Non-variational methods - I

1 Many-Body Perturbation Method

Can perturbative methods be used to take care of the shortcoming of the HF method? In other words, can we systematically introduce the effects of configurations neglected in the HF method in perturbative framework? It turns out that it is indeed possible to do so. The basic problem here is to define a suitable zeroth order Hamiltonian (H_0) and the corresponding Zeroth order wave function for the state concerned (ψ_0). Once that is done, we can invoke the standard Rayleigh Schrodinger Perturbation Theory (RSPT) to introduce corrections to the zeroth order energy and the wave function at different orders. The resulting systematism has been known as many-body Perturbation theory.

A common way of choosing the zeroth order Hamiltonian H_0 of a many electron system is to take it as the sum of Fock operators for all the electrons. With this choice

$$H_0 = \sum_{i=1}^{n_e} f_i = \sum_{i=1}^{n_e} \{h_i + \sum_{j=1}^{n_e} 2J_j - K_j\} \tag{1}$$

$$= \sum_{i=1}^{n_e} h_{ii} + \sum_{i=1}^{n_e}\sum_{j=1}^{n_e} \langle g_{ij} \rangle, \ (2J_{ij} - k_{ij} = \langle g_{ij} \rangle)$$

$$= \sum_{i=1}^{n_e} h_{ii} + 2\langle V_{ee} \rangle$$

(2)

On the other hand $H = \sum_{i=1}^{n_e} h_{ii} + \sum_{i=1}^{n_e}\sum_{j>i}^{n_e} g_{ij} = h_1 + V_{ee}$

[Note the double count of electron repulsion in equation (2)

The perturbation V is then easily seen to be

$$V = H - H_0 = \sum_i \sum_{j>i} g_{ij} - \sum_{i=1}^{n_e} \sum_{j=1}^{n_e} \langle g_{ij} \rangle$$

$$= V_{ee} - 2\langle V_{ee} \rangle \tag{3}$$

The zeroth order wave function is just the HF (single determinant wave function, ψ_0) and zeroth order energy is

$$E_0 = \langle \psi_0 | H_0 | \psi_0 \rangle = \sum_i \langle \psi_0 | f_i | \psi_0 \rangle$$

$$= \sum_{i=1}^{n_e} \varepsilon_i \tag{4}$$

that is, just the sum of the energies of all the occupied orbitals.

The first order correction $\Delta E^{(1)}$ to E_0 is the expectation value of the perturbation V, i.e.,

$$\Delta E^{(1)} = \langle \psi_0 | V | \psi_0 \rangle$$

$$= \langle V_{ee} \rangle - \langle 2V_{ee} \rangle$$

$$= -\langle V_{ee} \rangle \tag{5}$$

which takes care of the double counting of electron-repulsion in the zeroth order energy (E_0). Therefore,

$$E_0 + \Delta E^{(1)} = (E_0^{HF}) \tag{6}$$

which means that with the specific choice of H_0 and V, the correct HF energy is recovered at the first order. Electron correlation effects begin to appear only at the next higher order for example, in the 2nd order correction to E_0. The perturbation theory that we are discussing here has been known as Moller-Plesset perturbation theory.

Let us work out the second order energy correction $\Delta E^{(2)}$. According to the Rayleigh Schrodinger Perturbation theory (RSPT),

$$\Delta E^{(2)} = \sum_i \frac{\langle \psi_0 | V | \psi_i \rangle \langle \psi_i | V | \psi_0 \rangle}{E_0 - E_i} \tag{7}$$

ψ_i s are all possible excited states of the system. Now $\langle \psi_i | V | \psi_0 \rangle = 0$, if ψ_i is a singly excited state (with respect to the HF ground state), by virtue of Billouin's theorem and orthogonality of canonical HF orbitals. If ψ_i s are triply, quadruply or higher excited states, with respect to the HF

ground state, $\langle \psi_i | V | \psi_0 \rangle = 0$, as V contains only two-electron operators. This leads to a compact expression for $\Delta E^{(2)}$ that involves computation of matrix elements of V between the HF ground state and all the doubly excited singlet state wave functions of the system.

$$\text{So, } \Delta E^{(2)} = \sum_{i<j}^{occ} \sum_{p<q}^{unocc} \frac{\langle \psi_0 | V | \psi_{ij}^{pq} \rangle \langle \psi_{ij}^{pq} | V | \psi_0 \rangle}{E_0 - E_{ij}^{ab}}$$

$$= \sum_{i<j} \sum_{p<q} \frac{| \langle \phi_i \phi_j \| \phi_p \phi_q \rangle - \langle \phi_i \phi_j \| \phi_q \phi_p \rangle |^2}{(\varepsilon_i + \varepsilon_j - \varepsilon_p - \varepsilon_q)}$$

$$= \Delta E(MP2) \qquad (8)$$

The second order MOller-Plesset perturbation theoretical correction to the energy is easily computed once the relevant two electron integrals over the MOs (only the integrals that involve two occupied and two unoccupied MOs) are available. This entails computational labour that grows as $(N_{basis})^5$. Approximately 80-90 percent of the correlation energy can be recovered by an MP2 calculation at a computational cost more or less similar to the cost of calculation of HF energy of the system. One can go to higher orders (MP3, MP4, ...), at a higher computational cost.

Note: AO-MO transformation:

All post-Hartree Fock methods require 2-electron integrals over MO basis, a typical integral being $\langle \phi_i \phi_j | \phi_k \phi_l \rangle$. $\langle \phi_i \phi_j | \phi_k \phi_l \rangle = \sum_p^N \sum_q^N \sum_r^N \sum_s^N C_{pi} \left[C_{qi} \left[C_{rk} \left[C_{sl} \langle \chi_p \chi_q | \chi_r \chi_s \rangle \right] \right] \right]$. The evaluation is best carried out by performing the transforming one index at a time as indicated by [] reducing the bottle neck to a N5 dependence approximately, from the N8 dependence.