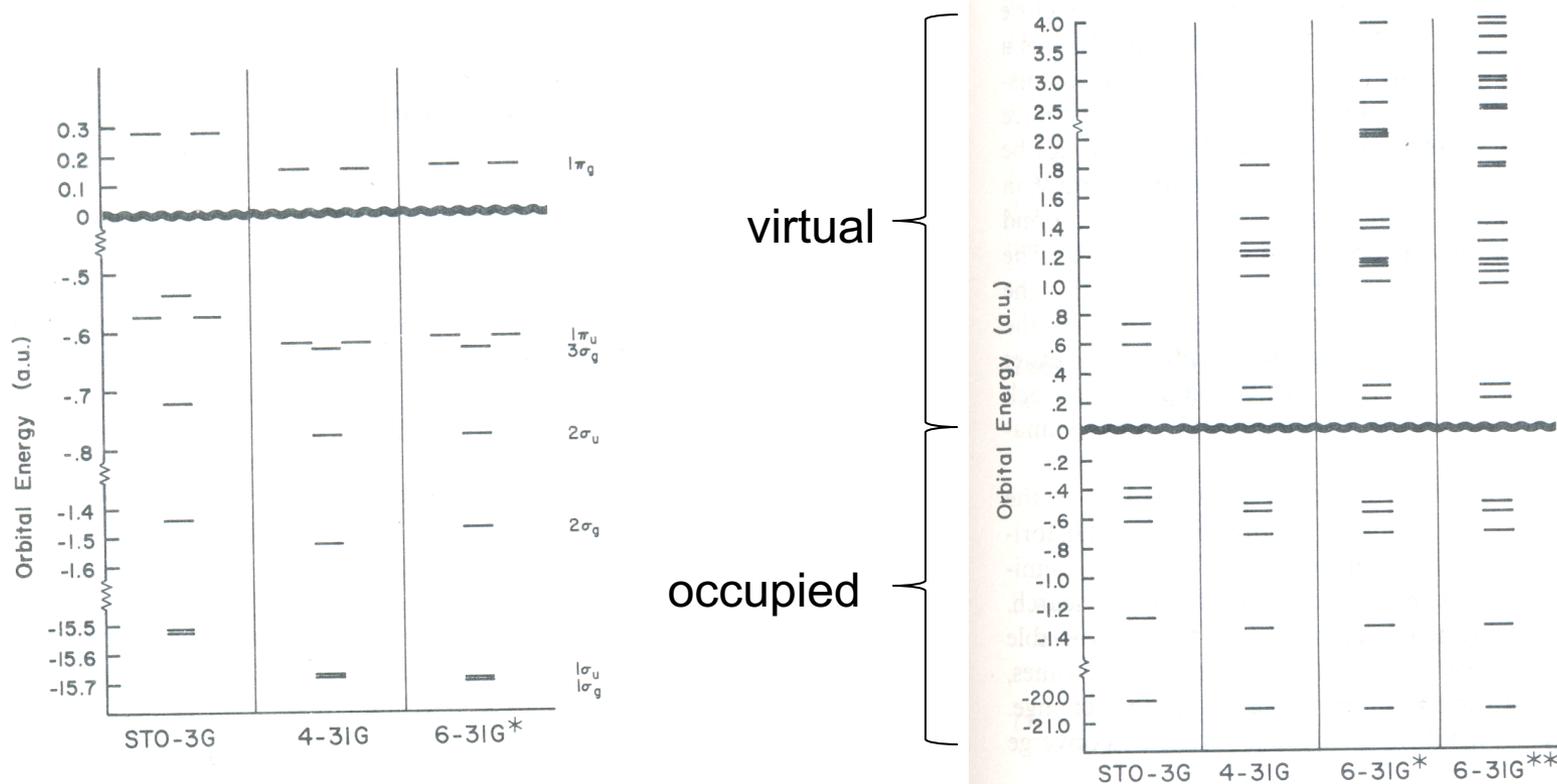
HF orbital energies of N_2

HF occupied and virtual orbital energies of H_2O

Ab initio Jargons: Closed vs. Open Shell
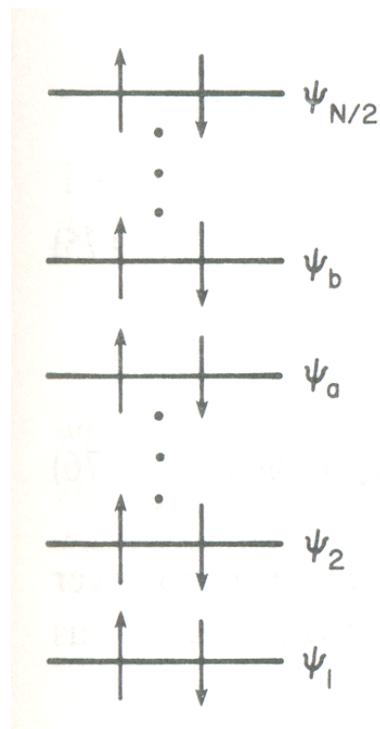
Closed shell
Opposite-spin electrons are all paired up!
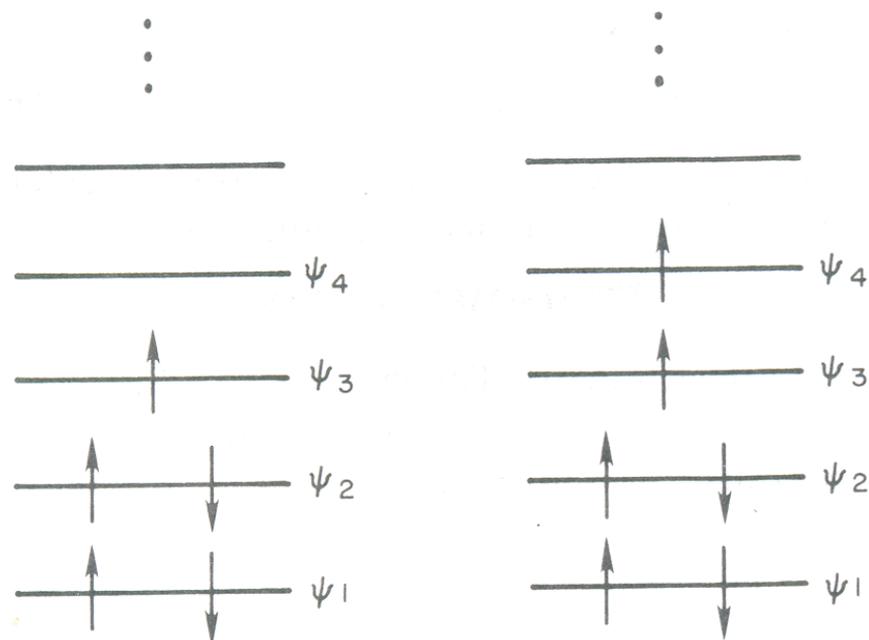
Open shell
There remain unpaired electron spins

