Coupled Cluster Theory

The basic ansatz of coupled cluster theory is that the exact many-electron wavefunction may be generated by the operation of an exponential operator on a single determinant.

$$\Psi = e^{\hat{T}} \Phi_0$$

where Ψ is the exact wavefunction, \hat{T} is an excitation operator, Φ_0 and is a single determinant wavefunction, usually the Hartree-Fock determinant. The excitation operator can be written as a linear combination of single, double, triple, etc excitations, up to N fold excitations for an N electron system.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_N$$

where

and

 $\hat{T}_2 \Phi_0 = \sum_{i>j}^{occ} \sum_{a>b}^{virt} t_{ij}^{ab} \Phi_{ij}^{ab}$

 $\hat{T}_1 \Phi_0 = \sum_i^{occ} \sum_a^{virt} t_i^a \Phi_i^a$

and

$$\hat{T}_3 \Phi_0 = \sum_{i>j>k}^{occ} \sum_{a>b>c}^{virt} t_{ijk}^{abc} \Phi_{ijk}^{abc}$$

etc. The coefficients, t_i^a , t_{ij}^{ab} , t_{ijk}^{abc} ,... of the various determinants are called the amplitudes.

The exponential operator is defined by the usual expansion

$$e^{\hat{T}} = \sum_{N=0}^{\infty} \frac{\hat{T}^{N}}{N!} = 1 + T + \frac{1}{2}T^{2} + \frac{1}{3!}T^{3} + \frac{1}{4!}T^{4} + \dots$$

and so

$$e^{\hat{T}} = 1 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...) + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...)^2 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...)^3 + ...$$

Gathering orders of excitation

$$e^{\hat{T}} = 1 + \hat{T}_1 + (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) + (\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3) + (\hat{T}_4 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \hat{T}_1\hat{T}_3 + \frac{1}{24}\hat{T}_1^4) + \dots$$

We see that there is only one way to have a single excitation, \hat{T}_1 , but two ways to generate double excitations. We may have a pure double excitation, \hat{T}_2 , or two successive

single excitations $\hat{T}_1 \hat{T}_1 = \hat{T}_2^2$. Similarly there are three ways to generate triply excited determinants, a pure triple, \hat{T}_3 , or a single and a double, $\hat{T}_1 \hat{T}_2$ or three singles, $\hat{T}_1 \hat{T}_1 = \hat{T}_1^3$, etc.

We may define an operator for each of these classes of excitations

$$\hat{C}_{1} = \hat{T}_{1}, \text{ single excitations}$$

$$\hat{C}_{2} = \hat{T}_{2} + \frac{1}{2}\hat{T}_{1}^{2}; \text{ double excitations}$$

$$\hat{C}_{3} = \hat{T}_{3} + \hat{T}_{1}\hat{T}_{2} + \frac{1}{6}\hat{T}_{1}^{3}; \text{ triple excitations}$$

$$\hat{C}_{4} = \hat{T}_{4} + \frac{1}{2}\hat{T}_{2}^{2} + \frac{1}{2}\hat{T}_{1}^{2}\hat{T}_{2} + \hat{T}_{1}\hat{T}_{3} + \frac{1}{24}\hat{T}_{1}^{4}; \text{ four fold excitations}$$

and so on.

We may then write the exponential operator as

$$e^{\hat{T}} = 1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \hat{C}_4 + \dots$$

Given that one knows the solution to the Hartree-Fock equations for a system, one knows all of the occupied and virtual orbitals and therefore all of the determinants. To construct the coupled cluster wavefunction one must then determine the various amplitudes, $t_i^a, t_{ij}^{ab}, t_{ijk}^{abc}, \dots$

The Energy of a Coupled Cluster Wavefunction.

Let's first obtain the equation that determines the energy, E.

