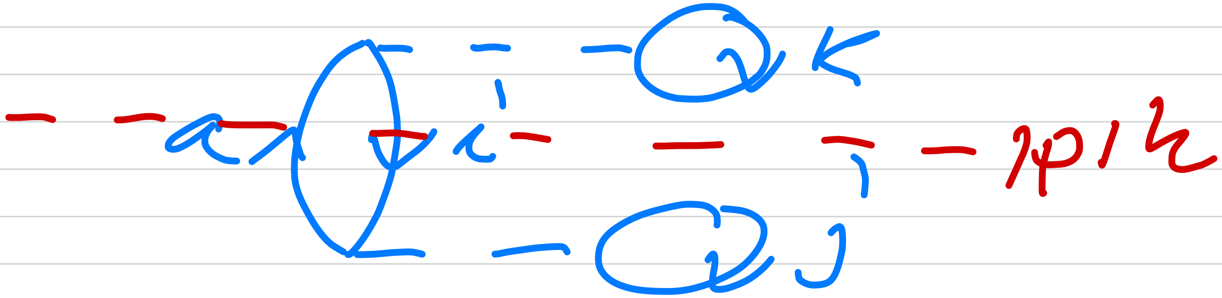
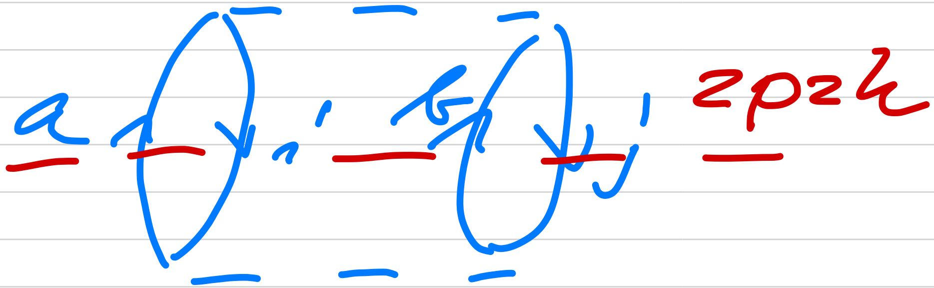
FYS4480/9480, lecture November 13, 2025

FYS4480/9480 November 13

MBPT (2)





$$\sum_{aijk} \frac{\langle ik|v|ak\rangle\langle aj|v|ij\rangle}{\varepsilon_i - \varepsilon_a}$$

$$\frac{1}{4}\sum_{abij} \frac{\langle ij|v|ab\rangle\langle ab|v|ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

$n_h = 3$

$n_e = 3$

$n_{ep} = 0 \quad \left(\frac{1}{2}\right)^0$

$n_h = 2 \quad n_e = 2$

$n_{ep} = 2 \rightarrow \left(\frac{1}{2}\right)^2$

$$\Delta E_0^{(2)} = \langle \Phi_0 | \hat{H}_I \underbrace{\frac{\hat{Q}}{\varepsilon_0}}_{\hat{R}} \hat{H}_I | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \hat{H}_I \hat{R} \hat{H}_I | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \hat{H}_I | \Psi_0^{(1)} \rangle$$

$$|\Psi_0^{(1)}\rangle = \hat{R} \hat{H}_I | \Phi_0 \rangle$$

$$\hat{R} \hat{H}_I | \Phi_0 \rangle = \sum_{M>0} \overbrace{\frac{|\Phi_M\rangle\langle\Phi_M|}{E_0 - E_M}}^{\hat{R}} \hat{H}_I | \Phi_0 \rangle$$

$$|\Psi^{(1)}\rangle = \frac{1}{4}\sum_{\substack{ab\\ij}} \frac{\langle ab|v|ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b} |\Phi_{ij}^{ab}\rangle$$

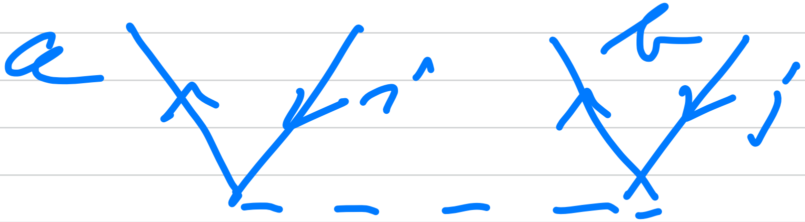
$$+ \sum_{ai} \frac{\langle a|f|i\rangle}{\varepsilon_i - \varepsilon_a} |\Phi_i^a\rangle$$

