

FYS 4480, NOV 3, 2022

Rayleigh-Schrödinger pert theory

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

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

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

$$\Delta E^{(2)} = \sum_m \frac{\langle\Phi_0|\hat{H}_1|\Phi_m\rangle\langle\Phi_m|\hat{H}_1|\Phi_0\rangle}{E_0 - E_m}$$

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

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

$$E_0^{ref} = \sum_{i \leq F} \langle i|w_0|i\rangle + \frac{1}{2} \sum_{ij} \langle i|w|i\rangle_{AS}$$

$$\begin{aligned} H_N &= \sum_{pq} \langle p|\hat{f}|q\rangle a_p^\dagger a_q \\ &+ \frac{1}{4} \sum_{pqrs} \langle pq|w|rs\rangle a_p^\dagger a_q^\dagger a_s a_r \end{aligned}$$

$$E_{MBPT}^{ref} = W_0 \quad \hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle$$

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

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

$$\begin{aligned} \Delta E^{(3)} = & \sum_{mn} \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_n \rangle}{(W_0 - W_m)(W_0 - W_n)} \\ & \times \langle \Phi_n | H_1 | \Phi_0 \rangle \\ & - \sum_m \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_0 \rangle}{(W_0 - W_m)^2} \\ & \times \langle \Phi_0 | H_1 | \Phi_0 \rangle \end{aligned}$$

wave operator

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

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

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

$$\Omega^{(2)} = \sum_{mn} \frac{|\Phi_m\rangle \langle \Phi_m | H_1 | \Phi_n\rangle}{(\omega_0 - \omega_m)(\omega_0 - \omega_n)} \times \langle \Phi_n | H_1 | \Phi_0 \rangle$$

$$- \sum_m \frac{|\Phi_m\rangle \langle \Phi_m | H_1 | \Phi_0 \rangle}{(\omega_0 - \omega_m)^2} \times \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$\Delta E^{(2)} = \langle \Phi_0 | H_1 \Omega^{(1)} | \Phi_0 \rangle$$

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

$$\Delta E^{(2)} = \sum_{ai} \underbrace{\frac{|\langle \Phi_0 | H_1 | \Phi_i^a \rangle|^2}{\epsilon_i - \epsilon_a}}_{\text{1p1h contrib}}$$

$$+ \sum_{\substack{ab \\ ij}} \frac{|\langle \Phi_0 | H_1 | \Phi_{ij}^{ab} \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

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

$$\begin{aligned}\langle \Phi_0 | H_N | \Phi_n^a \rangle &= \langle i | f^1 | a \rangle \\ &= \underbrace{\langle i | h_0 | a \rangle}_{=0} + \sum_j \langle i'j | v | a_j \rangle_{AS}\end{aligned}$$

$$\begin{aligned}\langle \Phi_0 | H_N | \Phi_{ij}^{ab} \rangle &= \langle i'j | v | ab \rangle_{AS} \\ &= \langle \Phi_0 | H_I | \Phi_{ij}^{ab} \rangle\end{aligned}$$

$$\begin{aligned}\Delta E^{(2)} &= \sum_{a \neq i} \frac{|\langle i | f | a \rangle|^2}{\epsilon_i - \epsilon_a} \\ &\quad + \frac{1}{4} \sum_{a,b} \frac{|\langle i'j | v | ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\ &= \sum_{a \neq i} \frac{|\langle i'j | v | a_j \rangle|^2}{\epsilon_i - \epsilon_a} \\ &\quad + \frac{1}{4} \sum_{i'j'} \frac{\langle i'j | v | ab \rangle \langle ab | v | i'j \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \\ &\quad \quad \quad t_{ij}^{ab}\end{aligned}$$

$$t_{ij}^{ab} = \frac{\langle ab | r | i'j' \rangle}{\epsilon_{i'} + \epsilon_{j'} - \epsilon_a - \epsilon_b}$$

$$\begin{aligned} \mathcal{N}_{2ph}^{(1)} &= \sum_{\substack{ab \\ i'j'}} \frac{|ab\rangle \langle ab | r | i'j' \rangle}{\epsilon_{i'} + \epsilon_{j'} - \epsilon_a - \epsilon_b} \\ &= \sum_{\substack{ab \\ i'j'}} |ab\rangle t_{ij}^{ab} \end{aligned}$$

