

Post-Hartree Fock Methods:

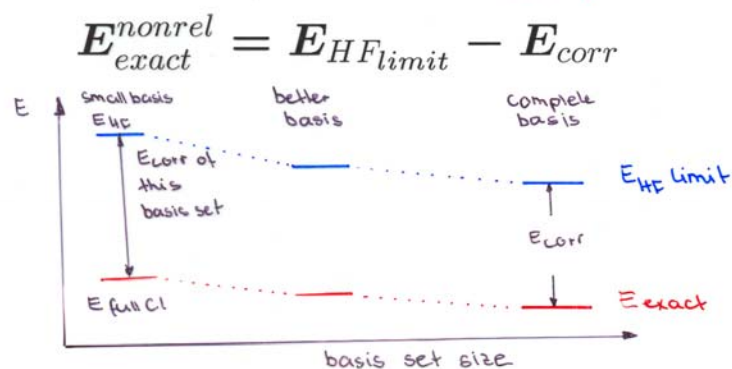
(Methods that go beyond Hartree-Fock, i.e. that take electron correlation into account)

1. Configuration Interaction (CI)

(Script: Chapter 5)

Electron Correlation

Chemist's definition of E_{corr} (Lowdin):



→ E_{corr} is basis set dependent!

Electron Correlation: Physicist's view

Probability distribution of a system with 2 electrons is not given by the product $\rho(1)\rho(2)$ only:

$$\rho_2(\vec{r}_1, \vec{r}_2) = \frac{1}{2}\rho(\vec{r}_1)\rho(\vec{r}_2)[1 + h(\vec{r}_1, \vec{r}_2)]$$

$h(\vec{r}_1, \vec{r}_2)$: pair correlation function

The presence of electron(1) modifies the probability distribution for electron(2):

→ exchange-correlation hole

$$\rho_{xc}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_2)h(\vec{r}_1, \vec{r}_2)$$

(exchange-correlation hole created by an electron at \vec{r}_1).

→ correlated motion of electrons

(electrons 'avoid each other' → electron-electron repulsion is lowered)

→ HF_{limit} is higher than the true total energy of the system

Post-Hartree-Fock Methods

Methods use a Hartree-Fock calculation as starting point and try to improve the HF results by taking account of **electron correlation**:

- Configuration Interaction (CI)
- Møller-Plesset Perturbation (MP)
- Coupled-Cluster (CC)

Configuration Interaction (CI)

Improved Ansatz for the Many-Body Wavefunction:

$$\Psi_j^{CI}(x_1, x_2, x_3 \dots x_N) = \sum_m C_{m_1, m_2, m_3 \dots m_N} \underbrace{|\phi_{m_1}(x_1)\phi_{m_2}(x_2)\phi_{m_3}(x_3)\dots\phi_{m_N}(x_N)\rangle}_{|\Phi_i\rangle}$$

where $x_i = (\vec{r}_i, s_i)$.

If we use the symbol $|\Phi_i\rangle$ for the Slater determinant i , we can also write this as

$$|\Psi_j^{CI}\rangle = \sum_i C_{ij} |\Phi_i\rangle$$

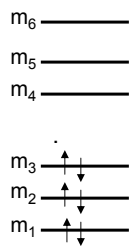
Instead of describing the many-electron wavefunction with a single Slater determinant (like in Hartree-Fock), we describe it with a **linear combination of Slater determinants**.

How do we get more than one Slater determinant?

In the Hartree-Fock case, we constructed a Slater determinant that corresponds to the electronic configuration in the ground state (i.e. all the electrons occupy the lowest possible molecular orbitals). However, the system can also exist in electronically excited states where electrons occupy molecular orbitals that are higher in energy. For each such electronically excited configuration we can construct a corresponding Slater determinant and include them in our expansion for the many electron wavefunction. Each Slater determinant corresponds to a different electronic configuration (therefore the name **Configuration Interaction (CI)**) that is generated by creating excited state configurations from the ground state Hartree-Fock wavefunction.

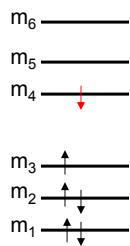
Let's look at an example:

HF ground state



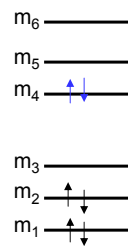
$$\Phi_0 = \left| \phi_{m_1}^2 \phi_{m_2}^2 \phi_{m_3}^2 \right|$$

single excitations 'S'



$$\Phi_1 = \left| \phi_{m_1}^2 \phi_{m_2}^2 \phi_{m_3} \phi_{m_4} \right|$$

double excitations 'D'



$$\Phi_2 = \left| \phi_{m_1}^2 \phi_{m_2}^2 \phi_{m_4}^2 \right|$$

All possible singly excited configurations in this example:

$$\Phi_1 = \left| \phi_{m_1}^2 \phi_{m_2}^2 \phi_{m_3} \phi_{m_4} \right|$$

$$\Phi_1 = \left| \phi_{m_1}^2 \phi_{m_2} \phi_{m_3}^2 \phi_{m_4} \right|$$

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$$\Phi_1 = \left| \phi_{m_1}^2 \phi_{m_2}^2 \phi_{m_3} \phi_{m_5} \right|$$

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$$\Phi_1 = \left| \phi_{m_1}^2 \phi_{m_2}^2 \phi_{m_3} \phi_{m_6} \right|$$

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$$\Phi_1 = \left| \phi_{m_1} \phi_{m_2}^2 \phi_{m_3}^2 \phi_{m_6} \right|$$

We often use the letters **a,b,c** etc.. for the **occupied molecular orbitals** from which we excite an electron, and the letters **r,s**, etc.. to label the **empty (virtual) orbitals** to which we excite electrons.