<u>FCI</u>

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

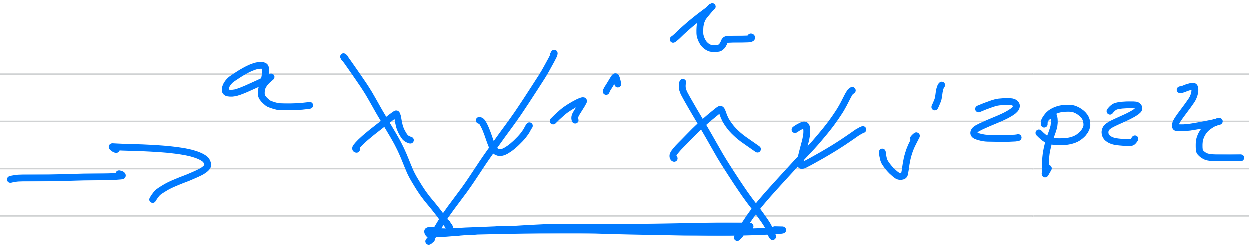
$$\hat{C} = \sum_{ai} C_i^a |\Phi_i^a\rangle + \sum_{\substack{ab\\ij}} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

$$+ \ldots$$



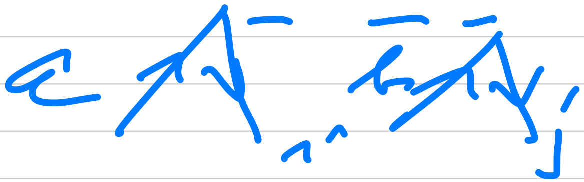
2p2h

$\langle ab | v | i'j' \rangle$

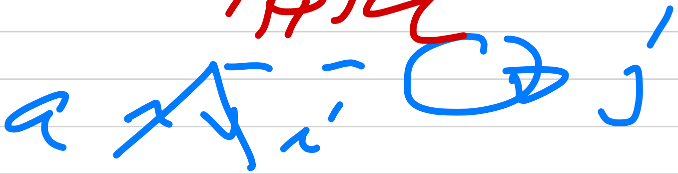


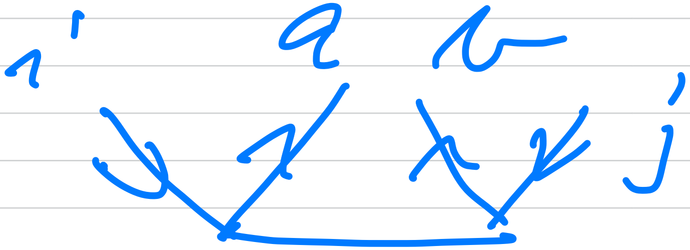
$$\frac{\langle ab | v | i'j' \rangle \, |\Phi_{ij}^{ab}\rangle}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_a - \varepsilon_b}$$

2p2h

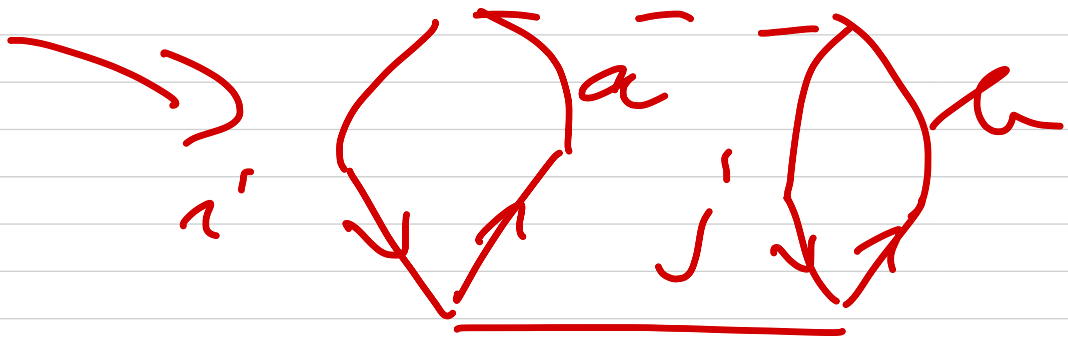


1p1h





2p2h



$$|\psi^{(2)}\rangle = \qquad |\Phi_M\rangle = |\Phi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i \times |\Phi_0\rangle$$

$$\sum_{MN>0} \frac{|\Phi_M\rangle\langle\Phi_M|\mathcal{H}_1|\Phi_N\rangle\langle\Phi_N|\mathcal{H}_1|\Phi_0\rangle}{(\varepsilon_0-\varepsilon_M)(\varepsilon_0-\varepsilon_N)}$$

