FYS 4480, NOV 3, 2022

Rayleigh-Schrödinger pert theory

$$\Delta E = \sum_{i=1}^{\infty} \Delta E^{(i)} \qquad \hat{P} = |\Phi_0\rangle\langle\Phi_0| \qquad \hat{P}|\psi_0\rangle = |\Phi_0\rangle$$

$$\Delta E^{(1)} = \langle\Phi_0|H_1|\Phi_0\rangle$$

$$= \frac{1}{2}\sum_{ij}\langle ij|v|ij\rangle_{AS}$$

$$\Delta E^{(2)} = \sum_m \frac{\langle\Phi_0|\hat{H}_1|\Phi_m\rangle\langle\Phi_m|\hat{H}_1|\Phi_0\rangle}{W_0 - W_m}$$

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$= H_N + E_0^{ref}$$

$$E_0^{ref} = \sum_{i \le F}\langle i|h_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|v|ij\rangle_{AS}$$

$$\hat{H}_N = \sum_{pq}\langle p|\hat{f}|q\rangle a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs}\langle pq|v|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

$$E^{ref}_{MBPT} = W_0 \qquad \hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle$$

$$\Delta E_{MBPT} = E - W_0$$

$$\Delta E_{FCI} = E - E_0^{ref} = E - (W_0 + \Delta E^{(1)})$$

$$\Delta E^{(3)} = \sum_{mn} \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_n \rangle \times \langle \Phi_n | H_1 | \Phi_0 \rangle}{(W_0 - W_m)(W_0 - W_n)}$$

$$- \sum_m \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_0 \rangle}{(W_0 - W_m)^2} \times \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

wave operator

$$\Omega = \sum_{i=1}^{\infty} \Omega^{(i)}$$

$$\Omega |\Phi_0\rangle = Q |\Psi_0\rangle$$

$$\Omega^{(1)} = \sum_m \frac{|\Phi_m\rangle \langle \Phi_m | H_1 | \Phi_0 \rangle}{W_0 - W_m}$$

$$\Omega^{(2)} = \sum_{mn} \frac{|\Phi_m\rangle\langle\Phi_m|H_1|\Phi_n\rangle \times \langle\Phi_n|H_1|\Phi_0\rangle}{(W_0 - W_m)(W_0 - W_n)}$$

$$- \sum_{m} \frac{|\Phi_m\rangle\langle\Phi_m|H_1|\Phi_0\rangle}{(W_0 - W_m)^2} \times \langle\Phi_0|H_1|\Phi_0\rangle$$

$$\Delta E^{(i+1)} = \langle\Phi_0|H_1\Omega^{(i)}|\Phi_0\rangle$$

Example: $\Delta E^{(2)}$

$$\Delta E^{(2)} = \underbrace{\sum_{ai} \frac{|\langle\Phi_0|H_I|\Phi_i^a\rangle|^2}{\varepsilon_i - \varepsilon_a}}_{\text{1p1h contrib}}$$

$$+ \sum_{\substack{ab \\ ij}} \frac{|\langle\Phi_0|H_1|\Phi_{ij}^{ab}\rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$H_1 = \frac{1}{4} \sum_{pqrs} \langle pq|v|rs\rangle_{AS} \, a_p^\dagger a_q^\dagger a_s a_r$$

$$\langle \Phi_0 | H_N | \Phi_i^a \rangle = \langle i | \hat{f} | a \rangle$$

$$= \underbrace{\langle i | h_0 | a \rangle}_{=0} + \sum_j \langle ij | v | aj \rangle_{AS}$$

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

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

$$\Delta E^{(2)} = \sum_{ai} \frac{|\langle i | f | a \rangle|^2}{\varepsilon_i - \varepsilon_a}$$

$$+ \frac{1}{4} \sum_{\substack{ab \\ ij}} \frac{|\langle ij | v | ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$= \sum_{aij} \frac{|\langle ij | v | aj \rangle|^2}{\varepsilon_i - \varepsilon_a}$$

$$+ \frac{1}{4} \sum_{\substack{ab \\ ij}} \langle ij | v | ab \rangle \underbrace{\frac{\langle ab | v | ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}}_{t_{ij}^{ab}}$$

