

Quantum chemistry

Long history

Highest reliability

Computational complexity

A central “technology” of MOLECULAR MODELING

Molecular modeling:

Properties of molecules in the gas phase and in the condensed phase

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Quantum chemistry

Properties of molecules in the gas phase and in the condensed phase

Depends on electronic wavefunction Ψ or electron density ρ

$$\rho(\vec{r}) = |\Psi(\vec{r})|^2$$

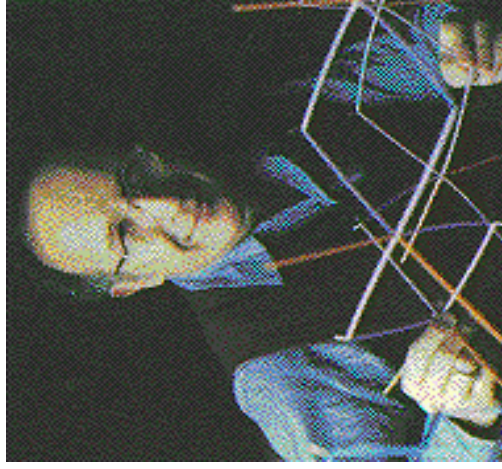
Today - traditional *ab initio* methods: Ψ
- density functional theory (DFT): ρ

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Nobel Prizes for Computational Chemistry



Mulliken, 1966



Hoffmann, 1981



Fukui, 1981



Kohn, 1998



Pople, 1998

MOTIVATION

Computer HARDWARE development
(powerful and cheap PC's available)

SOFTWARE development

“Black box” tools for computational chemistry available

Number of theoretical/computational papers increases dramatically

- Calculations of various properties for almost any type of systems

Goal

- increase the overlap between theory and experiment
- interpretation of experimental data at atomic scale level

- Reliability ranges from “quite reasonable” to “rather poor”

=> Judging the reliability of theoretical work becomes very important but difficult

GOAL:

- Basic overview of QC methods
(for non-experts in computational chemistry)
- Reliability of QC methods

Quantum mechanics – axiomatic character

- postulates
- wave function Ψ
- time dependent Schrödinger equation
- stationary Schrödinger equation

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

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

Solving the stationary Schrödinger equation

⇒ Traditional *ab initio*

⇒ DFT

MODEL

“A set of simplifying approximations adopted for the description of a specific system”

- (i) A set of atomic nuclei representing the system
- (ii) A set of constraints applied
(*boundary conditions, geometry constraints, etc.*)
- (iii) Number of electrons explicitly treated
- (iv) Interaction potentials between particles in the system

MODEL

METHOD

METHODS

Hierarchy based on a *number of electrons explicitly treated*:

- 1) no electrons
Inter-atomic potential functions (**IPF**)
(force field, molecular mechanics)
- 2) valence electrons only
Semi-empirical methods (*NDO, AM1, PM3*)
Ab initio with pseudopotentials
(plane-wave DFT)
- 3) all electrons considered
Ab initio (Hartre-Fock, post-HF, DFT)

METHODS

Hierarchy based on a *number of electrons explicitly treated*:

1) no electrons

Inter-atomic potential functions (IPF)
(force field, molecular mechanics)

Inter-atomic potential functions

Electrostatic interaction

- polarizable potentials
- *core-shell model - ion-pair potential*

$$1/2 k_2 r^2 + 1/24 k_4 r^4$$

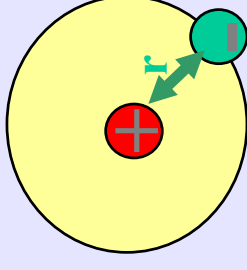
Two-body

- Buckingham potential

$$A \exp(-r/\rho) - C r^{-6}$$

Three-body

$$1/2 k_2 (q - q_0)^2 + 1/6 k_3 (q - q_0)^3 + 1/2 k_4 (q - q_0)^4$$



METHODS

Hierarchy based on a *number of electrons explicitly treated*:

1) no electrons

Inter-atomic potential functions (IPF)
(force field, molecular mechanics)

Inter-atomic potential functions

Advantages

- computationally simple and cheap
- large number of atoms in model
- molecular dynamics - effect of temperature

Disadvantages

- reliability
- chemical reactions

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Semi-empirical methods

- rarely used nowadays
- suitability questionable

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Stationary Schrödinger equation

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

CCSD(T)

Non-relativistic Hamiltonian
 Born-Oppenheimer approximation
 Electron Density $\rho(\vec{r}) = \sum_i^{occ} |\varphi_i(\vec{r})|^2$
 One-el. Functions $\varphi_i(1) = \sum_{\mu} c_{i\mu} \chi_{\mu}(1)$

Hybrid functionals
 B3LYP, B3PW91, ...

Generalized gradient approximation (GGA)
 $E \equiv E[\rho, \nabla\rho]$
 PW91, BP86, BLYP, PBE, ...

MP2

Electron correlation

Expansion over Slater det.
 $\Phi = C_0\Psi_0 + C_S\Psi_S + C_D\Psi_D + \dots$

Traditional \longleftrightarrow DFT
Ab initio

Model of independent electrons
 $\hat{H}^{el}(i, j) \equiv \sum_i V^{eff}(i)$

Post-HF methods

Hartree-Fock method
 $\phi_1(1) \dots \text{HF orbitals}$
 $\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \det|\varphi_1(1)\varphi_2(2)\dots\varphi_n(n)|$
 Electron correlation neglected

Non-interacting reference system
 Kohn-Sham orbitals

Local density approximation
 LDA (LSD, SVWN)
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Time independent Schrödinger equation

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

Wave function describing the system

Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}$$

Derived from classical Hamilton's function

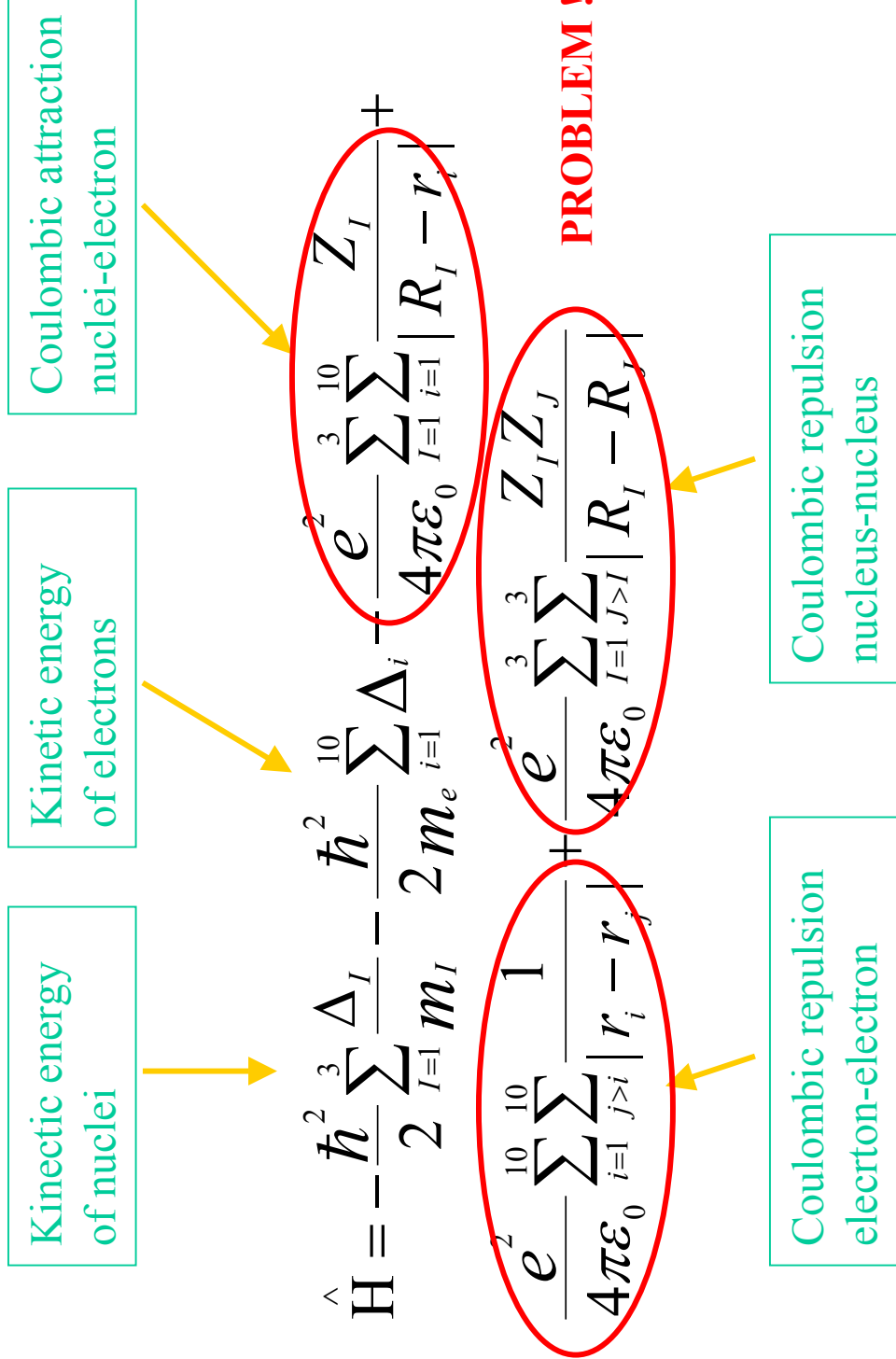
Molecular Hamiltonian $\hat{H} = \hat{T}_J + \hat{T}_e + \hat{V}_{JJ} + \hat{V}_{Je} + \hat{V}_{ee}$