Ab initio Jargons: Restricted vs. Unrestricted
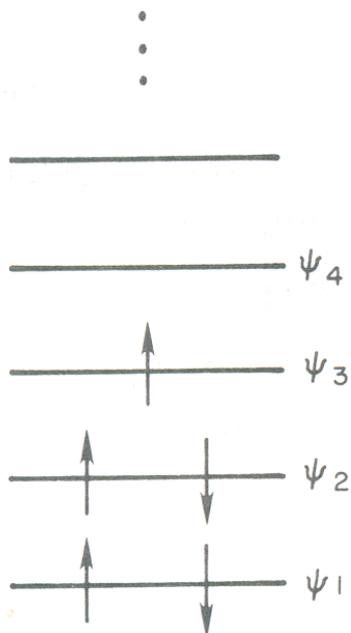
Restricted Hartree-Fock (RHF)
$\alpha-$ and $\beta-$spin orbitals have common spatial part
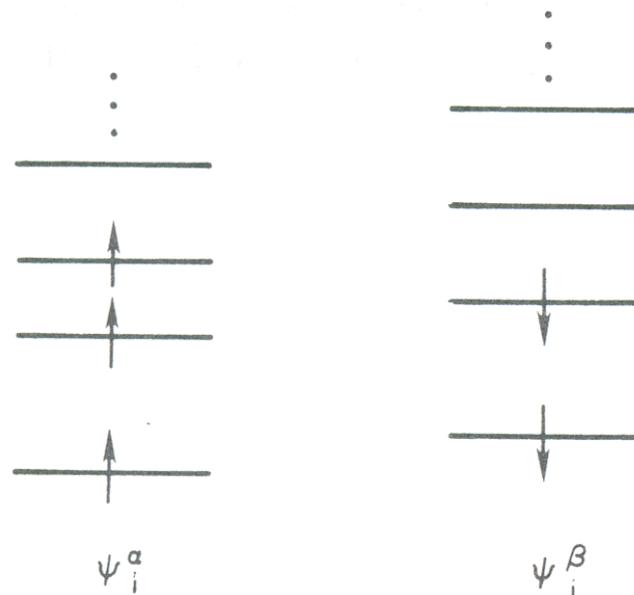
Unrestricted Hartree-Fock (UHF)
$\alpha-$ and $\beta-$spin orbitals can have different spatial parts

Open shell & unrestricted important for bond breaking events!

What can be calculated?

$$\hat{H}\Psi = E\Psi$$

From Prof. Dr. Frank Neese, http://www.thch.uni-bonn.de/tc

Koopmans' Theorem

For example, HF MO energies give the ionization potential and electron affinity:

N ➔ N-1

E=0

Ionization potential

Usually accurate

occupied orbitals

N ➔ N+1

virtual orbitals

Usually quite bad

electron affinity

E=0
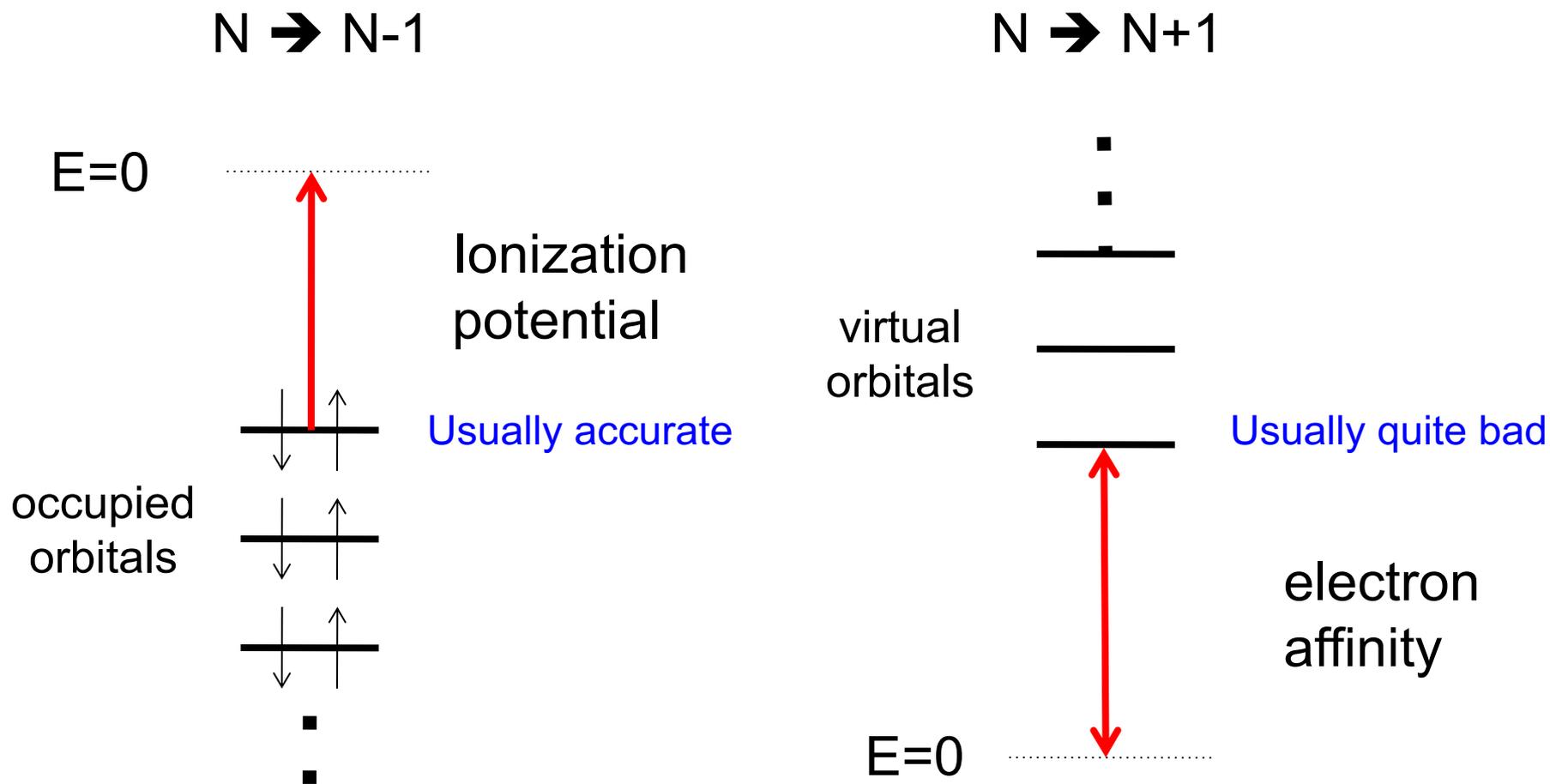
Equilibrium Structures

System	X–H bond length		H–X–H bond angle	
	Theory	Experiment	Theory	Experiment
H_2	0.730	0.742		
CH_3	1.072	1.079	120.0	120.0
CH_4	1.082	1.085	109.5	109.5
NH_2	1.015	1.024	108.6	103.4
NH_3	0.991	1.012	116.1	106.7
OH	0.967	0.971		
H_2O	0.948	0.957	111.5	104.5
HF	0.921	0.917		

Lengths in Angstroms and angles in degrees for small molecules
(from Daudel et al., 1983).

Calculated by "geometry optimization"

Vibrational Frequencies

System	Theory	Experiment
H_2	4644	4405
CH_3	3321	3184
	3125	3002
	1470	1383
	776	580
CH_4	3372	3019
	3226	2917
	1718	1534
	1533	1306
NH_2	3676	3220
	3554	3173
	1651	1499
NH_3	3985	3444
	3781	3336
	1814	1627
	597	950
OH	3955	3735
H_2O	4143	3756
	3987	3657
	1678	1595
HF	4150	4138

The frequencies with H-F are overestimated

Vibrational frequencies for small molecules in cm^{-1} (from Daudel et al., 1983).

HF-SCF with a large basis set.

