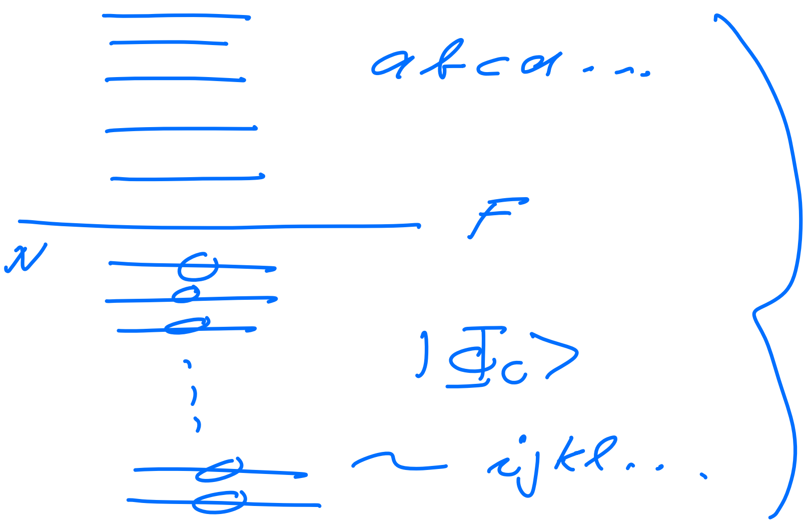
FYS4480 Sept 29, 2022

New vacuum state

$|c\rangle = |\Phi_0\rangle$ N-body state



$$\hat{H} = \sum_{pq} \{a_p^\dagger a_q\} \langle p|\hat{f}|q\rangle$$

$$+ \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle_{AS} \times \{a_p^\dagger a_q^\dagger a_s a_r\}$$

$$+ E_0^{Ref}$$

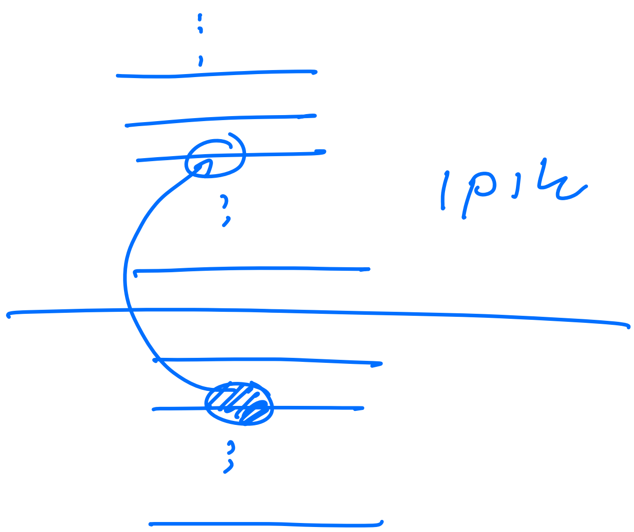
$$= \hat{F}_N + \hat{V}_N + E_0^{Ref},$$

$$E_0^{Ref} = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij} \langle ij|\hat{v}|ij\rangle_{AS}$$

$$= \langle \Phi_0 | H | \Phi_0 \rangle$$

$$\hat{F}_N = \sum_{pq} \langle p | \hat{h}_0 | q \rangle \{ a_p^\dagger a_q \} + \sum_{pqi} \langle p i | \hat{v} | q i \rangle \{ a_p^\dagger a_q \}$$

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle$$ 1p1h



1p1h

$$|\Phi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle$$

2p2h

$\vdots$

$$|\Phi_{i_1 i_2 \dots i_N}^{a_1 a_2 \dots a_N}\rangle = a_{a_1}^\dagger a_{a_2}^\dagger \cdots a_{a_N}^\dagger a_{i_N} a_{i_{N-1}} \cdots a_{i_1} \times |\Phi_0\rangle$$

