Moller Plesset Perturbation Theory

In Moller-Plesset (MP) perturbation theory one takes the unperturbed Hamiltonian for an atom or molecule as the sum of the one particle Fock operators

$$\hat{H}^0 = \sum_{i=1}^{N} \hat{F}(i)$$

where the eigenfunctions of $\hat{F}$ are the occupied and virtual Hartree-Fock orbitals of the system and the eigenvalues the associated one electron energies.

$$\hat{F}\varphi_i = \varepsilon_i \varphi_i$$

The Hartree-Fock wavefunction

$$\psi_0(1,2,\cdots,N) = \hat{\mathcal{A}}\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)$$

is an eigenfunction of $\hat{H}^0$ with an eigenvalue equal to the sum of the one electron energies of the occupied spin orbitals

$$E_0 = \sum_{i=1}^{N} \varepsilon_i$$

The essential observation in MP perturbation theory is that all Slater determinants formed by exciting electrons form the occupied to the virtual orbitals are also eigenfunctions of $\hat{H}^0$ with an eigenvalue equal to the sum of the one electron energies of the occupied spin orbitals. So a determinant formed by exciting from the i^{th} spin orbital in the Hartree-Fock ground state into the a^{th} virtual spin orbital

$$\psi_i^a = \hat{\mathcal{A}}\varphi_1(1)\varphi_2(2)\varphi_{i-1}(i-1)\varphi_a(i)\varphi_{i+1}(i+1)\cdots\varphi_N(N)$$

has the eigenvalue

$$E_i^a = E_0 + \varepsilon_a - \varepsilon_i$$

Similarly, the doubly excited determinant, ψ_{ij}^{ab} has the eigenvalue

$$E_{ij}^{ab} = E_0 + \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$$

and so on. With N electrons we have N ground state spin orbitals $(i = 1, 2, \cdots, N)$ while the number of virtual orbitals depends on the number of functions in the expansion basis. Lets say we have N_V virtual orbitals $(a = 1, 2, \cdots, N_V)$. We then have NN_V single excitations, $\left(\frac{N}{2}\right)\left(\frac{N_V}{2}\right)$ double excitations, $\left(\frac{N}{3}\right)\left(\frac{N_V}{3}\right)$ triples, etc. up to $\left(\frac{N}{N}\right)\left(\frac{N_V}{N}\right)$ N fold excitations. The total number of excited determinants and therefore the total number of excited eigenfunctions of $\hat{H}^0$ is

$$N_{total} = \sum_{k=1}^{N} \left(\frac{N}{k}\right)\left(\frac{N_V}{k}\right)$$

Knowing all of the eigenvalues and eigenfunctions of $\hat{H}^0$ we can use Rayleigh-Schrodinger perturbation theory to find the energies and eigenfunctions of $\hat{H}$. We write the perturbation as the difference between the perturbed and unperturbed Hamiltonians.

$$\hat{V} = \hat{H} - \hat{H}^0$$

As usual

$$\hat{H} = \sum_{i=1}^{N} \hat{f}(i) + \sum_{i<j}^{N} g(i,j)$$

The Fock operator has the form

$$\hat{F}(1) = \hat{f}(1) + \hat{V}_{HF}(1)$$

where the Hartree-Fock potential is given by

$$\hat{V}_{HF}(1) = \sum_{j=1}^{N} \int d\tau(2) \varphi_j^*(2) g(1,2)(1 - \hat{P}_{12}) \varphi_j(2)$$

The one electron operators, $\hat{f}$ in $\hat{H}$ & $\hat{H}^0$ are identical and cancel in taking the difference resulting in the perturbation

$$\hat{V} = \sum_{i<j}^{N} g(i,j) - \sum_{j=1}^{N} \hat{V}_{HF}(j)$$

which is the difference between the instantaneous and average electron-electron interaction. This perturbation is sometimes called the fluctuation potential as one imagine that it measures the deviation from the mean of the electron-electron interaction.