"vibrational/normal mode analysis"

Electron Densities

Li$_2$ B$_2$ C$_2$ N$_2$ O$_2$ F$_2$
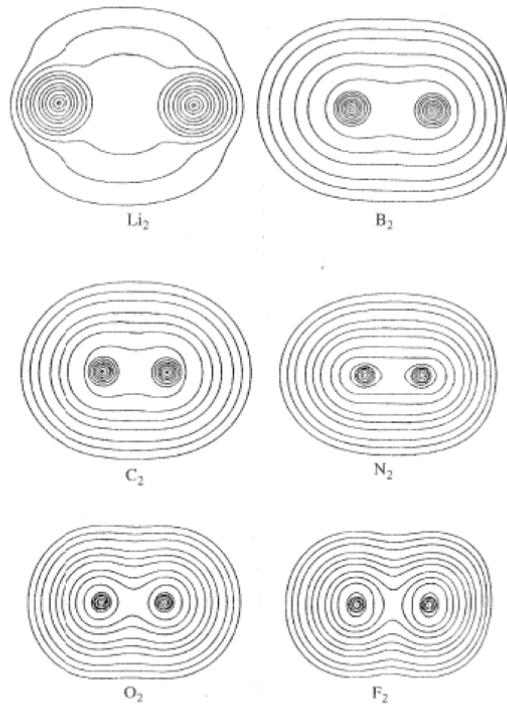
From R. F.W. Bader

$$\rho(\vec{r}) = \sum_{i=1}^{N} |\phi_i(\vec{r})|^2$$

➤ The electron densities computed are structure-less. They resemble the densities of superposed atoms.

➤ The chemical bonds are hardly visible.

Limitations of HF-SCF

- The Hartree-Fock SCF method is limited by the single Slater determinant approximation

- HF-SCF calculation does not include the effects of electron correlation

$$E_{corr} = E_{exact} - E_{HF}$$

E_{corr}: correlation energy

Advanced QC: Electron Correlation

♦ Hartree-Fock is a mean field theory

♦ As a result, for two electrons

$$P(r_1, r_2) = P(r_1)P(r_2)$$

Figure 3. The interelectronic cusp

r1-r2

Peter Knowles

http://www.fz-juelich.de/nic-series/Volume3/Volume3.html
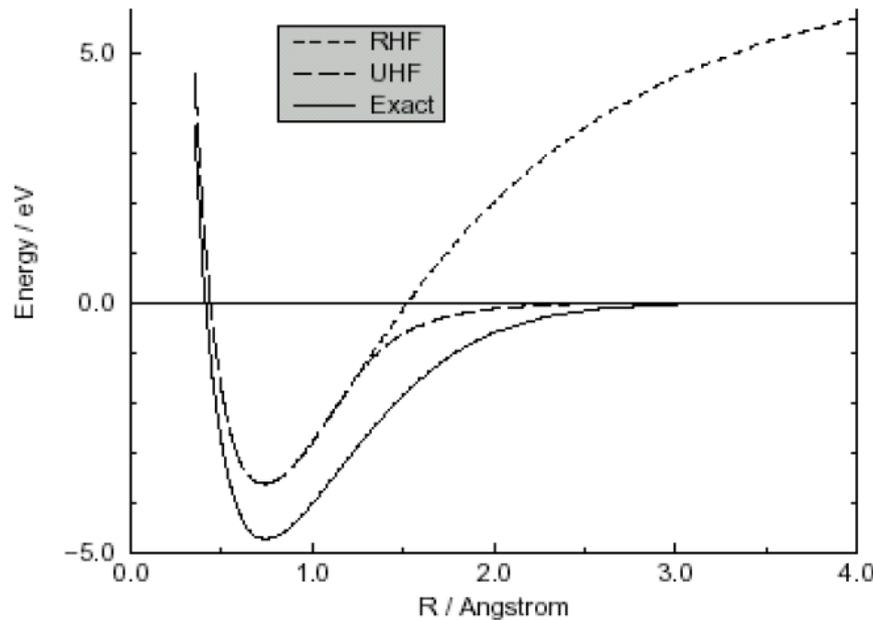
♦ Overestimate ionic states at long distances and the probability to
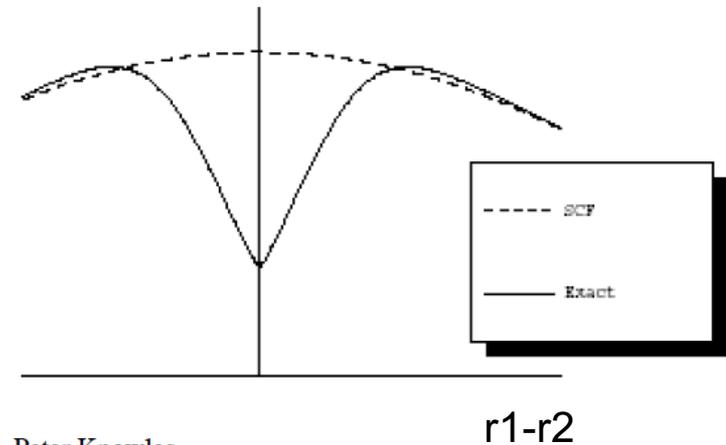
find two electrons close together
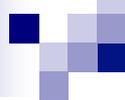
Electron Correlation Methods

- Electron correlations can be accounted for by considering a combination of Slater determinants – post-HF
  - Configuration Interactions (CI)
  - Coupled-Cluster (CC)
  - Møller-Plesset Perturbation Theory (MP)
  - Multi-Configuration Self-Consistent Field (MC-SCF)
  - Density Functional Theory (DFT)

Basics of Density Functional Theory

Brief History of DFT

- 1926: Old DFT -- Thomas-Fermi theory and extensions.

- 50's-60's: Slater and co-workers develop Xα as crude KS-LDA.

- 1965: Modern DFT begins with Kohn-Sham equations. By introducing orbitals, get 99% of the kinetic energy right, get accurate $n(\mathbf{r})$, and only need to approximate a small contribution, $E_{XC}[n]$.

- 1965: KS also suggested local density approximation (LDA) and gradient expansion approximation.

- 1993: More modern functionals (GGA's and hybrids) shown to be usefully accurate for thermochemistry

- 1995-: TDDFT & hybrid DFT methods

- 1998: Kohn and Pople win Nobel prize in chemistry

- 2000-: DFT with dispersion/long-range corrected DFT

- 2010: DFT in materials science, geology, soil science, astrophysics, protein folding,...