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

$$\Omega^{(1)}_{2p2h} = \sum_{\substack{ab\\ij}} \frac{|ab\rangle\langle ab|v|ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

$$= \sum_{\substack{ab\\ij}} |ab\rangle\, t_{ij}^{ab}$$

computational topics:

$$\Delta E^{(2)} = \sum_{\substack{ab\\ij}} \frac{\langle ij|v|ab\rangle\langle ab|v|ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

Def: $I = \{(ij)\}$ 2h configs

$J = \{(ab)\}$ 2p configs

Def $V_{IJ} = \langle ij|v|ab\rangle_{AS}$

Def $T_{JI} = \frac{\langle ab|v|ij\rangle_{AS}}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$

$$\Delta E^{(2)} = \sum_{IJ} V_{IJ} T_{JI}$$

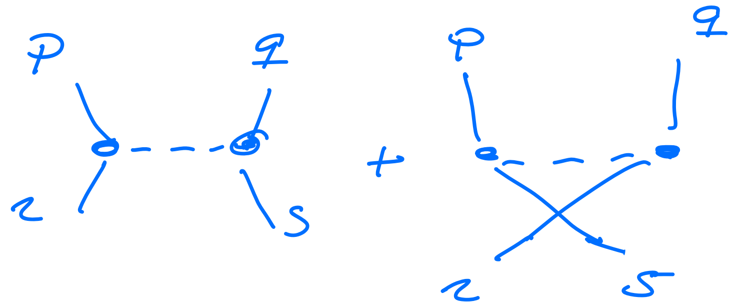
$$\sum_{ai} \frac{|\langle i|f|a\rangle|^2}{\varepsilon_i - \varepsilon_a}$$

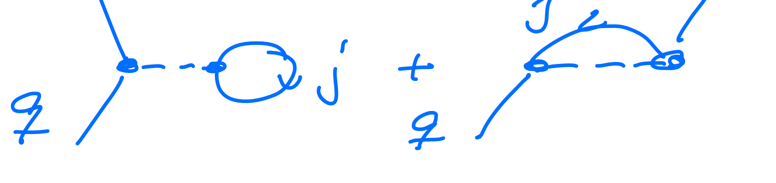
$$\langle i|f|a\rangle = \sum_j \langle ij|v|aj\rangle_{AS}$$

Diagrammatic representation.

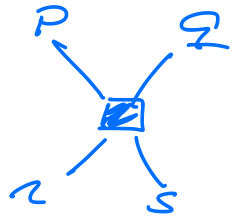
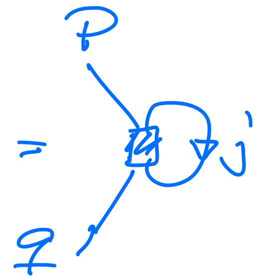
Definitions

$$H_I = \hat{V}_N + F_N = \overbrace{\frac{1}{4}\sum_{pqrs} \langle pq|v|rs\rangle_{AS}\, a_p^\dagger a_q^\dagger a_s a_r}^{V_N} + \underbrace{\sum_{pqj} \langle pj|v|qj\rangle_{AS}\, a_p^\dagger a_q}_{F_N}$$

$\hat{V}_N =$ 

$\hat{F}_N =$ 

with anti-symmetrized mtx elements

$V_N =$  $F_N =$ 

we have left h_0

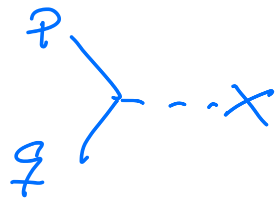
$h_0 =$ 

Diagram rules

1. For a diagram with n-V interactions, each vertex contains an anti-symmetrized vertex, indicated by  or in terms of direct and exchange parts 
onebody operators are indicated as 

② Draw all topologically distinct diagrams to a given order by linking up all particle and hole lines with various vertices. Two diagrams can be made topologically equivalent by deformation of fermion lines under the restrictions:

(i) Particle lines remain particle lines, same for holes

(ii) Ordering of vertices not altered.

