Rayleigh-Schrödinger perturbation theory (Part 2)

Expanding $\Psi_0^{(1)}$ in the basis $\Psi_n^{(0)}$ with $n = 0, 1, 2, \ldots, \infty$

$$|\Psi_0^{(1)}\rangle = \sum_n c_n^{(1)} |\Psi_n^{(0)}\rangle \quad \Rightarrow \quad c_m^{(1)} = \langle \Psi_m^{(0)} | \Psi_0^{(1)} \rangle$$

Therefore,

$$|\Psi_0^{(1)}\rangle = \sum_{n \neq 0} |\Psi_n^{(0)}\rangle \langle \Psi_m^{(0)} | \Psi_0^{(1)} \rangle$$

Using results from the previous slide, one can show that

$$\boxed{E_0^{(2)} = \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \mathbf{H}_1 | \Psi_n^{(0)} \rangle^2}{E_0^{(0)} - E_n^{(0)}}}$$

$$\boxed{E_0^{(3)} = \sum_{n,m \neq 0} \frac{\langle \Psi_0^{(0)} | \mathbf{H}_1 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \mathbf{H}_1 | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \mathbf{H}_1 | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} - E_0^{(1)} \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \mathbf{H}_1 | \Psi_n^{(0)} \rangle^2}{(E_0^{(0)} - E_n^{(0)})^2}}$$

Møller-Plesset (MP) perturbation theory

In Møller-Plesset perturbation theory, the partition is

$$\mathbf{H}^{(0)} = \sum_{i=1}^{N} f(i) = \sum_{i=1}^{N} [h(i) + v^{\text{HF}}(i)], \qquad \mathbf{H}^{(1)} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i} v^{\text{HF}}(i)$$

Therefore,

$$E_0^{(0)} = \sum_{i}^{\text{occ}} \varepsilon_i, \qquad E_0^{(1)} = -\frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle \quad \Rightarrow \quad \boxed{E_{\text{HF}} = E_0^{(0)} + E_0^{(1)}}$$

The first information about the correlation energy is given by the 2nd-order energy

$$\boxed{E_0^{(2)} = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{virt}} \frac{\langle ij || ab \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}}$$

This is the MP2 energy!!

There's a similar expression for the MP3 energy, but I was too lazy to type it.

MP3 energy

The third-order correction is a bit ugly...

$$\boxed{\begin{aligned} E_0^{(3)} &= \frac{1}{8} \sum_{ijkl} \sum_{ab} \frac{\langle ij||ab\rangle \langle kl||ij\rangle \langle ab||kl\rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b)} \\ &+ \frac{1}{8} \sum_{ij} \sum_{abcd} \frac{\langle ij||ab\rangle \langle ab||cd\rangle \langle cd||ij\rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_d)} \\ &+ \sum_{ijk} \sum_{abc} \frac{\langle ij||ab\rangle \langle kb||cj\rangle \langle ac||ik\rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_c)} \end{aligned}}$$

NB:
MP2 and MP3 only requires only doubly excited determinants
MP4 does need singly, doubly, triply and quadruply excited determinant!

Be careful!
The MP2 and MP3 correlation energies are given by

$$E_c^{\text{MP2}} = E_0^{(2)} \qquad E_c^{\text{MP3}} = E_0^{(2)} + E_0^{(3)}$$

Illustration for the Be atom

Correlation energy of Be

Level	ΔE_c	%	Level	ΔE_c	%
MP2	0.053174	67.85			
MP3	0.067949	86.70	CISD	0.075277	96.05
MP4	0.074121	94.58			
MP5	0.076918	98.15	CISDT	0.075465	96.29
MP6	0.078090	99.64			
MP7	0.078493	100.15	CISDTQ	0.078372	100

- MPn is not a variational method, i.e. you can get an energy lower than the true ground state energy!
- MPn fails for systems with small HOMO-LUMO gap
- The MPn series can oscillate around the exact energy
- MPn is size-consistent!

Cost of correlated methods

Scaling of CI and MP correlation methods

Scaling	CI methods	MP methods
K^5	CIS	MP2
K^6	CISD	MP3
K^7		MP4
K^8	CISDT	MP5
K^9		MP6
K^{10}	CISDTQ	MP7
$\exp(K)$	FCI	

Problem: H_2 in minimal basis

"Using a minimal basis (like previously), could you calculate the MP2 and MP3 energy of the H_2 molecule?"

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We have calculated the CID correlation energy previously

$$E_c = \Delta - \sqrt{\Delta^2 + K_{12}^2} = -0.0206$$

where

$$\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$

The MP2 correlation energy is

$$E_c^{\text{MP2}} = E^{(2)} = \frac{\langle 11|22\rangle^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} = -0.0132$$

The MP3 correlation energy is

$$E^{(3)} = \frac{K_{12}(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} = -0.0048$$

$$E_c^{\text{MP3}} = E^{(2)} + E^{(3)} = -0.0181$$