Eletronic Structure Theory Notes (WFT)

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1 Many-Body Perturbation Theory

Now we introduce a different method which is not variational but size consistent at each level, called perturbation theory. We divide the total Hamiltonian into two pieces: a zeroth-order $\mathcal{H}_0$ and a perturbation part $\mathcal{V}$.

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{V} \tag{1}$$

where λ is a parameter.
Now the exact eigenfunction to be solved is

$$\mathcal{H}\left|\Phi\right\rangle = \mathcal{E}\left|\Phi\right\rangle \tag{2}$$

and we only know

$$\mathcal{H}_0\left|\Psi_i^0\right\rangle = E_i^0\left|\Psi_i^0\right\rangle \tag{3}$$

We can expand the exact wavefunction and energy

$$\begin{aligned}\mathcal{E} &= E_i^0 + \lambda E_i^1 + \lambda^2 E_i^2 + \cdots \\ \left|\Phi\right\rangle &= \left|\Psi_i^0\right\rangle + \lambda\left|\Psi_i^1\right\rangle + \lambda^2\left|\Psi_i^2\right\rangle + \cdots\end{aligned} \tag{4}$$

By defining the normalization of $\left\langle\Psi_i^0\right|\left|\Phi\right\rangle = 1$, one can easily derive that

$$\left\langle\Psi_i^0\right|\left|\Psi_i^n\right\rangle = 0 \tag{5}$$

Substitute the expansion into the eigenfunction and equate coeffcients of λ^n, we find (to simplify the equation, let $\left|i^n\right\rangle = \left|\Psi_i^n\right\rangle$)

$$\begin{aligned}\mathcal{H}_0\left|i^0\right\rangle &= E_i^0\left|i^0\right\rangle \\ \mathcal{H}_0\left|i^1\right\rangle + \mathcal{V}\left|i^0\right\rangle &= E_i^0\left|i^1\right\rangle + E_i^1\left|i^0\right\rangle \\ \mathcal{H}_0\left|i^2\right\rangle + \mathcal{V}\left|i^1\right\rangle &= E_i^0\left|i^2\right\rangle + E_i^1\left|i^1\right\rangle + E_i^2\left|i^0\right\rangle\end{aligned} \tag{6}$$

Multiply these equations by $\langle i^0|$, we can get the nth-order energies

$$\begin{aligned} E_i^0 &= \langle i^0| \mathcal{H}_0 |i^0\rangle \\ E_i^1 &= \langle i^0| \mathcal{V} |i^0\rangle \\ E_i^2 &= \langle i^0| \mathcal{V} |i^1\rangle \end{aligned} \tag{7}$$

To get the first-order wavefunction,we expand $|i^1\rangle$ in terms of the eigenfunctions of $\mathcal{H}_0$

$$|i^1\rangle = \sum_n c_n^1 |n\rangle \tag{8}$$

$$|i^1\rangle = \sum_n \frac{\langle n| \mathcal{V} |i\rangle}{E_i^0 - E_n^0} \tag{9}$$

the second-order energy

$$E_i^2 = \sum_n \frac{|\langle i| \mathcal{V} |n\rangle|^2}{E_i^0 - E_n^0} \tag{10}$$

After the above introduction of perturbation theory, we now consider how to improve Hatree-Fock energy. We defind the Hamiltonian

$$\mathcal{H}_0 = \sum_i f_i = \sum_i [h(i) + v^{HF}(i)] \tag{11}$$

$$\mathcal{V} = \sum_{i<j} r_{ij}^{-1} - \sum_i v^{HF}(i) \tag{12}$$

this method is called **Moller-Plesset** theory. The first-order energy can be calculated

$$\begin{aligned} E_0^1 &= \langle \Psi_0| \mathcal{V} |\Psi_0\rangle \\ &= \langle \Psi_0| \sum_{i<j} r_{ij}^{-1} |\Psi_0\rangle - \langle \Psi_0| \sum_i v^{HF} |\Psi_0\rangle \\ &= \frac{1}{2} \sum_{ab} \langle ab| |ab\rangle - \sum_a \langle a| v^{HF} |a\rangle \\ &= -\frac{1}{2} \sum_{ab} \langle ab| |ab\rangle \end{aligned} \tag{13}$$

The sum of the zero and first-order energies is Hatree-Fock energy

$$E_{HF} = E_0^0 + E_0^1 = \sum_a \epsilon_a - \frac{1}{2} \sum_{ab} \langle ab| |ab\rangle \tag{14}$$

so the first correction occurs in the second-order energy

$$\begin{aligned} E_0^2 &= \sum_n \frac{|\langle 0|\,\mathcal{V}\,|n\rangle|^2}{E_0^0 - E_n^0} \\ &= \sum_n \frac{|\langle \Psi_0|\,\mathcal{V}\,|\Psi_{ab}^{rs}\rangle|^2}{E_0^0 - E_n^0} \\ &= \sum_{a<b,r<s} \frac{|\langle ab|\,|rs\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \\ &= \frac{1}{4}\sum_{abrs} \frac{|\langle ab|\,|rs\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \end{aligned} \tag{15}$$

2 One-Particle Many-Body Green Function