

C7790 Introduction to Molecular Modelling

TSM Modelling Molecular Structures

Lesson 12 Quantum Chemistry I

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Context

macroworld

states

(thermodynamic properties, G, T,...)

phenomenological thermodynamics

equilibrium (equilibrium constant)

kinetics (rate constant)

free energy
(Gibbs/Helmholtz)



partition function

statistical thermodynamics

microstates

(mechanical properties, E)

microstate \neq microworld

microworld

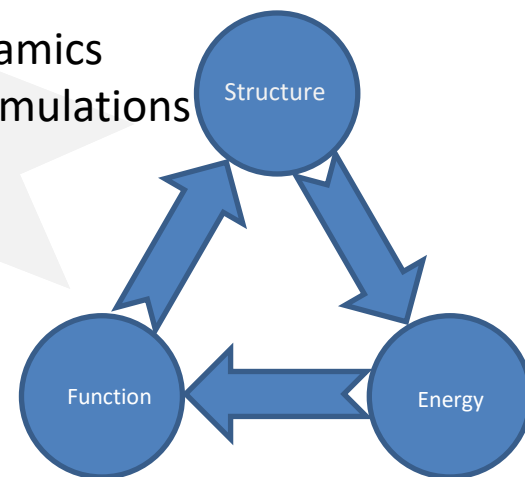
Description levels (model chemistry):

quantum mechanics

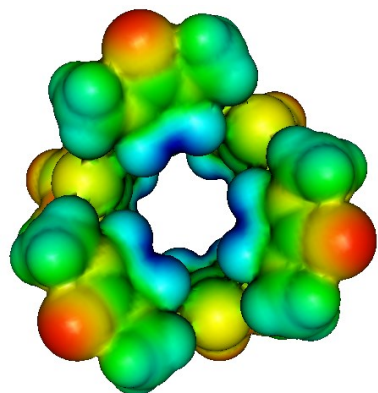
- semiempirical methods
- ab initio methods
- post-HF methods
- DFT methods
- molecular mechanics
- coarse-grained mechanics

Simulations:

- molecular dynamics
- Monte Carlo simulations
- docking
- ...



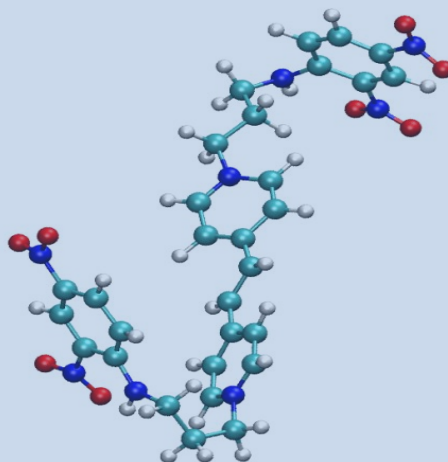
Method overview (model chemistry)



QM (Quantum mechanics)

$$E(\mathbf{R})$$

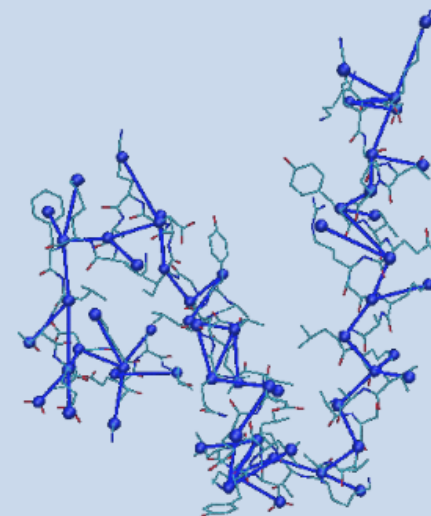
R - position of atom nuclei



MM (Molecular mechanics)

$$E(\mathbf{R})$$

R - position of atoms



CGM (Coarse-grained mechanics)

$$E(\mathbf{R})$$

R - position of beads

Quantum chemistry I

Multi-electron systems

Approximations:

- Born-Oppenheimer approximation
- **One-electron approximation**
- **Basis functions**

Finding the solution

SE is complicated differential equation:

$$\hat{H}\psi_k(\mathbf{r}, \mathbf{R}) = E_k(\mathbf{R})\psi_k(\mathbf{r}, \mathbf{R})$$

(the devil is a kinetic operator)

- Instead of searching for all possible solutions, let's focus on a ground state.
- The **ground state** is the state with the lowest energy E_0 .
- Since E_k are electronic states, it can be expected that for the most systems that the ground state will determine the essential behavior of the system.

$$E_0 < E_1 < E_2 < \dots$$


The ground state can be found by a variational method.

Alternative: a perturbation method.

Variational method

$$\hat{H}\psi_k(\mathbf{r}, \mathbf{R}) = E_k(\mathbf{R})\psi_k(\mathbf{r}, \mathbf{R}) \quad \text{differential form}$$

The **variational method** employs variational calculus. The method essence is to find the local extreme of **functional**, which is the way how to transform functions on real numbers. Such a representation is the relationship between energy and wave function expressed in integral form:


$$E(\mathbf{R}) = \frac{\int_{\Omega} \Psi^*(\mathbf{r}, \mathbf{R}) \hat{H} \Psi(\mathbf{r}, \mathbf{R}) d\tau}{\int_{\Omega} \Psi^*(\mathbf{r}, \mathbf{R}) \Psi(\mathbf{r}, \mathbf{R}) d\tau}$$

integral form (fully equivalent to SE)

$$d\tau = d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_n$$

integrates across all electrons and the entire space Ω

Variational method

$$E_k = E[\Psi_k] = \frac{\int \Psi_k^* \hat{H} \Psi_k d\tau}{\int \Psi_k^* \Psi_k d\tau} = \text{min!}$$

The wave function, which provides the minimum value of the integral, is a solution of the Schrödinger equation. **The global minimum of a functional is the energy of the ground state**, which implies:

$$\Psi \neq \Psi_0$$

$$E > E_0$$

The inaccurate wave function always provides a higher value of energy.

Hartree-Fock method

Finding a wave function

Finding of wavefunction is practically impossible because it is a function of all electron positions. Possible simplification is **one-electron approximation**:

Hartree's method

$$\Psi(r_1, r_2, \dots, r_n) = \varphi_1(r_1)\varphi_2(r_2)\dots\varphi_n(r_n)$$

Similar approach was employed for:

- time-independent SE
- BO approximation

Finding a wave function

Finding of wavefunction is practically impossible because it is a function of all electron positions. Possible simplification is **one-electron approximation**:

Hartree's method

$$\Psi(r_1, r_2, \dots, r_n) = \varphi_1(r_1)\varphi_2(r_2)\dots\varphi_n(r_n)$$

Hartree's method does not consider important properties of multi-electron systems. Electrons are **indistinguishable fermions** (particles with half spin), which they must comply with **Pauli Exclusion Principle**:

no two indistinguishable fermions can be in the same quantum state

The wave function of the system must be **antisymmetric**. Antisymmetric wave functions can be obtained by all permutations between one-electron functions and spatial and spin coordinates.

Antisymmetric wave function:

$$\Psi(r_1, r_2, \dots, r_n, \sigma_1, \sigma_2, \dots, \sigma_n) = -\Psi(r_1, r_2, \dots, r_n, \sigma_2, \sigma_1, \dots, \sigma_n)$$

$$\Psi(r_1, r_2, \dots, r_n, \sigma_1, \sigma_2, \dots, \sigma_n) = -\Psi(r_2, r_1, \dots, r_n, \sigma_1, \sigma_2, \dots, \sigma_n)$$

↑
spatial coordinates of electrons

↑
spin coordinates of electrons (z-component of spin)

