① Coupled-cluster theory review (for excited-state CC)

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

$$\hat{H}|\Psi\rangle = E_{cc}|\Psi\rangle \quad \text{or} \quad \hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{cc}e^{\hat{T}}|\Phi_0\rangle$$

is true in the same det. space reached by $1+\hat{T}$ from $|\Phi_0\rangle$

For instance, if $\hat{T} = \hat{T}_2$

$$\langle\Phi_0|\hat{H}e^{\hat{T}_2}|\Phi_0\rangle = E_{CCD}\langle\Phi_0|e^{\hat{T}_2}|\Phi_0\rangle$$

$$\langle\Phi_{ij}^{ab}|\hat{H}e^{\hat{T}_2}|\Phi_0\rangle = E_{CCD}\underbrace{\langle\Phi_{ij}^{ab}|e^{\hat{T}_2}|\Phi_0\rangle}_{t_{ij}^{ab}}$$

connected

same

disconnected (simple product)

$$\langle\Phi_0|\hat{H}e^{\hat{T}_2}|\Phi_0\rangle = \langle\Phi_0|\underbrace{(\hat{H}e^{\hat{T}_2})_C}_{\bar{H}}|\Phi_0\rangle + \underbrace{\langle\Phi_0|\hat{H}|\Phi_0\rangle}_{E_{HF}}\langle\Phi_0|e^{\hat{T}_2}|\Phi_0\rangle$$

CCD effective Hamiltonian

same

$$\langle\Phi_{ij}^{ab}|\hat{H}e^{\hat{T}_2}|\Phi_0\rangle = \langle\Phi_{ij}^{ab}|(\hat{H}e^{\hat{T}_2})_C|\Phi_0\rangle + \overbrace{\langle\Phi_0|\hat{H}|\Phi_0\rangle}^{E_{HF}}\underbrace{\langle\Phi_{ij}^{ab}|e^{\hat{T}_2}|\Phi_0\rangle}_{t_{ij}^{ab}}$$

connected   disconnected

$$+\underbrace{\langle\Phi_0|\hat{H}\hat{T}_2|\Phi_0\rangle}_{E_{CCD}^{corr}}\underbrace{\langle\Phi_{ij}^{ab}|\hat{T}_2|\Phi_0\rangle}_{t_{ij}^{ab}}$$

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

$$\langle\Phi_0|\bar{H}|\Phi_0\rangle = E_{CCD}^{corr}$$

$$\langle\Phi_{ij}^{ab}|\bar{H}|\Phi_0\rangle = 0$$

$$\boxed{\overbrace{(He^{\hat{T}})_C}^{\bar{H}}|\Phi_0\rangle = E_{CC}^{corr.}|\Phi_0\rangle \quad \text{in } (1+\hat{T})|\Phi_0\rangle \text{ space}}$$

② Excited-state CC = Equation of motion CC (EOM-CC)
CC linear response (CCLR)
Sym-adapted cluster CI (SAC-CI)

Ⓘ Linear response

i) Initial state = CC ground state

$$\hat{H}^{(0)} e^{\hat{T}^{(0)}} |\Phi_0\rangle = E_{cc}^{(0)} e^{\hat{T}^{(0)}} |\Phi_0\rangle$$

$\langle\Phi_0|$

$$\langle\Phi_0| \hat{H}^{(0)} e^{\hat{T}^{(0)}} |\Phi_0\rangle = E_{cc}^{(0)}$$

time dep.

$$\hat{H}^{(0)} e^{\hat{T}^{(0)}} |\Phi_0\rangle e^{-iE_{cc}^{(0)}t} = E_{cc}^{(0)} e^{\hat{T}^{(0)}} |\Phi_0\rangle e^{-iE_{cc}^{(0)}t}$$

ii) Turn on perturbation = time oscillating electric field at ω

$$\hat{H} = \hat{H}^{(0)} + \underbrace{\hat{g}^{(1)} e^{-i\omega t} + \hat{g}^{(1)\dagger} e^{i\omega t}}_{\text{perturbation = real } \propto \cos\omega t}$$

iii) Response in $\hat{T}$, E_{cc}

$$\hat{T} = \hat{T}^{(0)} + \lambda \hat{C}^{(1)} e^{-i\omega t} + \lambda \hat{C}^{(1)\dagger} e^{i\omega t} + \cdots \rightarrow O(\lambda^2) \text{ neglect}$$

