FYS4480/9480, November 22: CC-theory

Reminder from lecture Nov. 21

The wave operator in FCI

$$|\Psi_0\rangle = (1+\hat{C})|\Phi_0\rangle$$

$$= \sum_{PH} C_H^P |\Phi_H^P\rangle$$

example $\sum_{ai} C_i^a \underbrace{a_a^\dagger a_i |\Phi_0\rangle}_{|\Phi_i^a\rangle}$

Exponential ansatz

$$|\Psi_0\rangle = \exp\{T\}|\Phi_0\rangle$$

"Famous" example (Thouless' theorem)

$$T = T_1 = \underbrace{\sum_{ai} c_i^a a_a^\dagger a_i}$$

spin operator (single excitations)

$$|\Psi_0\rangle = \exp\left\{\sum_{ai} c_i^a a_a^\dagger a_i\right\} |\Phi_0\rangle$$

in general

$$T = T_1 + T_2 + T_3 + \cdots$$ TRUNCATE

singles

doubles

triples

Famous approximations

(i) CCS $T = T_1$, singles

(ii) CCD $T = T_2$, doubles

(iii) CCSD $T = T_1 + T_2$, singles & doubles

(iv) CCSDT : $T = T_1 + T_2 + T_3$

Note also that $[T_i, T_j] = 0$

We will focus on the CCD approximation first.

Exponential ansatz

$$|\Phi_H^P\rangle \xrightarrow{2p2h} (a_a^\dagger a_i)(a_b^\dagger a_j)|\Phi_0\rangle$$

$$= |\Phi_{ij}^{ab}\rangle$$

$$= - a_a^\dagger a_b^\dagger a_i a_j |\Phi_0\rangle$$

$$= a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle$$

$$T_2 = \frac{1}{4}\sum_{\substack{ab\\ij}} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

write pair cluster

$$\Big[\prod_{a>b}\big(1+t_{ij}^{ab}\underbrace{A_{ij}^{ab}}_{a_a^\dagger a_b^\dagger a_j a_i}\big)\Big]a_i^\dagger a_j^\dagger|0\rangle$$

$$= a_i^\dagger a_j^\dagger|0\rangle + \sum_{a>b} t_{ij}^{ab}\, a_a^\dagger a_b^\dagger|0\rangle$$

in general we have a double excitation

$$\prod_{\substack{a>b\\ i>j}}\big(1+t_{ij}^{ab}A_{ij}^{ab}\big)|\Phi_0\rangle$$

A_{ij}^{ab} commute with each other

The generalized CC function

$$|\Psi_0\rangle_{CC} = \left[\prod_{PH} (1 + t_H^P A_H^P)\right] |\Phi_0\rangle$$

$$|\Psi_0\rangle_{FCI} = \left(1 + \sum_{PH>0} c_H^P A_H^P\right) |\Phi_0\rangle$$

$$|\Psi_0\rangle_{RSPT} = \sum_{k=0}^{\infty} \left[(RH_I)^k |\Phi_0\rangle \right]_L$$

$$(A_H^P)^2 = 0 \qquad \left[A_H^P |\Phi_0\rangle \right.$$

$$(1 + t_H^P A_H^P) = \exp(t_H^P A_H^P)$$

$$T = \sum_{PH} t_H^P A_H^P$$

$$|\Psi_0\rangle_{CC} = \prod_{PH} (1 + t_H^P A_H^P) |\Phi_0\rangle$$

$$= \exp(T) |\Phi_0\rangle$$

$$T_1 = \sum_{ai} t_i^a a_a^+ a_i$$

$$T_2 = \frac{1}{(2!)^2} \sum_{\substack{ab \\ ij}} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i$$

$$t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}$$

$$T_3 = \frac{1}{(3!)^2} \sum_{\substack{abc \\ ijk}} t_{ijk}^{abc} \left(a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i \right)$$

$$\underbrace{e^{T} |\Phi_0\rangle} = \overbrace{\sum_i c_i |\Phi_0\rangle}^{\text{FCI}}$$