Density Functional Theory for Pedestrians

Electron density function (much simpler object than wave function):

$$\rho(\vec{r}_1) = \int \Psi^*(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N, \sigma_1, \sigma_2 \ldots \sigma_N) \cdot \Psi(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N, \sigma_1, \sigma_2 \ldots \sigma_N) d^3 r_2 d^3 r_3 \ldots d^3 r_N d\sigma_1 d\sigma_2 \ldots d\sigma_N$$

Hohenberg-Kohn Theorem (1964)

1. $V_{ext}(\vec{r}) = V_{ext}[\rho(\vec{r})]$

$$\rho_0 \Rightarrow \{N, Z_A, R_A\} \Rightarrow \hat{H} \Rightarrow \Psi_0 \Rightarrow E_0 \text{(and other properties)}$$

Therefore, instead of Ψ dependent on 4N coordinates we would need just ρ_0 dependent on just 3 coordinates

2. The variational principle for DFT

$$E[\bar{\rho}] \geq E[\rho_0]$$

$$E[\rho] = T_k[\rho] + E_{Ne}[\rho] + E_{ee}[\rho] \text{ or}$$
$$E[\rho] = T_k[\rho] + E_{Ne}[\rho] + J[\rho] + E_{xc}[\rho]$$

If we would know how to express each of those four terms

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2; \quad E_{Ne}[\rho] = -\sum_{m=1}^{M} Z_m \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{R}_m|} d\vec{r}$$

Density Functional Theory for Pedestrians

Kohn-Sham formalism → represent ρ(r) using a fictitious non-interacting system, i.e. a single Slater determinant. This resolves the problem with the kinetic energy term (Kohn-Sham orbitals):

$$T_k = -\frac{1}{2}\sum^N \int \varphi_i^*(\vec{r})\nabla^2\varphi_i(\vec{r})dr$$

$$\rho(\vec{r}) = \sum^N |\varphi_i(\vec{r})|^2$$

The big unknown left is the exchange-correlation functional

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho] \qquad \text{(X: exchange, C: correlation)}$$

We know exact E$_{xc}$ exists but nobody knows its functional form → approximations!!

The Hartree-Fock case:

$$E_X^{HF} = -\frac{1}{2}\sum_{i,j}\iint \frac{\varphi_i(\vec{r}_1)\varphi_j(\vec{r}_1)\varphi_i(\vec{r}_2)\varphi_j(\vec{r}_2)}{r_{12}}d\vec{r}_1 d\vec{r}_2; \qquad E_C[\rho] = 0$$

Approximations for E_{xc} (Jacob's ladder)

$$E_{\mathrm{xc}} = \int \epsilon_{\mathrm{xc}}(\mathbf{r}) \, d^3 r$$

1. Local density approximation (LDA): $\quad \epsilon_{\mathrm{xc}} = f(\rho)$

2. Generalized gradient approximation (GGA): $\epsilon_{\mathrm{xc}} = f(\rho, \nabla\rho)$

3. Meta-GGA: $\quad \epsilon_{\mathrm{xc}} = f\left(\rho, \nabla\rho, \nabla^2\rho, t\right), \; t = \frac{1}{2}\sum_i |\nabla\psi_i|^2$

4. The use of occupied orbitals (e.g., Hartree-Fock)

5. The use of unoccupied orbitals (e.g., RPA)

- **Local density approximation (LDA)**
  - Uses only $n(\mathbf{r})$ at a point,

$$E_{\text{XC}}^{\text{LDA}}[n] = \int d^3r \; e_{\text{XC}}^{\text{unif}}(n(\mathbf{r}))$$

- **Generalized gradient approx (GGA)**
  - Uses both $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$

$$E_{\text{XC}}^{\text{GGA}}[n] = \int d^3r \; e_{\text{XC}}(n(\mathbf{r}), |\nabla n|)$$

  - Examples are PBE and BLYP

- **Hybrid:**

$$E_{\text{XC}}^{\text{hyb}}[n] = a(E_{\text{X}} - E_{\text{X}}^{\text{GGA}}) + E_{\text{XC}}^{\text{GGA}}[n]$$

  - Mixes some fraction of HF, a usually about 25%
  - Examples are B3LYP and PBE0
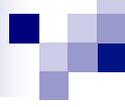
Electron Correlations

- Dynamical correlation (captured by DFT): interactions between energetically separated configurations

- Static correlation (not in DFT): mixing of near-degenerate configurations → multiconfigurational character is necessary

Mix GGA with Hartree-Fock exchange.

Kohn-Sham theory (1965) – equation for orbitals:

$$\left(T + V_{ne} + V_{ee} + \boxed{\frac{\partial F_x}{\partial \rho}} + \frac{\partial F_c}{\partial \rho} \right) \varphi_i = \varepsilon_i \varphi_i$$

Compare Hartree-Fock theory (1930):

$$\left(T + V_{ne} + V_{ee} + \boxed{V_x^{HF}} \right) \varphi_i = \varepsilon_i \varphi_i$$

Advantages: Attractive HF exchange cancels self-interaction in V_{ee}

Hybrid DFT (Becke 1993):

$$\left(T + V_{ne} + V_{ee} + \boxed{\frac{X}{100} V_x^{HF} + (1 - \frac{X}{100}) \frac{\partial F_x}{\partial \rho}} + \frac{\partial F_c}{\partial \rho} \right) \varphi_i = \varepsilon_i \varphi_i$$

(39,000+ citations in March 2013)

Mean (unsigned) errors in kcal/mol

	Bond energies	Barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18
Correct thru 2nd order: SOGGA	7	13
GGA: BLYP (1988)	1.5	8
Hybrid: B3LYP (1993)	0.9	4

Becke–3 parameter–Lee-Yang-Parr

"chemical accuracy" for main-group bond energies, bond lengths, ...

Calculations on a set of main-group molecules.

B3LYP is enormously popular.

Sousa, Fernandes, Ramos, *JPC A* (2007)
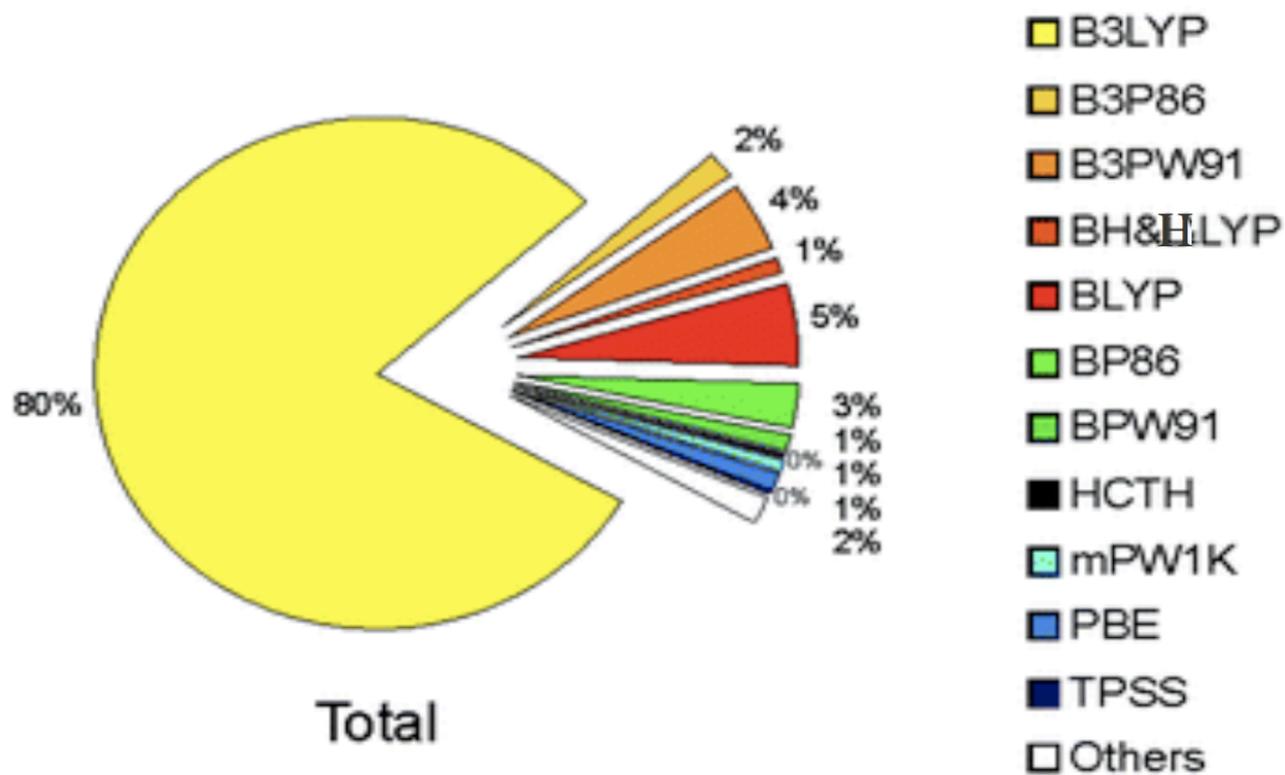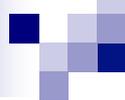
Limitations of the current Exchange and Correlation functionals