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=1}^n \frac{\Delta_i}{m_i}$$

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^n \sum_{j=1}^n \frac{z_i z_j}{|r_i - r_j|}$$

Example - water molecule Hamiltonian

Water molecule Hamiltonian



Stationary Schrödinger eq. - easy to set up, problem to solve

One-electron atoms:

- exact (analytical) solution
- hydrogen-like atoms --> atomic orbitals



Manyelectron systems:

- Problematic components: depends on the coordinates of more than one particle
- We cannot separate variables and solve the equation

Quest for approximative solution: finding approximations which can be controlled

1. Born-Oppenheimer approximation
2. Model of independent electrons
3. MO LCAO

BOA

Separation of
electronic and nuclear
degrees of freedom

Potential energy
surface

Stationary Schrödinger equation

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Kohn-Sham orbitals

Local density approximation
LDA (LSD, SVWN)
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Born-Oppenheimer approximation

Positions of nuclei are fixed $E_{kin}^J = 0$

$$\hat{H} = \cancel{\hat{T}_J} + \hat{T}_e + \hat{V}_{JJ} + \hat{V}_{Je} + \hat{V}_{ee}$$

$= 0 = \text{const.}$

Depends only on electronic coordinates

$$\hat{H} = \hat{T}_e + \hat{V}_{Je} + \hat{V}_{ee} + \text{konst.}$$

One-electron part

Two-electron part

Electrons move in the potential of nuclei at fixed positions R:

$$\hat{H} \Psi_i(r, R) = E_i(R) \Psi_i(r, R)$$

POTENTIAL ENERGY SURFACE (PES)

Complete separation of nuclear and electronic motion
Dynamics of atomic nuclei is investigated on PES - quantum or classical dynamics

Water molecule Hamiltonian

Kinetic energy of nuclei

Kinetic energy of electrons

Coulombic attraction nuclei-electron

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{I=1}^3 \Delta_I - \frac{\hbar^2}{2m_e} \sum_{i=1}^{10} \Delta_i - \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^3 \sum_{i=1}^{10} \frac{Z_I}{|R_I - r_i|} +$$

$$\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{10} \sum_{j>i}^{10} \frac{1}{|r_i - r_j|} + \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^3 \sum_{J>I}^3 \frac{Z_I Z_J}{|R_I - R_J|}$$

Coulombic repulsion electron-electron

Coulombic repulsion nucleus-nucleus

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{10} \Delta_i - \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^3 \sum_{i=1}^{10} \frac{Z_I}{|R_I - r_i|} + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{10} \sum_{j>i}^{10} \frac{1}{|r_i - r_j|} + konst.$$

PROBLEM !!

Stationary Schrödinger equation

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

n -electron wavefunction expressed in terms of n one-electron functions:

$$\Psi(1,2,\dots,n) = \prod_{i=1}^n \varphi_i(i)$$

Non-relativistic Hamiltonian
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Electron Density $\rho(\vec{r}) = \sum_i^{occ} |\varphi_i(\vec{r})|^2$
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Expansion over Slater det.
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Traditional *Ab initio*

DFT

Model of independent electrons
 $\hat{H}^{el}(i,j) \equiv \sum_i V^{eff}(i)$

Post-HF methods

Hartree-Fock method
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$$\Psi(1,2,\dots,n) = \frac{1}{\sqrt{n!}} \det |\varphi_1(1)\varphi_2(2)\dots\varphi_n(n)|$$

Electron correlation neglected

Hybrid functionals
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Non-interacting reference system
 Kohn-Sham orbitals

Local density approximation
 LDA (LSD, SVWN)
 $E \equiv E[\rho]$

Model of independent electrons

Hamiltonian can be expressed as a sum of one- and two-electronic contributions:

$$\hat{H} = \sum_i \hat{h}_i(1) + \sum_i \sum_{j>i} \hat{v}_{ij}(1,2)$$



$T_i + V_{ij}$

V_{ee}

Hinders the separation of variables

$$\sum_{i=1}^n \sum_{j>i}^n \hat{v}_{ij}(1,2) \approx \sum_{i=1}^n \hat{V}_i(1)$$



Effective potential - electron moves in an averaged field of all other electrons of the system

$$\hat{H} \approx \sum_{i=1}^n [\hat{h}(i) + \hat{V}(i)] = \sum_{i=1}^n \hat{H}'(i)$$



Each member of this Hamiltonian operates only on a single electron



Separation of variables: Overall wave-function can be expressed as product of one-electron functions

$$\sum_{i=1}^n \hat{H}(i) \Psi(1, 2, \dots, n) = E \Psi(1, 2, \dots, n)$$


$$\Psi(1, 2, \dots, n) = \prod_{i=1}^n \varphi_i(i)$$

Original Schrödinger eq. is splitted to **n** one-electron equations

It is not enough to take just a product function.

To satisfy the antisymmetrization postulate we express a wave function in the form of SLATER DETERMINANT

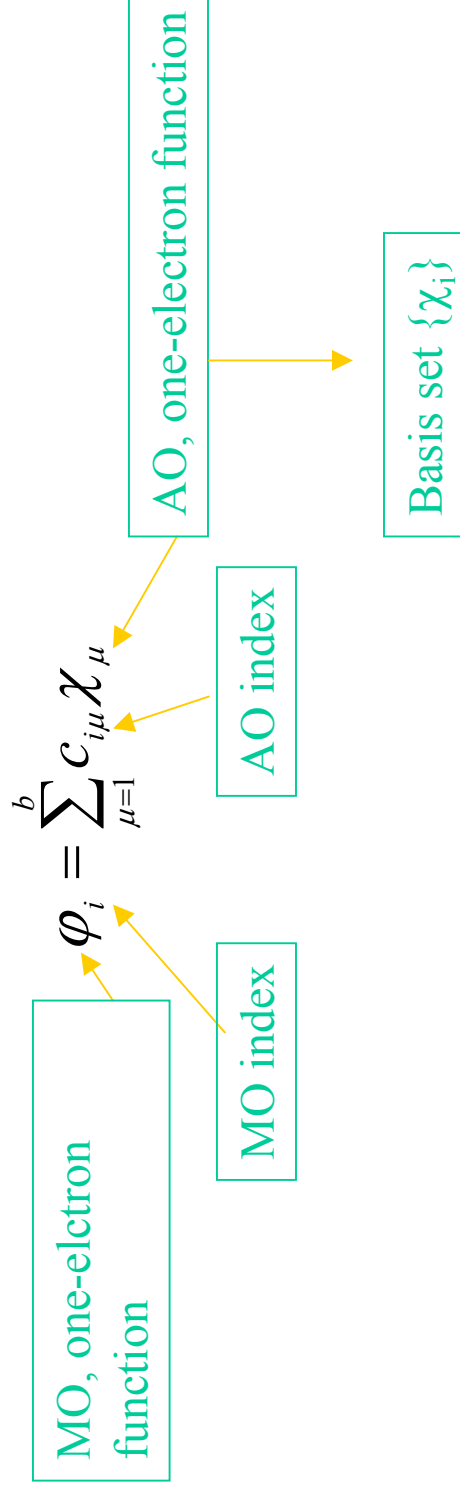
$$\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \det(\varphi_i) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(n) & \varphi_2(n) & \dots & \varphi_n(n) \end{vmatrix}$$

Overall wave function describing the system is in the form of the product of one electron functions φ_i (MO)

One-electron functions φ_i -

- MOLECULAR ORBITALS - in the form of linear combination of atomic orbitals

MO LCAO



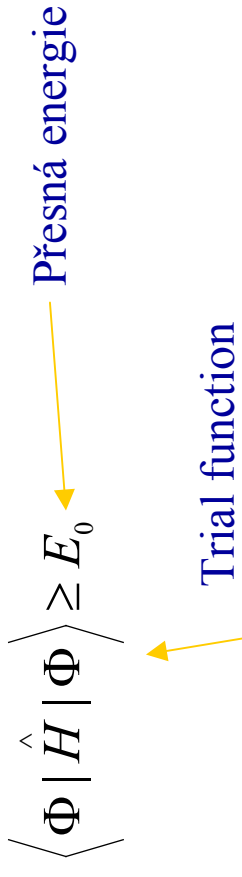
- we get just n MO when we use n AO
- increasing the basis set size - convergence control
- energy is minimized as a function of $c_{i\mu}$

Variation theorem

$$\langle \Phi | \hat{H} | \Phi \rangle \geq E_0$$

Trial function

Přesná energie



Trial function gives energy that is always higher than true energy

Linear variation function

$$\Phi = \sum_k c_k f_k$$

The best function (giving the lowest energy) must satisfy:

$$\frac{\partial W}{\partial c_i} = 0$$

\Rightarrow it leads to secular equations :

$$\sum_{k=1}^b [H_{ik} - WS_{ik}] c_k = 0$$

$$H_{ik} = \langle f_i | \hat{H} | f_k \rangle \quad S_{ik} = \langle f_i | f_k \rangle$$

System of N linear homogeneous equations - non-trivial solution only for $\det=0$

Stationary Schrödinger equation

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

CCSD(T)

Non-relativistic Hamiltonian
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Expansion over Slater det.
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MP2

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Ab initio

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Hartree-Fock method
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Local density approximation
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 $E \equiv E[\rho]$