$$T = T_1 + T_2 + T_3 + \dots \; T_{N_{p}N_{h}}$$

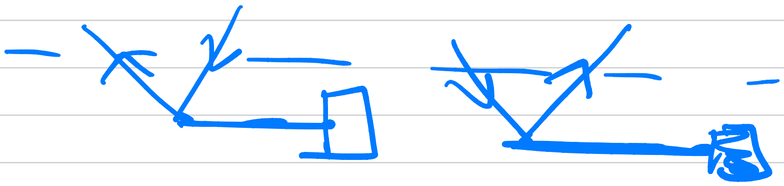
$$c_0 = 1$$

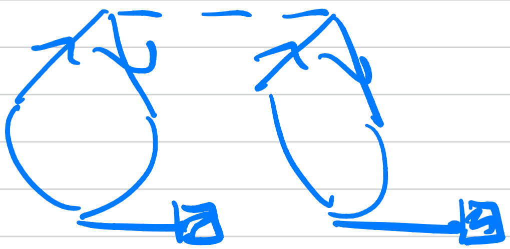
$$c_1 = T_1 \quad (1p1h)$$

$$c_2 = T_2 + \frac{1}{2} T_1^2 \quad (2p2h)$$

$$C_2 = \overline{T_2} + \frac{1}{2}\overline{T_1}^2$$

$\overline{T_1} =$ 

$\overline{T_1}^2 =$  $-$ 2p2h



$$C_3 = \overline{T_3} + \overline{T_1}\,\overline{T_2} + \frac{1}{6}\overline{T_1}^3$$

$$H|\Psi_0\rangle_{CC} = E_0|\Psi_0\rangle_{CC}$$

$$He^T|\Phi_0\rangle = E_0 e^T|\Phi_0\rangle$$

$$E_{min} = \underset{t_H^P}{\operatorname{argmin}} \frac{\langle\Phi_0|e^{T^\dagger} H e^T|\Phi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}$$

$|\Psi_0\rangle$ depends on t_H^P in a non-linear. Optimizing E_{min} as function of t_H^P, leads to an intractable set of non-linear equations

Projected approach

$$He^{T}|\Phi_0\rangle = E_0 e^{T}|\Phi_0\rangle$$

Set up $\binom{n}{N}$ amplitude equations to find energy and amplitudes by left-projecting by each determinant:

$$\langle\Phi_0|He^{T}|\Phi_0\rangle = E_0 \qquad e^{T}|\Phi_0\rangle = |\Psi_0\rangle$$

$$\langle\Phi_0|\Psi_0\rangle = 1$$

$$\langle pH | H e^{T} | \Phi_0 \rangle = E_0 \langle pH | e^{T} | \Phi_0 \rangle$$

$$\left(\langle \Phi_n^a | H e^{T} | \Phi_0 \rangle = E_0 \langle \Phi_n^a | e^{T} | \Phi_0 \rangle \right)$$

For a truncated cluster operator

$$T_N < T \qquad \left(T = T_1 + T_2 \right)$$

$$H e^{T_N} | \Phi_0 \rangle \neq E_N e^{T_N} | \Phi_0 \rangle$$

For say $T = T_1 + T_2$

(i) $\langle \Phi_0 | H e^{T} | \Phi_0 \rangle = E_0$

(ii) $\langle \Phi_n^a | H e^{T} | \Phi_0 \rangle = E_0 \langle \Phi_n^a | e^{T} | \Phi_0 \rangle$

(iii) $\langle \Phi_{ij}^{ab} | H e^{T} | \Phi_0 \rangle =$

$$E_0 \langle \Phi_{ij}^{ab} | e^{T} \underline{| \Phi_0 \rangle}$$

$$H = E_0^{Ref} + \overbrace{F_N + V_N}^{H_N}$$

$$e^{-T} H e^{T} | \Phi_0 \rangle = e^{-T} E_0 e^{T} | \Phi_0 \rangle$$

$$\Delta E = E_0 - E_0^{Ref}$$

$$\langle \Phi_0 | \underbrace{e^{-T} H_N e^{T}} | \Phi_0 \rangle = \Delta E | \Phi_0 \rangle$$

$$T = -T^{+}$$

Projection :

$$\langle \Phi_0 | e^{-T} H_N e^{T} | \Phi_0 \rangle = \Delta E$$

$$\langle \Phi_i^a | e^{-T} H_N e^{T} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | e^{-T} H_N e^{T} | \Phi_0 \rangle = 0$$

Baker-Campbell-Hausdorff expansion

$$e^{-T} H_N e^{T} = H_N + [H_N, T] + \frac{1}{2} [[H_N, T], T] + \frac{1}{3!} [[[H_N, T], T], T] + \ldots$$

with a commutator like $[A, B]$ the result has a rank one less than the operator A, B

$$[H_N, T] \Rightarrow [F_N, T_1]$$

$$a_p^{\dagger} a_q \qquad a_a^{\dagger} a_{r'}$$

$$F_N T_1$$

$$= a_p^{\dagger}(\delta_{qa} - a_a^{\dagger} a_q) a_{r'}$$

$$- a_a^{\dagger}(\delta_{pr'} - a_p^{\dagger} a_{r'}) a_q$$

$$T_1 F_N$$

$$\delta_{qa} a_p^{\dagger} a_{r'} - \delta_{pr'} a_a^{\dagger} a_q$$

$$V_N \propto a_p^\dagger a_q^\dagger a_s a_r$$

$$\Delta E = \langle \Phi_0 | H_N | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | [H_N, T] | \Phi_0 \rangle$$