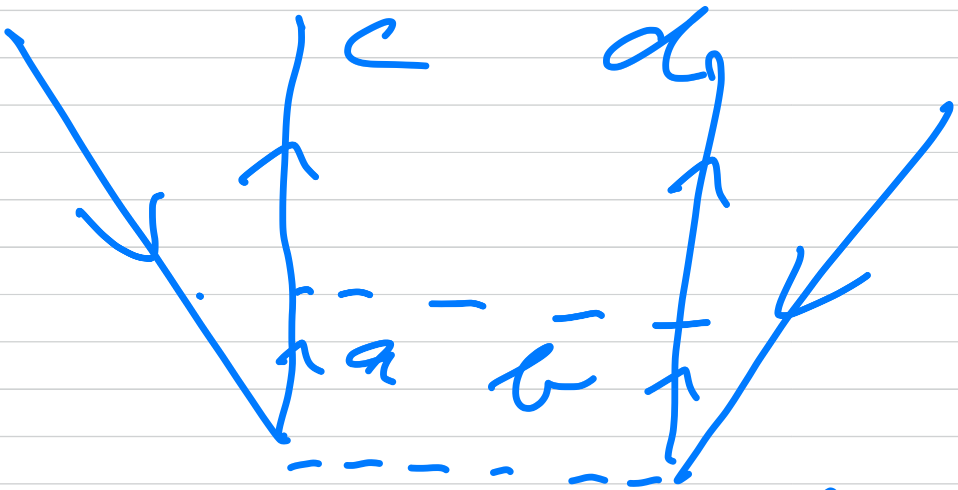
$$-\left\{\sum_{M>0} \frac{|\Phi_M\rangle\langle\Phi_M|\mathcal{H}_1|\Phi_0\rangle}{(\varepsilon_0-\varepsilon_M)^2}\right\}$$

$$\times \langle\Phi_0|\mathcal{H}_1|\Phi_0\rangle$$

To get $\Delta E_0^{(3)}$ multiply with $\langle\Phi_0|\mathcal{H}_I$

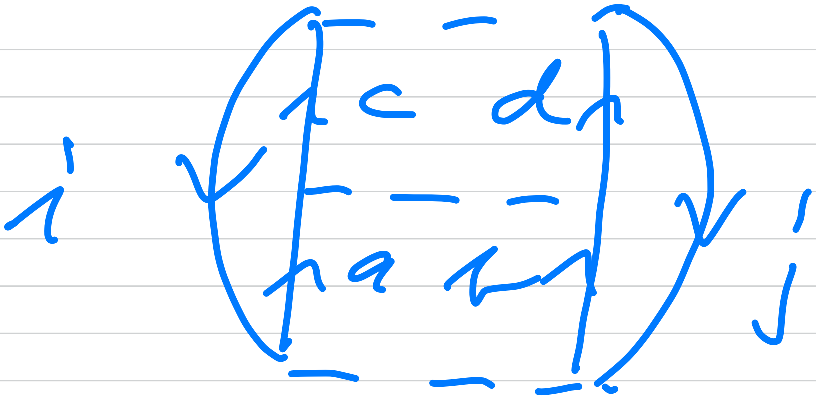
$$|\psi^{(2)}\rangle = \hat{R}\, H_I\, \hat{R}\, H_I\, |\Phi_0\rangle - \sum \frac{|\Phi_m\rangle\langle\Phi_m|H_1|\Phi_0\rangle}{(E_0 - E_m)^2} \times \langle\Phi_0|H_1|\Phi_0\rangle$$

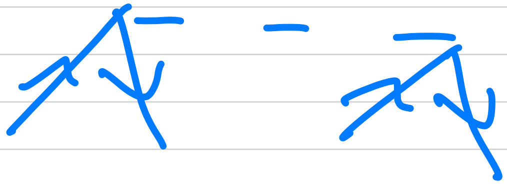
2p2h



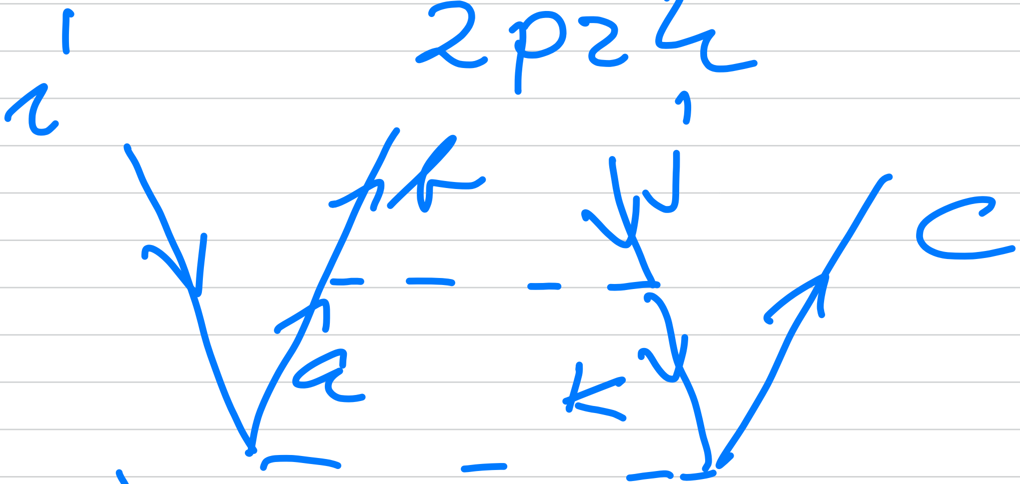
$$\frac{1}{4}\sum_{\substack{ab\\cd\\ij}} \frac{\langle cd|v|ab\rangle\langle ab|v|ij\rangle}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)} \times \frac{1}{(\varepsilon_i+\varepsilon_j-\varepsilon_c-\varepsilon_d)} |\Phi_{ij}^{cd}\rangle$$