Post-HF methods

Hartree-Fock method

$$\hat{H} = \sum_i \hat{h}_i(1) + \sum_{i,j>i} \hat{v}_{ij}(1,2)$$

$$\sum_{i=1}^n \sum_{j>i}^n \hat{v}_{ij}(1,2) \approx \sum_{i=1}^n \hat{V}_i(1)$$

$$\Psi(1,2,\dots,n) = \frac{1}{\sqrt{n!}} \det(\varphi_i) = \frac{1}{\sqrt{n!}}$$

$\varphi_1(1)$	$\varphi_2(1)$...	$\varphi_n(1)$
$\varphi_1(2)$	$\varphi_2(2)$...	$\varphi_n(2)$
...
$\varphi_1(n)$	$\varphi_2(n)$...	$\varphi_n(n)$

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

$$\delta E[\Psi] = 0$$

Neglect correlation of electronic motion !
 => Error ~ “correlation energy”

- HF methods offers technical solution of the problem:
- one electron equations are solved one by one
 - electrons move in the averaged field of all other electrons

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^n h_{ii} + \frac{1}{2} \sum_i^n \sum_j^n (J_{ij} - K_{ij})$$

One-electron integral $h_{ii} = \langle \varphi_i(1) | \hat{h}_1 | \varphi_i(1) \rangle$

Coulombic integral $J_{ij} = \langle \varphi_i(1)\varphi_j(2) | \hat{v}_{ij}(1,2) | \varphi_i(1)\varphi_j(2) \rangle$

Exchange integral $K_{ij} = \langle \varphi_i(1)\varphi_j(2) | \hat{v}_{ij}(1,2) | \varphi_j(1)\varphi_i(2) \rangle$

$\delta E[\Psi]=0 \Rightarrow$ **Fock's equations**

$$\hat{F} \varphi_i' = \varepsilon_i \varphi_i'$$

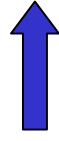
$$\hat{F}(1) = \hat{h}(1) + \sum_{j=1}^n \langle \varphi_j(2) | \hat{v}'(1,2) | \varphi_j(2) \rangle$$

Fock's equations are solved iteratively - SCF procedure
 CPU time formally depends on N^4 ($N \dots$ number of basis functions)

Hartree-Fock-Roothaan

MO LCAO

$$\varphi_i = \sum_{\mu=1}^L c_{\mu i} \chi_{\mu}$$



FOCK EQUATIONS

$$\hat{\mathbf{F}}(i) \sum_{\mu=1}^L c_{\mu i} \chi_{\mu} = \varepsilon_i \sum_{\mu=1}^L c_{\mu i} \chi_{\mu}$$



$$\sum_{\mu=1}^L \langle \chi_{\nu} | \hat{\mathbf{f}}(i) | \chi_{\mu} \rangle c_{\mu i} = \varepsilon_i \sum_{\mu=1}^L \langle \chi_{\nu} | \chi_{\mu} \rangle c_{\mu i}$$

SECULAR EQUATIONS

$$\sum_{\mu=1}^L F_{\mu\nu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^L S_{\mu\nu} c_{\mu i} \Rightarrow \sum_{\mu=1}^L c_{\mu i} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0$$

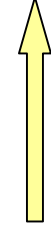
$$F_{\mu\nu} = \langle \chi_{\mu} | \hat{\mathbf{f}}(i) | \chi_{\nu} \rangle = h_{\mu\nu}^{core} + \sum_{\kappa=1}^B \sum_{\lambda=1}^B P_{\kappa\lambda} \left[(\mu\nu | \kappa\lambda) - \frac{1}{2} (\mu\lambda | \kappa\nu) \right]$$

SCF procedure:

- 1) Starting MO \sim set of $c_{\mu i}$
- 2) Calculate integrals $(\mu\nu|\kappa\lambda)$, $S_{\mu\nu}$, $h_{\mu\nu}$
- 3) Constructing $P_{\kappa\lambda}$
- 4) Constructing $F_{\mu\nu}$
- 5) Solving Fock equations \Rightarrow new set of $c_{\mu i}$
- 6) Check the convergence

[back to 3]

$$P_{\kappa\lambda} = 2 \sum_{j=1}^{n/2} c_{\kappa j}^* c_{\lambda j}$$



Let computer to do it !

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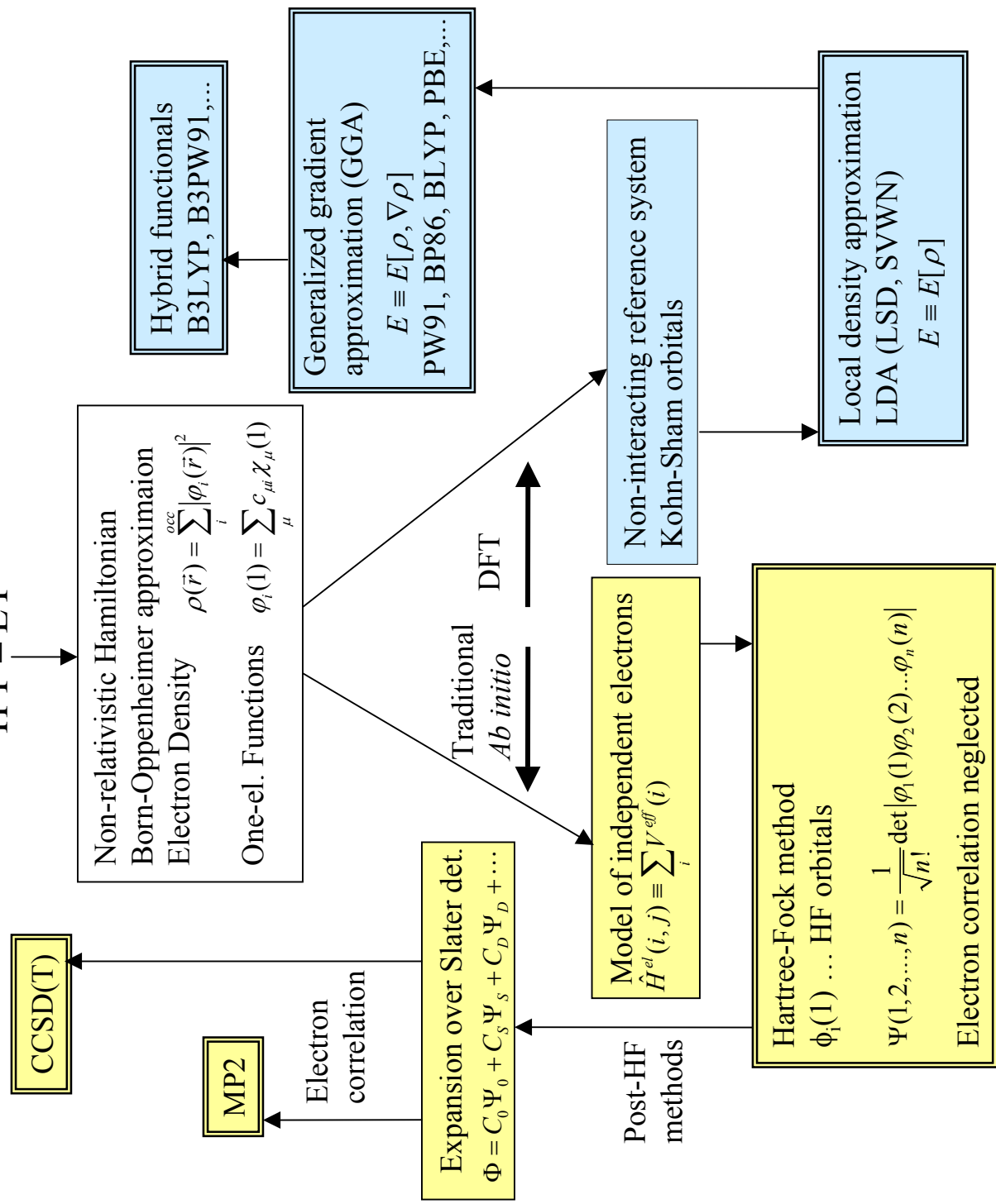
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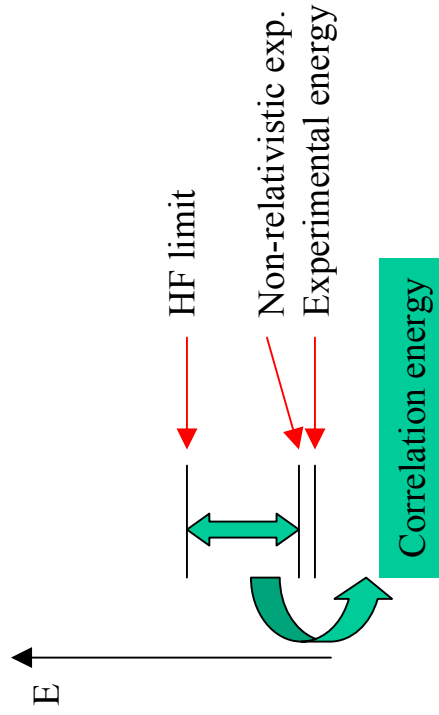
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Correlation energy



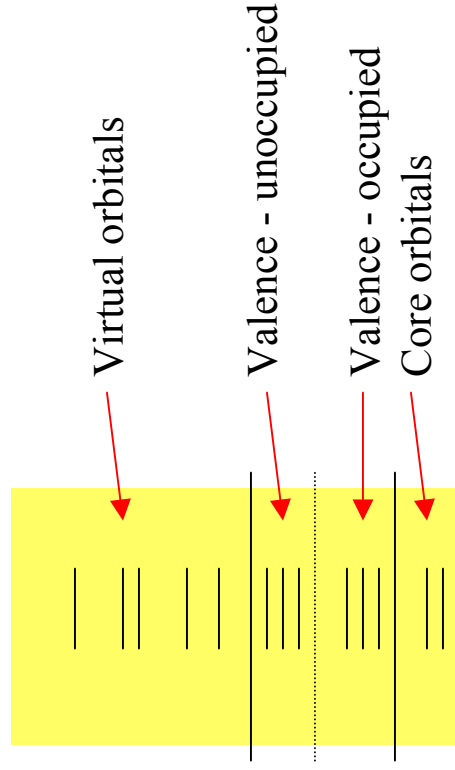
Importance of electron correlation strongly depend on the nature of studied system/process. It may partially cancel out.