$$+ \frac{1}{2!} \langle | [[H_N, T], T] | \rangle$$

$$+ \frac{1}{3!} \langle | [[[\cdots]]] | \rangle$$

$$+ \frac{1}{4!} \langle | [[[[\cdots]]]] | \rangle$$

$$\langle \Phi_0 | H_N T_i | \Phi_0 \rangle = 0$$

for $i > 2$ since H_N is at most a two-body operator

if we have an HF-basis

$$\langle \Phi_0 | H_N T_1 | \Phi_0 \rangle = \langle \Phi_0 | H_N | \Phi_i^a \rangle$$
$$= 0$$

$$T = T_1 + T_2 \quad / \quad \langle \Phi_0 | H_N | \Phi_0 \rangle = 0$$

$$\Delta E_0 = \langle \Phi_0 | [H_N, T_1 + T_2] | \Phi_0 \rangle$$
$$+ \frac{1}{2} \langle \Phi_0 | [[H_N, T_1], T_1] | \Phi_0 \rangle$$

Leave out $T_1 \Rightarrow T = T_2$

CC-doublet = CCD

$$\Delta E = \langle \Phi_0 | [H_N, T_2] | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{\substack{ab \\ ij}} \boxed{t_{ij}^{ab}} \langle ab || ij \rangle$$

$$= \Delta E_{CCD}$$

an iterative guess

$$t_{ij}^{ab}(0) = \frac{\langle ij || ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$\langle PH | e^{-T} H_N e^{T} | \Phi_0 \rangle = 0$$

which leads to (9.3)

$$\langle \Phi_{ij}^{ab} | H_N (1 + T_2 + \tfrac{1}{2} T_2^2) | \Phi_0 \rangle$$

$$= \Delta E_{CCD}\, t_{ij}^{ab}$$

<u>1st</u>

$$\langle \Phi_{ij}^{ab} | H_N | \Phi_0 \rangle = \langle ab | v | ij \rangle$$

<u>2nd</u>

$$\langle \Phi_{ij}^{ab} | H_N T_2 | \Phi_0 \rangle$$

$$= \sum_{\substack{k>l \\ c>d}} \langle \Phi_{ij}^{ab} | H_N | \Phi_{kl}^{cd} \rangle t_{kl}^{cd}$$

$$= \underbrace{\langle \Phi_{ij}^{ab} | H_0 - E_0^{Ref} | \Phi_{ij}^{ab} \rangle}_{L_0} t_{ij}^{ab}$$

$$+ \sum_{\substack{k>l \\ c>d}} \underbrace{\langle \Phi_{ij}^{ab} | U_N^{HF} | \Phi_{kl}^{cd} \rangle}_{L_1} t_{kl}^{cd}$$

$$+ \sum_{\substack{k>l \\ c>d}} \underbrace{\langle \Phi_{ij}^{ab} | V_N | \Phi_{kl}^{cd} \rangle}_{L_2} t_{kl}^{cd}$$

$$U_N^{HF} = \sum_{pq} \langle p | u^{HF} | q \rangle a_p^\dagger a_q \quad \Big| \quad u_{pq}^{HF} = \sum_{m<F} \langle pm | V | qm \rangle$$

$$L_0 = \Big(-(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b) + \frac{1}{2}\sum_{\substack{kl \\ ab}} \langle kl \| kl \rangle \Big) \times t_{ij}^{ab}$$

collecting all term

$$\Big\{ \langle \Phi_0 | a_i^\dagger a_j^\dagger a_b a_a \, a_p^\dagger a_q \, a_c^\dagger a_d^\dagger a_l a_k | \Phi$$

$$\varepsilon_{ij}^{ab} t_{ij}^{ab} = \langle ab \| ij \rangle + \frac{1}{2}\sum_{cd} \langle ab \| cd \rangle t_{ij}^{cd}$$

$$(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b) \quad + \frac{1}{2}\sum_{kl} \langle ij \| kl \rangle t_{kl}^{ab}$$

$$+$$

$$- \sum_{kc} \Big(\langle bk|v|cj\rangle t_{ik}^{ac} - \langle bk|v|ci\rangle \times t_{jk}^{ac}$$

one body

$$- \langle ak|v|cj\rangle t_{ik}^{bc} + \langle ak|v|ci\rangle t_{jk}^{bc} \Big)$$

$$+ \sum_{\substack{kl \\ cd}} \langle kl|v|cd\rangle \Big[\frac{1}{4} t_{ij}^{cd} t_{kl}^{ab}$$

$$- \frac{1}{2} \left(t_{ij}^{ac} t_{kl}^{bd} + t_{ij}^{bd} t_{kl}^{ac} \right)$$

$$- \frac{1}{2} \left(t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab} \right)$$

$$+ \left(t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac} \right) \Big]$$