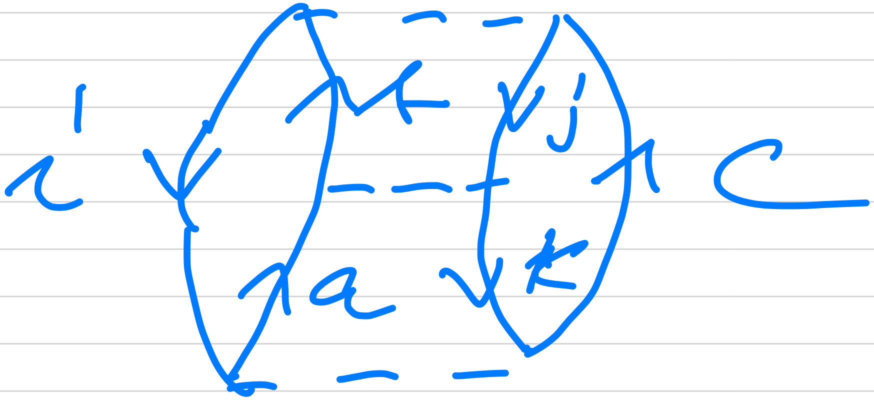
$$\langle\Phi_0|H_1|\psi^{(2)}\rangle$$

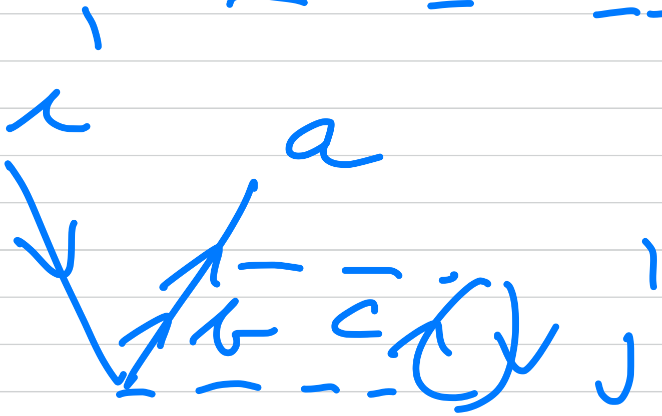


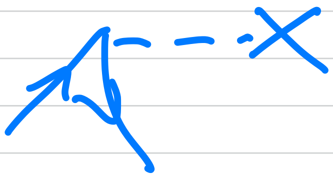


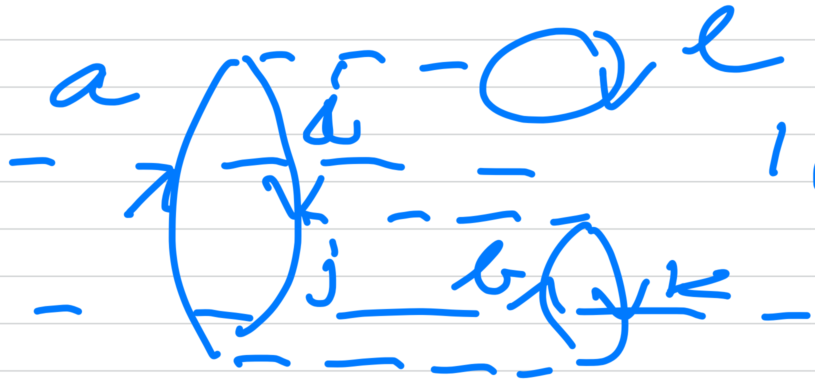
2p2h











1p2h

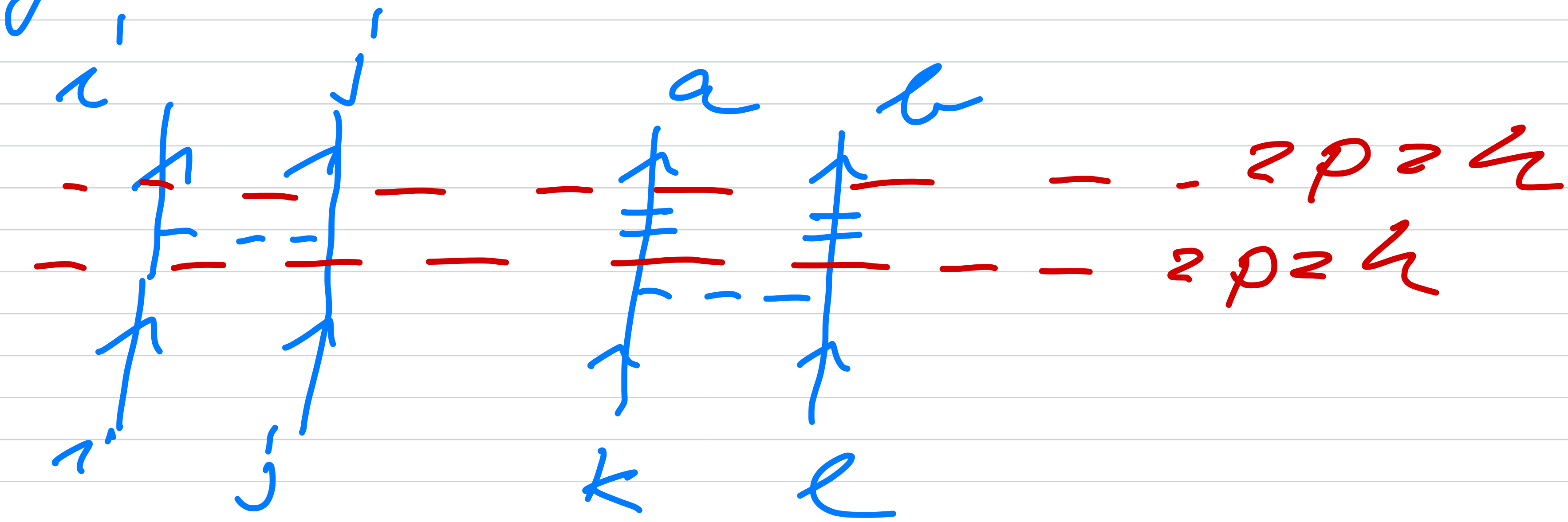
2p2h

$n_e = 3 \quad n_h = 4 \quad (-1)^7 = -1$