Electron correlation raises from the close proximity of electrons.

To include electron correlation electrons must have a chance to escape away from other electrons.

Instead of using single Slater determinant we use combination of more Slater determinants in the wavefunction of the system.

	SINGLE	DOUBLE
$\sigma^* 2b_2$	—	—
$\sigma^* 4a_1$	—	—
$\pi 1b_1$	$\uparrow \uparrow$	$\uparrow \downarrow$
$n 3a_1$	$\uparrow \uparrow$	—
$\sigma 1b_2$	$\uparrow \downarrow$	$\uparrow \downarrow$
$\sigma 2a_1$	$\uparrow \downarrow$	$\uparrow \downarrow$
core $1a_1$	$\uparrow \downarrow$	$\uparrow \downarrow$



=> single Slater determinant is replaced by linear combination of many determinants

$$\Phi = \sum_I C_I \Psi_I$$

Various methods differ in the specification of Slater determinants in linear expansion and in the criteria used in search for optimal coefficients C_I

If all Slater determinant that can be created with the given basis set are considered
full CI (configuration interaction)

Number of SD in given
basis set:

$$B=100, n=50 \quad N_{\text{full}}^{\text{SD}} \sim 10^{45}$$

$$N_{\text{full}}^{\text{SD}} \sim \frac{B!(B+1)!}{(n/2)!(n/2+1)!(b-n/2)!(b-n/2+1)!}$$

Brillouin's theorem: $\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = 0$

Slater-Condon's rules: *majority of integrals formed by different Slater determinant vanishes*

Monoexcited determinants:

$$\Psi^S = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} c_i^a \Psi_i^a$$

Biexcited determinants:

$$\Psi^D = \sum_i^{\text{occ}} \sum_{j \neq i}^{\text{unocc}} \sum_a^{\text{occ}} \sum_{b \neq a}^{\text{unocc}} c_{ij}^{ab} \Psi_{ij}^{ab}$$

Tri- and tetra-excitation

$$\Psi_0 = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots \\ \varphi_1(n) & \dots & \varphi_n(n) \end{vmatrix} \quad \longrightarrow \quad \Psi_i^a = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \dots & \varphi_a(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \dots & \varphi_a(2) & \dots & \varphi_n(2) \\ \dots & \dots & \dots & \dots & \dots \\ \varphi_1(n) & \dots & \varphi_a(n) & \dots & \varphi_n(n) \end{vmatrix}$$

Configuration interaction (CI)

Wavefunction in the form:

$$\Phi^{CI} = c_0 \Psi_0 + \Psi^S + \Psi^D + \Psi^T + \Psi^Q + \dots$$

Variation theorem applied

Search only for C coefficients of CI expansion

MO are kept fixed (coefficients c does not change)

Various implementations (CID, CISD, CISDTQ,..)

Not size consistent !

Davidson correction for size consistency: $(1-c_0)^2 \cdot E_{\text{correl}}$

Applications

Modern variant of CI method: AQCC, ACPF

CISD - 2e1 ~ 100% E(corr)
 - 100e1 ~ 60% E(corr)

Example: He...He

Coupled Clusters (CC)

$$|\Psi\rangle = e^{\hat{T}} |\Psi_{HF}\rangle \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \dots \hat{T}_N \quad e^{\hat{T}} = 1 + \hat{T} + (2!)^{-1}\hat{T}^2 + (3!)^{-3}\hat{T}^3 + \dots = \sum_k \frac{\hat{T}^k}{k!}$$

Wave function

Taylor expansion

$$|\Psi\rangle = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots) |\Psi_{HF}\rangle$$

Eg., double excitation

$$\begin{aligned} \hat{T}_2 \Psi &= \sum_i \sum_{j < i} \sum_a \sum_{b < a} t_{ij}^{ab} \Psi_{ij}^{ab} \\ \hat{T}_2^2 \Psi &= \hat{T}_2 \left(\sum_i \sum_{j < i} \sum_a \sum_{b < a} t_{ij}^{ab} \Psi_{ij}^{ab} \right) \\ &= \sum_i \sum_{j < i} \sum_k \sum_{l < k} \sum_a \sum_{b < a} \sum_c \sum_{d < c} t_{ij}^{ab} t_{kl}^{cd} \Psi_{ijkl}^{abcd} \end{aligned}$$

CID $\Phi^{CID} = (1 + \hat{T}_2) \Psi_{HF}$

CCD $\Phi^{CCD} = (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2) \Psi_{HF}$

Makes it size-consistent !

**CCSD
CCSD(T), CCSDT**

- quite precise
- size consistent
- best routine method for description of dynamic el. correlation

QCISD(T) - neglects some of T_1T_2 cross-terms - only small computer saving,
lost of accuracy

PERTURBATION THEORY

Rayleigh-Schrödinger formulation (non-degenerate systems)

System of interest:

$$\hat{H}\Psi_n = E_n\Psi_n$$

“Reference” (known) system:

$$\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

Perturbation (small !):

$$\hat{V} \equiv \hat{H}' = \hat{H} - \hat{H}_0$$

Introducing an ordering parameter λ and expand eigenfunctions and eigenvalues in Taylor series:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

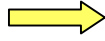
$$\Psi_n = \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \dots$$

$$\Psi_n^{(k)} = \frac{1}{k!} \frac{\partial^k \Psi_n}{\partial \lambda^k} \Big|_{\lambda=0}$$

$$E_n^{(k)} = \frac{1}{k!} \frac{\partial^k E_n}{\partial \lambda^k} \Big|_{\lambda=0}$$

PT for electron correlation - Moller-Plesset formulation

$$\text{Perturbation} \quad \hat{H}' = \sum_{i < j} r_{ij}^{-1} - \sum_i v_i^{HF} (i)$$



$$E^{MP2} = \underbrace{E^{(0)} + E^{(1)}}_{=E^{HF}} + E^{(2)} = E^{HF} + \sum_a^{occ} \sum_b^{virt} \sum_r \sum_s \frac{|\langle ab | rs \rangle - \langle ab | sr \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Can be close to 0 !

Size-consistent, non-variational

MP2, MP3, MP4

MP2 - cheapest post-HF method for electron correlation
Most popular method

Stationary Schrödinger equation

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

CCSD(T)

Non-relativistic Hamiltonian
 Born-Oppenheimer approximation
 Electron Density $\rho(\vec{r}) = \sum_i^{occ} |\varphi_i(\vec{r})|^2$
 One-el. Functions $\varphi_i(1) = \sum_\mu c_{i\mu} \chi_\mu(1)$

Hybrid functionals
 B3LYP, B3PW91, ...

Generalized gradient approximation (GGA)
 $E \equiv E[\rho, \nabla\rho]$
 PW91, BP86, BLYP, PBE, ...

Expansion over Slater det.
 $\Phi = C_0\Psi_0 + C_S\Psi_S + C_D\Psi_D + \dots$

MP2

Electron correlation

Traditional *Ab initio* DFT

Model of independent electrons
 $\hat{H}^{el}(i, j) \equiv \sum_i V^{eff}(i)$

Non-interacting reference system
 Kohn-Sham orbitals

Hartree-Fock method
 $\phi_1(1) \dots \phi_n(n)$
 $\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \det|\varphi_1(1)\varphi_2(2)\dots\varphi_n(n)|$
 Electron correlation neglected

Post-HF methods

Local density approximation
 LDA (LSD, SVWN)
 $E \equiv E[\rho]$

BASIS SET

1. Hydrogen atom orbitals:

$$\phi = Nr^l e^{-Zr/na_0} \sum_{j=0}^{n-l-1} b_j r^j Y_{l,m}(\vartheta, \varphi)$$

2. Slater-type orbitals:

$$\phi_{STO} = \frac{[2\zeta/a_0]^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_{l,m}(\vartheta, \varphi)$$