In this way, we can write the linear combination of Slater determinants that describe the many electron wavefunction Ψ as

$$\left| \Psi^{CI} \right\rangle = C_0 \left| \Phi_0 \right\rangle + \sum_a \sum_r C_a^r \left| \Phi_a^r \right\rangle + \sum_a \sum_b \sum_r \sum_s C_{ab}^{rs} \left| \Phi_{ab}^{rs} \right\rangle + \dots$$

If we include Slater determinants for **all possible excitations**, the method is called **full CI** and The result is **exact** (within a chosen basis set)!

$\left| \Phi_0 \right\rangle$ Hartree-Fock ground-state determinant

$\left| \Phi_a^r \right\rangle$ singly-excited determinants

$\left| \Phi_{ab}^{rs} \right\rangle$ doubly-excited determinants

r,s: indices for virtual orbitals

a,b: indices for occupied orbitals

If we include all possible excited state configuration where one electron is promoted from the occupied to the unoccupied orbitals, the method is called **CIS**, if we include all possible single and double excitations it is **CISD** etc.. (**CISDT**, **CISDTQ**...). By allowing for this increased flexibility of the wavefunction, we are able to capture the modifications of the electronic distribution caused by correlation effects. If we include all possible excited state configurations, the method is called **full CI** and the results is exact.

So in theory we now know how to solve a many-electron Schrodinger equation exactly:

Like for Hartree-Fock, we can calculate the expectation value of the total energy of the system:

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle$$

Where Ψ is a linear combination of Slater determinants generated from the Hartree-Fock orbitals

$$\left| \Psi^{CI} \right\rangle = C_0 \left| \Phi_0 \right\rangle + \sum_a \sum_r C_a^r \left| \Phi_a^r \right\rangle + \sum_a \sum_b \sum_r \sum_s C_{ab}^{rs} \left| \Phi_{ab}^{rs} \right\rangle + \dots$$

To find Ψ^{CI} , we use the **variational theorem** that tells us that the best wavefunction is the one that minimizes the total energy E_{el} :

If we **minimize E** with respect to the **coefficients C** (but leave the one electron orbitals untouched, i.e. equal to the Hartree-Fock orbitals), the method is called **CI** (it takes account of **dynamic correlation**).

If we include only few determinants and **minimize with respect to the coefficients C and the one-electron MOs Φ_i** , the method is called **multireference CI (MRCI)** (it is specially good for taking **static correlation effects** into account).

We get the matrix equation

$$HC = CE$$

with the Hamiltonian matrix elements:

$$H_{KL} = \langle \Phi_K | H | \Phi_L \rangle$$

All we have to do is to diagonalize this matrix and we have found the exact solution of the many-electron Schrodinger equation in a given basis!

We do not have to calculate all of the Hamiltonian matrix elements because some of them are zero. There are simple rules (Slater rules) that help us to know which ones (see script):

$$H = \begin{matrix} \langle \Phi_0 | \\ \langle S | \\ \langle D | \\ \langle T | \\ \langle Q | \\ \vdots \end{matrix} \begin{bmatrix} \langle \Phi_0 | H | \Phi_0 \rangle & & & & & \dots \\ 0 & \langle S | H | S \rangle & & & & \dots \\ \langle D | H | \Phi_0 \rangle & \langle D | H | S \rangle & \langle D | H | D \rangle & & & \dots \\ 0 & \langle T | H | S \rangle & \langle T | H | D \rangle & \langle T | H | T \rangle & & \dots \\ 0 & 0 & \langle Q | H | D \rangle & \langle Q | H | T \rangle & \langle Q | H | Q \rangle & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

In practice: the number of determinants we have to include to do a full CI calculations is intractable in most cases!

$$\approx \binom{N_{SO}}{N_{electrons}} = \frac{N_{SO}!}{N_{el}!(N_{SD}-N_{el})!}$$

Ex.: Benzene with 6-311G** basis:

$$\# \text{ of determinants} \quad \binom{288}{42} \approx 10^{52}$$

We would have to calculate, store and diagonalize a $10^{52} \times 10^{52}$ Matrix (ca. 10^{93} TByte!)

Full CI calculations have been performed as benchmarks studies for very small molecules. CIS is sometimes used for approximate excited state calculations. Otherwise CI is not used very often because it is simply too expensive and other correlated methods give results of comparable quality for a lower computational cost.

Percentage of Correlation energy:

Molecule	Basis Set	CISD	CISDT	CISDTQ
BH	DZP	94.91	n/a	99.97
H ₂ O (R _e)	DZ	94.70	95.47	99.82
H ₂ O (1.5 R _e)	DZ	89.39	91.15	99.48
H ₂ O (2.0 R _e)	DZ	80.51	83.96	98.60
NH ₃	DZ	94.44	95.43	99.84
HF	DZP	95.41	96.49	99.86
H ₇ ⁺	DZP	96.36	96.87	99.96

- **doubles** contribute most to gs correlation energy
- **quadruples** are more important than triples (at least for energy)
- at stretched geometries CISD and CISDT markedly poorer, CISDTQ ok

Number of CSF's:

Molecule	Basis set	CISD	CISDT	CISDTQ
BH	DZP	568	n/a	28 698
H ₂ O	DZ	361	3 203	17 678
NH ₃	DZ	461	4 029	19 925
HF	DZP	552	6 712	48 963
H ₇ ⁺	DZP	1 271	24 468	248 149

(Handy et al., CPL 95, 386 (1983)
Schaefer et al., JCP 100, 8132 (1994))