Computational steps:

$$\Delta E^{(2)} = \sum_{\substack{ab \\ i'j'}} \frac{\langle i'j' | r | ab \rangle \langle ab | r | i'j' \rangle}{\epsilon_{i'} + \epsilon_{j'} - \epsilon_a - \epsilon_b}$$

$$\text{Def: } \mathcal{I} = \{ (i'j') \}_{2h \text{ configs}}$$

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

$$\text{Def } V_{\mathcal{I}\mathcal{J}} = \langle i'j' | r | ab \rangle_{AS}$$

$$\text{Def } T_{\mathcal{J}\mathcal{I}} = \frac{\langle ab | r | i'j' \rangle_{AS}}{\epsilon_{i'} + \epsilon_{j'} - \epsilon_a - \epsilon_b}$$

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

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

$$\langle i | f | a \rangle = \sum_j \langle ij | w | aj \rangle_A$$

Diagrammatic representation.

Definitions -

$$H_I = \underbrace{\hat{V}_N + \hat{F}_N}_{\text{circled}} = \frac{1}{4} \sum_{pqrs} \langle pq | v | rs \rangle_A \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s + \sum_{pqj'} \langle pj | w | qj \rangle_A \hat{a}_p^\dagger \hat{a}_q \hat{a}_{j'}$$

\hat{V}_N

\hat{F}_N

$$\hat{V}_N = \text{Diagram 1} + \text{Diagram 2}$$

Diagram 1: Two vertices connected by a dashed line. The left vertex has two incoming lines labeled p and r, and two outgoing lines labeled q and s. The right vertex has two incoming lines labeled q and s, and two outgoing lines labeled p and r.

Diagram 2: Two vertices connected by a dashed line. The left vertex has two incoming lines labeled p and r, and two outgoing lines labeled q and s. The right vertex has two incoming lines labeled p and r, and two outgoing lines labeled q and s, with the lines crossing each other.

$$\hat{F}_N = \text{Diagram 3} + \text{Diagram 4}$$

Diagram 3: A vertex with two incoming lines labeled p and q, and two outgoing lines labeled r and s. It is connected by a dashed line to a circle labeled j'. The circle has two incoming lines labeled p and q, and two outgoing lines labeled r and s.

Diagram 4: A vertex with two incoming lines labeled p and q, and two outgoing lines labeled r and s. It is connected by a dashed line to another vertex. The second vertex has two incoming lines labeled p and q, and two outgoing lines labeled r and s, with a curved line connecting the two incoming lines.

with anti-symmetrized
matrix elements

$$V_N = \begin{array}{c} p \quad q \\ \diagdown \quad \diagup \\ \boxed{\text{X}} \\ \diagup \quad \diagdown \\ r \quad s \end{array} \quad F_N = \begin{array}{c} p \\ \diagdown \\ \boxed{\text{X}} \quad \text{---} j \\ \diagup \\ q \end{array}$$

we have left h_0

$$h_0 = \begin{array}{c} p \\ \diagdown \\ \quad \quad \text{---} X \\ \diagup \\ q \end{array}$$

Diagram rules

- ① For a diagram with n - V interactions, each vertex can be an anti-symmetrized vertex, indicated by $\boxed{\text{X}}$ or in terms of direct and exchange parts $\bullet \text{---} \bullet$ one-body operators as indicated as $\bullet \text{---} X$

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.

