C7790 Introduction to Molecular Modelling
TSM Modelling Molecular Structures

Lesson 12
Quantum Chemistry I

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Context

| **macroworld** | **microworld** |

states

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

Description levels (model chemistry):

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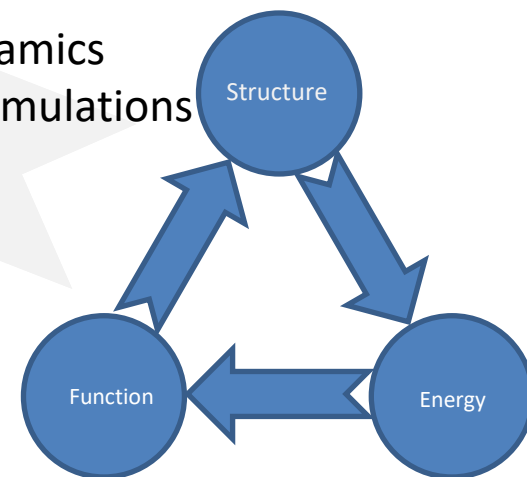
- quantum mechanics
 - semiempirical methods
  - ab initio methods
  - post-HF methods
  - DFT methods
- molecular mechanics
- coarse-grained mechanics

equilibrium (equilibrium constant)
kinetics (rate constant)

free energy
(Gibbs/Helmholtz)

Simulations:

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

partition function

statistical thermodynamics

microstates

(mechanical properties, E)

microstate ≠ microworld

Structure

Function

Energy

Method overview (model chemistry)
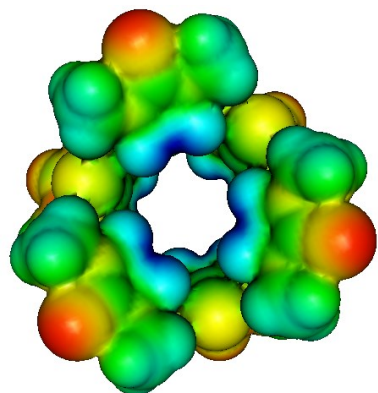
QM (Quantum mechanics)	MM (Molecular mechanics)	CGM (Coarse-grained mechanics)
$E(\mathbf{R})$	$E(\mathbf{R})$	$E(\mathbf{R})$
R - position of atom nuclei	R - position of atoms	R - position of beads
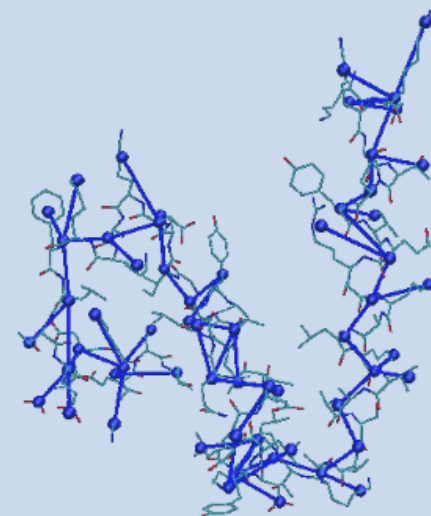
Quantum chemistry I

Multi-electron systems

Approximations:
- ➢ Born-Oppenheimer approximation
- ➢ **One-electron approximation**
- ➢ **Basis functions**

Chemical system

Hamiltonian of chemical system consisting of N nuclei of mass M and charge Z and n electrons is given by:

kinetic energy operator   potential energy

$$\hat{H} = -\frac{1}{2m}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{Z_i Z_j}{r_{ij}} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i}{r_{ij}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

electrons   nucleus-nucleus   electron-electron

electron-nucleus

Nuclei motion is not considered in the BO approximation.

Schrödinger equation:

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

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, lets 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.

$$\boxed{E_0} < E_1 < E_2 < \ldots$$

The ground state can be found be a variational method.

Alternative: a perturbation method.