isomorphic if $\hat{T} = SD$, $\hat{C} = SD$

$$E_{cc} = E_{cc}^{(0)} + \lambda \underbrace{E_{cc}^{(1)}}_{e^{-i\omega t}} + O(\lambda^2) \rightarrow \text{neglect}$$

$$e^{\hat{T}^{(0)} + \lambda \hat{C}^{(1)} e^{-i\omega t}} = e^{\hat{T}^{(0)}} \left(1 + \lambda \hat{C}^{(1)} e^{-i\omega t} + O(\lambda^2)\right)$$

$$E_{cc} = \langle\Phi_0| \hat{H}^{(0)} e^{\hat{T}^{(0)} + \lambda C^{(1)} e^{-i\omega t}} |\Phi_0\rangle \approx \underbrace{\langle\Phi_0| \hat{H}^{(0)} e^{\hat{T}^{(0)}} |\Phi_0\rangle}_{E_{cc}^{(0)}} + \lambda \underbrace{\langle\Phi_0| \hat{H}^{(0)} e^{\hat{T}^{(0)}} \hat{C}^{(1)} |\Phi_0\rangle}_{E_{cc}^{(1)}} e^{-i\omega t}$$

$(\because \hat{g}^{(1)} \rightarrow 0)$

iv) Substitute in time-dep. SE, collect terms w/ $e^{-iE_{cc}t-i\omega t}$

$$\left(\hat H^{(0)}+\hat g^{(1)}e^{-i\omega t}+\cdots\right)\left(e^{\hat T^{(0)}}\left(1+\hat C^{(1)}e^{-i\omega t}\right)|\Phi_0\rangle e^{-iE_{cc}t}\right)$$

$$=i\frac{\partial}{\partial t}\left(e^{\hat T^{(0)}}\left(1+\hat C^{(1)}e^{-i\omega t}\right)|\Phi_0\rangle e^{-iE_{cc}t}\right)$$

$\to E_{cc}\, e^{\hat T^{(0)}}|\Phi_0\rangle e^{-iE_{cc}t}$

$\hookrightarrow \left(E_{cc}^{(0)}+\lambda E_{cc}^{(1)}e^{-i(\omega t)}\right) e^{\hat T^{(0)}}|\Phi_0\rangle$

$$\hat H^{(0)}e^{\hat T^{(0)}}\hat C^{(1)}|\Phi_0\rangle+\underbrace{\hat g^{(1)}e^{\hat T^{(0)}}|\Phi_0\rangle}_{0}=\left(E_{cc}^{(0)}+\omega\right)e^{\hat T^{(0)}}\hat C^{(1)}|\Phi_0\rangle \quad \longrightarrow ☆$$

$$+\,E_{cc}^{(1)}\,e^{\hat T^{(0)}}|\Phi_0\rangle$$

$E_{cc}^{(1)} = \langle\Phi_0|\hat H e^{\hat T^{(0)}}\hat C^{(1)}|\Phi_0\rangle$

(∵ finite response w/ zero pert.)

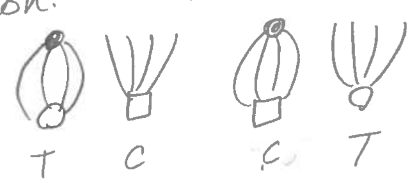
v) ☆ is true in some det. space, e.g. if $\hat T$ = SD, SD space

if $\hat T=\hat C=D$

$$\langle\Phi_{ij}^{ab}|\hat H^{(0)}e^{\hat T^{(0)}}\hat C^{(1)}|\Phi_0\rangle=\left(E_{cc}^{(0)}+\omega\right)\underbrace{\langle\Phi_{ij}^{ab}|e^{\hat T^{(0)}}\hat C^{(1)}|\Phi_0\rangle}_{C_{ij}^{ab}}$$