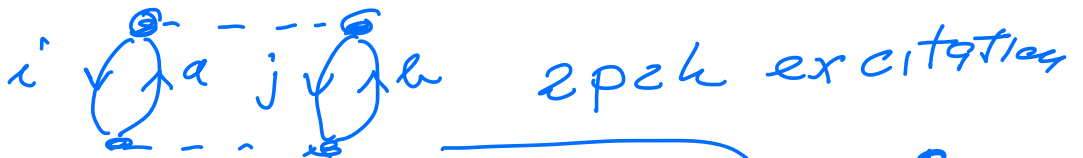
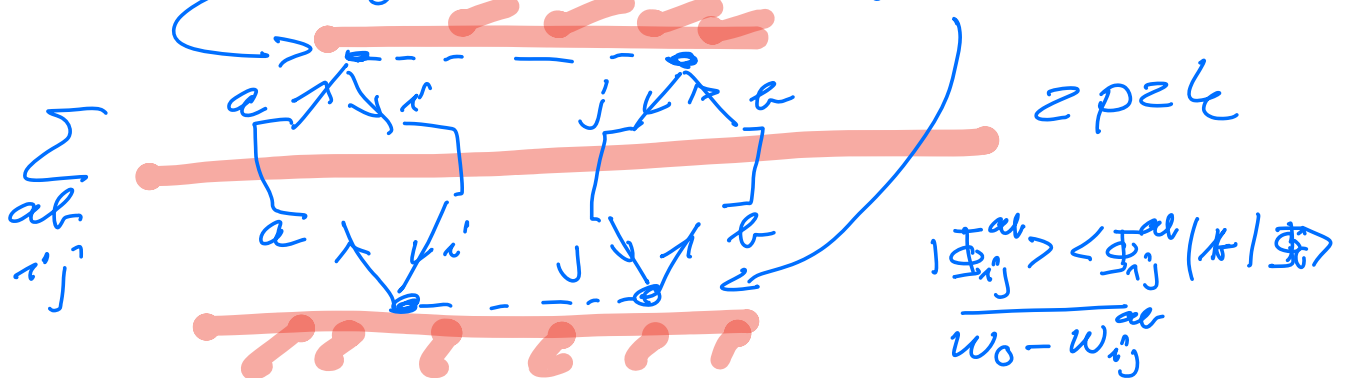
Example

$$\frac{1}{4} \sum_{\substack{a,b \\ i,j}} \frac{\langle ij | r | ab \rangle_{AS} \langle ab | r | ij \rangle_{AS}}{E_i + E_j - E_a - E_b}$$

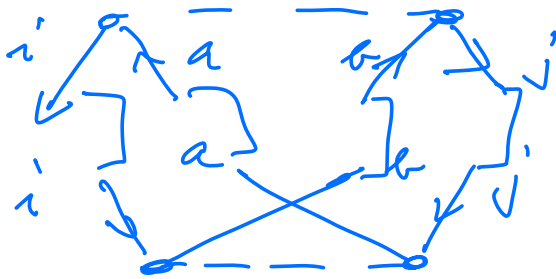
$$(\langle ij|v|ab\rangle - \langle ij|v|ba\rangle) \times$$

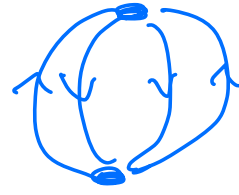
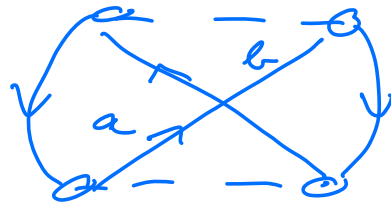
$$(\langle a|v|v_j \rangle - \langle b|v|v_j \rangle)$$