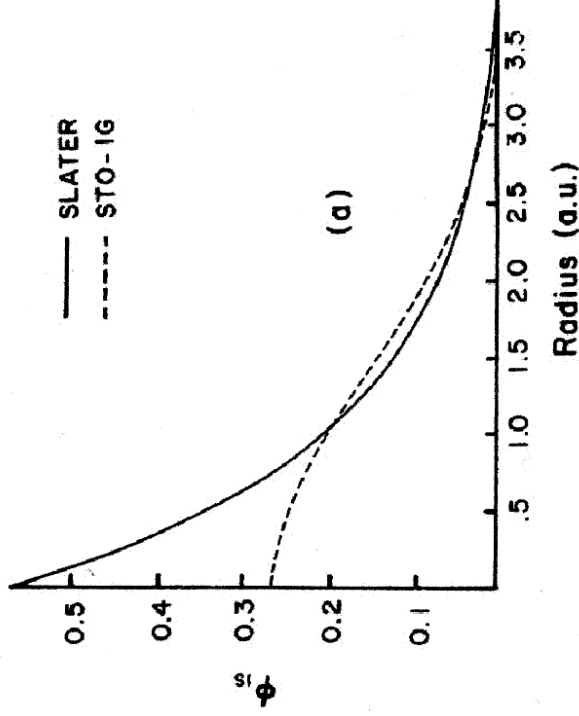
3. Gaussian orbitals:

$$\phi_{GTO} = Nx^l x^l y^l z^l e^{-\alpha r^2}$$

- i+j+k=0 ... s
- i+j+k=1 ... p
- i+j+k=2 ... d

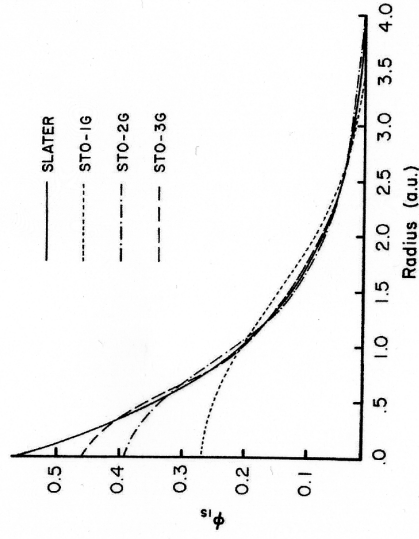
(! 6 d-components)

[Boys (Proc. R. Soc. A, 200 (1950) 542)]



Significant differences between GTO and STO description of electrons close to the nucleus

Contracted GTO orbitals:



$$\begin{aligned} \phi_{STO}^{1s} (\zeta = 1.24) &\simeq 0.44\phi_{GTO}^{1s} (\alpha = 0.17) \\ &+ 0.54\phi_{GTO}^{1s} (\alpha = 0.62) \\ &+ 0.15\phi_{GTO}^{1s} (\alpha = 3.43) \end{aligned}$$

Example: STO-3G for C atom

```
S 3 1.00
0.7161683735D+02 0.1543289673D+00
0.1304509632D+02 0.5353281423D+00
0.3530512160D+01 0.4444634542D+00
SP 3 1.00
0.2941249355D+01 -0.9996722919D-01 0.1559162750D+00
0.6834830964D+00 0.3995128261D+00 0.6076837186D+00
0.2222809159D+00 0.7001154689D+00 0.3919573931D+00
```

α exponent

Contr. coef.
for s

Contr. coef.
for p

Basis set classification:

- minimal basis set
- double- ζ bs
- valence double - ζ bs
- triple- ζ bs
- polarization function
- diffuse function

Basis Set	Applies to	Polarization Functions	Diffuse Functions
STO-3G	H-Xe	*	
3-21G	H-Xe	* <i>or</i> **	+
6-31G	H-Kr	(3df,3pd)	++
6-311G	H-Kr	(3df,3pd)	++
D95	H-Cl <i>except Na and Mg</i>	(3df,3pd)	++
D95V	H-Ne	(d) <i>or</i> (d,p)	++
LanL2MB	H-Ba, La-Bi		
LanL2DZ	H, Li-Ba, La-Bi		
SDD, SDDAll	<i>all but Fr and Ra</i>		
cc-pV(DTQ5)Z	H-He, B-Ne, Al-Ar, Ga-Kr	<i>included in definition</i>	<i>added via AUG- prefix</i>
cc-pV6Z	H, B-Ne	<i>included in definition</i>	<i>added via AUG- prefix</i>
SV and SVP	H-Kr	<i>included in definition</i>	
TZV and TZVP	H-Kr	<i>included in definition</i>	
EPR-II, EPR-III	H, B, C, N, O, F	<i>included in definition</i>	

Example: 6-31G(d) basis set for carbon atom:

Standard basis: 6-31G(d) (5D, 7F)
Basis set in the form of general basis input:

```
1 0
S   6 1.00
    0.3047524880D+04  0.1834737130D-02
    0.4573695180D+03  0.1403732280D-01
    0.1039486850D+03  0.6884262220D-01
    0.2921015530D+02  0.2321844430D+00
    0.9286662960D+01  0.4679413480D+00
    0.3163926960D+01  0.3623119850D+00
SP  3 1.00
    0.7868272350D+01 -0.1193324200D+00  0.6899906660D-01
    0.1881288540D+01 -0.1608541520D+00  0.3164239610D+00
    0.5442492580D+00  0.1143456440D+01  0.7443082910D+00
SP  1 1.00
    0.1687144782D+00  0.1000000000D+01  0.1000000000D+01
D   1 1.00
```

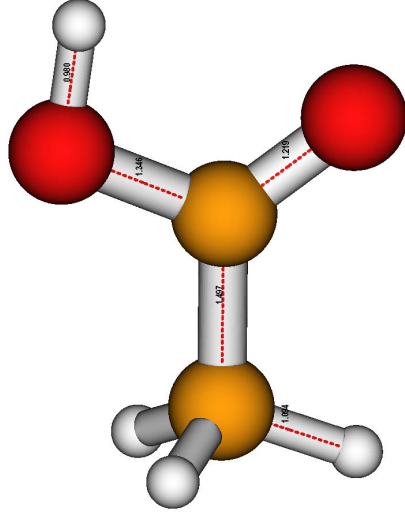
α exponent

Contr. coef.
for s

Contr. coef.
for p

CH₃COOH

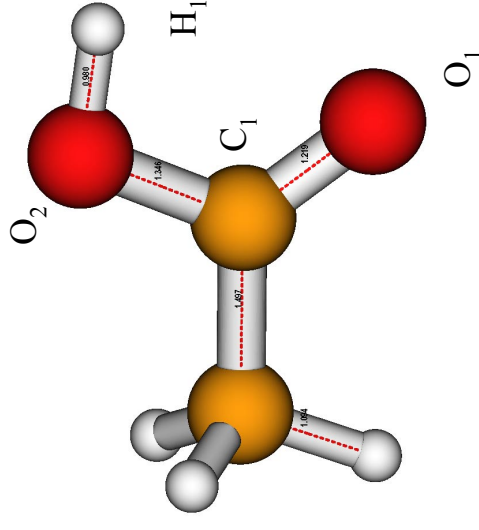
[Geometry: HF/6-31G(d)]



Basis set	No. of bf	E(HF) (a.u.)	E(homo) (a.u.)	Dipole Moment (Debey)	CPU (s)
sto-3g	24	-224.801626	-0.34416	0.8712	6
3-21G	44	-226.532063	-0.44189	1.5629	6
6-31G	44	-227.698149	-0.45659	1.7389	6
6-311G	64	-227.759343	-0.45900	1.7689	7
6-31G(d)	64	-227.809095	-0.44890	1.7908	8
6-31G(d,p)	76	-227.821273	-0.44824	1.8164	10
D95	48	-227.741903	-0.46203	1.8180	7
D95V	44	-227.741397	-0.46190	1.8184	7
LanI2DZ	44	-227.741398	-0.46207	1.8192	7
cc-pvdz	76	-227.834149	-0.44646	1.8149	12
cc-pvtz	176	-227.904686	-0.45319	1.9120	191
cc-pvqz	340	-227.922078	-0.45486	1.9486	2075

Exp = 1.74 D

CH₃COOH



Mulliken charge distribution

	STO-3G	3-21G	6-31G	6-311G	6-31G* 6-31G**	cc- pVDZ	cc- pVTZ	cc- pVQZ	
C ₁	0.343	0.830	0.688	0.667	0.771	0.752	0.290	0.397	0.572
O ₁	-0.287	-0.601	-0.528	-0.487	-0.561	-0.564	-0.358	-0.385	-0.464
O ₂	-0.321	-0.709	-0.693	-0.661	-0.731	-0.615	-0.282	-0.325	-0.411
H ₁	0.225	0.408	0.431	0.422	0.476	0.363	0.174	0.241	0.262
C	-0.214	-0.680	-0.513	-0.582	-0.587	-0.412	-0.017	-0.278	-0.272
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.085	0.249	0.204	0.214	0.215	0.162	0.062	0.125	0.124

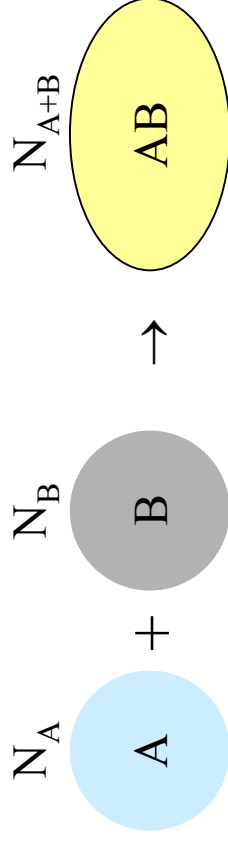
Basis sets

Atom-centered basis sets

Gaussian Type Orbitals (GTO)

Slater Type Orbitals (STO)

Numerical basis set



Inherent problem: Basis set superposition error (BSSE)

Correction for BSSE - counterpoise correction method

Plane-wave basis set - for periodic systems

- no BSSE

He atom - various approaches

$$\hat{H}^{He} = -\frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$e' = -\frac{e}{\sqrt{4\pi\epsilon_0}}$$

$$\hat{H}^{He} = \underbrace{-\frac{\hbar^2}{2m_e}\Delta_1 - \frac{Ze^{\prime 2}}{r_1}}_{\hat{h}_1} + \underbrace{-\frac{\hbar^2}{2m_e}\Delta_2 - \frac{Ze^{\prime 2}}{r_2}}_{\hat{h}_2} + \underbrace{\frac{e^{\prime 2}}{r_{12}}}_{\hat{v}_{12}}$$

Exact value: $E^{He^+} + IP(He) = 2.000 + 0.90357 = 2.90357$ a. u.