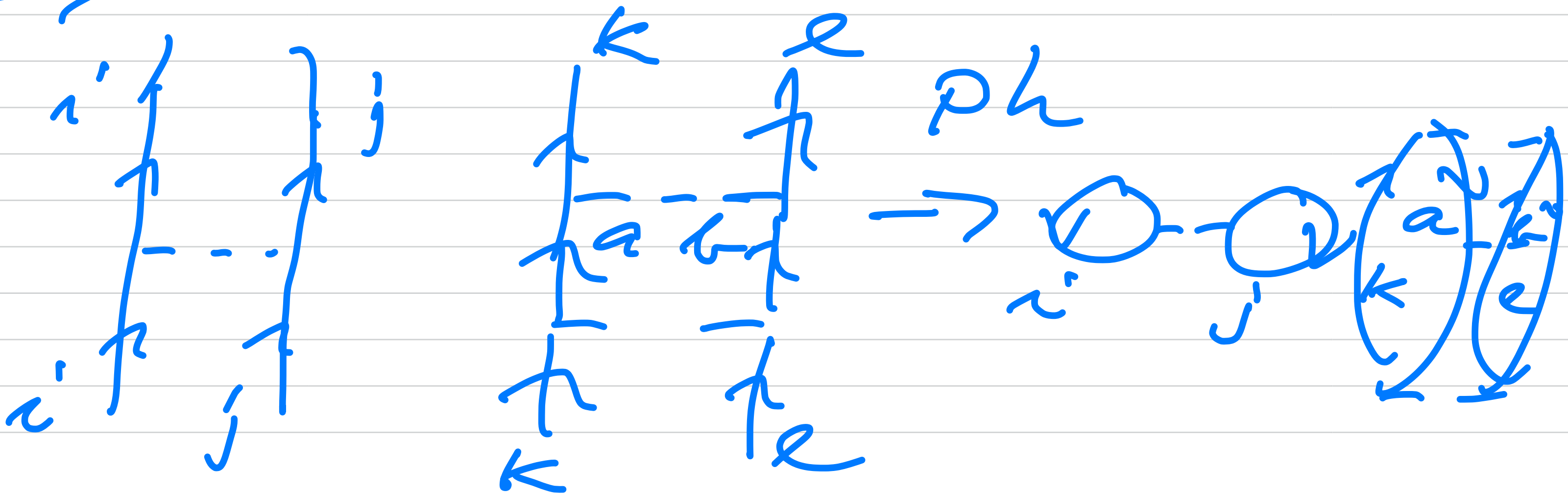
$n_{ep} = 1 \rightarrow \frac{1}{2}$

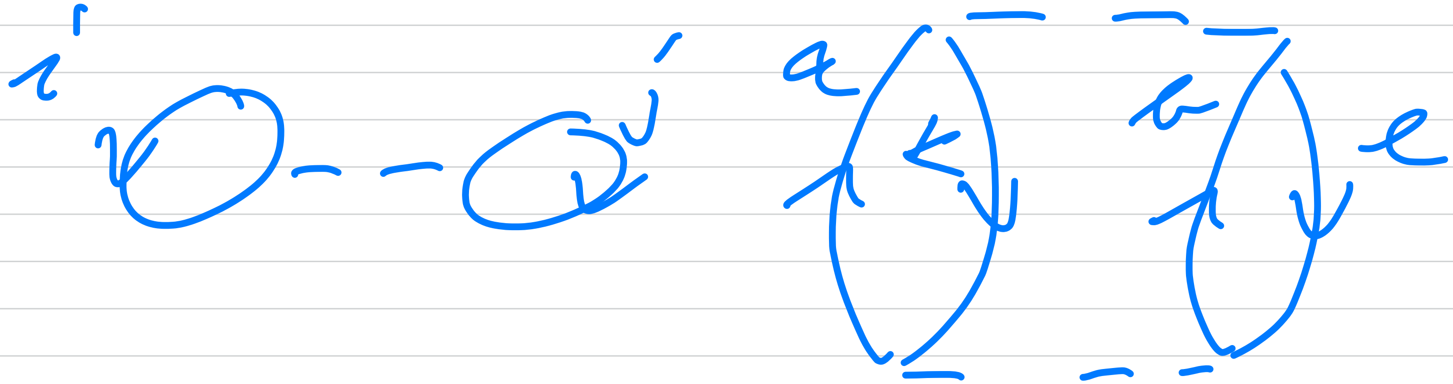
$$-\frac{1}{2}\sum_{\substack{ab\\ ijk\ell}} \frac{\langle i\ell|v|a\ell\rangle\langle jk|v|ib\rangle\langle ab|v|jk\rangle}{(\varepsilon_j+\varepsilon_k-\varepsilon_a-\varepsilon_b)(\varepsilon_i-\varepsilon_a)}$$