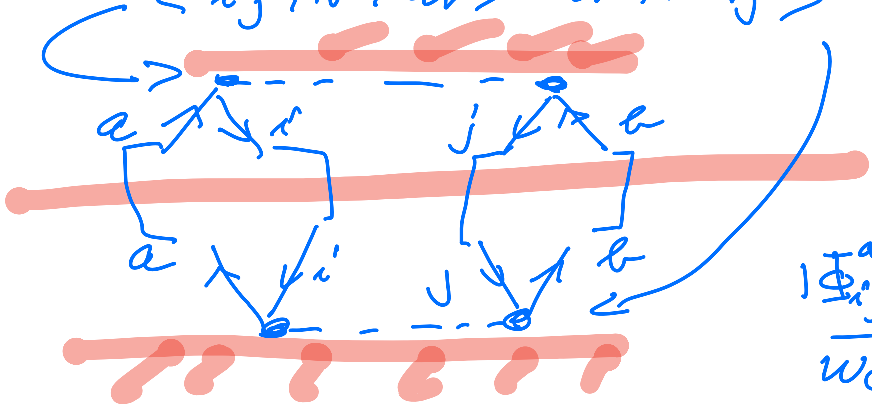
Example

$$\frac{1}{4} \sum_{\substack{ab \\ ij}} \frac{\langle ij|v|ab\rangle_{AS} \langle ab|v|ij\rangle_{AS}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$(\langle ij|v|ab\rangle - \langle ij|v|ba\rangle) \times (\langle ab|v|ij\rangle - \langle ba|v|ij\rangle)$$

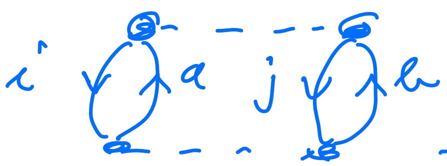
$$\langle ij|v|ab\rangle\langle ab|v|ij\rangle$$

$$\sum_{ab\,ij}$$

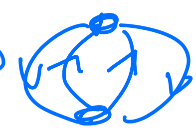


2p2h

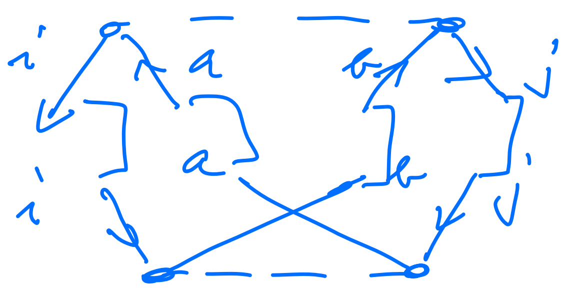
$$\frac{|\Phi_{ij}^{ab}\rangle\langle\Phi_{ij}^{ab}|V|\Phi_0\rangle}{W_0 - W_{ij}^{ab}}$$