Experiment

Exact energy of He^+ :

$$E_{He^+} = -\frac{Z^2}{n^2} \cdot 0.5 a.u.$$

1 a.u. = 27.2114 eV = 627.51 kcal/mol

4. Hartree-Fock description

He atom

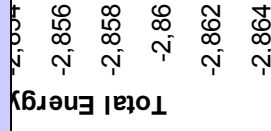
Hartree-Fock description

BASIS SET	No. of bf	No. of prim. G	HF Energy	Orbital En.
sto-3g	1	3	-2.807783	-0.87604
3-21G	2	3	-2.835679	-0.90357
6-31G	2	4	-2.855160	-0.91413
6-311G	3	5	-2.859895	-0.91687
6-31G(d,p)	5	7	-2.855160	-0.91413
tzvp	6	8	-2.859895	-0.91687
cc-pvdz	5	7	-2.855160	-0.91415
cc-pvtz	14	18	-2.861153	-0.91763
cc-pvqz	30	38	-2.861514	-0.91785
cc-pv5z	55	73	-2.861624	-0.91792

NOTE:

- only s-functions play a role

HF limit



basis set size : cc-pVDZ - cc-pV5Z

5. Post-HF description

Method	6-311G	6-311G(d,p)
hf	-2.859895	-2.859895
mp2	-2.872802	-2.884577
mp3	-2.875503	-2.889403
mp4	-2.876169	-2.890341
CID	-2.876289	-2.890484
CISD	-2.876418	-2.890571
CCD	-2.876289	-2.890484
CCSD	-2.876418	-2.890571

Notes:

- CID/CCD and CISD/CCSD gives the same energies
- CID and CISD does not give the same energies

CPU dependence on the size of the system:

Basis set	# BF	E(HF)	full CI
cc-pvdz	5	-2.855160	-2.88759
cc-pvtz	14	-2.861153	-2.90023
cc-pvqz	30	-2.861514	-2.90241
cc-pv5z	55	-2.861624	-2.90315

Method	Formal	Actual
SCF	B^4	$B^{2.7}$
MP2	OB^4	O^2B^3
MP4, QCISD(T)	O^3V^4	O^3V^4
Full CI	$((O+V)!/O!V!)^2$	
B...	total number of basis functions	
O...	number of occupied orbitals	
V...	number of unoccupied orbitals	

Stationary Schrödinger equation

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

CCSD(T)

Non-relativistic Hamiltonian
Born-Oppenheimer approximation
Electron Density $\rho(\vec{r}) = \sum_i^{occ} |\varphi_i(\vec{r})|^2$
One-el. Functions $\varphi_i(1) = \sum_{\mu} c_{i\mu} \chi_{\mu}(1)$

Hybrid functionals
B3LYP, B3PW91, ...

Generalized gradient approximation (GGA)
 $E \equiv E[\rho, \nabla\rho]$
PW91, BP86, BLYP, PBE, ...

Expansion over Slater det.
 $\Phi = C_0\Psi_0 + C_S\Psi_S + C_D\Psi_D + \dots$

MP2

Electron correlation

Traditional \longleftrightarrow DFT
Ab initio

Model of independent electrons
 $\hat{H}^{el}(i, j) \equiv \sum_i V^{eff}(i)$

Non-interacting reference system
Kohn-Sham orbitals

Hartree-Fock method
 $\phi_1(1) \dots$ HF orbitals
 $\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \det|\varphi_1(1)\varphi_2(2)\dots\varphi_n(n)|$
Electron correlation neglected

Local density approximation
LDA (LSD, SVWN)
 $E \equiv E[\rho]$

Post-HF methods

Density functional theory

Traditional *ab initio*: finding the N-electron wavefunction $\Psi(1,2,\dots,N)$ depending on 4N coord.
DFT: finding the total electron spin-densities depending on 8 coordinates

Hohenberg & Kohn:

Theorem I: Energy of the system is unique functional of electron density

$$\rho(\vec{r}) \Rightarrow N_{el}, \{R_J, Z_J\} \Rightarrow V_{ext} \Rightarrow \hat{H} \Rightarrow E, \Psi$$

Theorem II: Variational principle $E_0[\rho] \leq E[\tilde{\rho}]$

$$E_0[\rho_0] = \underbrace{\int \rho_0(\vec{r}) V_{Ne} d\vec{r}}_{\text{system dependent}} + \underbrace{T[\rho_0] + E_{ee}[\rho_0]}_{\text{universally valid}}$$

Hohenberg-Kohn functional:

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + F_{HK}[\rho_0]$$

Kinetic energy of electron
Coulomb repulsion
Non-classical interaction
(self-interaction, exchange, and correlation)

All properties are determined by the ground state density
H&K only proved that F_{HK} exist, however, we do not know it
H&K do not give a direction how can we find density

H&K theorems allow us to construct the rigorous many-body theory using density as a fundamental properties

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{ncI}[\rho(\vec{r})]$$

Kohn-Sham method:

In analogy with HF method they introduce non-interacting reference system with effective local potential V_s :

$$\hat{H}_s = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_s(\vec{r}_i)$$

$\frac{1}{\sqrt{N!}}$	$\varphi_1(\vec{x}_1)$	$\varphi_2(\vec{x}_1)$...	$\varphi_N(\vec{x}_1)$
	$\varphi_1(\vec{x}_2)$	$\varphi_2(\vec{x}_2)$		$\varphi_N(\vec{x}_2)$
	\vdots	\vdots		\vdots
	$\varphi_1(\vec{x}_N)$	$\varphi_2(\vec{x}_N)$...	$\varphi_N(\vec{x}_N)$

$$\hat{f}^{KS} \quad \varphi_i = \varepsilon_i \varphi_i$$

Kohn-Sham equations

$$\hat{f}^{KS} = -\frac{1}{2} \nabla^2 + V_s(\vec{r})$$

Problematic kinetic energy term is divided between non-interacting system and exchange-correlation functional:

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})]$$

$$E_{xc}[\rho] \equiv (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{ncl}[\rho]$$

$T_c = T - T_s$... the residual part of kinetic energy

How does it work:

$$\begin{aligned}
 E[\rho(\vec{r})] &= T_s[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho] = T_s[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] + \int V_{Ne} \rho(\vec{r}) d\vec{r} \\
 &= -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \iint |\varphi_i(\vec{x}_1)|^2 \frac{1}{r_{12}} |\varphi_j(\vec{x}_2)|^2 d\vec{x}_1 d\vec{x}_2 + E_{XC}[\rho(\vec{r})] - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{iA}} |\varphi_i(\vec{x}_1)|^2 d\vec{x}_1
 \end{aligned}$$

Applying variational principle we solve Kohn-Sham equations in iterative way

Everything “unknown” is in E_{XC}

If we know E_{XC} we have an EXACT method

E_{XC} is not know => we have to rely of approximate exchange correlation functionals

Exchange-correlation functionals:

- I. local density approximation - $E_{XC}[\rho]$
- II. Generalized Gradient approx. - $E_{XC}[\rho, \nabla\rho]$
- III. Meta GGA - $E_{XC}[\rho, \nabla\rho]$ ($E_{XC} = E_x + E_c + E_{tc}$)
- IV. Hybrid density functionals - $E_{XC}[\rho, \nabla\rho]$ + combines with “exact”=HF exchange

Local Density Approximation: (LDA ~ LSD ~ SWWN)

E_{XC} derived for the model of uniform electron gas

$$\begin{aligned}
 E_{XC}^{LDA}[\rho] &= \int \rho(\vec{r}) \varepsilon_{XC}(\rho(\vec{r})) d\vec{r} \\
 \varepsilon_{XC}(\rho(\vec{r})) &= \varepsilon_X(\rho(\vec{r})) + \varepsilon_C(\rho(\vec{r}))
 \end{aligned}$$

$$\varepsilon_X = -\frac{3}{4} \sqrt{\frac{3}{\pi} \rho(\vec{r})}$$

S ... used by Slater

ε_C (fit of QMC data) **VWN**

Generalized Gradient Approximation: (GGA)

E_{XC} depends not only on density but also on the density gradients

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla \rho_\alpha, \nabla \rho_\beta) d\vec{r}$$

Particular forms of GGA functionals should be rather viewed as mathematical concept

$$E_X^{GGA} = E_X^{LSD} - \sum_\sigma \int F(s_\sigma) \rho_\sigma^{4/3}(\vec{r}) d\vec{r} \quad s_\sigma(\vec{r}) = \frac{|\nabla \rho_\sigma(\vec{r})|}{\rho_\sigma^{4/3}(\vec{r})}$$

Reduced density gradient

$$F^B = \frac{\beta s_\sigma^2}{1 + 6\beta s_\sigma \sinh^{-1} s_\sigma}$$

Example: E_X derived by Becke ... **B (=B88)**
 $\beta=0.0042$ (empirical)

Hybrid Density Functionals:

HF exchange is mixed into the functional form

$$E_{XC}^{B3} = E_{XC}^{LSD} + a(E_{XC}^{\lambda=0} - E_X^{LSD}) + bE_X^B + cE_C^{PW91}$$

Example: B3PW91 (Becke)
a, b, and c - fitted parameters

Several most commonly used functionals

Abbreviation	Type	Exchange part	Correlati on part	Authors
S	LDA	+	-	Slater (Dirac)
VWN	LDA	-	+	Vosko, Wilk, Nusair (1980)
B, B88	GGA	+	-	Becke (1988)
LYP	GGA	-	+	Lee, Young, Parr (1988)
PW91	GGA	+	+	Perdew, Wang (1992)
P86 (P)	GGA	-	+	Perdew (1986)
PBE	GGA	+	+	Perdew, Burke, Ernzerhof (1996)
B3	Hybrid	+	-	Becke

Dipole moments for selected molecules [in D, 1 D = 0.3934 a.u.]