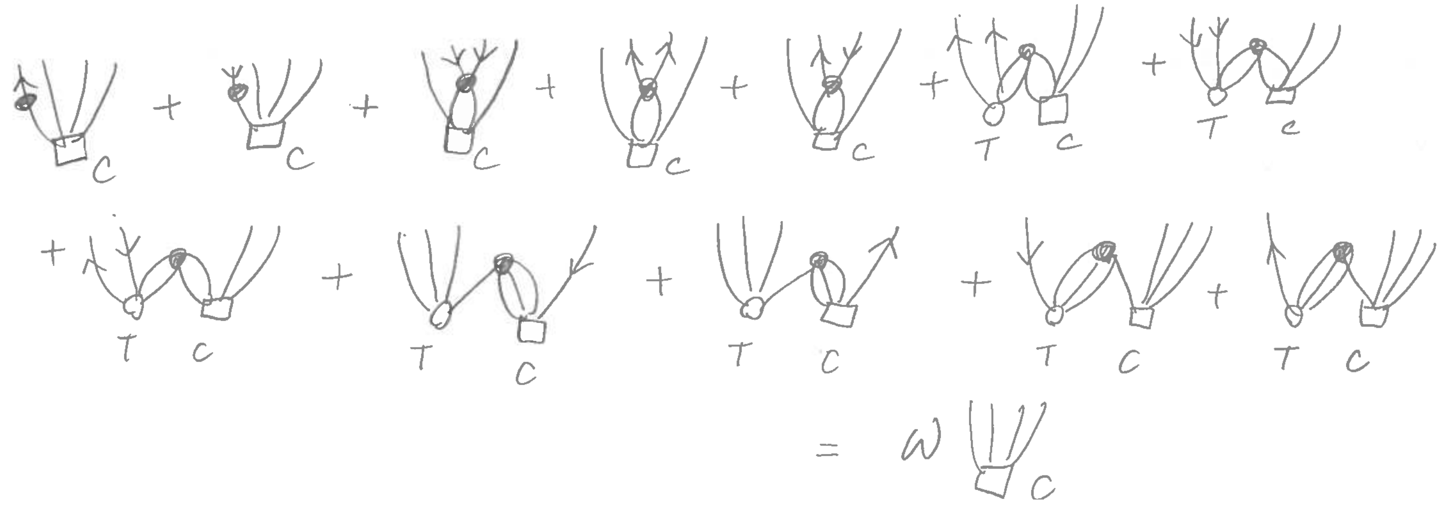
contains

discon.



$$+\underbrace{\langle\Phi_0|\hat H e^{\hat T^{(0)}}\hat C^{(1)}|\Phi_0\rangle}\langle\Phi_{ij}^{ab}|e^{\hat T^{(0)}}|\Phi_0\rangle$$

connected only!



(II) Equation of motion

GS: $\hat{H} e^{\hat{T}} |\Phi_0\rangle = E_{CCD} e^{\hat{T}} |\Phi_0\rangle$

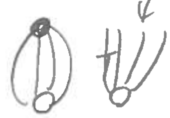
$\langle\Phi_0|$: $\langle \Phi_0 | H e^{\hat{T}} | \Phi_0 \rangle = E_{CCD} \langle \Phi_0 | e^{\hat{T}} | \Phi_0 \rangle = E_{CCD}$ → $\langle \Phi_0 | (He^T)_c | \Phi_0 \rangle = \Delta E_{CCD}$

→ discon. E_{HF}

$\langle\Phi_{ij}^{ab}|$: $\langle \Phi_{ij}^{ab} | H e^{\hat{T}} | \Phi_0 \rangle = E_{CCD} \langle \Phi_{ij}^{ab} | e^{\hat{T}} | \Phi_0 \rangle = E_{CCD}\, T_{ij}^{ab}$

E_{CCD} → E_{HF} + 

discon. $E_{HF} T_{ij}^{ab}$



T

→ $\langle \Phi_{ij}^{ab} | (He^T)_c | \Phi_0 \rangle = 0$

$$\bar{H} = (H e^T)_c \quad \text{CC effective Hamiltonian}$$

$\bar{H} |\Phi_0\rangle = \Delta E_{CCD} |\Phi_0\rangle$; HF-like eq. w/ energy $= \Delta E_{CCD}$

$\langle\Phi_0|$: $\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = \Delta E_{CCD}$

$\langle\Phi_{ij}^{ab}|$: $\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0$