Variational method

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

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:

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

integral form (fully equivalent to SE)

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

integrates across all electrons and the entire space Ω

Variational method

$$E_k = E[\Psi_k] = \frac{\displaystyle\int_{\boldsymbol{\Omega}} \Psi_k^* \hat{H} \Psi_k \, d\boldsymbol{\tau}}{\displaystyle\int_{\boldsymbol{\Omega}} \Psi_k^* \Psi_k \, d\boldsymbol{\tau}} = \min!$$

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

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

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

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

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:

$$\Psi(r_1, r_2, ..., r_n, \sigma_1, \sigma_2, ..., \sigma_n) = -\Psi(r_1, r_2, ..., r_n, \sigma_2, \sigma_{1,}..., \sigma_n)$$

$$\Psi(r_1, r_2, ..., r_n, \sigma_1, \sigma_2, ..., \sigma_n) = -\Psi(r_2, r_1, ..., r_n, \sigma_1, \sigma_{2,}..., \sigma_n)$$

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

One-electron approximation

Hartree-Fock method

$$\Psi(r_1, r_2, ..., r_n, \sigma_1, \sigma_{2,} ..., \sigma_n) = \sum_P sign(P)\{\varphi_1(r_1)\chi_1(\sigma_1)\varphi_2(r_2)\chi_2(\sigma_2)...\varphi_n(r_n)\chi_n(\sigma_n)\}$$

all permutations

z-component of spin (spin coordinate)

spin part of one-electron function

Alternative notation: **Slater determinant**

$$\Psi(r_1, r_2, ..., r_n, \sigma_1, \sigma_{2,} ..., \sigma_n) = \begin{vmatrix} \varphi_1(r_1)\chi_1(\sigma_1) & \varphi_2(r_1)\chi_2(\sigma_1) & \varphi_n(r_1)\chi_n(\sigma_1) \\ \varphi_1(r_2)\chi_1(\sigma_2) & \varphi_2(r_2)\chi_2(\sigma_2) & \varphi_n(r_2)\chi_n(\sigma_2) \\ & & \\ \varphi_1(r_n)\chi_1(\sigma_n) & \varphi_2(r_n)\chi_2(\sigma_n) & \varphi_n(r_n)\chi_n(\sigma_n) \end{vmatrix}$$

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

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

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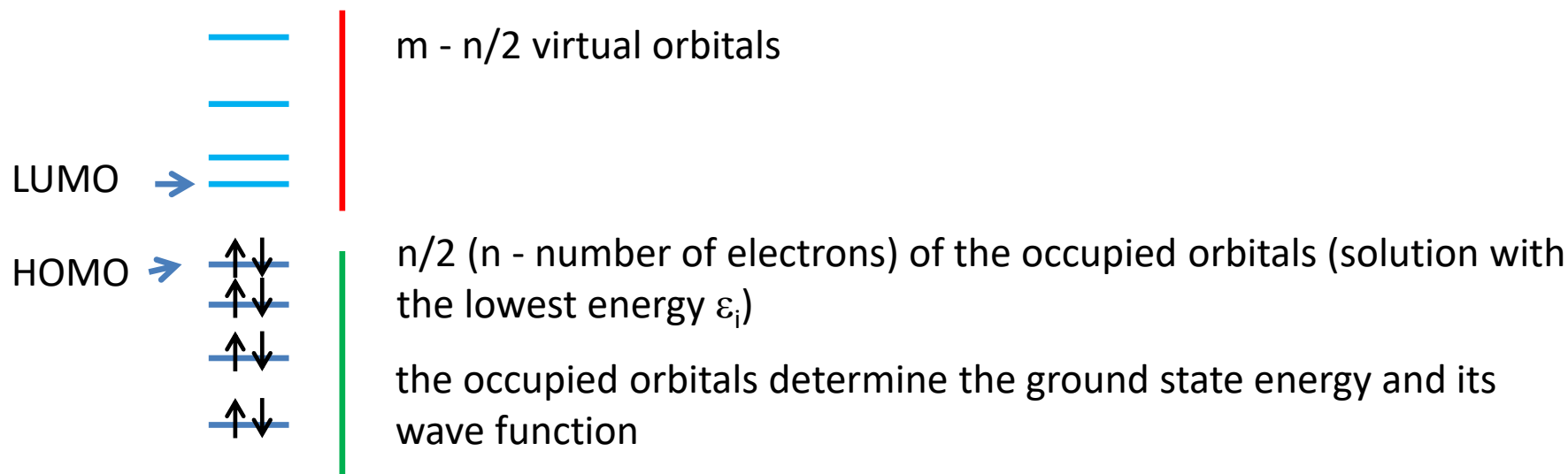
variational method