Molecule	HF POL ^a	MP2 POL ^a	SVWN numerical ^b	SVWN TZVP-FIP ^c	BLYP TZVP-FIP ^c	BLYP POL ^a	BLYP 6-31G(d) ^d	B3LYP cc-pVTZ	B3LYP POL ^a	Exp.
CO	-0.25	0.31	0.23	0.24	0.19	0.19	0.15	0.13	0.10	0.11
H ₂ O	1.98	1.85	1.86	1.88	1.83	1.80	2.04	1.92	1.86	1.85
H ₂ S	1.11	1.03	1.15	1.15	1.07	0.97		1.19	1.01	0.97
HF	1.92	1.80	1.80	1.81	1.76	1.75	1.81	1.83	1.80	1.83
HCl	1.21	1.14				1.08		1.21	1.12	1.11
NH ₃	1.62	1.52	1.53	1.57	1.52	1.48	1.90	1.59	1.52	1.47
PH ₃	0.71	0.62				0.59		0.53	0.62	0.57
SO ₂	1.99	1.54				1.57		2.01	1.67	1.63

^a taken from Cohen and Tanirungrotechai, 1999;^b taken from Dickson and Becke, 1996 ^c taken from Calaminici, Jug and Köster, 1998, ^d taken from Johnson, Gill and Pople, 1993

Barrier heights of H₂ + H → H + H₂ [in kcal/mol]

Method	barrier without SIC	barrier with SIC
LSD	-2.3	5.7
BLYP	2.9	12.6
BPW91	4.7	14.3
B3LYP	4.1	11.1
exp.		9.7

Taken from Johnson, 1995 and Csonka and Johnson, 1998

Compilation of mean absolute deviations for bond lengths [Å] / bond angles [degrees] for small main group molecules from different sources.

32 first row species, 6-31G(d) basis set, Johnson, Gill, and Pople, 1993			
HF	0.020 / 2.0	SVWN	0.021 / 1.9
MP2	0.014 / 1.8	BLYP	0.020 / 2.3
QCISD	0.013 / 1.8		

13 species, Martin, El-Yazal, and François, 1995a			
CCSD(T)/cc-pVDZ	0.018 / 2.2	B3LYP/cc-pVDZ	0.009 / 1.7
CCSD(T)/cc-pVTZ	0.014 / 0.6	B3LYP/cc-pVTZ	0.004 / 0.3
CCSD(T)/cc-pVQZ	0.002 / 0.4	B3LYP/cc-pVQZ	0.004 / 0.3

40 species cont. third row elements, 6-31G(d) basis set, Redfern, Blauddau and Curtiss, 1997			
MP2	0.022 / 0.4	B3LYP	0.030 / 0.5
BLYP	0.048 / 1.0	B3PW91	0.020 / 0.5
BPW91	0.020 / 0.5		

^a uncontracted aug-cc-pVTZ basis

Deviations between computed atomization energies and experiment for the JGP test set employing the 6-31G(d) basis set [in kcal/mol]. Taken from Johnson, Gill and Pople, 1993.

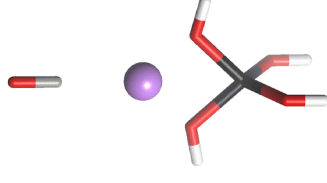
	HF	MP2	QCISD	SVWN	SLYP	BVWN	BLYP
mean abs. dev. ^a	86	22	29	36 (40) ^a	38	4 (4) ^a	6
mean dev.	-86	-22	-29	36 (40) ^a	38	0 (4) ^a	1

^a Basis set free results taken from Becke, 1992.

EXAMPLE #1 - Reliability of methods for interaction energies

Interaction energy (kJ/mol) for $\text{CO} + \text{M}^+ \text{Al}(\text{OH})_4^-$

		Na^+		Cu^+	
Method	Basis set	$E_{(\text{BSSE})}$	E	$E_{(\text{BSSE})}$	E
Post HF	CCSD(T)	-26	-192	-159	
	MP2	-28	-242	-209	
HF	cc-pVQZ ^a	-22	-26	-21	
DFT	LDA	-34	-288	-262	
	PBE	-29	-240	-210	
	BP86	-23	-232	-205	
	BLYP	-25	-216	-186	
	hybrid	B3LYP	-26	-180	-155



1-T cluster model

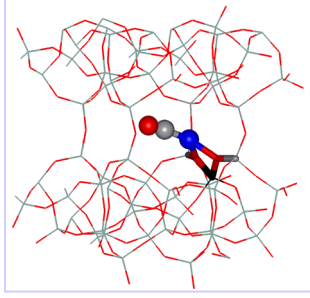
- CCSD(T) - reference energies
- HF - complete failure !
- Hybrid DFT (B3LYP) - remarkable agreement
- LDA - systematic overestimation
- GGA, MP2 - good agreement for simple interaction (Na^+), 20% error (overestimated) for complicated system (Cu^+)

EXAMPLE #2 - Model convergence for interaction energies

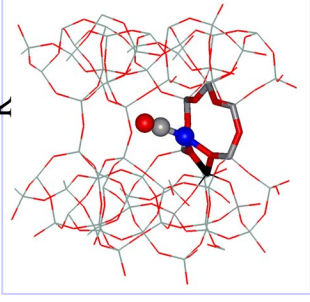
CO interaction energies with Cu⁺/FER
Cu⁺ at the P6/T1 site

ΔE^{el} (kJ/mol)

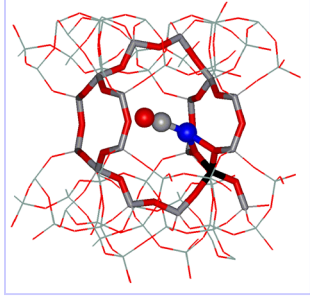
3-T



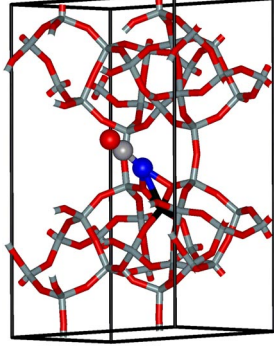
6-T_R



17-T



periodic UC



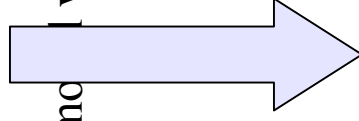
-201

-135

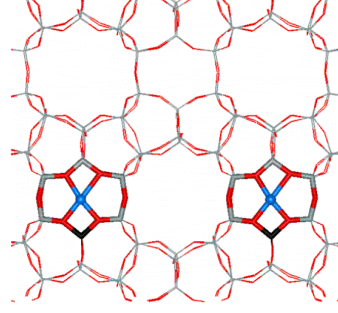
-139

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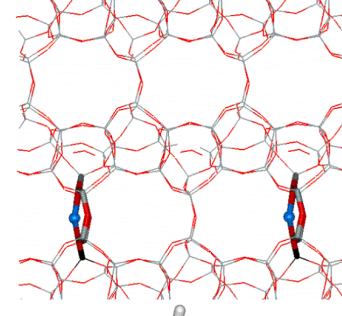
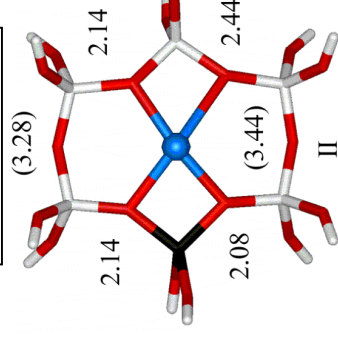
Combined QM/MM model with increasing inner part size
PBE/VTZP + BSSE



6-T cluster model:
-148 kJ/mol



P6/T1 site

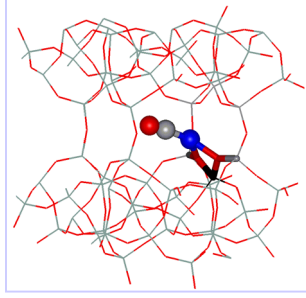


EXAMPLE #2 - Model convergence for interaction energies

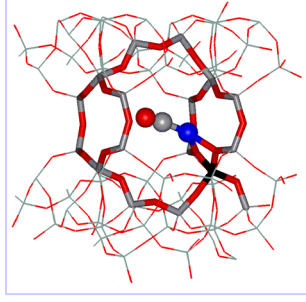
CO interaction energies with Cu⁺/FER
Cu⁺ at the P6/T1 site

ΔE^{el} (kJ/mol)

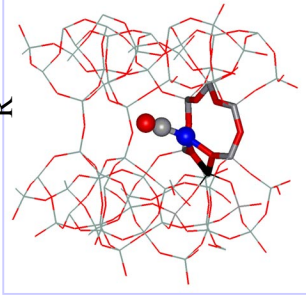
3-T



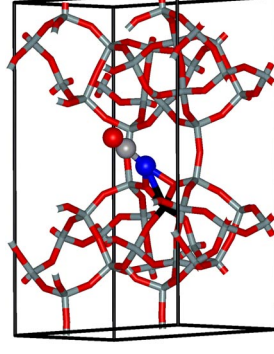
17-T



6-T_R



periodic UC



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Combined QM/MM model with increasing inner part size
PBE/VTZP + BSSE

!