One-electron approximation

Hartree-Fock method

$$\Psi(r_1, r_2, \dots, r_n, \sigma_1, \sigma_2, \dots, \sigma_n) = \sum_P \text{sign}(P) \{ \varphi_1(r_1) \chi_1(\sigma_1) \varphi_2(r_2) \chi_2(\sigma_2) \dots \varphi_n(r_n) \chi_n(\sigma_n) \}$$

all permutations

z-component of spin (spin coordinate)

spin part of one-electron function

Alternative notation: **Slater determinant**

$$\Psi(r_1, r_2, \dots, r_n, \sigma_1, \sigma_2, \dots, \sigma_n) = \begin{vmatrix} \varphi_1(r_1) \chi_1(\sigma_1) & \varphi_2(r_1) \chi_2(\sigma_1) & \dots & \varphi_n(r_1) \chi_n(\sigma_1) \\ \varphi_1(r_2) \chi_1(\sigma_2) & \varphi_2(r_2) \chi_2(\sigma_2) & \dots & \varphi_n(r_2) \chi_n(\sigma_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(r_n) \chi_1(\sigma_n) & \varphi_2(r_n) \chi_2(\sigma_n) & \dots & \varphi_n(r_n) \chi_n(\sigma_n) \end{vmatrix}$$

One-electron functions

- Even with one-electron approximation, finding one-electron functions is difficult.
- Thus, one-electron functions are expressed using a linear combination of basis functions.
- This description is **exact** if we use **complete system of basis functions** (infinitely large set of orthonormal functions).
- The problem is then reduced to finding linear coefficients c , which determine extent of given basis functions to searched one-electron functions.

$$\varphi_i(\mathbf{r}_i) = \sum_{j=1}^m c_{ij} \chi_j(\mathbf{r}_i)$$

one-electron function
(molecular/atomic orbital)

for multielectron atoms

searched numbers

pre-defined basis functions

The diagram illustrates the equation $\varphi_i(\mathbf{r}_i) = \sum_{j=1}^m c_{ij} \chi_j(\mathbf{r}_i)$. A blue arrow points from the text 'one-electron function (molecular/atomic orbital)' to the symbol $\varphi_i(\mathbf{r}_i)$. Another blue arrow points from the text 'for multielectron atoms' to the same symbol. A blue arrow points from the text 'searched numbers' to the coefficient c_{ij} . Two blue arrows point from the text 'pre-defined basis functions' to the basis function symbols $\chi_j(\mathbf{r}_i)$.

Basis functions

$$\varphi_i(\mathbf{r}_i) = \sum_{j=1}^m c_{ij} \chi_j(\mathbf{r}_i)$$

← pre-defined basis functions

From a practical (numerical) point of view, it is necessary to use **limited number of basis functions**.

Basis function choice affects **speed** of calculation and **accuracy** of achieved results.

Basis set types:

- atomic orbitals (atom centered) are usually derived from simplified SE solution for hydrogen atom
 - GTO - Gaussian Type Orbital
 - STO - Slater Type Orbital (more accurate but more complicated)
- plane waves - solid state physics

HF method

The HF method tries to find such c , which minimizes energy functional.

one-electron molecular orbitals

$$\varphi_i(\mathbf{r}_i) = \sum_{j=1}^m c_{ij} \chi_j(\mathbf{r}_i)$$

occupied orbitals

system WF

$$\Psi_0(r_1, r_2, \dots, r_n, \sigma_1, \sigma_2, \dots, \sigma_n) = \sum_P \text{sign}(P) \{ \varphi_1(r_1) \chi_1(\sigma_1) \varphi_2(r_2) \chi_2(\sigma_2) \dots \varphi_n(r_n) \chi_n(\sigma_n) \}$$

