

Advanced Physical Chemistry (fizkemhk17em)

Electronic Structure

Péter G. Szalay
ELTE Eötvös Loránd University
Institute of Chemistry
szalay@chem.elte.hu



Correlated methods

Reminder: The Hartree–Fock method

Wave function: a Slater-determinant corresponding to a configuration:

$$\begin{array}{c}
 \text{-----} \\
 \text{---}\uparrow\downarrow\text{---} \\
 \text{---}\uparrow\downarrow\text{---}
 \end{array}$$

$$\Psi_{HF} = \hat{A}(\varphi_1(1) \varphi_2(2) \varphi_3(3) \dots \varphi_n(n))$$

antisymmetrizer - Pauli principle

Reminder: The Hartree–Fock method

Wave function: a Slater-determinant corresponding to a configuration:

$$\begin{array}{c}
 \text{-----} \\
 \text{---}\uparrow\downarrow\text{---} \\
 \text{---}\uparrow\downarrow\text{---}
 \end{array}$$

$$\Psi_{HF} = \hat{A}(\varphi_1(1) \varphi_2(2) \varphi_3(3) \dots \varphi_n(n))$$

antisymmetrizer - Pauli principle

Molecular orbitals (φ_i) obtained from:

$$\hat{f} \varphi_i = \varepsilon_i \varphi_i$$

$$\varphi_i = \sum_{\alpha} c_{i\alpha} \chi_{\alpha} \quad \chi_{\alpha} : \text{basis functions}$$

Reiminder: The Hartree–Fock method

Advantages:

- Independent particle approximation → concept of orbitals
- not very expensive

Problems:

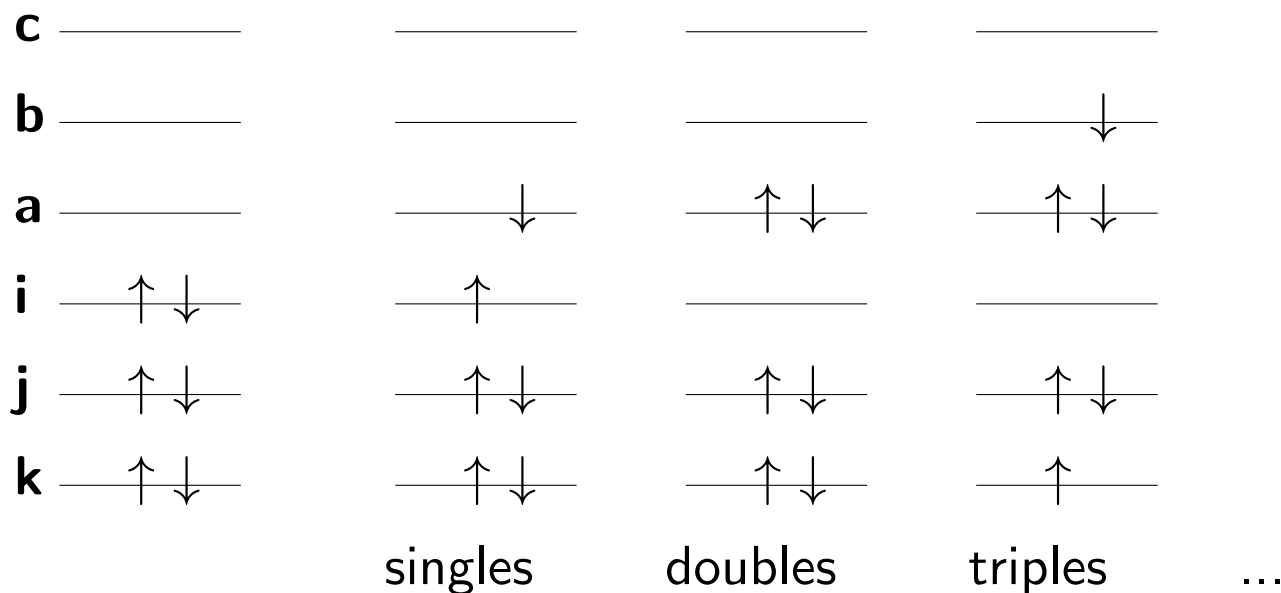
- do not describe the proper interaction of electrons
→ lack of „**electron correlation**”
- accuracy is limited

