IIc.   Möller-Plesset perturbation theory

While the configuration interaction method is clearly a rigorous way to add correlation to the Hartree-Fock results, the method is computationally very demanding because of the large number of excited Slater determinants that need - at least in principle - to be included. Another commonly used estimate of the correlation energy is based on perturbation theory rather than variational calculations and is usually referred to as Möller-Plesset perturbation theory, MPN, where N stands for the order of the perturbation included in the calculations. It is not clear how to reach the exact result with this approach. In fact, the perturbation expansion has been shown not to converge as N becomes larger in some cases. Still, MP2 and MP4 are commonly used approximations.

The Hamiltonian is partitioned as

$$H = H_0 + P$$

where H_0 is the Hartree-Fock Hamiltonian

$$H_0 = \sum_i f(i) = \sum_i [h(i) + v^{HF}(i)]$$

and

$$P = \sum_{i<j} r_{ij}^{-1} - \sum_i v^{HF}(i)$$

is the perturbation. Here, $v^{HF}(i)$ denotes the Coulomb and exchange interaction of electron i with the rest of the electrons in the Hartree-Fock approximation. From the expression for the Hartree-Fock energy, one can see that

$$v^{HF}\chi_a(x_1) = \sum_b \int dx_2 \frac{|\chi_b(x_2)|^2}{r_{12}} \chi_a(x_1) - \sum_b \int dx_2 \frac{\chi_b^*(x_2)\chi_a(x_2)}{r_{12}} \chi_b(x_1)$$

$$= \sum_b [b|r_{12}^{-1}|b]\chi_a(x_1) - \sum_b [b|r_{12}^{-1}|a]\chi_b(x_1)$$

and the expectation value of v^{HF} for orbital a is

$$[a|v^{HF}|a] = \sum_b [aa|bb] - [ab|ba] .$$

The indices i and j are used for electrons, while a and b point to orbitals.

The Hartree-Fock Slater determinant, $|\Psi_0 >$, is an eigenfunction of H_0

$$H_0 |\Psi_0 > = E_0^{(0)} |\Psi_0 >$$

with eigenvalue

$$E_0^{(0)} = \sum_a \epsilon_a$$

where ϵ_a is the orbital energy for orbital a. This is the zeroth order perturbation energy. Note that this is not the same as the Hartree-Fock estimate of the energy of the system, $E_0^{HF} = < \Psi_0|H|\Psi_0 >$, which involves the exact Hamiltonian.

To first order, the correction to the energy is

$$E_0^{(1)} = < \Psi_0|P|\Psi_0 >$$

$$= < \Psi_0| \sum_{i<j} r_{ij}^{-1}|\Psi_0 > - < \Psi_0| \sum_i v^{HF}(i)|\Psi_0 >$$

$$= \frac{1}{2} \sum_a \sum_b ([aa|bb] - [ab|ba]) - \sum_a [a|v^{HF}|a]$$

The second sum is just twice the first sum so the final result is

$$E_0^{(1)} = -\frac{1}{2} \sum_a \sum_b [aa|bb] - [ab|ba] .$$

This shows that the Hartree-Fock energy is the sum of the zeroth and first order perturbation energy

$$E_0^{HF} = E_0^{(0)} + E_0^{(1)} = \sum_a \epsilon_a - \frac{1}{2} \sum_{ab} [aa|bb] - [ab|ba] .$$

In order to introduce correlation, one needs to go to second order or higher in the perturbation. The second order energy is

$$E_0^{(2)} = \sum_n \frac{| < 0|P|n > |^2}{E_0^{(0)} - E_n^{(0)}}$$

where the sum runs over all states except the ground state of the system. Here, $|0 >$ denotes $|\Psi_0 >$ and $|n >$ is a Slater determinant corresponding to higher energy electron configurations. It turns out that single excitation Slater determinants do not give a non-zero contribution to $E_0^{(2)}$, i.e.

$$< \Psi_0|P|\Psi_a^r > = 0 .$$

Also, the triple and higher order excitation determinants do not give a non-zero contribution because the perturbation includes only pairwise interactions. Only the double excitation determinants, $|\Psi_{ab}^{rs} >$, give a non-zero contribution. The matrix elements are (see table 2 for matrix elements of Slater determinants)

$$< \Psi_0| \sum_{i<j} r_{ij}^{-1}|\Psi_{ab}^{rs} > = [ar|bs] - [as|br]$$

and the energy eigenvalue of the double excitation determinants is $E_0^{(0)} - \epsilon_a - \epsilon_b + \epsilon_r + \epsilon_s)$, that is

$$H_0|\Psi_{ab}^{rs} > = (E_0^{(0)} - \epsilon_a - \epsilon_b + \epsilon_r + \epsilon_s) |\Psi_{ab}^{rs} > .$$

The expression for the second order energy then becomes

$$E_0^{(2)} = \sum_{a<b} \sum_{r<s} \frac{|<\Psi_0| \sum_{i<j} r_{ij}^{-1} |\Psi_{ab}^{rs}>|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

$$= \sum_{a<b} \sum_{r<s} \frac{|[ar|bs] - [as|br]|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \ .$$

Note that the second-order energy can be expressed as a sum over contributions from each pair of electrons in occupied orbitals

$$E_0^{(2)} = \sum_{a<b} e_{ab}$$

and the contribution from each pair involves a sum over pairs of virtual orbitals

$$e_{ab} = \sum_{r<s} \frac{|[ar|bs] - [as|br]|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \ .$$

The estimate of the energy to second order is referred to as the MP2 approximation to the energy of the system

$$E_0^{MP2} = E_0^{(0)} + E_0^{(1)} + E_0^{(2)}.$$