> Ground state DFT functionals

- Long history on ground state functionals
  LDA/GGA/Meta-GGA/Hybrid functional (with exact exchange)

- but still many problems to solve:
  → long-range asymptotic (1/r)
  → biradical states
  → self-interaction correction (SIC)
  → non-locality/exact exchange

- **The original DFT formulation is only for the ground state → How to treat excited states?**

The Jacob's Ladder
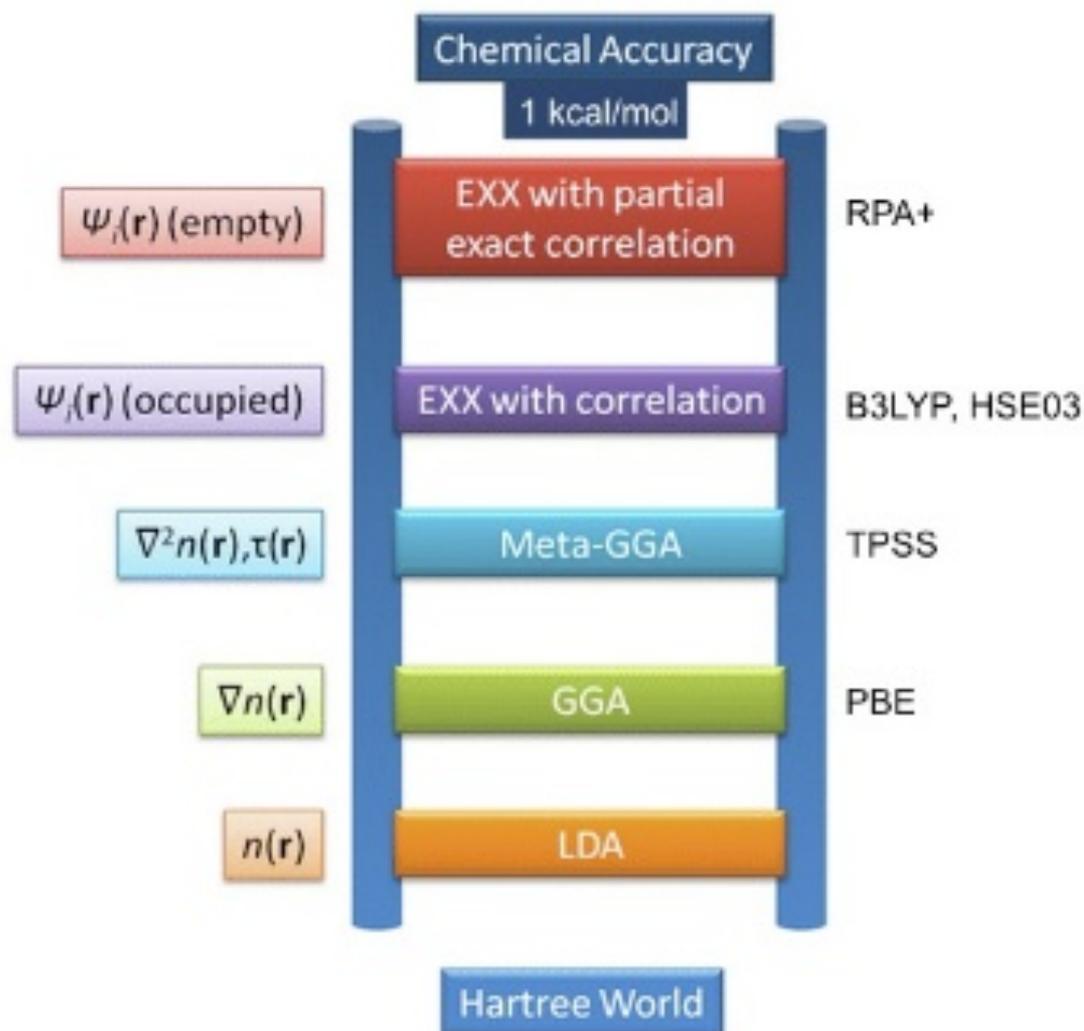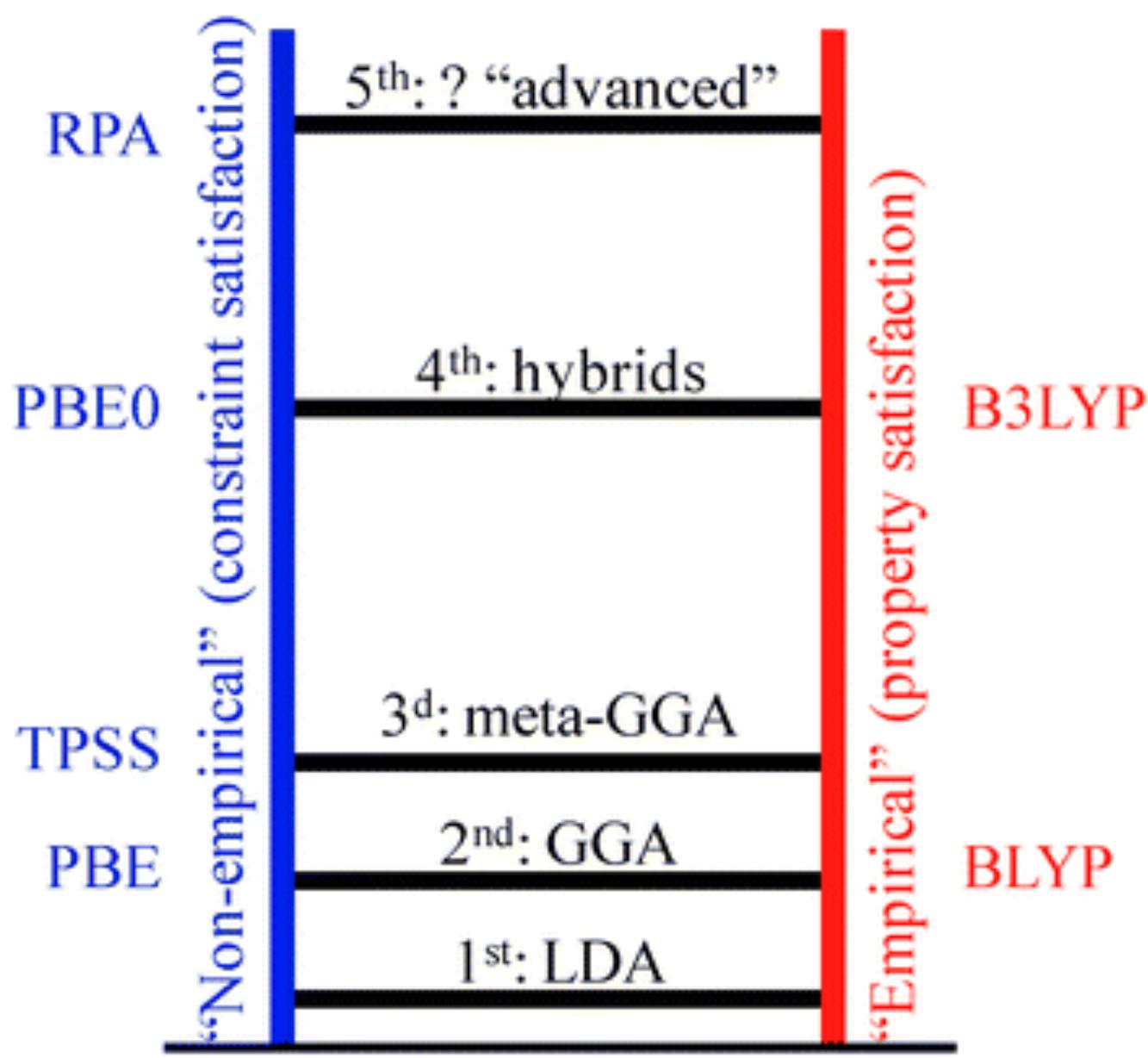
Popular combinations of $E_x[\rho]$ and $E_c[\rho]$