↓ CI w/ $\bar{H}$ for excited states

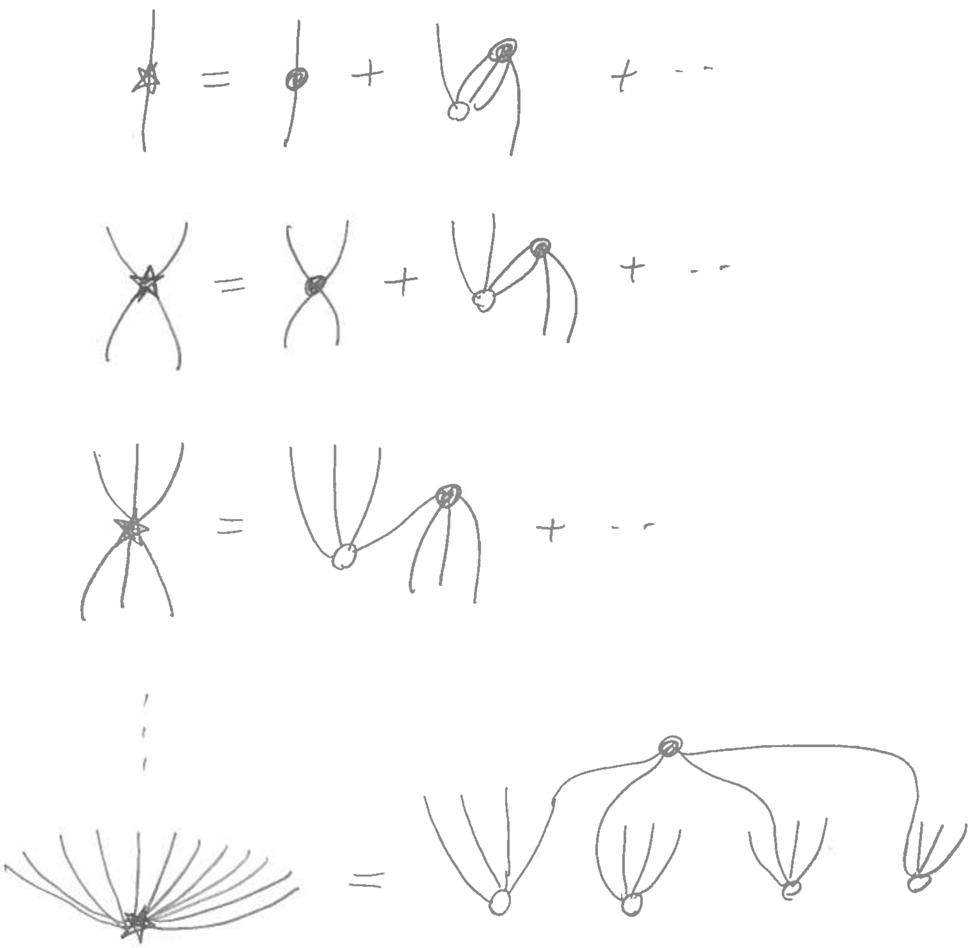
$\hat{C}$: $\bar{H} \hat{C} |\Phi_0\rangle = (\Delta E_{CCD} + \omega) \hat{C} |\Phi_0\rangle$

$\hat{C} \bar{H} |\Phi_0\rangle = \Delta E_{CCD} \hat{C} |\Phi_0\rangle$

$[\bar{H}, \hat{C}] |\Phi_0\rangle = \omega \hat{C} |\Phi_0\rangle$

$\langle\Phi_{ij}^{ab}|$: $\langle \Phi_{ij}^{ab} | (\bar{H} \hat{C})_c | \Phi_0 \rangle = \omega\, C_{ij}^{ab}$

$$\bar{H} = (\hat{H} e^{\hat{T}})_c = \hat{H} + (\hat{H}\hat{T})_c + (\hat{H}\hat{T}^2/2!)_c + (\hat{H}\hat{T}^3/3!)_c + (\hat{H}\hat{T}^4/4!)_c$$