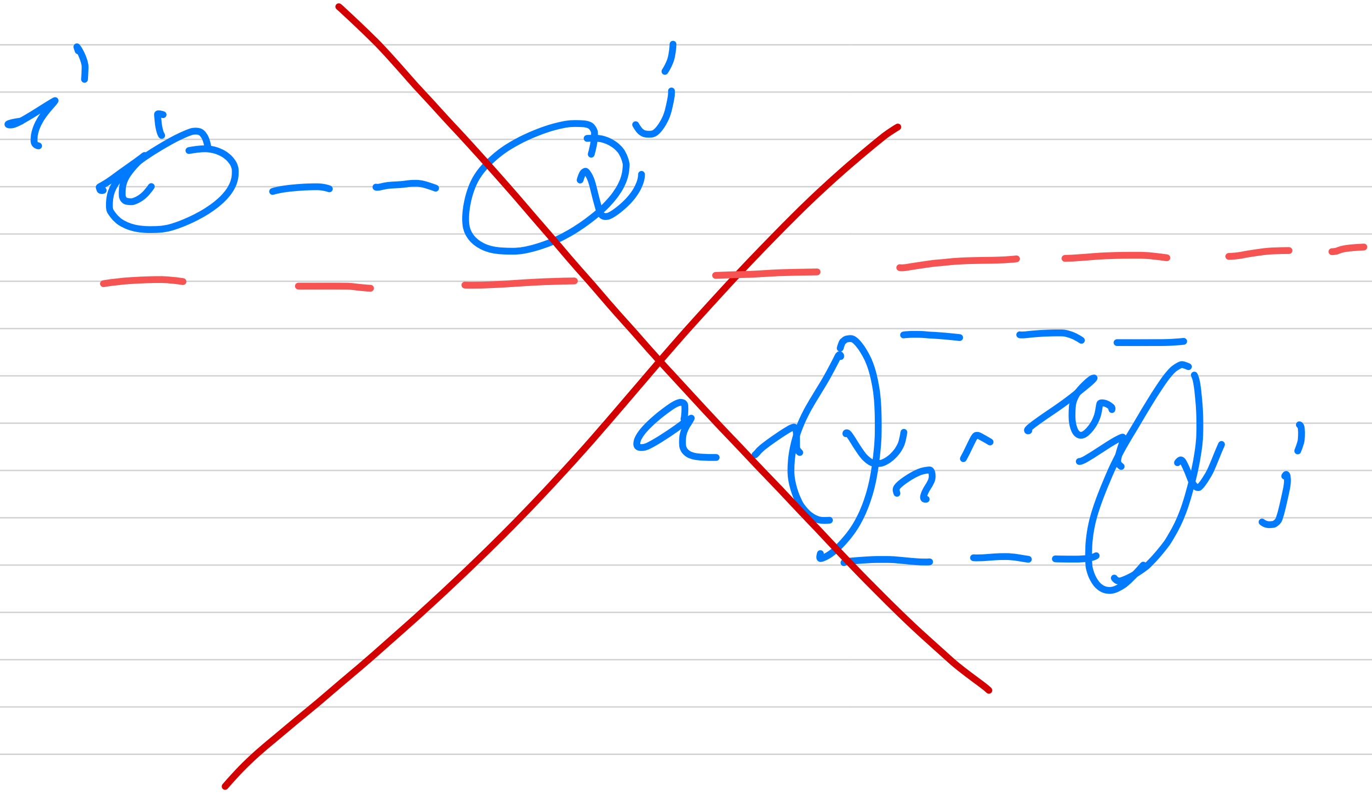
Unlinked term in particle-formalism



$\langle \Phi_c | H_1 | \Phi_c \rangle$

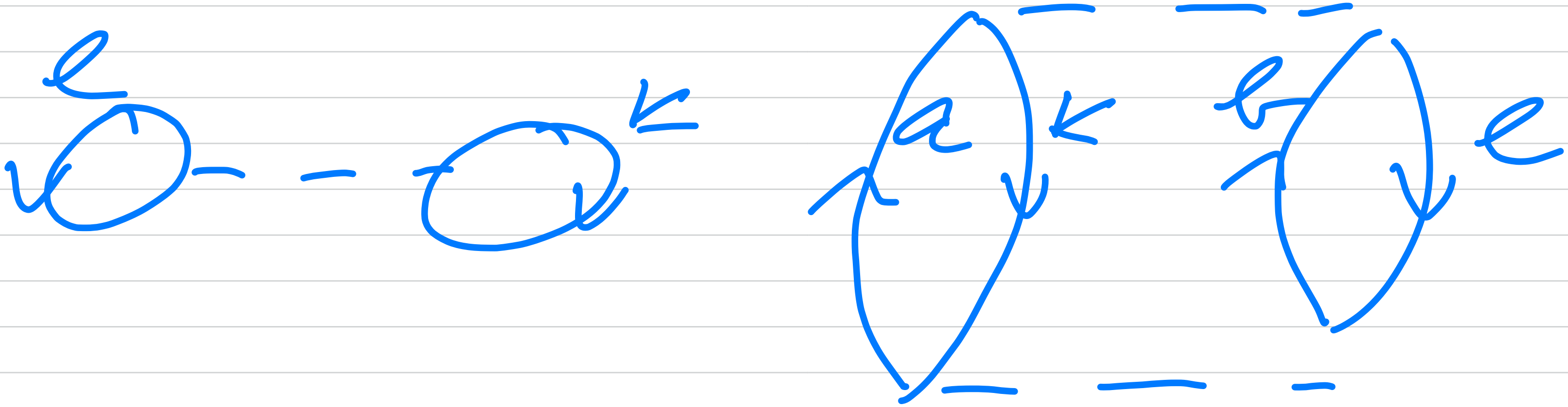




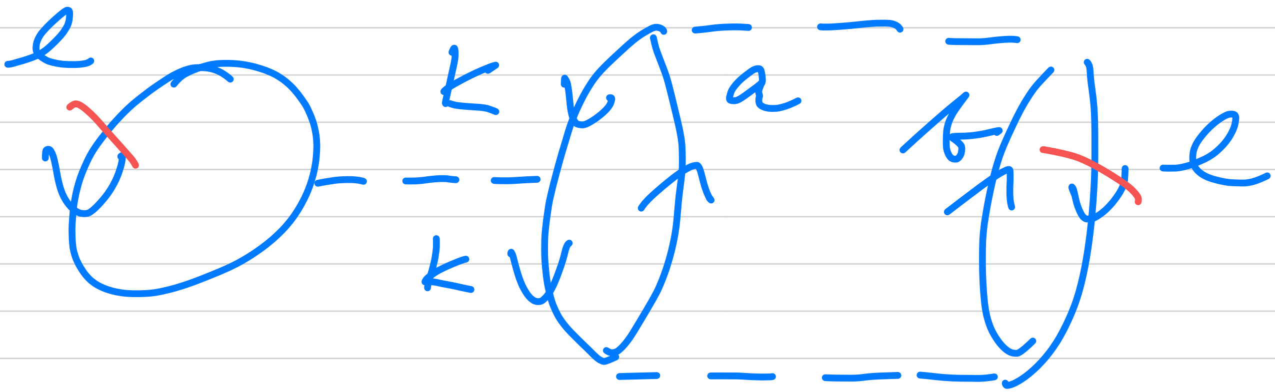


intermediate states have to belong to

$$\hat{Q} = \sum_m |\phi_m\rangle\langle\phi_m|$$



unlinked



linked

Violates Pauli principle

Unlinked diagrams in MBPT (RS) are not size extensive contribution to the energy

$$E \sim N$$

Electron gas

$$\langle \vec{k}_i \vec{k}_j | v | \vec{k}_m \vec{k}_n \rangle$$

$$= \delta_{\vec{k}_i + \vec{k}_j, \vec{k}_m + \vec{k}_n} \times \frac{1}{V}$$

$$\times \int v(\vec{r}_{12})\, d\vec{r}_{12}\, e^{i(\vec{k}_i - \vec{k}_j)\vec{r}_{12}}$$

$$\propto \frac{1}{V}$$

$$\Delta E_0^{(1)} = \overset{\vec{k}_i}{\bigcirc} - - - \overset{\vec{k}_j}{\bigcirc}$$

$$= \frac{1}{2} \sum_{\vec{k}_i \vec{k}_j \leq k_F} \langle \vec{k}_i \vec{k}_j | v | \vec{k}_i \vec{k}_j \rangle$$

$$\sum_{k} \to \frac{V}{(2\pi)^3} \int d\vec{k} \Rightarrow$$

$$\frac{V}{(2\pi)^3} \int_0^{k_F} \int_0^{\pi} \int_0^{2\pi} d\vec{k} = N \qquad \rho = \frac{N}{V}$$