Going beyond Hartree-Fock

- Density Functional Theory - DFT
- Configuration Interaction (CI) - expand the wave function on several determinants
 - orbitals form a complete set \rightarrow determinants build from orbitals also form a complete set
 - expanding the wave function on this set gives the „exact” solution
- Perturbation Theory (PT) - use HF as start
- Coupled Cluster (CC) - exponential expansion of the wave function

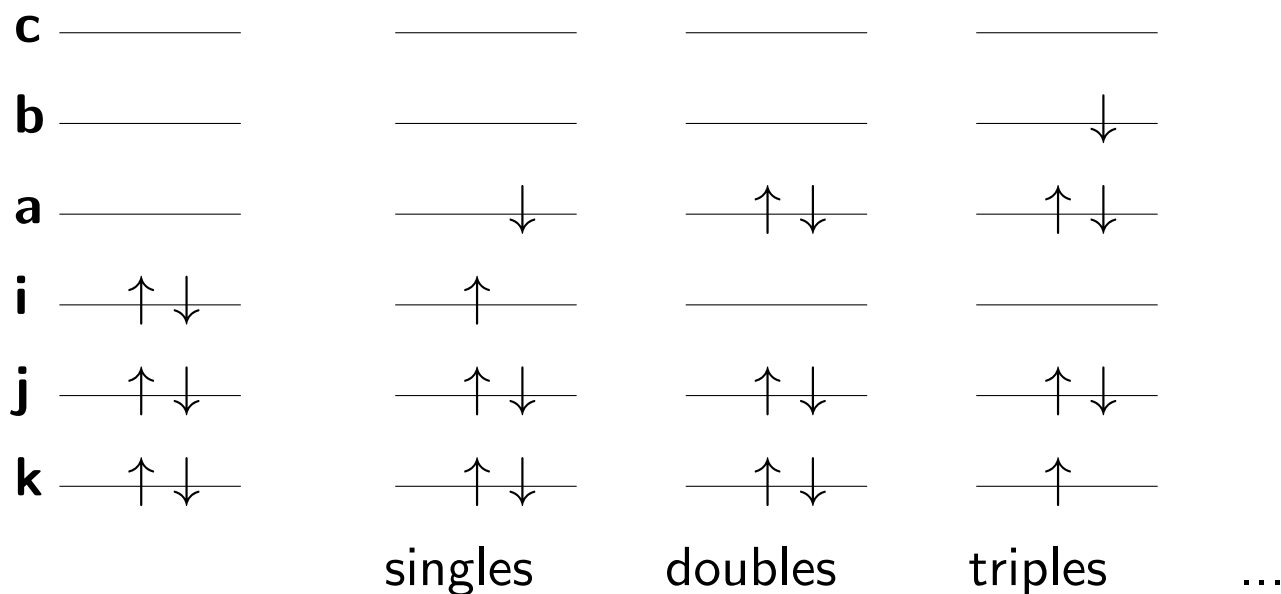
The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants



The Configuration Interaction (CI) method

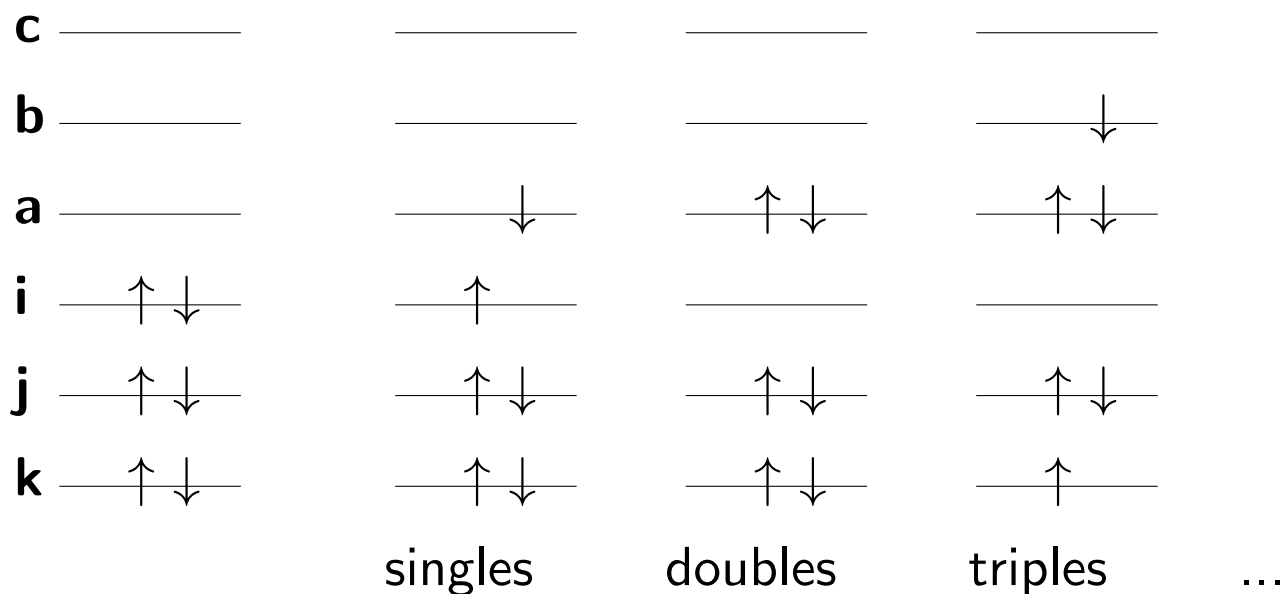
Wave function: linear combination of Slater-determinants