variational method

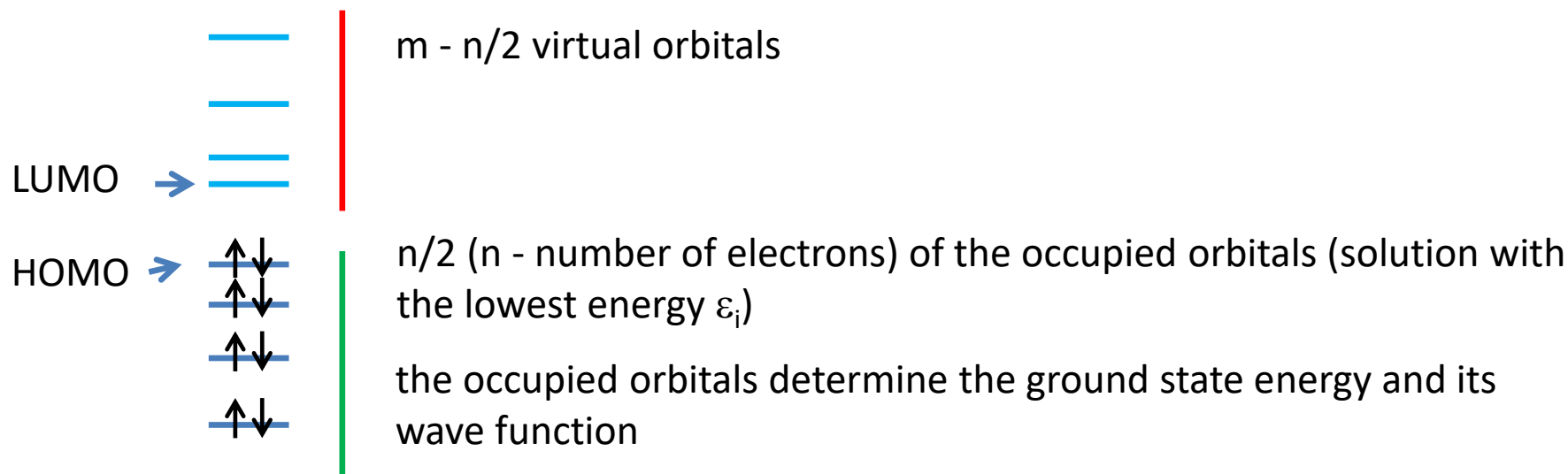
$$E_0 = E[\Psi_0] = \min!$$

RHF method

RHF - (**Restricted Hartree-Fock Method**) is applicable to closed systems (closed shell systems), where each molecular orbital contains exactly two electrons with opposite spin. Using the variational method, one-electron approximation and linear combination of basis functions, the solution can be found solving a generalized eigenproblem:

$$\mathbf{F}\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_i$$

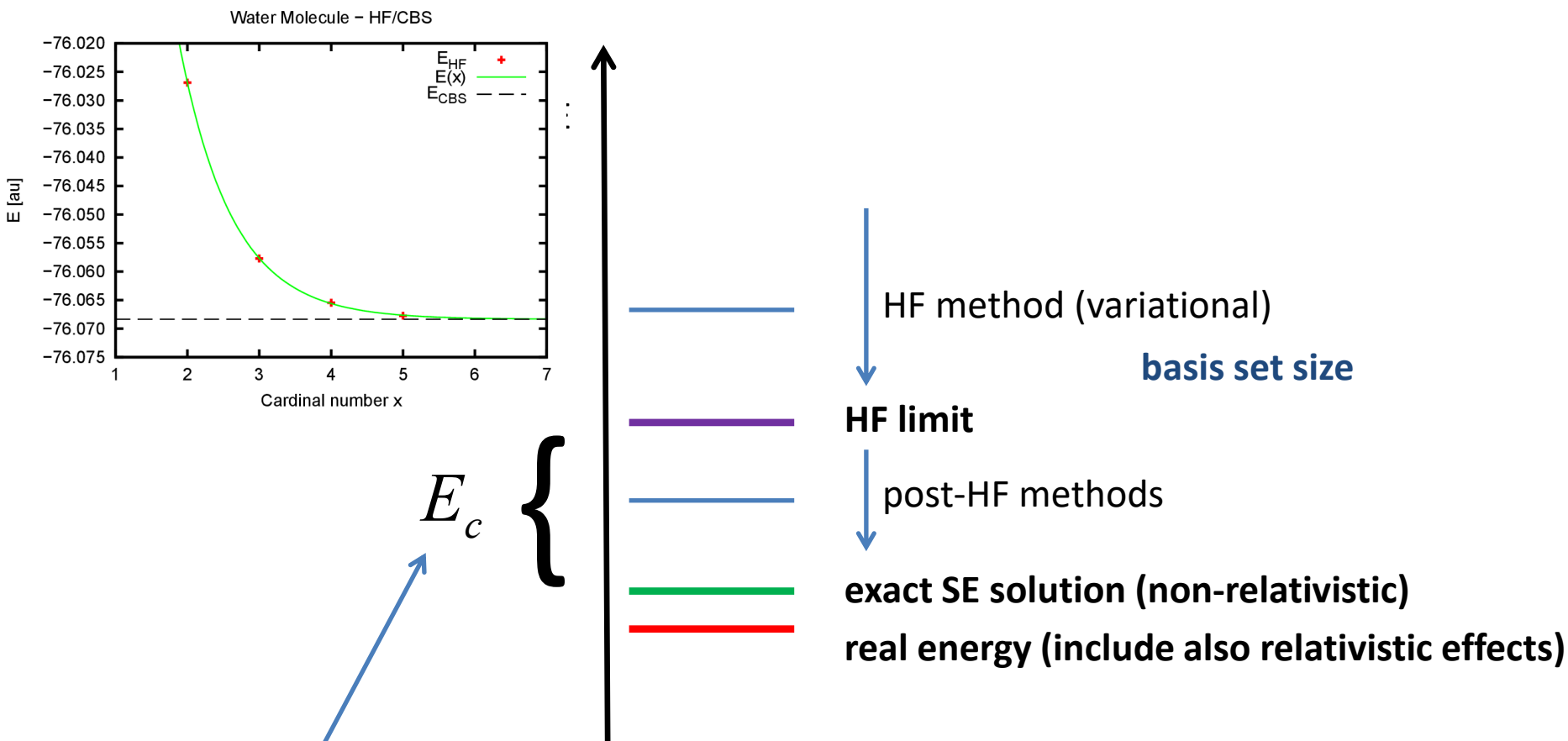
The solution is m (basis set size) of eigenvalues ε and vectors \mathbf{c} . Eigenvalues ε represent the energy of one-electron functions (orbitals).



Summary

- The HF method is starting point for other QM methods
- HF is a variational method
- It uses two approximations:
 - one-electron approximation (**very bad approximation**)
 - **correlation energy** (post-HF methods)
 - finite number of basis functions
 - correction is possible by extrapolation to a complete basis