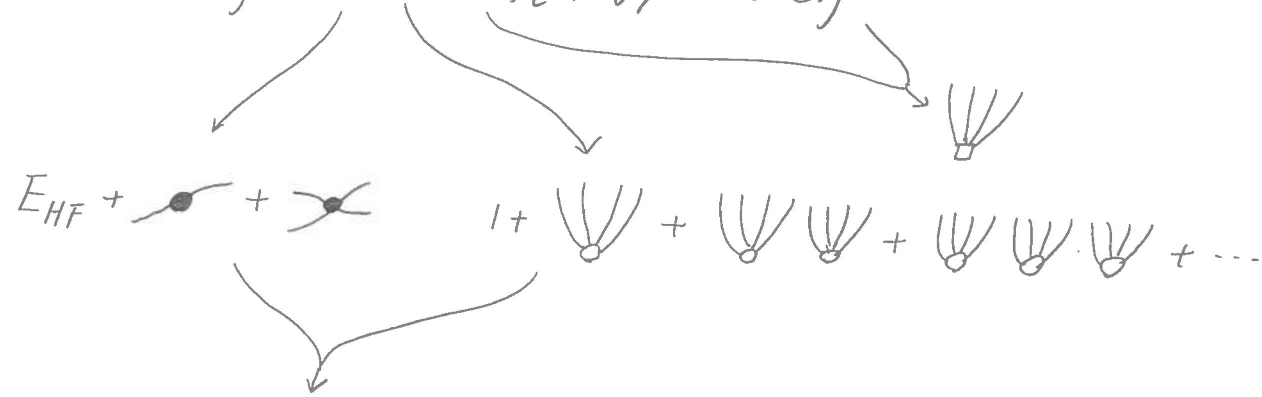


6-electron op.

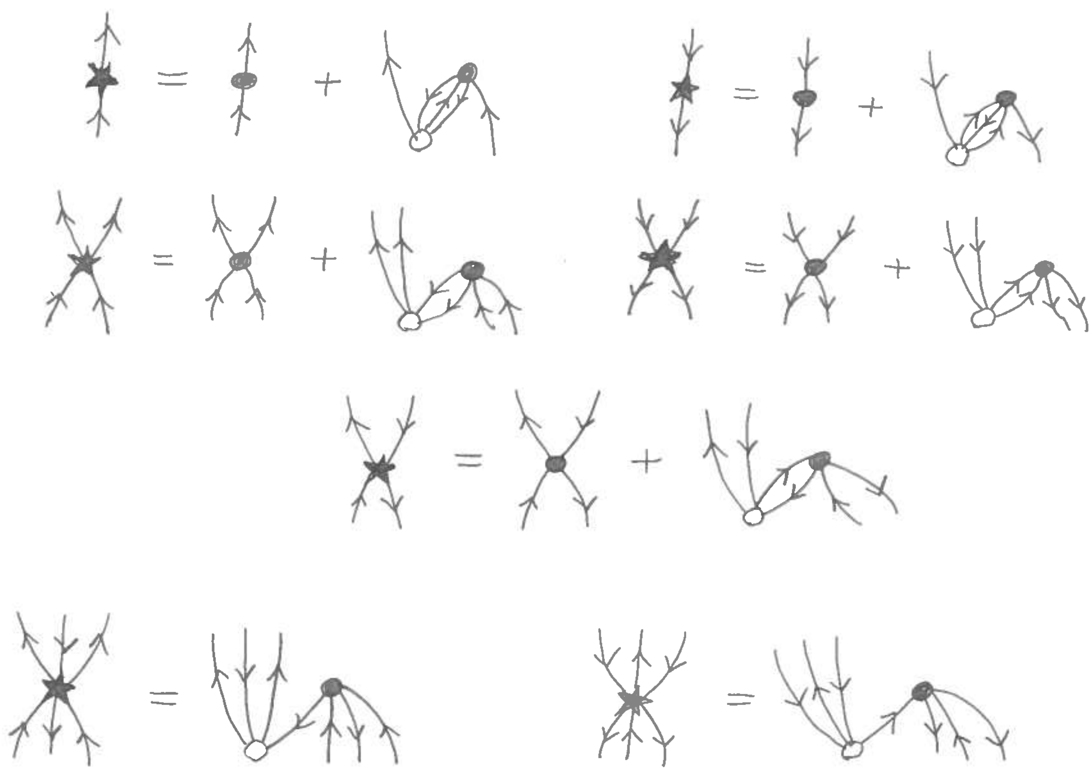
③ EOM-CCD (though it's unrealistic not to have single excitations)

