

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)
- Many Body Perturbation Theory (Møller-Plesset (MPn))

Magnitude of Correlation Contributions

Example: Methane CH₄ (6-311G* Basis set)

	Total Energy	
Hartree-Fock	-40.202409 au	
exact	-40.372946 au	
E _{corr}	-0.170537 au	→ -107.0 kcal/mol
	(0.4%)	

Typical estimate of electron correlation energies:

~ 100kJ/mol for a localized electron pair

General: < 1% of total energy

Many-Body Perturbation Theory (MBPT)

General idea:

in case correlation effects are relatively small \rightarrow HF solutions $|\Psi_i\rangle_{HF}$ and $\{E_i\}_{HF}$ are already close approximations to the exact $|\Psi_i\rangle$ and $\{E_i\}$

\rightarrow correlation effects can be considered as perturbation to the HF solutions and treated via perturbation theory

Perturbation Theory:

Given: Hamiltonian \mathcal{H}^0
with eigen functions $|\Psi_i^0\rangle$
and eigen values E_i^0

True Hamiltonian \mathcal{H} partitioned into:

$$\mathcal{H} = \mathcal{H}^0 + \lambda \mathcal{H}' = \mathcal{H}^0 + \lambda \mathcal{V} \quad (\mathcal{V} \ll \mathcal{H}^0)$$

$\lambda=0 \rightarrow \hat{H} = \hat{H}_0$
 $\lambda=1 \rightarrow \hat{H} = \hat{H}_0 + \hat{H}'$

\uparrow exact Hamiltonian
 \uparrow unperturbed system
 \uparrow scaled perturbation

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

$$\mathcal{H}_0 \Phi_i = E_i^0 \Phi_i, \quad i = 0, 1, 2, 3, \dots, \infty$$

\downarrow complete set of orthonormal (eigen)functions

Let's consider the non-degenerate ground state of a time-independent system:

Schrödinger Equation for the perturbed system:

$$\mathcal{H} \Psi(\lambda) = E(\lambda) \Psi_i(\lambda)$$

For $\lambda = 0$, $\Psi(0) = \Phi_0$ and $E(\lambda) = E_0$

$\rightarrow \lambda$ can be varied smoothly from the unperturbed ($\lambda=0$) to the fully perturbed ($\lambda=1$) case

⇒ Taylor expansion of E_i and $|\Psi_i\rangle$ around $\lambda = 0$

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

$$|\Psi_i\rangle = \lambda^0 |\Psi_i^{(0)}\rangle + \lambda^1 |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots$$

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle$$

Indices (0),(1),(2)..(n): refer to the unperturbed system (0th order correction), the 1st order correction, 2nd order correction...nth order correction → MP2,MP3, MP4 etc...

Series does not necessarily converge!

Normalization condition:

overlap of perturbed wfc with unperturbed wfc chosen to be 1!

$$\langle \Psi | \Phi \rangle = 1$$

$$\langle \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} \dots | \Phi \rangle = 1$$

$$\langle \Psi^{(0)} | \Phi \rangle + \lambda^1 \langle \Psi^{(1)} | \Phi \rangle + \lambda^2 \langle \Psi^{(2)} | \Phi \rangle + \dots = 1$$


 $\langle \Psi^{(i \neq 0)} | \Phi \rangle = 0$

All corrections are orthogonal
To unperturbed solution

n-th order Perturbation Equations:

$$(\mathcal{H}_0 + \lambda \mathcal{H}')(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots) =$$

$$(\lambda^0 E^{(0)} + \lambda^1 E^{(1)} + \lambda^2 E^{(2)} + \dots)(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots)$$

Collect terms with same power in λ :

$$\lambda^{(0)} : \mathcal{H}_0 \Psi^{(0)} = E^{(0)} \Psi^{(0)}$$

$$\lambda^{(1)} : \mathcal{H}_0 \Psi^{(1)} + \mathcal{H}' \Psi^{(0)} = E^{(0)} \Psi^{(1)} + E^{(1)} \Psi^{(0)}$$

$$\lambda^{(2)} : \mathcal{H}_0 \Psi^{(2)} + \mathcal{H}' \Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi^{(0)}$$

...

$$\lambda^{(n)} : \mathcal{H}_0 \Psi^{(n)} + \mathcal{H}' \Psi^{(n-1)} = \sum_{j=0}^n E^{(j)} \Psi^{(n-j)}$$

$\Psi^{(n)}$, $E^{(n)}$: n-th order correction to the wavefunction and to the energy

Rayleigh-Schrödinger Perturbation Formula

For example 1st order perturbation:

$$(\mathcal{H}_0 - E^{(0)})\Psi^{(1)} + (\mathcal{H}' - E^{(1)})\Phi_0 = 0$$

Contains 2 unknowns

General solution: expand wavefunction correction in complete set of unperturbed wavefunctions:

$$\Psi^{(1)} = \sum_{i=0}^{\infty} c_i \Phi_i$$

If we introduce this Ansatz for the wavefunction in the equation above, we obtain:

$$E^{(1)} = \langle \Phi_0 | \mathcal{H}' | \Phi_0 \rangle \quad \text{1st order correction to the energy}$$

By multiplying on the left with a given Φ_j and integrating, we obtain the coefficients c_j for the 1st order correction to the wavefunction:

$$\Psi^{(1)} = \sum_{i=0}^{\infty} c_i \Phi_i \quad \text{with} \quad c_j = \frac{\langle \Phi_j | \mathcal{H}' | \Phi_0 \rangle}{E_0 - E_j} \quad \text{1st order correction to the wavefunction}$$

In addition, from the normalization condition we get $c_0 = 0$.