Correlation energy



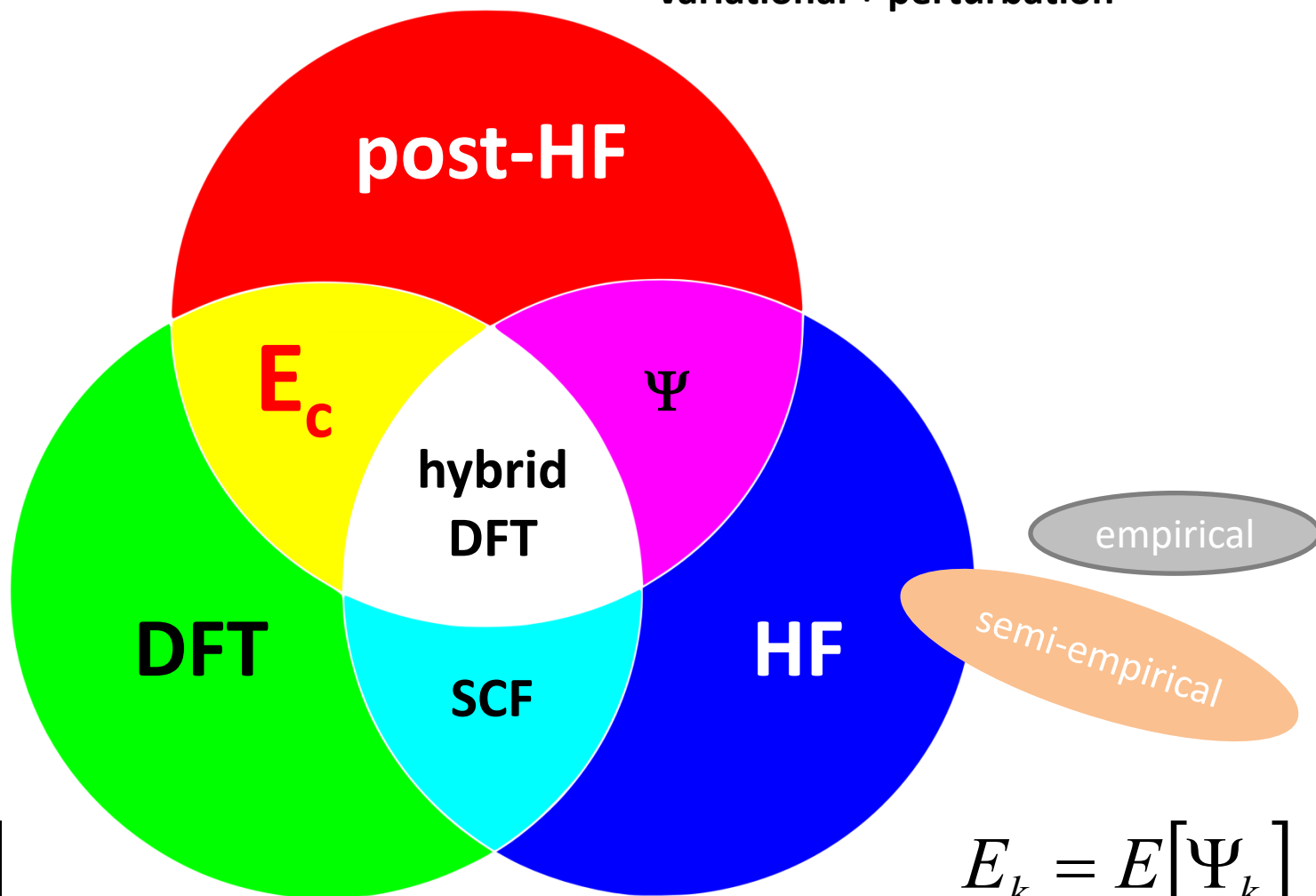
correlation energy – it is not included in the HF method **because one-electron approximation**

correlation energy is always negative because electron repulsion is overestimated by the HF method

Quantum chemical methods

Method classification

variational + perturbation



$$E_k = E[\rho_k]$$

$$E_k = E[\Psi_k]$$

variational

Andrew Gilbert

Quantum chemistry

time-independent Schrödinger equation

$$\hat{H}_e \psi_k(\mathbf{r}, \mathbf{R}) = E_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R})$$

| Formal scaling | Methods | | | |
|---------------------------------------|---------|------------|---------------|--------------------------|
| | HF | CI methods | MP methods | CC methods |
| $N^4 \rightarrow N^2 \rightarrow N^1$ | HF, DFT | | | |
| N^5 | | | MP2 | CC2 (iterative) |
| N^6 | | CISD | MP3, MP4(SDQ) | CCSD (iterative) |
| N^7 | | | MP4 | CCSD(T), CC3 (iterative) |
| N^8 | | CISDT | MP5 | CCSDT |
| N^9 | | | MP6 | |
| N^{10} | | CISDTQ | MP7 | CCSDTQ (iterative) |