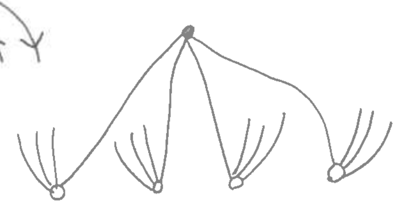
$$\langle \Phi_{ij}^{ab} | (\bar{H} \hat{C}_2)_c | \Phi_0 \rangle = \omega C_{ij}^{ab}$$

$$\langle \Phi_{ij}^{ab} | (\hat{H} e^{\hat{T}_2} \hat{C}_2)_c | \Phi_0 \rangle = \omega C_{ij}^{ab}$$



the part of $\bar{H} = (\hat{H} e^{\hat{T}_2})_c$ that can contribute here is net zero excitation:

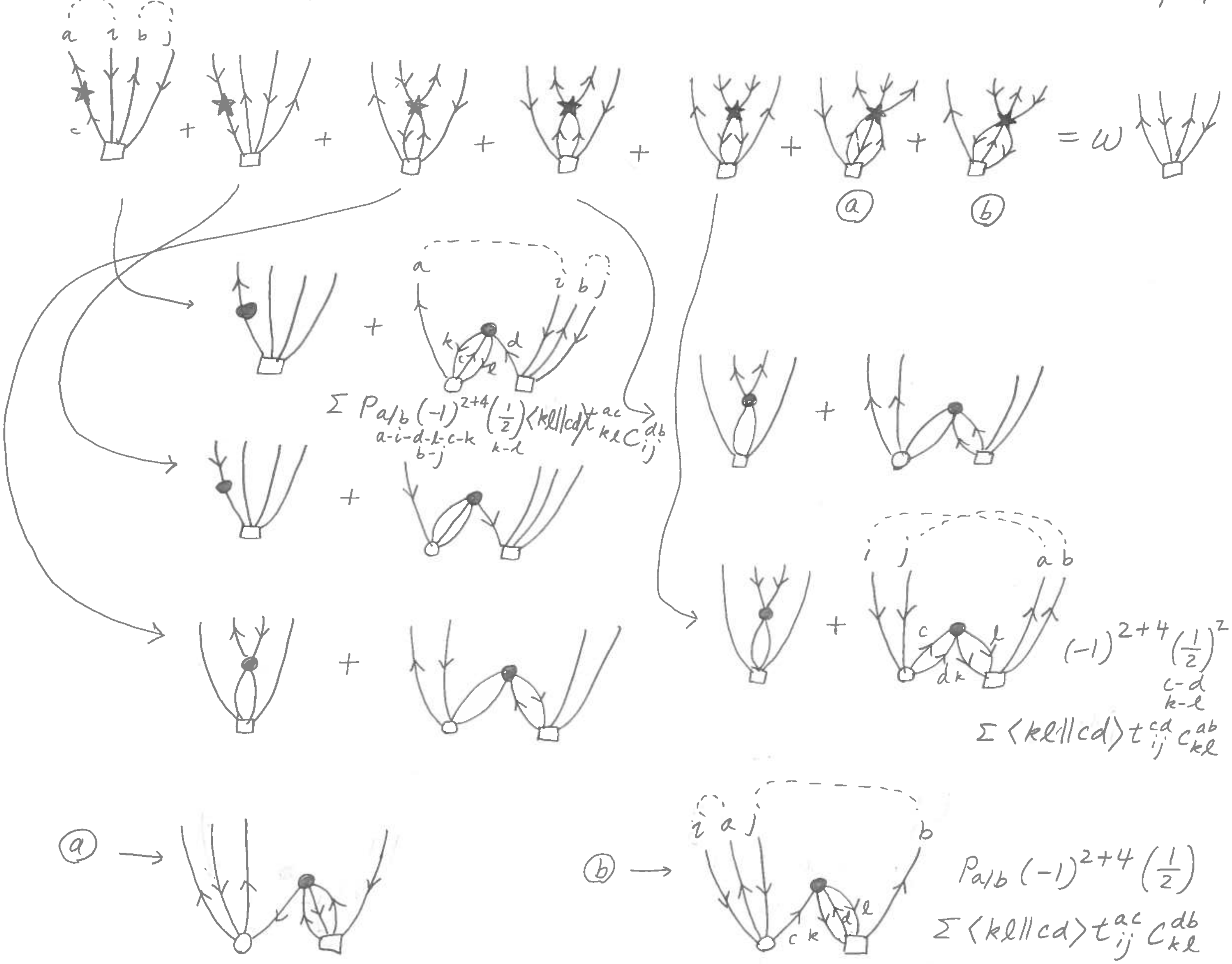




$\bar{H}$ has 3-electron operator!