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

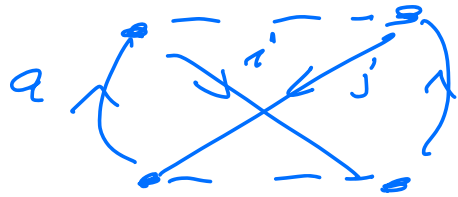


$$\langle i'j' | v | ab \rangle \langle ba | v | i'j' \rangle$$

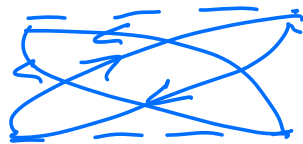




with antisym
mtx elements



$$b = -\langle ij | r | kl \rangle \langle a | r | ji \rangle$$



$$\begin{aligned} & \langle ji | r | ba \rangle \langle ba | r | ji \rangle \\ & = \langle ij | r | ab \rangle \langle ab | r | ij \rangle \end{aligned}$$

③

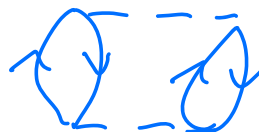
there is a factor

$$(-)^{n_h + n_e}$$

$n_e = \#$ 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

$$\frac{1}{\sum_{j=1}^{m_k} \varepsilon_j - \sum_{a=1}^{m_p} \varepsilon_a}$$

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

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

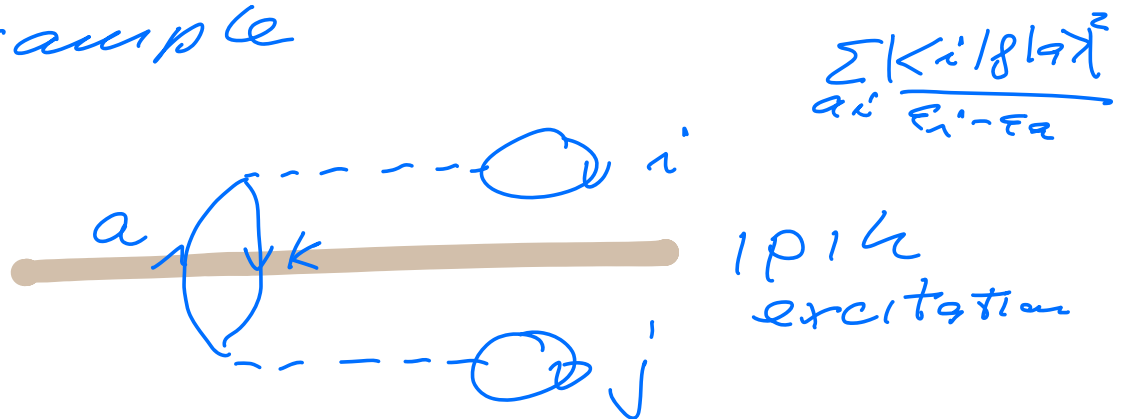

 $n_{ep} = 2$

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

⑥ Sum freely over all intermediate states

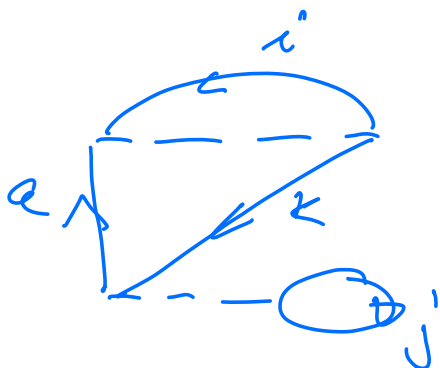
(7) Label all vertices with the different particle/hole states and assign labels to all lines + arrows for hole and particle lines;

Example



$$+ \sum_{\substack{jk \\ a}} \frac{\langle k_i | v | a_i \rangle_{\text{H}} \langle a_j | v | k_j \rangle_{\text{H}}}{\epsilon_k - \epsilon_a}$$

$$\# n_h = 3 \quad \# n_e = 3$$



$$= - \sum_{\substack{ijk \\ a}} \frac{\langle i|k|a\rangle \langle a|j|k\rangle}{\epsilon_k - \epsilon_a}$$