The first order correction to the energy is the average of the perturbation over the unpertubed wavefunction. In this context this is given by

$$E_0^{(1)} = \langle \psi_0 | \hat{V} | \psi_0 \rangle = \langle \psi_0 | \sum_{i<j}^{N} g(i,j) - \sum_{j=1}^{N} \hat{V}_{HF}(j) | \psi_0 \rangle$$

From the Slater-Condon rules we have

$$\langle \psi_0 | \sum_{i<j}^{N} g(i,j) | \psi_0 \rangle = \sum_{i<j}^{N} \left\langle \varphi_i \varphi_j \left| g(1,2)(1-\hat{P}_{12}) \right| \varphi_i \varphi_j \right\rangle$$

and

$$\langle \psi_0 | \sum_{i=1}^{N} \hat{V}_{HF} | \psi_0 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_i \varphi_j \left| g(1,2)(1-\hat{P}_{12}) \right| \varphi_i \varphi_j \right\rangle$$

resulting in

$$E_0^{(1)} = -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_i \varphi_j \left| g(1,2)(1-\hat{P}_{12}) \right| \varphi_i \varphi_j \right\rangle$$

We note that the energy through first order is simply the Hartree-Fock energy.

$$E_{HF} = \langle \psi_0 | \hat{H} | \psi_0 \rangle = E_0 + E_0^{(1)} = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_i \varphi_j \left| g(1,2)(1-\hat{P}_{12}) \right| \varphi_i \varphi_j \right\rangle$$

The second order correction to the ground state energy depends on the first order correction to the wavefunction. This in turn depends on matrix elements of the perturbation between the unperturbed ground and excited states of $\hat{H}^0$. In this context this is

$$E_0^{(2)} = \sum_{\nu \neq 0} \frac{\left| V_{\mu\nu} \right|^2}{E_{0\nu}} = E^S + E^D + E^T + \cdots + E^N$$

The single excitations contribute

$$E^S = \sum_{i=1}^{N} \sum_{a=1}^{N_V} \frac{\left| \langle \psi_0 | \hat{V} | \psi_i^a \rangle \right|^2}{\varepsilon_i - \varepsilon_a}$$

Since

$$\left\langle \psi_0 \middle| \sum_{i<j}^{N} g(1,2) \middle| \psi_k^a \right\rangle = \pm \sum_{i=1}^{N} \left\langle \varphi_k \varphi_i \middle| g(1,2)(1-\hat{P}_{12}) \middle| \varphi_a \varphi_i \right\rangle \text{ and}$$

$$\left\langle \psi_0 \middle| \sum_{j=1}^{N} \hat{V}_{HF} \middle| \psi_k^a \right\rangle = \pm \sum_{i=1}^{N} \left\langle \varphi_k \varphi_i \middle| g(1,2)(1-\hat{P}_{12}) \middle| \varphi_a \varphi_i \right\rangle$$

so

$$\left\langle \psi_0 \middle| \sum_{i<j}^{N} g(1,2) - \sum_{j=1}^{N} \hat{V}_{HF} \middle| \psi_k^a \right\rangle = 0 \text{ and } E^S = 0 .$$

The double excitations contribute

$$E^D = \sum_{i<j}^{N} \sum_{a<b}^{N_V} \frac{\left| \left\langle \psi_0 \middle| \hat{V} \middle| \psi_{ij}^{ab} \right\rangle \right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

Because $\sum_{j=1}^{N} \hat{V}_{HF}$ is a one electron operator all matrix elements between ψ_0 & ψ_{ij}^{ab} vanish and only $\sum_{i<j}^{N} g(1,2)$ contributes

$$\left\langle \psi_0 \middle| \sum_{i<j}^{N} g(1,2) \middle| \psi_{kl}^{ab} \right\rangle = \pm \left\langle \varphi_k \varphi_l \middle| g(1,2)(1-\hat{P}_{12}) \middle| \varphi_a \varphi_b \right\rangle$$

and therefore

$$E^D = \sum_{i<j}^{N} \sum_{a<b}^{N_V} \frac{\left| \left\langle \varphi_i \varphi_j \middle| g(1,2)(1-\hat{P}_{12}) \middle| \varphi_a \varphi_b \right\rangle \right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

All matrix elements of the perturbation involving triple or higher excitations vanish and so

$$E^T + E^Q + \cdots + E^N = 0$$

and

$$E_0^{(2)} = E^D = \frac{1}{4}\sum_{i,j}^{N}\sum_{a,b}^{N_V} \frac{\left|\left\langle \varphi_i\varphi_j \left| g(1,2)(1-\hat{P}_{12}) \right| \varphi_a\varphi_b \right\rangle\right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

We have rewritten the summations as unrestricted sums and note that the $i = j \ \& \ a = b$ terms vanish. Note also that denominator is always negative so $E_0^{(2)} < 0$, as required.