- SVWN=LSDA
- SVWN5
- BLYP

Hybrid functionals

- B3LYP

$$E_{xc}^{hybr} = a_0 E_x^{HF} + (1 - a_0) E_x^{LDA} + a_x \Delta E_x^{B88} + E_c^{LDA} + a_c \Delta E_c^{GGA}$$

$$a_0 = 0.2; \ a_x = 0.72; \ a_c = 0.81$$

- B3P86, B3PW91, B1B95 (1 parameter), B1LYP, MPW1PW91, B98, B971, B972, PBE1PBE etc.

- You can even construct your own. Gaussian provides such a functionality:
$E_{xc} = P_2 E_X^{HF} + P_1(P_4 E_X^{Slater} + P_3 \Delta E_x^{non\text{-}local}) + P_6 E_C^{local} + P_5 \Delta E_C^{non\text{-}local}$
IOP(3/76),IOP(3/77) and IOP(3/78) setup P_1 - P_6

B3LYP =
BLYP IOp(3/76=1000002000) IOp(3/77=0720008000) IOp(3/78=0810010000)

DFT references

1. W. Koch, M.C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH Verlag GmbH, 2001)

2. M.E. Casida in *Recent Advances in Density Functional Methods, Part 1* (World Scientific, Singapore, 1995)

3. M.E. Casida in *Recent Developments and Applications of Modern Density Functional Theory, Theoretical and Computational Chemistry*, vol 4., ed. by J.M. Seminario (Elsevier, Amsterdam, 1996).

4. Marques M.A.L. and Gross E.K.U. Annu. Rev. Phys. Chem **55**, 427 (2004).

Applicability of DFT
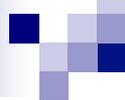
A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions†

Lars Goerigk[ab] and Stefan Grimme*[a]

Validation of electronic structure methods for isomerization reactions of large organic molecules

Sijie Luo,[a] Yan Zhao[b] and Donald G. Truhlar*[a]

PERFORMANCE: MOLECULAR GEOMETRIES

- ## Main group compounds

		HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H_2	R_0(H-H)	1.379	1.446	1.398	1.414	1.395	1.410	1.401
HF	R_0(H-F)	1.722	1.776	1.778	1.786	1.782	1.765	1.733
H_2O	R_0(O-H)	1.790	1.844	1.842	1.850	1.829	1.831	1.810
	θ_0 (H-O-H)	105.5	103.6	102.9	102.7	104.0	104.0	103.9
NH_3	R_0(N-H)	1.891	1.938	1.937	1.944	1.920	1.925	1.910
	θ_0 (H-N-H)	107.2	106.0	105.8	104.8	106.4	106.0	106.0
CH_4	R_0(C-H)	2.046	2.078	2.071	2.076	2.057	2.065	2.092
$\overline{E}$	R_0(44)	-0.010	0.014	0.018	0.020	0.010	0.012	—
$|\overline{E}|$	R_0(44)	0.020	0.021	0.018	0.020	0.014	0.013	—

6-31G* (Gill, 1993); 32 molecules; in Å and ^{o}

- ## Rules of thumb

  ❶ LDA (HF) bond lenghts slightly too long (short)

  ❷ Gradient corrections and post-HF slightly better

Peter Saalfrank (Universität Potsdam)

PERFORMANCE: TRANSITION METALS

- **Geometries:** $M(CO)_6$

method	HF	MP2/ECP	CCSD(T)	SVWN	BP86	B3LYP	exp.
$Cr(CO)_6$	1.970-2.010	1.862	1.939	1.865	1.910	1.921	1.918
$Mn(CO)_6$	–	2.031	–	2.035	2.077	2.068	2.063
$W(CO)_6$	–	2.047	–	2.060	2.116	2.078	2.058

M-C distance (in Å); extended basis sets, most at least of TZ quality; Koch /Holthausen (1999)

- **Dissociation energies $MH^+ \rightarrow M+H^+$; excitation energies $M \rightarrow M^*$**

	SVWN	BP86	B3LYP	MCPF	PCI-80	exp.
MAD diss. en. (kcal/mol)	12	8	4-5	6	2	±2
MAD exc. en. (eV)	0.75		0.33			

M=Sc-Cu; details see Koch / Holthausen, *A Chemist's Guide to DFT* (1999)

- **Rules of thumb**

  ❶ LDA (HF) bond lenghts too short (long)

  ❷ Gradient corrections and post-HF perform better

  ❸ Errors generally larger than for main group compounds

  ❹ Accurate low-spin / high-spin splittings very difficult (role of exact exchange)

PERFORMANCE: VIBRATIONAL FREQUENCIES

- **For some main group compounds**

		HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H_2		4646	4207	4461	4373	4534	4367	4401
FH		4358	3912	3841	3810	4041	4020	4139
CO		2439	2169	2105	2105	2125	2176	2170
H_2O	SS	4070	3657	3597	3568	3776	3751	3832
	BI	1827	1646	1698	1682	1735	1745	1648
	AS	4189	3789	3721	3690	3918	3878	3943
NH_3	SS	3689	3372	3332	3305	3504	3457	3506
$\overline{E}$	(213)	165	-51	-47	-63	69	12	–
$|\overline{E}|$	(213)	168	75	61	73	99	42	–

harmonic frequencies; 6-31G*; in cm^{-1}; 213 vibrations of 32 molecules (Gill, 1993)

- **Rules of thumb**

❶ LDA (HF) slightly too "soft" ("hard")

❷ Gradient-corrected DFT, QCISD perform well

❸ scaling factors (6-31G*): 0.895 (HF), 0.943 (MP2), 0.995 (BLYP), 0.9614 (B3LYP)