scaling, time complexity: http://en.wikipedia.org/wiki/Time_complexity

HF - Hartree-Fock method, DFT - density theory functionals,

CI - configuration interaction method, MP - Møller-Plesset perturbation method,

CC - coupled-clusters method, N - number of basis functions

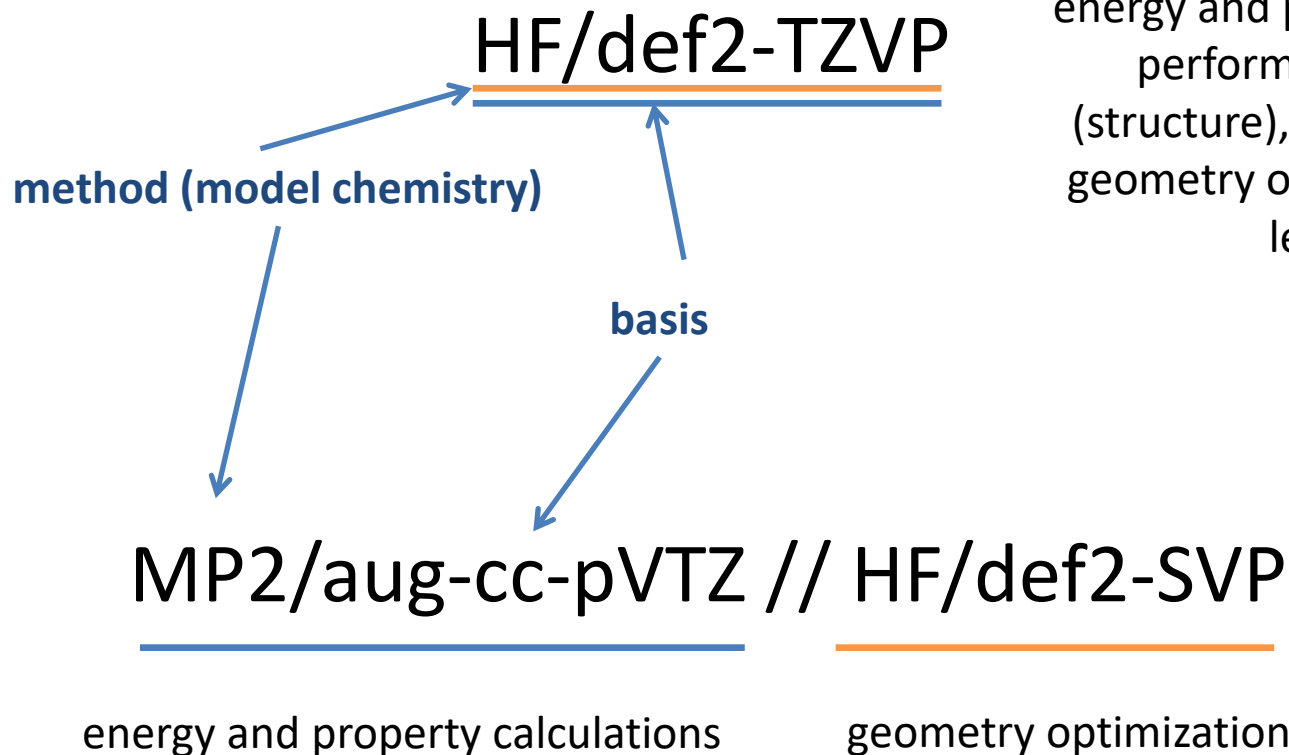
Jensen, F. Introduction to computational chemistry; 2nd ed.; John Wiley & Sons: Chichester, England; Hoboken, NJ, 2007.

QM method overview

Classification by theoretical approaches and approximations:

- empirical methods
 - extended Hückel method (EHT)
 -
- semi-empirical methods
 - AM1
 - PM3, PM6, PM7
 - ...
- ***ab initio* methods**
 - Hartree-Fock (HF) method
 - post-HF methods
 - Møller-Plesset method (MP2, MP3, ...)
 - coupled-clusters method (CC)
 - ...
- **density functional theory (DFT)**
 - LDA
 - GGA (BLYP, TPSS, PBE, ...)
 - hybrid (B3LYP, M06-2X, ...)

Method designation



energy and property calculations are performed on the geometry (structure), which was obtained by geometry optimization at the same level of theory