

Non-variational methods - II

2 Coupled Cluster Methods

We have seen how the many body perturbation methods take care of different configurations neglected in the Hartree-Fock theory (singles, doubles, etc.), each upto a given order. Could we have a method in which all corrections of a particular type are accounted for upto infinite order ? The answer leads us to what has been known in literature as the coupled cluster (CC) methods.

Starting with the closed-shell ground state HF wave function $\phi_0 = \psi_{HF}$ as the reference wave function, the coupled cluster wave function is written as

$$\psi_{cc} = e^T \phi_0 \quad (9)$$

$$= \sum_{m=0}^{\infty} \frac{1}{m!} T^m \phi_0, \quad (10)$$

$$\text{where } T = T_1 + T_2 + T_3 + \dots T_n \quad (11)$$

T is an excitation operator, that has been resolved into a sum of one (T_1), two (T_2), three (T_3), . . . $n(T_n)$ electron excitation operators. The k -electron excitation operator (T_k) acts on the HF reference wave function ϕ_0 to generate all the Slater determinants that represent k -electron excitation with respect to ϕ_0 . Typically,

$$T_1 \phi_0 = \sum_{i=1}^{noc} \sum_{p=noc+1}^{unocc} t_i^p \phi_i^p \quad (12)$$

$$T_2 \phi_0 = \sum_{i=1}^{noc} \sum_{p=noc+1}^{unocc} t_{ij}^{pq} \phi_{ij}^{pq}, \text{ etc} \quad (13)$$

The basic unknowns in the CC theory are the cluster amplitudes $\{t_i^p\}, \{t_{ij}^{pq}\}, \{t_{ijk}^{pqr}\}$, **of one, two, three electron excited determinants etc.** Using (10) and (11), the exponential operator (e^T) acting on ϕ_0 may be written as

$$e^T \phi_0 = \{ \mathbb{I} + T_1 + (T_2 + \frac{1}{2} T_1^2 + (T_3 + T_2 T_1 + \frac{1}{6} T_1^3) + \dots) \phi_0 \quad (14)$$

The first term (\mathbb{I}) in the above expression generates the HF function (ϕ_0) while all the singly excited (w.r.t. ϕ_0) configurations are produced by the action of T_1 on ϕ_0 . The group of terms generated by $(T_2 + \frac{1}{2} T_1^2) \phi_0$ include all connected double excitations ($T_2 \phi_0$) and also all disconnected double excitation ($T_1^2 \phi_0$). Similarly, the group of terms generated by $(T_3 + T_2 T_1 + \frac{1}{6} T_1^3) \phi_0$ represent all triply excited states which include the conventional or direct triples ($T_3 \phi_0$) or product triples ($T_2 T_1 \phi_0$ or $T_1^3 \phi_0$) and, so on for quadruply excited configurations.

Following the CC recipe, the Schrodinger equation for the stationary states of H can be written in the form

$$H | e^T \phi_0 \rangle = E | e^T \phi_0 \rangle \quad (15)$$

Projecting equation 34 on $\langle \phi_0$, we have

$$\langle \phi_0 | H e^T | \phi_0 \rangle = \tilde{E}_0 \langle \phi_0 | e^T | \phi_0 \rangle \quad (16)$$

$$= \tilde{E}_0 \langle \phi_0 | 1 + T_1 + T_2 + \dots | \phi_0 \rangle \quad (17)$$

where $\tilde{E}_0 = \langle \phi_0 | H e^T | \phi_0 \rangle$ is the coupled cluster energy of the system in the ground state.

We note here that the atomic/molecular many electron Hamiltonian contains only one $\left(\frac{1}{r_i}\right)$ and two-electron interaction operators $\left(\frac{1}{r_{ij}}\right)$ and conclude that we can write the following

expression for the CC energy (Note: $H e^T = H(\mathbb{1} + T_1 + T_2 + \frac{1}{2}T_1^2)$, since only one and two electron interactions are operating)

$$\begin{aligned} \tilde{E}_0 &= \left\langle \phi_0 \left| H \left(1 + T_1 + T_2 + \frac{1}{2} T_1^2 \right) \right| \phi_0 \right\rangle \\ &= \langle \phi_0 | H | \phi_0 \rangle + \langle \phi_0 | H | T_1 \phi_0 \rangle + \langle \phi_0 | H | T_2 \phi_0 \rangle + \frac{1}{2} \langle \phi_0 | H | T_1^2 \phi_0 \rangle \\ &= E_0 + \sum_{i=1}^{nocc} \sum_{nocc+1}^{imocc} t_i^p \langle \phi_0 | \phi_i^p \rangle + \sum_{i<j}^{nocc} \sum_{p<q}^{imocc} (t_{ij}^{pq} + t_i^p t_j^q - t_i^q t_j^p) \langle \phi_0 | H | \phi_{ij}^{pq} \rangle \end{aligned} \quad (18)$$

Since ϕ_0 is the HF determinant E_0 is just the Hartree-Fock energy of the ground state.