The Schrodinger equation is

or

 $\hat{H}\Psi = E\Psi$

$$(\hat{H} - E_0)\Psi = (E - E_0)\Psi$$

where we have subtracted the Hartree-Fock energy

$$E_0 = \left\langle \Phi_0 \left| \hat{H} \right| \Phi_0 \right\rangle$$

from both sides. We then define

 $\hat{H}_{\scriptscriptstyle N}=\hat{H}-E_{\scriptscriptstyle 0}$, and the correlation energy $\Delta E=E-E_{\scriptscriptstyle 0}$

and then write the Schrodinger equations as

$$\hat{H}_N \Psi = \Delta E \Psi$$

If we insert the CC ansatz for the wavefunction, muliply both sides of this equation with Φ_0 , and integrate we have

$$\left\langle \Phi_{0} \left| \hat{H}_{N} \right| (1 + \hat{C}_{1} + \hat{C}_{2} + \hat{C}_{3} + \hat{C}_{4} + \dots) \Phi_{0} \right\rangle = \Delta E \left\langle \Phi_{0} \left| (1 + \hat{C}_{1} + \hat{C}_{2} + \hat{C}_{3} + \hat{C}_{4} + \dots) \Phi_{0} \right\rangle$$

Because of the definition of \hat{H}_N , $\langle \Phi_0 | \hat{H}_N | \Phi_0 \rangle = 0$ and because Φ_0 is the Hartree Fock determinant, Brillouins theorem requires $\langle \Phi_0 | \hat{H}_N | \hat{C}_1 \Phi_0 \rangle = 0$. The Slater Condon rules then dictate that only the double excitation term on the left and the zero excitation term on the right survive. Accordingly we have

$$\left\langle \Phi_{0}\left|\hat{H}_{N}\right|\hat{C}_{2}\Phi_{0}\right\rangle =\Delta E$$

Now

$$\hat{C}_2 \Phi_0 = (\hat{T}_2 + \frac{1}{2} \hat{T}_1^2) \Phi_0$$

Now

$$\hat{T}_2 \Phi_0 = \sum_{i>j}^{occ} \sum_{a>b}^{virt} t^{ab}_{ij} \Phi^{ab}_{ij}$$

and

$$\hat{T}_1^2 \Phi_0 = \hat{T}_1 \sum_i^{occ} \sum_a^{virt} t_i^a \Phi_i^a = \sum_i^{occ} \sum_a^{virt} t_i^a \hat{T}_1 \Phi_i^a = \sum_i^{occ} \sum_a^{virt} t_i^a \sum_j^{occ} \sum_b^{virt} t_j^b \Phi_{ij}^{ab}$$

Eliminating the unrestricted summations and using the symmetry of the doubly excited determinant, $\Phi_{ij}^{ab} = -\Phi_{ji}^{ab} = -\Phi_{ij}^{ab} = \Phi_{ji}^{ba}$ results in

$$\hat{T}_{1}^{2}\Phi_{0} = 2\sum_{i>j}^{occ}\sum_{a>b}^{virt} (t_{i}^{a}t_{j}^{b} - t_{i}^{b}t_{j}^{a})\Phi_{ij}^{ab}$$

and

$$\hat{C}_{2}\Phi_{0} = \sum_{i>j}^{occ} \sum_{a>b}^{virt} (t_{ij}^{ab} + t_{i}^{a}t_{j}^{b} - t_{i}^{b}t_{j}^{a})\Phi_{ij}^{ab}$$

and finally.

$$\Delta E = \left\langle \Phi_0 \left| \hat{H}_N \right| \hat{C}_2 \Phi_0 \right\rangle = \sum_{i>j}^{occ} \sum_{a>b}^{virt} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \left\langle ia \right| \left| jb \right\rangle$$

So,

$$E = E_0 + \Delta E = E_0 + \sum_{i>j}^{occ} \sum_{a>b}^{virt} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle ia || jb \rangle$$

Where

$$\langle ia || jb \rangle = \int d\tau(1) d\tau(2) \varphi_i^*(1) \varphi_a^*(2) g(1,2)(1-\hat{P}_{12}) \varphi_j(1) \varphi_b(2)$$

Note that the single and double excitation amplitudes, just as in the configuration interaction method, determine the total energy. The question is then, how do we determine these amplitudes?

The determination of the excitation amplitudes.

One writes the Shrodinger equation as

 $\hat{H}_{N}\Psi = \Delta E\Psi$

substitutes the CC ansatz for the wavefunction, multiplies both sides by the singly excited determinant, Φ_m^e and then intergrates. The result is

$$\left\langle \Phi_m^e \left| \hat{H}_N \right| (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3) \Phi_0 \right\rangle = \Delta E \quad t_e^m$$

Where the Slater-Condon rules assure that no more than three fold excitations contribute to the left hand side and only the single excitation Φ_m^e contributes to the right hand side.