!

Experiment: -86 kJ/mol

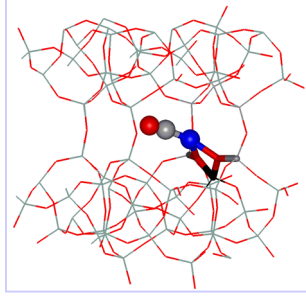
*TPD analysis - Stud. Surf. Sci. Catal., 158 (2005) 925.
(RTN-056)*

EXAMPLE #2 - Model convergence for interaction energies

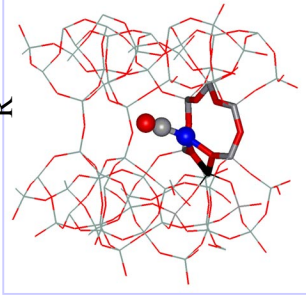
CO interaction energies with Cu⁺/FER Cu⁺ at the P6/T1 site

Experiment: $\Delta H^\circ(300) = -86$ kJ/mol

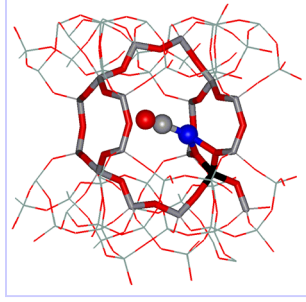
3-T



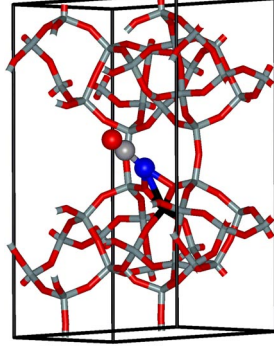
6-T_R



17-T



periodic UC



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1. PBE overestimates interaction energies

6-T_R QM/MM model reasonably good.

=> B3LYP QM/MM calculations with 6-T_R inner part

=> $\Delta E^{\text{el}} = -82$ kJ/mol

Interaction energy (kJ/mol) for CO + M⁺Al(OH)₄⁻

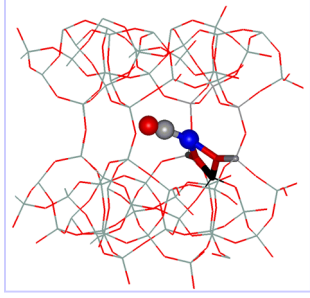
Method	Basis set	Na ⁺		Cu ⁺	
		E _(BSSE)	E	E	E _(BSSE)
Post HF	CCSD(T)	cc-pVQZ ^a	-26	-192	-159
	MP2	cc-pVQZ ^a	-28	-242	-209
HF	HF	cc-pVQZ ^a	-22	-26	-21
DFT	LDA	VTZP ^b	-34	-288	-262
	PBE	VTZP ^b	-29	-240	-210
	BP86	VTZP ^b	-23	-232	-205
	BLYP	VTZP ^b	-25	-216	-186
hybrid	B3LYP	VTZP ^b	-26	-180	-155

EXAMPLE #2 - Model convergence for interaction energies

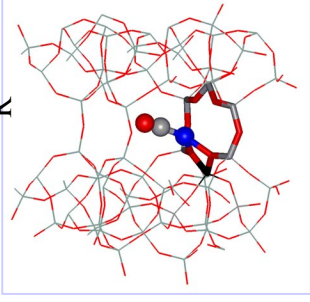
CO interaction energies with Cu⁺/FER
Cu⁺ at the P6/T1 site

Experiment: $\Delta H^\circ(300) = -86$ kJ/mol

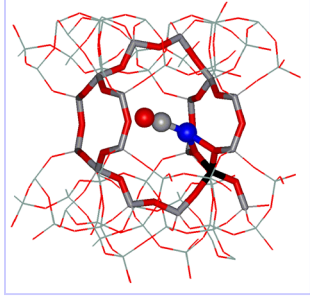
3-T



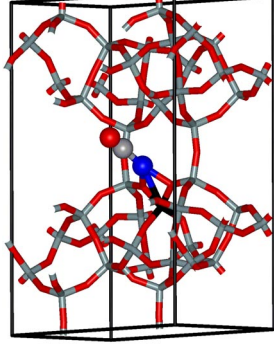
6-T_R



17-T



periodic UC



-201

-135

-139

-141

1. PBE overestimates interaction energies
2. Calculations: ΔE^{el}

$$\Delta H^\circ(300) = \Delta E^{\text{el}} + \Delta ZPE + \Delta U^\circ(\text{rot,trans}) + pV$$

(-82	+6	-6	-3)
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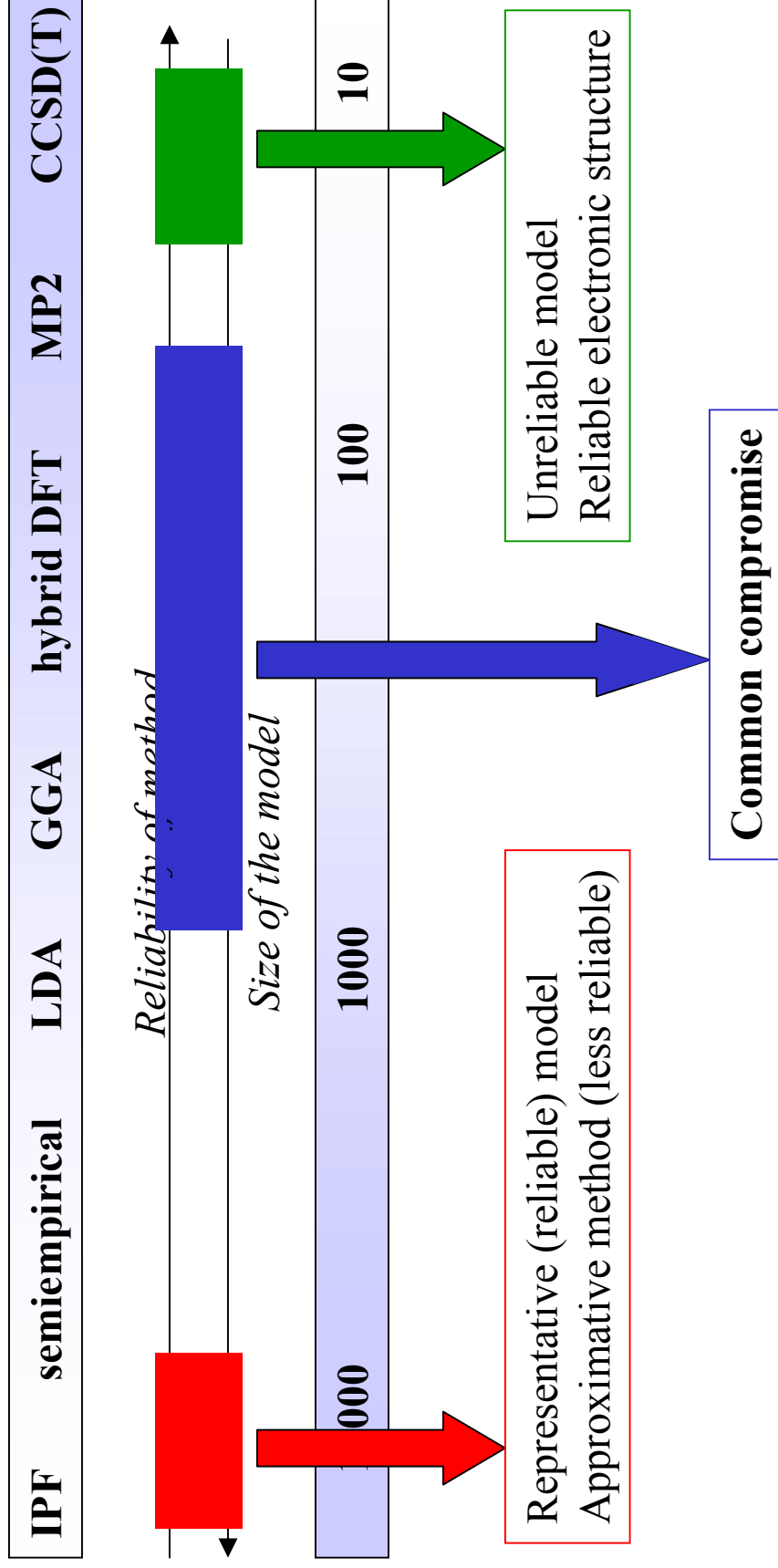
Calculations: $\Delta H^\circ(300) = -85$ kJ/mol

SUMMARY

- Almost every property can be calculated
- Qualitatively correct description (providing a reasonably appropriate model/method is used)
- Quantitative agreement with experiment - much more difficult to achieve
either a reliable method
or representative model

Selecting a proper model/method:

Compromise between model size and method reliability



SUMMARY

- Almost every property can be calculated
- Qualitatively correct description (providing a reasonably appropriate model/method is used)
- Quantitative agreement with experiment - much more difficult to achieve
*either a reliable method
or representative model*

=> in order to get quantitative agreement with experiment - extrapolation required

! • A perfect agreement between theory and experiment reached with approximate method or small cluster model is always suspicious (*error compensation*)

Literature:

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- P. Čársky a M. Urban: *Ab initio výpočty v chemii*, SNTL, Praha 1985.
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- A. Szabo a N. S. Ostlund: *Modern Quantum Chemistry*, McGraw-Hill, New York 1982.
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