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

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 **c**. Eigenvalues ε represent the energy of one-electron functions (orbitals).

m - n/2 virtual orbitals

LUMO

HOMO

n/2 (n - number of electrons) of the occupied orbitals (solution with the lowest energy ε_i)

the occupied orbitals determine the ground state energy and its wave function

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

Water Molecule − HF/CBS

E_{HF} — red +
$E(x)$ — green line
E_{CBS} — dashed line

E [au], Cardinal number x

HF method (variational)

basis set size

HF limit

post-HF methods

exact SE solution (non-relativistic)

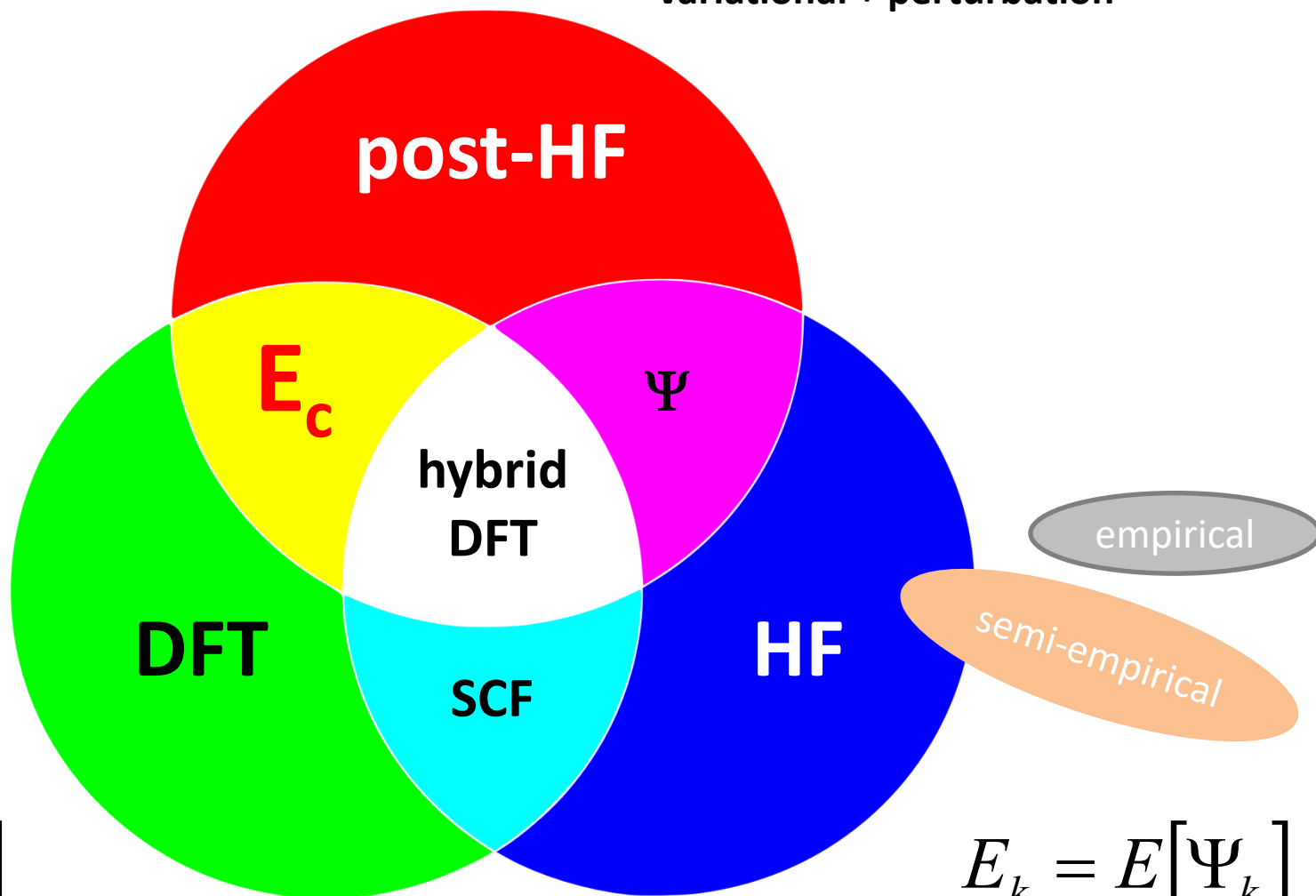**real energy (include also relativistic effects)**