$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants

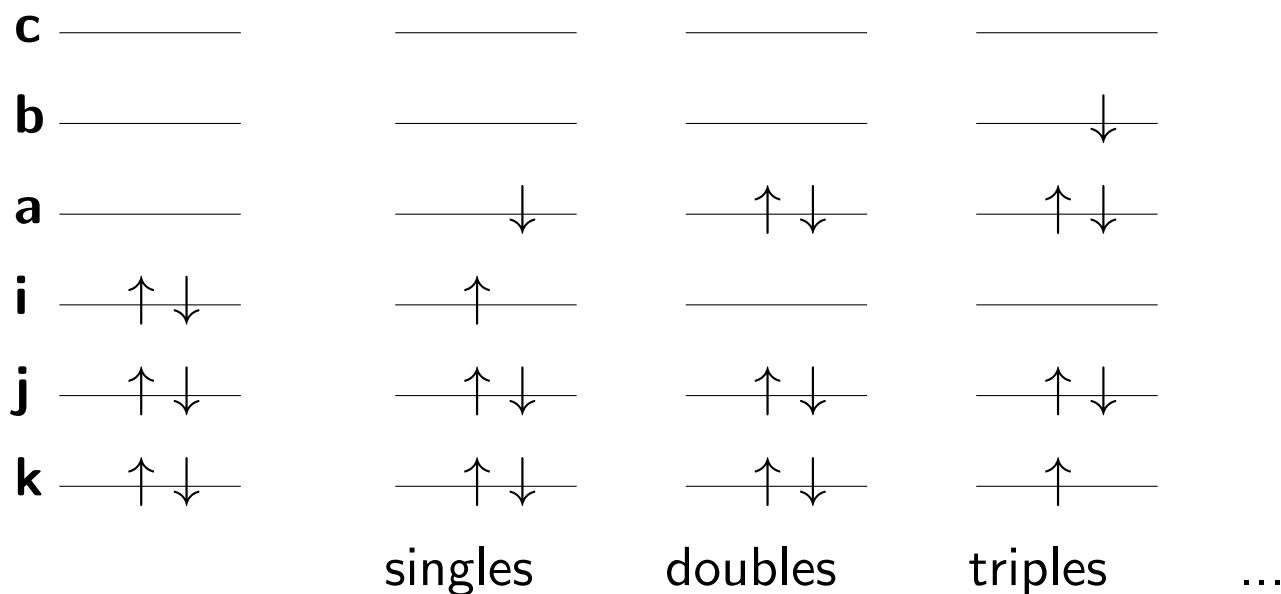


$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

↑ CIS

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants

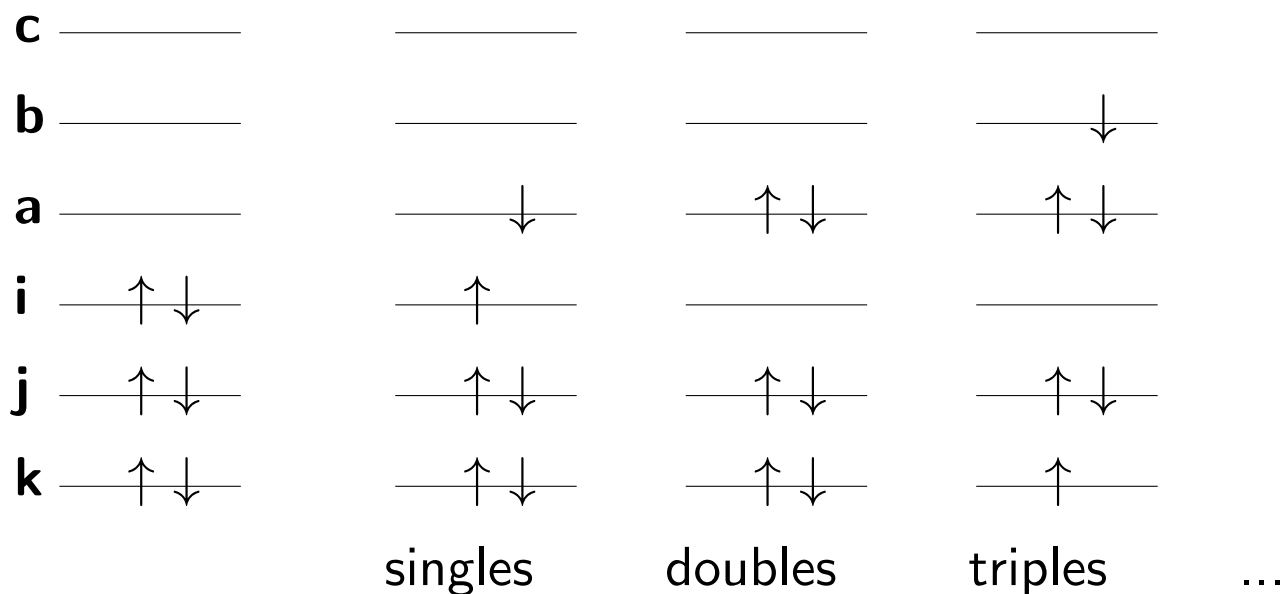


$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

↑ CISD

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants

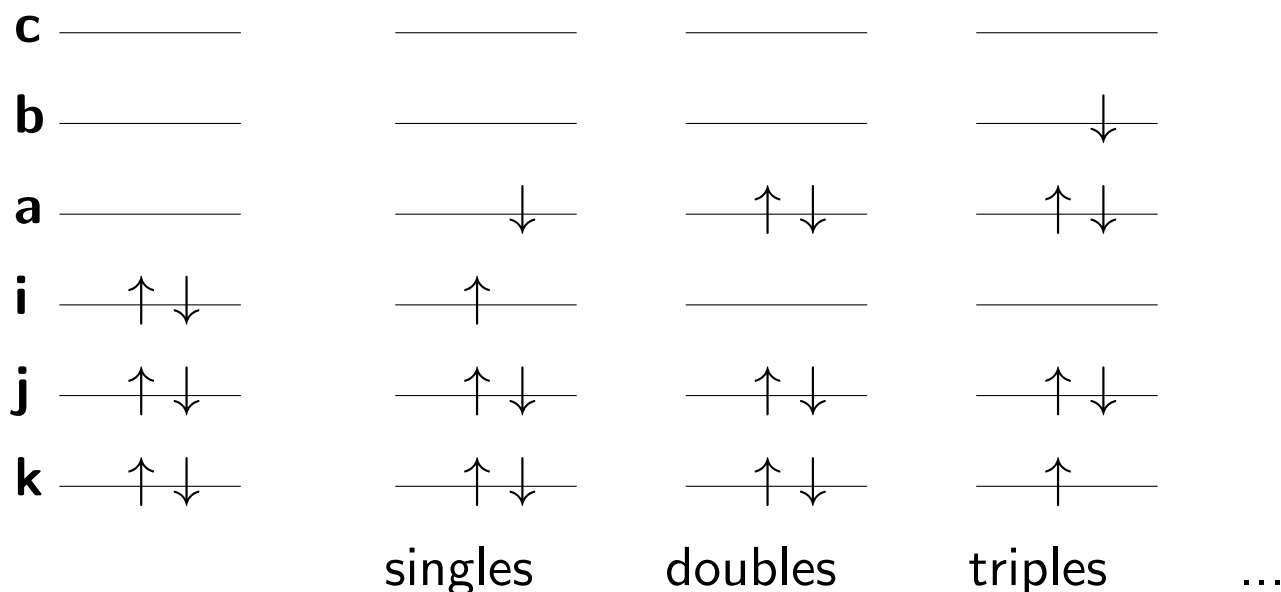


$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

↑ CISDT

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants



$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

Full CI

The CI equations

A general way of writing the CI wave function as linear combination of determinants:

$$\Psi_{CI} = \sum_p c_p \Phi_p$$

How can we obtain the coefficients? **Variationally**

This leads to a matrix eigenvalue equation:

$$\underline{\underline{H}} \underline{c} = E \underline{c}$$

where the matrix elements are:

$$H_{rp} = \langle \Phi_r | \hat{H} | \Phi_p \rangle$$

The elements of the eigenvector \underline{c} define the expansion in the first equation.

CI expansion space: Truncated CI

In practice: CISD - only single and double excitations

$$\Phi_{\text{CISD}} = c_0 \Phi_{\text{HF}} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab}$$

- Doubles, because these give the largest contribution to energy
- Singles also, because needed for one electron properties (not expensive anyway)

CI expansion space: Truncated CI

In practice: CISD - only single and double excitations

$$\Phi_{\text{CISD}} = c_0 \Phi_{\text{HF}} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab}$$

- Doubles, because these give the largest contribution to energy
- Singles also, because needed for one electron properties (not expensive anyway)

This approximation is valid if: $c_0 \sim 1$,

i.e. the wave function is dominated by the reference (HF) determinant

CI expansion space: Truncated CI

$$c_0 \sim 1$$

This is usually *satisfied*:

- ground electronic states at equilibrium geometry

Very often this is *not satisfied*:

- low lying virtual orbital
- dissociation, long bonds
- excited states
- etc.

Main problem with CI

Energy does not scale properly with the size of the system:

- not size-consistent
- not size-extensive

Size-consistency

Consider two subsystems at infinite separation. We have two choices:

- treat the two systems separately;
- consider only a super-system.

Provided that there is no interaction between the two systems, the two treatments should give the **same result, a basic physical requirement.**

Size-consistency

Let us use the CID wave function to describe this system!

For the super – system we have : $\Psi_{CID} = \Phi_{HF} + \Phi_D$

Φ_D is the sum of all double excitations out of Φ_{HF} (including coefficients).