PERFORMANCE: POTENTIAL CURVES

• **Chemical bond: Summary**
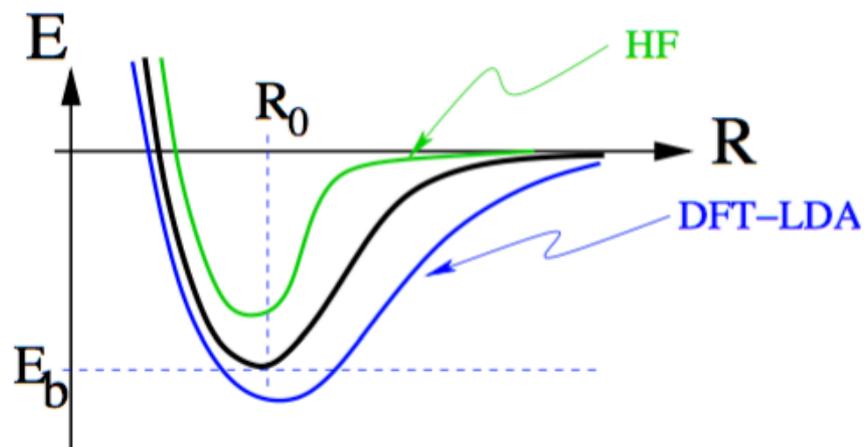
• **Van-der-Waals bond**

Ar_2, 6-311++G(3df,3dp)
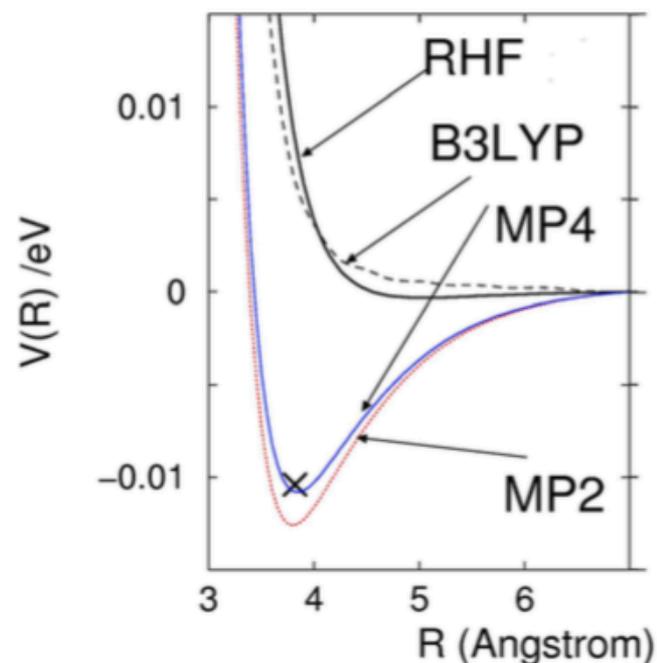
❶ HF too shallow, too steep

❷ LDA too deep, too flat

❸ GGA and post-HF perform better

❶ HF and B3LYP fail,
the former because lack of correlation,
the latter because $\lim_{r\to\infty} v_c(r)$ wrong

❷ Good basis sets needed

PERFORMANCE: NON-BONDING INTERACTIONS

- **Types**

  ❶ Hydrogen-Bonded systems

  ❷ Charge-Transfer systems

  ❸ Dipole-Interacting systems

  ❹ Weak Interactions

- **Systematic study (JCTC 1, 415 (2005))**

  - 44 DFT, 1 WFT (MP2), good basis sets

  - 4 data bases

  - W1 reference (CCSD(T), CBS)

- **Rules of thumb**

  ❶ MP2 $\approx$ hyper-GGA > meta-GGA > GGA > LDA

  ❷ There is always a functional . . .

Table 8. Overall Results (kcal/mol)[a]

rank	method	MMMUE HB	CT	DI	WI	MMMMUE[b]
1	MPWB1K	0.61	0.50	0.52	0.22	0.46
2	MP2	0.66	0.60	0.55	0.16	0.49
3	MPW1B95	0.71	0.56	0.53	0.25	0.51
4	PBE1KCIS	0.60	0.93	0.36	0.27	0.54
5	MPW1K	0.53	0.68	0.55	0.44	0.55
6	PBE1PBE	0.47	1.05	0.39	0.29	0.55
7	B98	0.61	0.95	0.38	0.28	0.55
8	B97-1	0.53	1.20	0.33	0.19	0.56
9	BHandHLYP	0.52	0.63	0.73	0.41	0.57
10	X3LYP	0.55	0.98	0.49	0.40	0.60
11	mPW1PW91	0.63	0.75	0.55	0.53	0.62
12	MPW3LYP	0.57	1.38	0.34	0.32	0.65
13	MPWKCIS1K	0.79	0.74	0.74	0.42	0.67
14	B3P86	0.46	1.10	0.53	0.68	0.69
15	TPSS1KCIS	0.71	1.22	0.50	0.40	0.71
16	B3LYP	0.77	0.80	0.78	0.60	0.74
17	TPSSh	0.63	1.43	0.53	0.45	0.76
18	MPW1KCIS	1.04	0.93	0.69	0.48	0.79
19	B97-2	1.32	0.75	0.86	0.56	0.87
20	BB1K	1.11	0.86	1.01	0.54	0.88
21	B3PW91	1.13	0.82	0.97	0.85	0.94
22	TPSS	0.66	2.15	0.54	0.47	0.95
23	TPSSKCIS	0.75	2.13	0.51	0.42	0.95
24	B1B95	1.37	0.73	1.11	0.65	0.96
25	PBEKCIS	0.70	2.60	0.41	0.27	1.00
26	mPWPBE	0.82	2.17	0.60	0.56	1.03
27	mPWB95	0.94	2.36	0.53	0.32	1.04
28	HCTH	1.76	1.45	0.59	0.36	1.04
29	mPWPW91	0.77	2.28	0.58	0.53	1.04
30	mPWKCIS	1.15	1.87	0.62	0.52	1.04
31	PBE	0.50	2.94	0.49	0.28	1.05
32	mPWLYP	0.72	2.71	0.41	0.40	1.06
33	XLYP	0.92	2.15	0.64	0.56	1.06
34	BP86	0.88	2.03	0.71	0.93	1.14
35	BLYP	1.29	1.72	1.00	0.81	1.21
36	BPW91	1.70	1.47	1.18	1.09	1.36
37	BB95	1.87	1.56	1.19	0.87	1.37
38	BPBE	1.74	1.45	1.20	1.11	1.38
39	VSXC	0.61	2.84	1.10	1.64	1.55
40	O3LYP	2.76	1.32	2.00	0.79	1.72
41	OLYP	3.60	1.60	2.40	0.93	2.13
42	G96LYP	2.95	1.33	2.56	1.89	2.18
43	SPWL	4.62	6.73	2.93	0.40	2.75
44	SVWN5	4.63	6.73	2.93	0.40	3.67
45	SVWN3	4.87	6.94	3.08	0.44	3.83
	average	1.28	1.78	0.92	0.56	1.14