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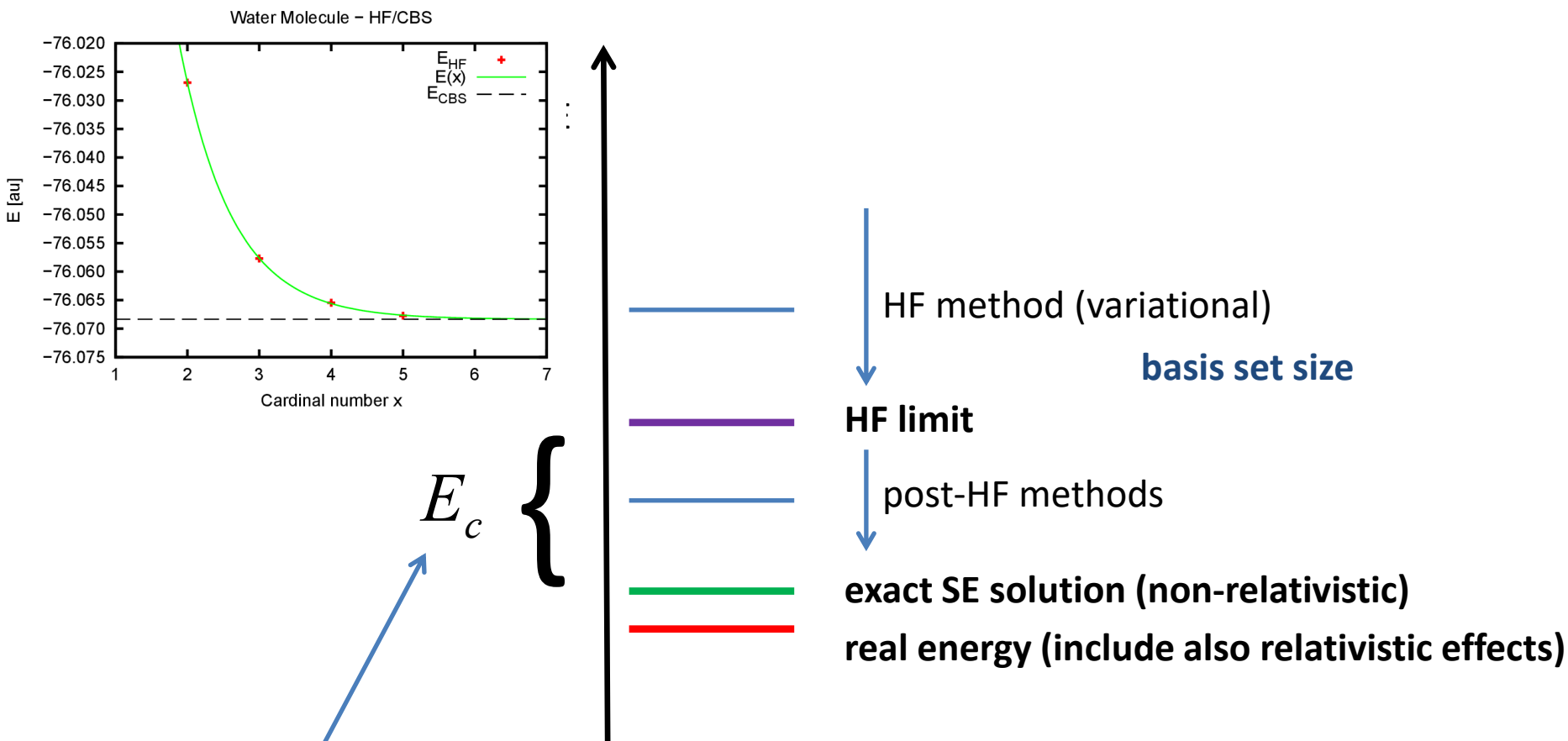
correlation energy – it is not included in the HF method **because one-electron approximation**