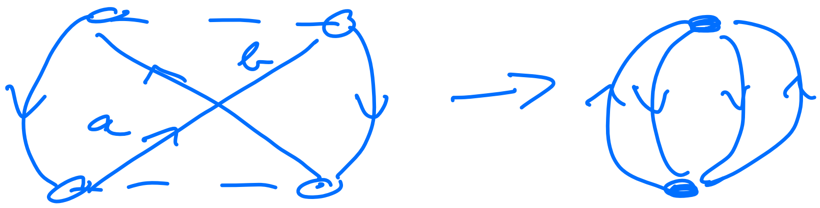


2p2h excitation

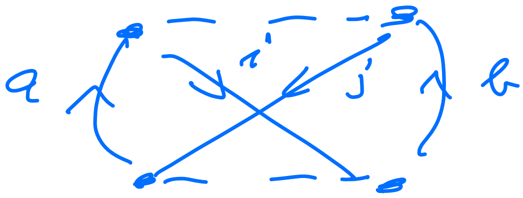


$$\langle ij|v|ab\rangle\langle ba|v|ij\rangle$$

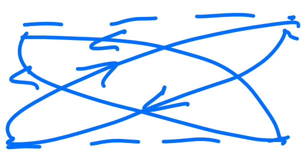




with antisym mtx elements



$= -\langle ij|v|ab\rangle\langle ab|v|ji\rangle$



$\langle ji|v|ba\rangle\langle ba|v|ji\rangle$

$= \langle ij|v|ab\rangle\langle ab|v|ij\rangle$

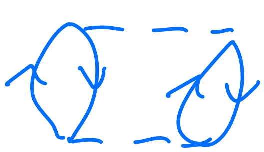
3 there is a factor

$(-)^{n_h+n_e}$

n_e = # closed loops

n_h = # hole lines

Example



$n_h = 2$

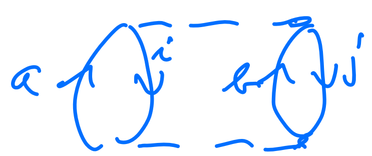
$n_e = 2$

(4) For each interval between two successive vertices, we have a factor

$$\frac{1}{\sum_{j=1}^{n_h} \varepsilon_j - \sum_{a=1}^{n_p} \varepsilon_a}$$

(5) There is a factor $\left(\frac{1}{2}\right)^{n_{ep}}$

where n_{ep} = # pairs of lines that start at the same interaction v and end at the same interaction v' and go in the same direction.



$n_{ep} = 2$

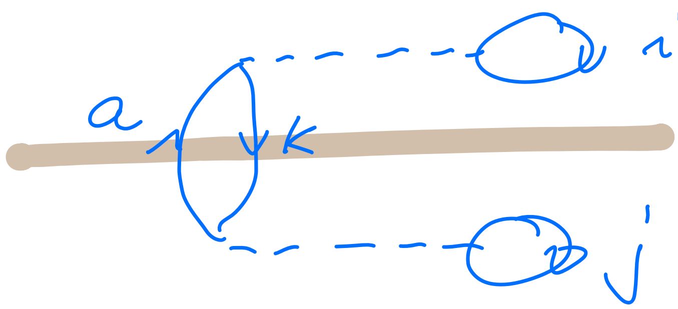
$$\sim \left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

(6) Sum freely over all intermediate states

(7) Label all vertices with the different particle/hole states and assign labels to all lines + arrows for hole and particle lines:

Example

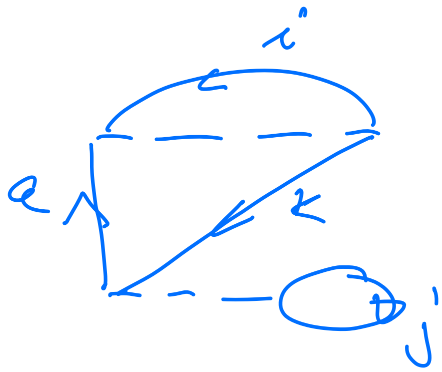
$$\sum_{ai} \frac{|\langle i|f|a\rangle|^2}{\varepsilon_i - \varepsilon_a}$$



1p1h excitation

$$+ \sum_{\substack{ijk \\ a}} \frac{\langle ki|v|ai\rangle_{AS}\langle aj|v|kj\rangle_{AS}}{\varepsilon_k - \varepsilon_a}$$

$\# n_h = 3 \qquad \# n_\ell = 3$



$$= -\sum_{\substack{ijk\\a}} \frac{\langle ik|v|ai\rangle\langle aj|v|kj\rangle}{\varepsilon_k - \varepsilon_a}$$