Coupled Cluster Theory

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October 17, 2023

1 Basic Concepts

Using second quantized operators, the excited state (configuration) can be represented as

$$|\Psi_i^a\rangle = a_a^\dagger a_i |\Psi_{HF}\rangle \tag{1}$$
$$|\Psi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_i a_j |\Psi_{HF}\rangle \tag{2}$$

In CI method, the exact wavefunction is the linear combination of these configuration. However, there are lots of problems in this method when facing strong corrleation system. Thus we will introduce a new method called CC (Coupled Cluster).
If the electrons have strong corrleation between each other, the independent-particle approximation is not good. We should imporve it by adding extra function which corrleates motions of pair electrons.

$$f_{ij}(x_m, x_n) = \sum_{a>b} t_{ij}^{ab} \phi_a(x_m)\phi_b(x_n) \tag{3}$$

For example, if we define the exact wavefunction as $|\Phi_0\rangle$, where

$$|\Phi_0\rangle = |\phi_i(x_1)\phi_j(x_2)\phi_k(x_3)\phi_l(x_4)\rangle \tag{4}$$

the improved function is

$$\begin{aligned}\Phi_{cc} &= |[\phi_i(x_1)\phi_j(x_2) + f_{ij}(x_1, x_2)]\phi_k(x_3)\phi_l(x_4)\rangle \\ &= |\Phi_0\rangle + \sum_{a>b} t_{ij}^{ab} |\phi_a(x_1)\phi_b(x_2)\phi_k(x_3)\phi_l(x_4)\rangle \end{aligned} \tag{5}$$

Tips: the above equation is just one combination, we need to consider all possiblities like $f_{ij}(x_3, x_4), f_{ij}(x_1, x_4) \cdots$ Moreover, we can also consider the corrleation among three or more electrons. Now it's easy to rewrite above things using second quantized operators

$$\begin{aligned} \hat{t}_i &= \sum_a t_i^a a_a^\dagger a_i \\ \hat{t}_{ij} &= \frac{1}{2}\sum_{ab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j \end{aligned} \tag{6}$$

the total operators can be written as

$$\begin{aligned} \hat{T}_1 &= \sum_i \hat{t}_i \\ \hat{T}_2 &= \frac{1}{4}\sum_{ij} \hat{t}_{ij} \\ \hat{T}_n &= (\frac{1}{n!})^2 \sum_{ij\cdots} \hat{t}_{ij\cdots} \end{aligned} \tag{7}$$

The new CC wavefunction is

$$|\Psi_{CC}\rangle = e^{\hat{T}_1+\hat{T}_2+\cdots} |\Psi_{HF}\rangle \tag{8}$$

2 Energy Equation

Since the equation of CC energy is very complicated, we shall introduce some technique to truncate it. We begin with the projection of the reference state Ψ_{HF}

$$\langle\Psi_{HF}| \hat{H} e^{\hat{T}} |\Psi_{HF}\rangle = E \tag{9}$$

expand the exponentiated operator in a power series we get

$$\begin{aligned} \langle\Psi_{HF}| \hat{H} |\Psi_{HF}\rangle + \langle\Psi_{HF}| \hat{H}\hat{T} |\Psi_{HF}\rangle + \langle\Psi_{HF}| \hat{H}\frac{\hat{T}^2}{2!} |\Psi_{HF}\rangle + \\ \langle\Psi_{HF}| \hat{H}\frac{\hat{T}^3}{3!} |\Psi_{HF}\rangle + \cdots = E \end{aligned} \tag{10}$$

According to Slater-Condon rules, the matrix elements between determinants that differ by more than two orbitals are zero. We have

$$\langle\Psi_{HF}| \hat{H} |\Psi_{HF}\rangle + \langle\Psi_{HF}| \hat{H}\hat{T} |\Psi_{HF}\rangle + \langle\Psi_{HF}| \hat{H}\frac{\hat{T}^2}{2!} |\Psi_{HF}\rangle = E \tag{11}$$

By multipling the equation by the inverse of the exponential operator, we obtain two new equations

$$\begin{aligned}\hat{H}e^{\hat{T}}\left|\Psi_{HF}\right\rangle &= Ee^{\hat{T}}\left|\Psi_{HF}\right\rangle \\ \left\langle\Psi_{HF}\right| e^{-\hat{T}}\hat{H}e^{\hat{T}}\left|\Psi_{HF}\right\rangle &= E\end{aligned} \tag{12}$$

and

$$\left\langle\Psi_{ij\cdots}^{ab\cdots}\right| e^{-\hat{T}}\hat{H}e^{\hat{T}}\left|\Psi_{HF}\right\rangle = 0 \tag{13}$$

It has great advantages that we decouple the energy equation and amplitude equation. What's more, the new transformed Hamiltonian can be simplfied via the **Campbell-Baker-Hausdorff** formula

