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))

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Magnitude of Correlation Contributions

Example: Methane CH_4 (6-311G* Basis set)

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

Typical estimate of electron correlation energies:

~ 100kJ/mol for a localized electron pair

General: < 1% of total energy

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Many-Body Perturbation Theory (MBPT)

Idea:
For the case electron correlation effects are relatively small, the Hartree-Fock solutions Φ_i^{HF} and E_i^{HF} are already close approximations to the exact solutions Ψ_i^{exact} and E_i^{exact}.

=> correlation effects can be considered as perturbation to the HF solution and treated via perturbation theory

Given:

$$\hat{H}^{(0)}\Phi_i^{(0)} = E_i^{(0)}\Phi_i^{(0)}$$

$\hat{H}^{(0)}$ zeroth order Hamiltonian with
$\Phi_i^{(0)}$ eigenfunctions and
$E_i^{(0)}$ eigenvalues

⟶ complete set of orthonormal (eigen)functions $i = 0,1,2,3,...,\infty$

Exact Hamiltonian $\hat{H}$ can be partitioned into:

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}' = \hat{H}^{(0)} + \lambda V$$

with $V << \hat{H}^{(0)}$

and $0 \leq \lambda \leq 1$

for λ = 0 $\hat{H} = \hat{H}^{(0)}$ for λ = 1 $\hat{H} = \hat{H}$

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Rayleigh-Schrödinger Perturbation Theory

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

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}'$$

⟶ λ can be varied smoothly from the unperturbed (λ = 0) to the fully perturbed (λ = 1) case

Schrödinger Equation for the perturbed system:

$$\hat{H}\Psi(\lambda) = E(\lambda)\Psi(\lambda)$$

Special notation for λ = 0 and i = 0:

$$\hat{H}^{(0)} = H_0$$
$$\Psi_0(\lambda = 0) = \Psi_0^{(0)} = \Phi_0$$
$$E_0(\lambda = 0) = E_0^{(0)} = E_0$$

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Expansion of Ψ and E in powers of λ

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

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

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

Series does not necessarily converge!

- Indices (0),(1),(2)..(n): refer to the unperturbed system (0th order correction), the 1st order correction, 2nd order correction…nth order correction, respectively → MP2, MP3, MP4 etc...
- Will concentrate on improving ground state wavefunction and energy i = 0

=> will leave out index i

Normalization condition: intermediate normalization

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

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

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

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

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

All corrections are orthogonal to the unperturbed solution

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n-th order Perturbation Equations

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

Collect terms with same power in λ:

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

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

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

$$\ldots$$

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

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

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Rayleigh-Schrödinger Perturbation Formulae

1st order perturbation:

$$\left(\hat{H}_0 - E^{(0)}\right)\Psi^{(1)} + \left(\hat{H}' - E^{(1)}\right)\Psi^{(0)} = 0$$

For improving ground-state solution Φ_0, E_0:

$$\left(\hat{H}_0 - E_0\right)\Psi^{(1)} + \left(\hat{H}' - E^{(1)}\right)\Phi_0 = 0$$

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:

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

1st order correction to the energy

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Quiz XIII: 1st order correction

1) Derive the expression for the 1st order correction to the energy starting from the equation gathering the λ^1 terms. Hint: multiply from the left with Φ_0 and integrate over all space.

2) Determine the expansion coefficients c_j for the first order correction to the wavefunction $\Psi^{(1)}$. Hint: multiply from the left with the basis function Φ_j ($j \neq 0$) and integrate over all space.

3) Why is $c_0 = 0$?

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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:

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

1st order correction to the wavefunction

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

2nd order perturbation:

$$\hat{H}_0 \Psi^{(2)} + \hat{H}' \Psi^{(1)} = E_0 \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Phi_0$$

2 unknowns

Expansion of the 2nd order correction to the wavefunction:

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

$c_0 = d_0 = 0$

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2nd order correction to the energy:

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

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

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:

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

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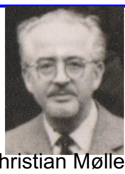
Møller-Plesset Perturbation Theory

unperturbed system:

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

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



Christian Møller (1904-1980)

Milton S.Plesset (1908-1991)

$$\mathcal{H}^0 = \sum^N \hat{f}(i) \qquad \hat{f}(i) = \hat{h}(i) + \sum_j^N \hat{J}_j - \hat{K}_j$$

perturbation:

$$\mathcal{V}' = \mathcal{H} - \mathcal{H}^0 = (\sum_i^N \hat{h}(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}) - \sum_i^N \hat{f}(i)$$

$$= (\sum_i^N \hat{h}(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}) - (\sum_i^N \hat{h}(i) + \sum_i^N \hat{v}_{HF}(i))$$

$$= \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \hat{v}_{HF}(i)$$

Difference between instantaneous and average e-e interaction: 'fluctuation potential'

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

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Quiz XIV: Møller-Plesset

1) What are the basis functions Φ_i in Moller-Plesset theory?
2) What is the 0^{th} order energy?
3) What is the 1^{st} order correction to the energy?

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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)

$$E^{(0)} = \sum_{i}^{N}\langle\phi_i|\hat{\mathcal{F}}_i|\phi_i\rangle = \sum_{i}^{N}\varepsilon_i^{\mathrm{HF}}$$

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

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

$$\mathrm{MP0:}\quad E(\mathrm{MP0}) = \sum_{a}^{N}\varepsilon_a^{\mathrm{HF}}$$

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

Note: First nontrivial energy correction at second order MP2 !

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Expansion of the perturbed wavefunction in doubly excited Slater determinants:

2nd order correction to the energy:

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

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Slater-Condon Rules

1. Identical Determinants: If the determinants are identical, then

$$\langle\Phi_1|\hat{H}|\Phi_1\rangle = \sum_m^N \langle m|\hat{h}|m\rangle + \sum_{m>n}^N \langle mn||mn\rangle \qquad (5.9)$$

2. Determinants that Differ by One Spin Orbital:

$$\begin{aligned} |\Phi_1\rangle &= |\cdots mn \cdots\rangle \\ |\Phi_2\rangle &= |\cdots pn \cdots\rangle \\ \langle\Phi_1|\hat{H}|\Phi_2\rangle &= \langle m|\hat{h}|p\rangle + \sum_n^N \langle mn||pn\rangle \end{aligned} \qquad (5.10)$$

3. Determinants that Differ by Two Spin Orbitals:

$$\begin{aligned} |\Phi_1\rangle &= |\cdots mn \cdots\rangle \\ |\Phi_2\rangle &= |\cdots pq \cdots\rangle \\ \langle\Phi_1|\hat{H}|\Phi_2\rangle &= \langle mn||pq\rangle \end{aligned} \qquad (5.11)$$

4. Determinants that Differ by More than Two Spin Orbitals:

$$\begin{aligned} |\Phi_1\rangle &= |\cdots mno \cdots\rangle \\ |\Phi_2\rangle &= |\cdots pqr \cdots\rangle \\ \langle\Phi_1|\hat{H}|\Phi_2\rangle &= 0 \end{aligned} \qquad (5.12)$$

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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

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