(actually it has $\underbrace{\text{6-electron}}_{\text{up to}}$ operator in CCD.)

$$P_{a/b}\,(-1)^2 \sum \langle a|f|c\rangle\, c^{cb}_{ij}$$



$$\sum P_{a/b} \underset{\substack{a-i-d-l-c-k\\ b-j}}{(-1)^{2+4}} \underset{k-l}{\left(\tfrac{1}{2}\right)} \langle kl\|cd\rangle\, t^{ac}_{kl}\, C^{db}_{ij}$$

$$(-1)^{2+4} \underset{\substack{c-d\\ k-l}}{\left(\tfrac{1}{2}\right)^2} \sum \langle kl\|cd\rangle\, t^{cd}_{ij}\, C^{ab}_{kl}$$

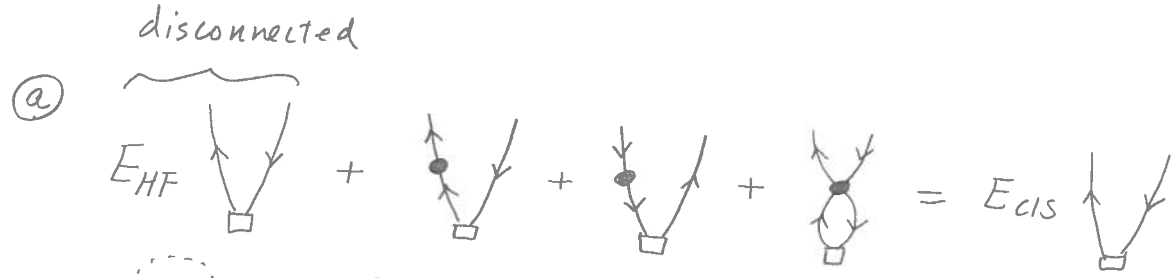
$$P_{a/b}\,(-1)^{2+4}\left(\tfrac{1}{2}\right) \sum \langle kl\|cd\rangle\, t^{ac}_{ij}\, C^{db}_{kl}$$

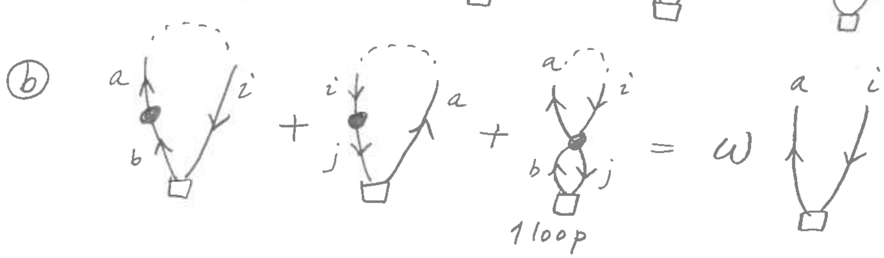
④ CIS redux

$$\langle \Phi_i^a | \hat{H} \hat{C}_1 | \Phi_0 \rangle = E_{CIS} \underbrace{\langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle}_{C_i^a} \qquad \text{——— ⓐ}$$

$$\rightarrow \langle \Phi_i^a | (\hat{H} \hat{C}_1)_c | \Phi_0 \rangle + \overbrace{\underbrace{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}_{E_{HF}} \underbrace{\langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle}_{C_i^a}}^{\text{disconnected}}$$

$$\rightarrow \langle \Phi_i^a | (\hat{H} \hat{C}_1)_c | \Phi_0 \rangle = \underbrace{\omega}_{= E_{CIS} - E_{HF}} C_i^a \qquad \text{——— ⓑ}$$





$$\sum_b \langle a | \hat{f} | b \rangle C_i^b - \sum_j \langle j | \hat{f} | i \rangle C_j^a - \sum_{b,j} \langle aj || bi \rangle C_j^b = \omega C_i^a$$

or

$$(\epsilon_a - \epsilon_i) C_i^a + \langle aj || ib \rangle C_j^b = \omega C_i^a$$

the same result as TDHF → CIS.