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2!}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{3!}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \cdots \tag{14}$$

which will naturally truncates in a manner somewhat analogous to the equation 11. We now give a simple prove, the electronic Hamiltonian is

$$\hat{H} = \sum_{pq} h_{pq}a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs}\left\langle pq\right|\left|rs\right\rangle a_p^\dagger a_q^\dagger a_s a_r \tag{15}$$

consider the second term in the expansion and only single-excitation operator

$$[\hat{H},\hat{T}] = [a_p^\dagger a_q, a_a^\dagger a_i] + [a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_i] \tag{16}$$

$$\begin{aligned}[a_p^\dagger a_q, a_a^\dagger a_i] &= a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \\ &= \delta_{qa}a_p^\dagger a_i - \delta_{iq}a_a^\dagger a_q\end{aligned} \tag{17}$$

$$\begin{aligned}[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_i] &= a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q^\dagger a_s a_r \\ &= \delta_{ar}a_p^\dagger a_q^\dagger a_s a_i + \delta_{iq}a_a^\dagger a_p^\dagger a_s a_r - \delta_{as}a_p^\dagger a_q^\dagger a_r a_i - \delta_{pi}a_a^\dagger a_q^\dagger a_s a_r\end{aligned} \tag{18}$$

if we go on with thrid term

$$[[a_p^\dagger a_q, a_a^\dagger a_i], a_b^\dagger a_j] = -\delta_{qa}\delta_{pj}a_b^\dagger a_i - \delta_{ip}\delta_{qb}a_a^\dagger a_j \tag{19}$$

$$\begin{aligned}&[[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_i], a_b^\dagger a_j] = \\ &\delta_{ar}[-\delta_{bs}a_p^\dagger a_q^\dagger a_i a_j - \delta_{pj}a_b^\dagger a_q^\dagger a_s a_i + \delta_{qj}a_b^\dagger a_p^\dagger a_s a_i] \\ &+\delta_{iq}[\delta_{br}a_a^\dagger a_p^\dagger a_s a_j - \delta_{pj}a_b^\dagger a_a^\dagger a_s a_r + \delta_{bs}a_a^\dagger a_p^\dagger a_r a_j] \\ &-\delta_{as}[-\delta_{br}a_p^\dagger a_q^\dagger a_i a_j - \delta_{pj}a_b^\dagger a_q^\dagger a_r a_i + \delta_{qj}a_b^\dagger a_p^\dagger a_r a_i] \\ &-\delta_{pi}[-\delta_{br}a_p^\dagger a_q^\dagger a_s a_j + \delta_{qj}a_b^\dagger a_a^\dagger a_s a_r - \delta_{bs}a_a^\dagger a_q^\dagger a_r a_i]\end{aligned} \tag{20}$$

the forth term

$$[[[a_p^\dagger a_q, a_a^\dagger a_i], a_b^\dagger a_j], a_c^\dagger a_k] = 0 \tag{21}$$

According to the above equation, we notice that one commutator we add, one operator in Hamiltonian will be eliminated. Because the Hamiltonian contains at most four operators, the expansion will naturally truncate after the fifth term

$$\frac{1}{4!}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] \tag{22}$$

Now we begin with CCSD approximation, which $\hat{T} = \hat{T}_1 + \hat{T}_2$, and define $\bar{H} \equiv e^{-\hat{T}} \hat{H} e^{\hat{T}}$, the Hamiltonian matrix is nonsymmertic

$$H_{CCSD} = \begin{bmatrix} E_{CCSD} & H_{0S} & H_{0D} \\ 0 & H_{SS} & H_{SD} \\ 0 & H_{DS} & H_{DD} \end{bmatrix} \tag{23}$$

Therefore we need to take the left-eigenvalue problem into consideration.

$$\langle \mathcal{L} | = \langle \Psi_{HF} | \hat{\mathcal{L}} \tag{24}$$

where

$$\begin{aligned} \hat{\mathcal{L}} &= 1 + \hat{\mathcal{L}}_1 + \hat{\mathcal{L}}_2 + \cdots \\ \hat{\mathcal{L}}_n &= (\frac{1}{n!})^2 \sum_{ij\cdots ab\cdots} l_{ab\cdots}^{ij\cdots} a_i^\dagger a_j^\dagger \cdots a_b a_a \end{aligned} \tag{25}$$

and we have

$$\begin{aligned} E &= \langle \Psi_{HF} | \hat{\mathcal{L}} \bar{H} | \Psi_{HF} \rangle \\ 1 &= \langle \Psi_{HF} | \hat{\mathcal{L}} | \Psi_{HF} \rangle \end{aligned} \tag{26}$$

3 Wick Theorem

It's hard to clearly explain Wick theorem and normal order in just a few sentences. Here we just use the conclusion.
If we define a HF ground state as the Fermi Vacuum. The operators can be divided into q-annihilation which annihilate holes and particles ($a_i^\dagger, a_a$) and q-creation which create holes and particles ($a_a^\dagger, a_i$). The contraction can be written as

$$\begin{aligned} \overbracket{a_i^\dagger, a_j} &= a_i^\dagger a_j - \{a_i^\dagger a_j\}_v = \delta_{ij} \\ \overbracket{a_a^\dagger, a_b} &= a_a^\dagger a_b - \{a_a^\dagger a_b\}_v = \delta_{ij} \end{aligned} \tag{27}$$