$\langle \phi_0 | H | \phi_i^p \rangle$, on the other hand is zero by virtue of Brillouin's theorem while

$$\langle \phi_0 | H | \phi_{ij}^{pq} \rangle = \sum_{i<j}^{nocc} \sum_{p<q}^{imocc} (t_{ij}^{pq} + t_i^p t_j^q - t_i^q t_j^p) \{ \langle \phi_i \phi_j | \phi_p \phi_q \rangle - \langle \phi_i \phi_j | \phi_q \phi_p \rangle \} \quad (19)$$

represents energy correction coming from double excitations. The coupled cluster energy is therefore fully determined once excitation amplitudes of all single and double excitations (t_i^p s and t_{ij}^{pq} s) and the relevant two-electron integrals over the MOs are computed. The equations determining the unknown amplitudes are obtained easily by noting that the equation

$$H e^T \phi_0 = E e^T \phi_0 \quad (20)$$

under a similarity transformation defined by e^T and e^{-T} reads

$$\tilde{H} | \phi_0 \rangle = e^{-T} H e^T | \phi_0 \rangle = \tilde{E} | \phi_0 \rangle$$

so that projecting on $\langle \phi_0$ | we get

$$\tilde{E} = \langle \phi_0 | e^{-T} H e^T | \phi_0 \rangle$$

Projecting on excited states $\langle \phi_k^p$ |, $\langle \phi_{kl}^{pq}$ |, etc. gives

$$\langle \phi_k^p | e^{-T} H e^T | \phi_0 \rangle = 0$$

$$\langle \phi_{kl}^{pq} | e^{-T} H e^T | \phi_0 \rangle = 0, \text{ etc.}$$

since $|\phi_0\rangle \perp |\phi_k^p\rangle \perp |\phi_{kl}^{pq}\rangle$, etc.

After a little manipulation, one is led to a complete set of non-linear algebraic equations

for the unknown cluster amplitudes (t_i^p, t_{ij}^{pq} , etc) which can be iteratively solved by a variety of techniques.

• **Notes:**

- (a) e^{-T} is interpreted as a de-excitation operator just as e^T is an excitation operator.
- (b) e^{-T} acts on functions on the left, for example on $\langle \phi_{ij}^{pq}$, etc.
- (c) \tilde{H} is a similarity transformed form of H . (Is \tilde{H} hermitian?)
- (d) In an n -electron system T contains upto n -electron excitation operators (T_N). If T is chosen as T_2 , the exact coupled cluster equations get replaced by an approximate coupled cluster equation, called coupled cluster doubles (CCD approximation). If T is set to be equal to T_1 plus T_2 the corresponding approximation is called coupled cluster singles and doubles (CCSD) approximation. Still higher order approximations are available.
- (e) CCD leads to substantial improvement in energy (relative to HF) but one-electron properties (like dipole moment) remain unaffected (why?).
- (f) CCSD leads to improvement of both energy and one electron properties relative to HF (why?).

(g) The CCSD case may be examined a bit more closely. In this case, $T=T_1+T_2$ and

$$e^T \approx e^{T_1+T_2} \approx 1 + T_1 + \left(T_2 + \frac{1}{2} T_1^2 \right) + \left(T_2 T_1 + \frac{1}{6} T_1^3 \right) + \dots$$

The CCSD energy is given by

$$E_{CCSD} = E_D + \sum_{i < j} \sum_{p < q}^{nocc} (t_{ij}^{pq} + t_i^p t_j^q) \left(\langle \phi_i \phi_j | \phi_p \phi_q \rangle - \langle \phi_i \phi_j | \phi_q \phi_p \rangle \right)$$

The CC amplitude equation are easily determined by the projection technique. Taking a singly excited configuration (e \rightarrow f) of ϕ_e^f for projection we get from equation 20

$$\left\langle \phi_e^f (1 - T_1) | H \left[1 + T_1 + \left(T_2 + \frac{1}{2} T_1^2 \right) + \left(T_2 T_1 + \frac{1}{6} T_1^3 \right) \right] \phi_0 \right\rangle = 0 \dots (i)$$

Using Brillouin's theorem we have (on the left only T_1 is retained as deexcitation below ϕ_0 is not possible)

$$\begin{aligned} & \left\langle \phi_e^f | H \left[T_1 + \left(T_2 + \frac{1}{2} T_1^2 \right) + \left(T_2 T_1 + \frac{1}{6} T_1^3 \right) \right] \phi_0 \right\rangle \\ & - t_e^f \left\langle \phi_0 | H \left[1 + \left(T_2 + \frac{1}{2} T_1^2 \right) \right] \phi_0 \right\rangle = 0 \dots \dots \dots (ii) \end{aligned}$$

Noting that

$$T_1|\phi_0\rangle = \sum_{i,p} t_i^p \phi_i^p$$

$$T_2|\phi_0\rangle = \sum_{i,j} \sum_{p,q} t_{ij}^{pq} \phi_{ij}^{pq}$$

it is now simple to arrive at the explicit algebraic equations for the SD cluster amplitudes.