PERFORMANCE: REACTIONS

- **An example: Diels-Alder reaction**
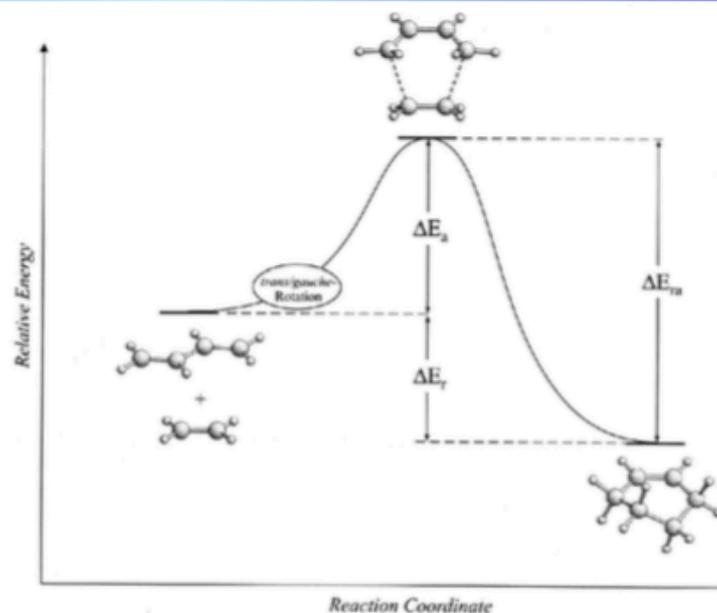
	Exp.	G2	HF	SVWN	BLYP	B3LYP
ΔE_a (kcal/mol)	27±2	25	51	5	26	28
ΔE_r (kcal/mol)	-38	-38	-30	-59	-14	-29

HF and DFT with 6-311+G(d,p), zero-point corrected

- **Rules of thumb**

  ❶ LDA (HF) activation energies much too small (much too high)

  ❷ LDA (HF) overbinds (underbinds)

  ❸ Gradient corrections and post-HF perform better

OTHER ISSUES AND SUMMARY

- **Things not touched upon here**

  ❶ Solids, in particular metals

  ### Why does the B3LYP hybrid functional fail for metals?

Joachim Paier, Martijn Marsman, and Georg Kresse
Faculty of Physics, Universität Wien and Center for Computational Materials Science, Sensengasse 8/12, A-1090 Wien, Austria

  ❷ Properties (electric, magnetic, . . .)

  ❸ Static correlation: Multi-determinant effects, conical intersections and all that

  ❹ Computational effort: Clear advantage for DFT

- **Conclusions**

  ❶ About $\approx 90\%$ calculations done with DFT: Good price / perfomance relation

  ❷ DFT has replaced semiempirical methods in electronic structure theory

  ❸ There is always a functional . . .

$$\hat{H}_e \, \Psi_{e,n}(r; R) = E_{e,n}(R) \, \Psi_{e,n}(r; R)$$

$n = 0$ (ground state), $n > 0$ (excited states)

Peter Saalfrank (Universität Potsdam)
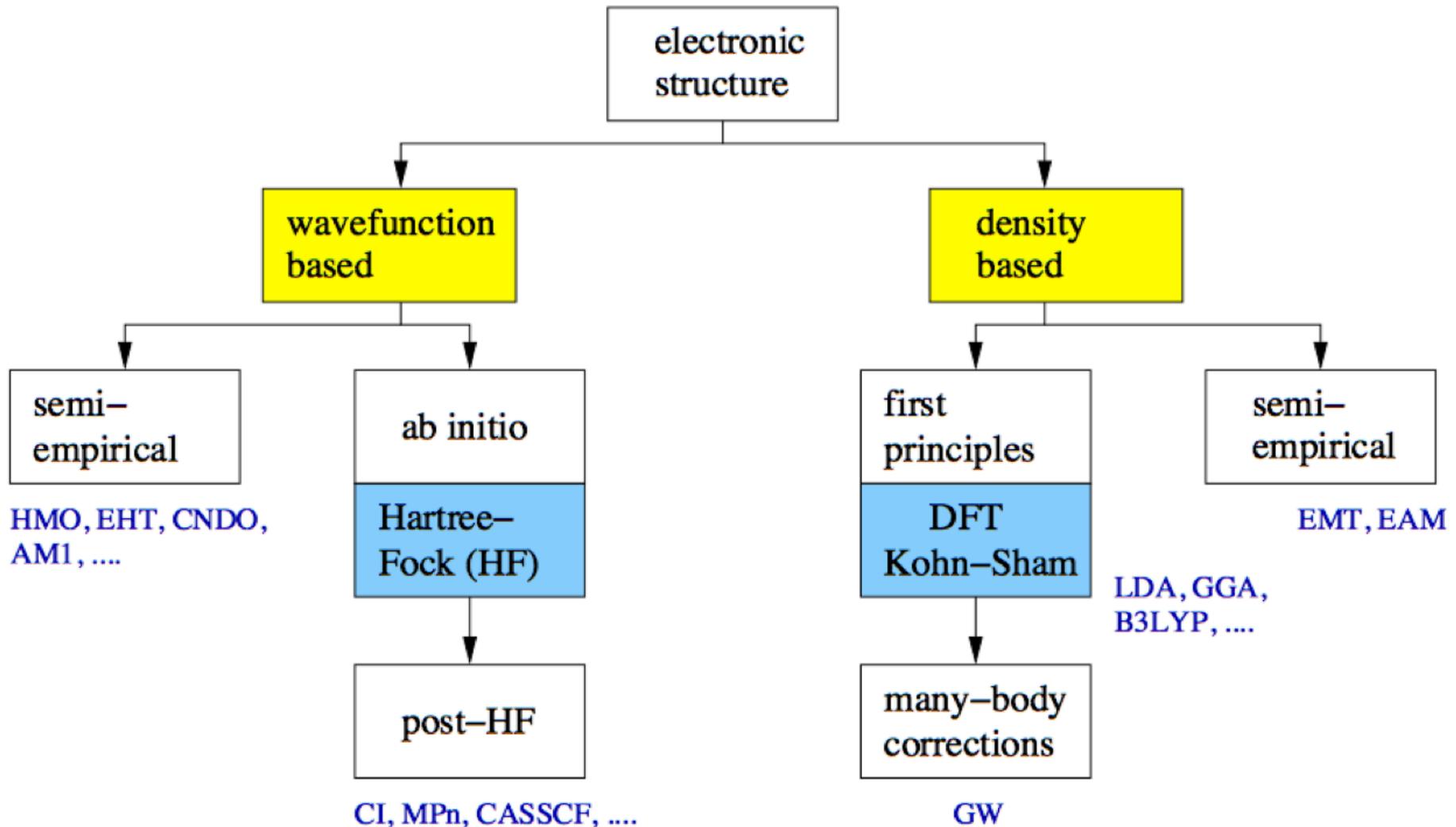
Conducting a Computational Project

- These questions should be answered
  - □ What do you want to know?
  - □ How accurate does the prediction need to be?
  - □ How much time can be devoted to the problem?
  - □ What approximations are being made?
- The answers to these questions will determine the type of calculation, method and basis set to be used ➔ Model Chemistry
- If good energy is the goal ➔ use extrapolation procedures to achieve `chemical accuracy': G1/2/3, W1/2/3, PCI-80… models
- DFT is always a good start for chemical systems

Variety of Methods in Computational Chemistry

	Quality	Size dependence

■ *Ab initio MO Methods*

- ☐ CCSD(T)   quantitative (1~2 kcal/mol) but expensive $\sim N^6$
- ☐ MP2   semi-quantitative and doable $\sim N^4$
- ☐ HF   qualitative $\sim N^{2-3}$

■ *Density Functional Theory*

- ☐ DFT   semi-quantitative and cheap $\sim N^{2-3}$

■ *Semi-empirical MO Methods*

- ☐ AM1, PM3, MNDO   semi-qualitative $\sim N^{2-3}$

■ Molecular Mechanics Force Field

- ☐ MM3, Amber, Charmm   semi-qualitative (no bond-breaking) $\sim N^{1-2}$

- So far we have described theories that allow us to obtain the ground state energy of a molecular system --- at a fixed molecular geometry

- How would this be useful??

- We will run some calculations next time!!