For the subsystems we can write:

$$\begin{aligned} {}^A\Psi_{CID} &= {}^A\Phi_{HF} + {}^A\Phi_D \\ {}^B\Psi_{CID} &= {}^B\Phi_{HF} + {}^B\Phi_D \end{aligned}$$

The product of these two wave functions gives the other choice for the wave function of the super-system:

$$\begin{aligned} {}^{A+B}\Psi_{CID} &= {}^A\Psi_{CID} {}^B\Psi_{CID} \\ &= {}^A\Phi_{HF} {}^A\Phi_{HF} + {}^A\Phi_{HF} {}^B\Phi_D + {}^B\Phi_{HF} {}^A\Phi_D + {}^A\Phi_D {}^B\Phi_D \\ &= \Phi_{HF} + \Phi_D + {}^A\Phi_D {}^B\Phi_D \end{aligned}$$

Size-consistency

This simple model enables us to identify the origin of the size-consistency error:

The difference of the two super-system wave functions:

$${}^A\Psi_{CID} {}^B\Psi_{CID} - \Psi_{CID} = {}^A\Phi_D {}^B\Phi_D$$

i.e. simultaneous double excitations on the subsystems are missing from the CI wave function.

Size-consistency

This simple model enables us to identify the origin of the size-consistency error:

The difference of the two super-system wave functions:

$${}^A\Psi_{CID} {}^B\Psi_{CID} - \Psi_{CID} = {}^A\Phi_D {}^B\Phi_D$$

i.e. simultaneous double excitations on the subsystems are missing from the CI wave function.

This error is present also if there is an interaction between A and B , but we cannot quantify it by two calculations

Size-consistency

This simple model enables us to identify the origin of the size-consistency error:

The difference of the two super-system wave functions:

$${}^A\Psi_{CID} {}^B\Psi_{CID} - \Psi_{CID} = {}^A\Phi_D {}^B\Phi_D$$

i.e. simultaneous double excitations on the subsystems are missing from the CI wave function.

This error is present also if there is an interaction between A and B , but we cannot quantify it by two calculations



lack of size-extensivity

The Coupled-Cluster method

Wave function:

$$\Psi_{CC} = e^{\hat{T}} \Phi_{HF}$$

where \hat{T}_n is an excitation operator:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$$

\hat{T} produces excited determinants, as in CI:

$$\hat{T}_n \Phi_0 = \frac{1}{n!} \sum_{abc\dots ijk\dots} t_{ijk\dots}^{abc\dots} \Phi_{ijk\dots}^{abc\dots}$$

The Coupled-Cluster method

Expanding the exponential

$$\Psi_{CC} = e^{\hat{T}} \Phi_{HF} = (1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \dots) \Phi_{HF}$$

which includes higher excitations, i.e. in case of Coupled-Cluster wave function higher excitations are included without increasing the number of parameters.

In particular, the quadruply excited term $\frac{1}{2} \hat{T}^2$ plays an important role (**simultaneous double excitation**).

The Coupled-Cluster method

Truncated versions:

- **CCSD** ($\hat{T} = \hat{T}_1 + \hat{T}_2$)
- **CCSD(T)** ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \text{approximate } \hat{T}_3$)
- **CCSDT** ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$)
- **CCSDTQ** ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$)

Widely used and very accurate for **ground** states!

CCSD(T) is considered as the **golden standard of quantum chemistry**

PERTURBATION THEORY

The starting point of Rayleigh-Schrödinger Perturbation Theory is the partitioning of the Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

with \hat{H}_0 being the zeroth order part of the Hamiltonian, \hat{V} is the perturbation. We need to know the solution for \hat{H}_0 , i.e.

$$\hat{H}_0\Psi_0 = E_0\Psi_0$$

with Ψ_0 and E_0 being the zeroth order wave function and energy, respectively.

PERTURBATION THEORY

In quantum chemistry we often use the so called Møller-Plesset (MP) partitioning:

$$\hat{H}_0 = \sum_i \hat{f}(i)$$

i.e. sum of the one-electron Fock-operators, since in this case:

Ψ_0 = Determinant from the Hartree – Fock calculation

$$E_0 = \sum_i \varepsilon_i$$

1st order: Hartree-Fock method

2nd order: MP2 or MBPT(2) method

3rd order: MP3 or MBPT(3) method

etc.



PERTURBATION THEORY

MP2: cheap way to include electron correlation

MP3: usually not any better than MP2

MP4: often very good but expensive

Main problems:

- **series may not converge**
- **gets very expensive**