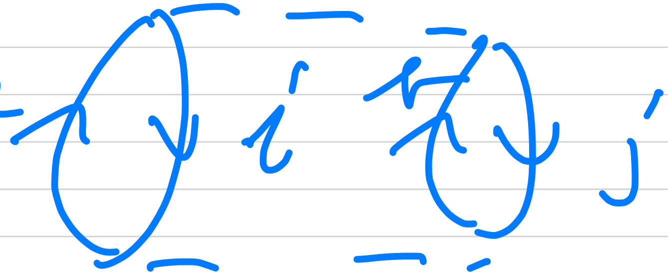
$$\Delta E_c^{(1)} = \frac{1}{2} \frac{V}{(2\pi)^3} \int_0^{k_F} d\vec{k}_1 \frac{V}{(2\pi)^3} \int_0^{k_F} d\vec{k}_2$$

$$\times \frac{1}{V} \underbrace{\int d r_{12} \, v(r_{12}) \cdots}_{\text{constant}}$$

$$\propto \quad N^2/V = N\rho$$

$$\frac{\Delta E_c^{(1)}}{N} \propto \rho$$

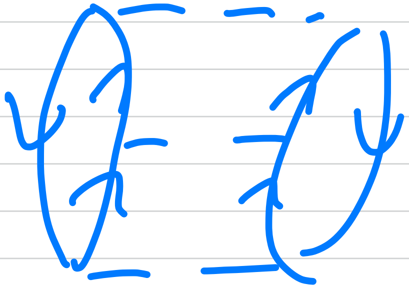
$$\Delta E_0^{(2)} = a$$



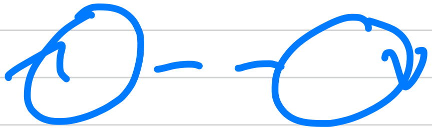
$$\sim N^2/V$$

$$= N\rho \implies$$

$$\frac{\Delta E_0^{(2)}}{N} \propto \rho \qquad \text{(size extensive)}$$

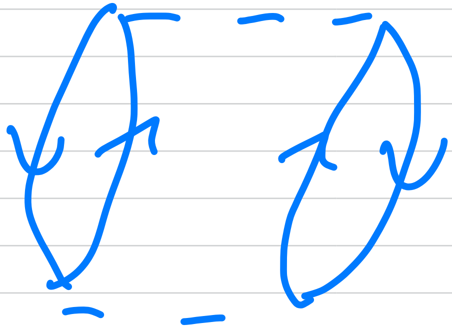


$$\sim \rho$$



$N^2\rho$

$N^2\rho^2$



$N\rho$

Coupled cluster theory

FCI

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

$$\hat{C}|\Phi_0\rangle = \sum_{ai} c_i^a |\Phi_i^a\rangle + \sum_{\substack{ab \\ ij}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

$$+ \ldots + NPNH$$

MBPT(RS)

$$\hat{C}|\Phi_0\rangle = \sum_{k=1}^{\infty} \left[(\hat{R}\hat{\mathcal{H}}_1)^k |\Phi_0\rangle \right]$$

$$\hat{R} = \sum_M \frac{|\Phi_M\rangle\langle\Phi_M|}{E_0 - E_M}$$

assumption:

$$\hat{C}\,|\Phi_0\rangle = \sum_{ar} C_r^a\,|\Phi_r^a\rangle$$

t_r^a amplitudes (1p1h excitations)

Thouless theorem

$$|\Psi_0\rangle = \exp\Big\{\sum_{ar} t_r^a\, a_a^\dagger a_r\Big\}|\Phi_0\rangle$$

$$\hat{T}_1 = \sum_{ai} t_i^a a_a^\dagger a_i$$

$$|\Psi_c\rangle = \exp(\hat{T}_1)|\Phi_c\rangle$$

$$= \left(1 + \hat{T}_1 + \frac{\hat{T}_1^2}{2!} + \frac{1}{3!}\hat{T}_1^3 + \dots\right)|\Phi_c\rangle$$

exponential ansatz,

1p1h excitations: singles

general ansatz

$$\hat{T} = \hat{T}_1 + \underbrace{\hat{T}_2}_{2p2h} + \underbrace{\hat{T}_3}_{3p3h} + \dots + \hat{T}_{N_p N_H}$$

exponential ansatz

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle$$

$$= \left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots \hat{T}_{N_{PART}} + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \ldots\right) \times |\Phi_0\rangle$$

$$\left[\hat{T}_{\mu_i}, \hat{T}_{\nu}\right] = 0$$

approximations

1) $T = T_1$ CCS 2) $T = T_2$ CCD

3) $T = T_1 + T_2$ CCSD 4) $T = T_1 + T_2 + T_3$ CCSDT