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

Quantum chemical methods

Method classification

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	HF	CI methods	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

HF/def2-TZVP

method (model chemistry)

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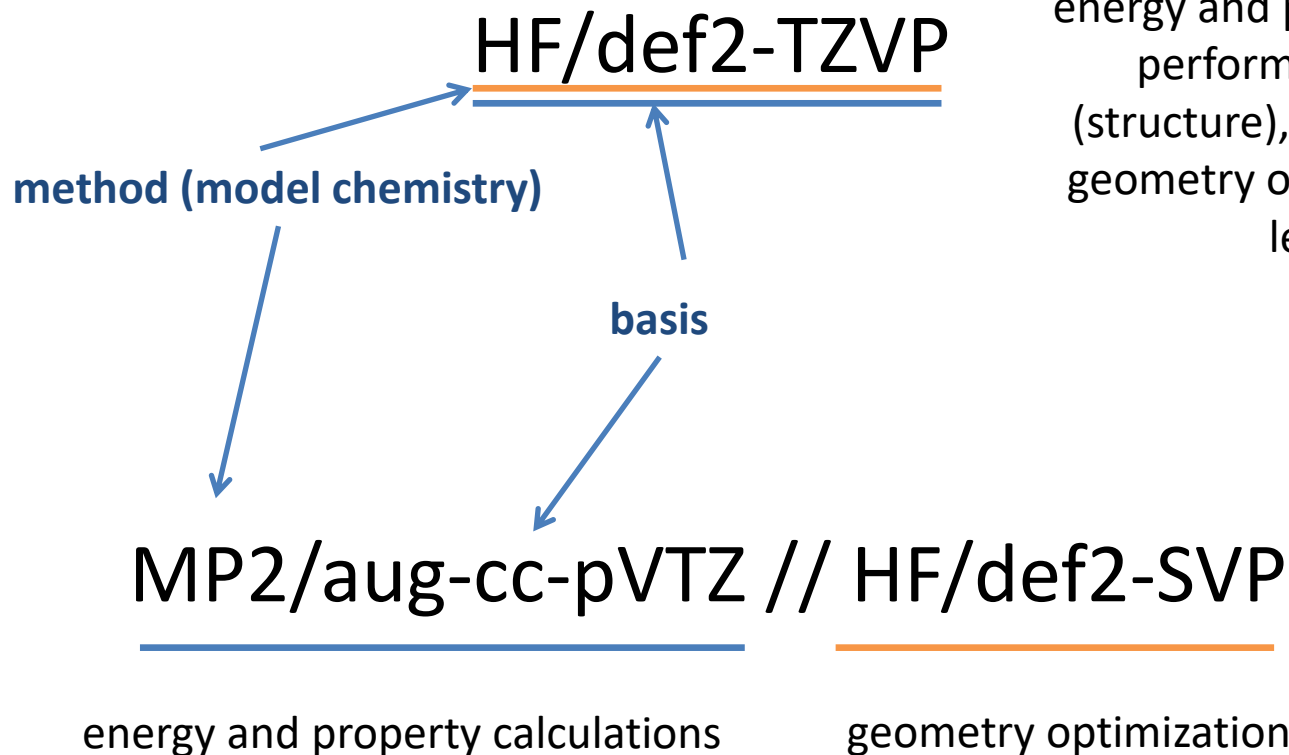
energy and property calculations are performed on the geometry (structure), which was obtained by geometry optimization at the same level of theory

MP2/aug-cc-pVTZ // HF/def2-SVP

energy and property calculations

geometry optimization