2nd order perturbation:

$$\mathcal{H}_0 \Psi^{(2)} + \mathcal{H}' \Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi^{(0)}$$

2 unknowns

Expansion of the 2nd order correction to the wavefunction:

$$\Psi^{(2)} = \sum_i d_i \Phi_i$$

$$c_0 = d_0 = 0$$

2nd order correction to the energy:

$$E^{(2)} = \langle \Phi_0 | H' | \Psi^{(1)} \rangle$$

$$E^{(2)} = \sum_i c_i \langle \Phi | \mathcal{H}' | \Phi_i \rangle = \sum_{i \neq 0} \frac{\langle \Phi_0 | \mathcal{H}' | \Phi_i \rangle \langle \Phi_i | \mathcal{H}' | \Phi_0 \rangle}{E_0 - E_i}$$

2nd order correction to the wfct:

$$d_j = \sum_{i \neq 0} \frac{\langle \Phi_j | \mathcal{H}' | \Phi_i \rangle \langle \Phi_i | \mathcal{H}' | \Phi_0 \rangle}{(E_0 - E_j)(E_0 - E_i)} - \frac{\langle \Phi_j | \mathcal{H}' | \Phi_0 \rangle \langle \Phi_0 | \mathcal{H}' | \Phi_j \rangle}{(E_0 - E_j)^2}$$

nth order correction to the energy:

$$E^{(n)} = \langle \Phi_0 | H' | \Psi^{(n-1)} \rangle$$

Møller-Plesset Perturbation Theory

unperturbed system:

$$\mathcal{H}^0 | \Psi^{(0)} \rangle = E_0^{(0)} | \Psi^{(0)} \rangle$$

\mathcal{H}^0 : Hartree-Fock Hamiltonian

$$\mathcal{H}^0 = \sum_i^N \hat{f}(i)$$

perturbation:

$$\begin{aligned} \mathcal{V}' &= \mathcal{H} - \mathcal{H}^0 = \left(\sum_i^N \hat{h}(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) - \sum_i^N \hat{f}(i) \\ &= \left(\sum_i^N \hat{h}(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) - \left(\sum_i^N \hat{h}(i) + \sum_i^N \hat{v}_{HF}(i) \right) \\ &= \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \hat{v}_{HF}(i) \end{aligned}$$

→ total e-e repulsion minus Hartree-Fock e-repulsion

Note that:

$$\langle \Phi_0 | \sum_{i < j}^N \hat{v}_{ij} | \Phi_0 \rangle = \frac{1}{2} \langle \Phi_0 | \sum_{i, j}^N \hat{v}_{ij}^{HF} | \Phi_0 \rangle \equiv \langle \mathbf{V}_{ee} \rangle$$

(the sum of the Fock operators counts the electron-electron repulsion twice!)

0th order energy:
(sum of HF eigenvalues)

$$E^{(0)} = \sum_i^N \langle \phi_i | \hat{F}_i | \phi_i \rangle = \sum_i^N \varepsilon_i^{\text{HF}}$$

1st order energy:
(correction for double counting electron-electron interaction)

$$\begin{aligned} E^{(1)} &= \langle \Phi_0 | \hat{\mathcal{H}}' | \Phi_0 \rangle = \langle \Phi_0 | \sum_{i < j}^N \hat{v}_{ij} | \Phi_0 \rangle - \langle \Phi_0 | \sum_{i, j=1}^N \hat{v}_{ij}^{HF} | \Phi_0 \rangle \\ &= \langle \mathbf{V}_{ee} \rangle - 2 \langle \mathbf{V}_{ee} \rangle = -\langle \mathbf{V}_{ee} \rangle \end{aligned}$$

$$\text{MP0 : } E(\text{MP0}) = \sum_a^N \varepsilon_a^{\text{HF}}$$

$$\text{MP1 : } E(\text{MP0}) + E(\text{MP1}) = E(\text{HF})$$

Note: First nontrivial energy correction at second order MP2 !

Expansion of the perturbed wavefunction in doubly excited Slater determinants:

2nd order correction to the energy:

$$E^{(2)} = \sum_{a < b}^{\text{occ.}} \sum_{r < s}^{\text{virt.}} \frac{\langle \Phi_0 | \hat{\mathcal{H}}' | \Phi_{ab}^{rs} \rangle \langle \Phi_{ab}^{rs} | \hat{\mathcal{H}}' | \Phi_0 \rangle}{E_0 - E_{ab}^{rs}}$$

$$E(\text{MP2}) = \sum_{a < b}^{\text{occ.}} \sum_{r < s}^{\text{virt.}} \frac{[\langle \phi_a \phi_b | \hat{v} | \phi_r \phi_s \rangle - \langle \phi_a \phi_b | \hat{v} | \phi_s \phi_r \rangle]^2}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

→ similar expressions can be derived for the nth order correction to the energy and to the wavefunction

Coupled Cluster (CC)

Yet another Ansatz for the Many-Body Wavefunction:

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle$$

where $|\Phi_0\rangle$ is a reference wavefunction. e.g. the Hartree-Fock determinant and \hat{T} is the cluster operator

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

\hat{T}_1 is the one-particle excitation operator which generates singly excited configurations.
 \hat{T}_2 is the two-particle excitation operator which generates doubly excited Slater determinants.
Etc..

In analogy to the terminology used in case of CI calculations, coupled clusters are labelled according to the order of excitations that is included e.g. **CCD**, **CCSD**, **CCSDT**, **CCSDTQ** etc.. Acronyms of the type **CCSD(T)** refer to a coupled cluster calculation including singles and doubles and a perturbatively treatment to include the effects of triple excitations. Calculations of the coupled cluster time are nowadays one of the most popular approaches for very high accuracy calculations.