NPNH

Ground state:

$$|\Psi_0\rangle = \sum_J c_{J0} |\Phi_J\rangle$$

$$c_{J0} = \langle \Psi_0 | \Phi_J \rangle$$

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

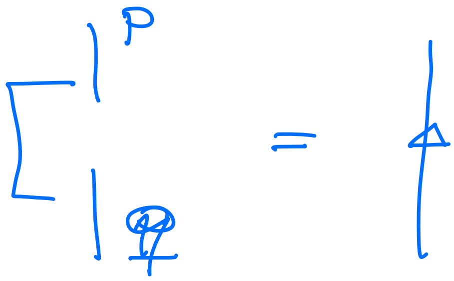
$$\langle \Phi_i^a | H | \Phi_i^a \rangle = \langle a | \hat{f} | a \rangle - \langle i | \hat{f} | i \rangle + E_0^{Ref}.$$

$$\langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle = \langle ij | w | ab \rangle_{AS}$$

Diagrammatic representation

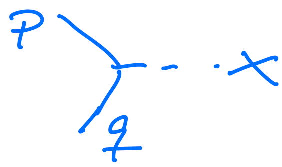
vacuum $|0\rangle$

$\overbrace{a_p a_q^+} = \delta_{pq}$ only non-zero

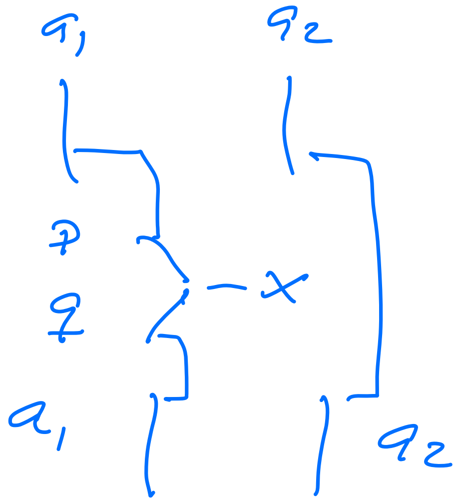


$$= \quad \Rightarrow \quad a_p a_q^{\dagger}$$

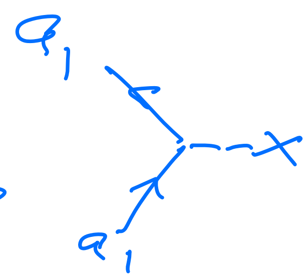
$$\hat{h}_0 \longrightarrow$$



$$\sum_{pq} \langle p | h_0 | q \rangle a_p^{\dagger} a_q$$

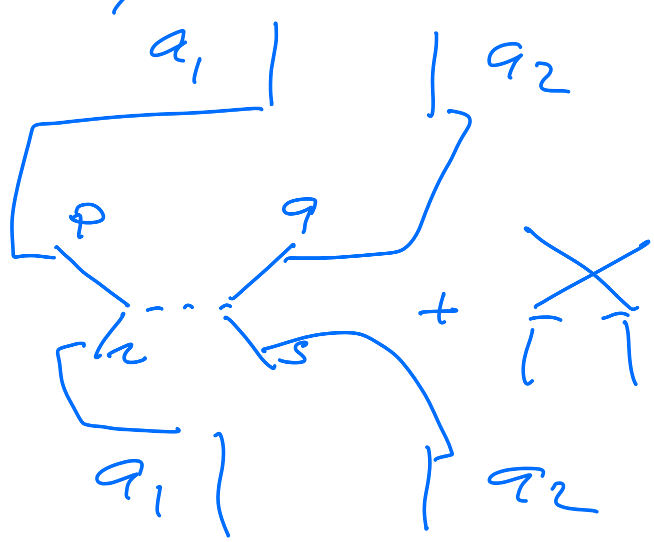


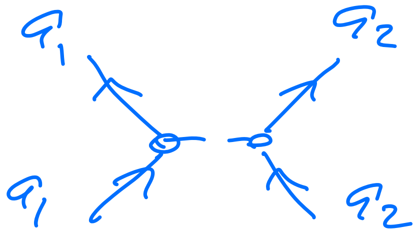
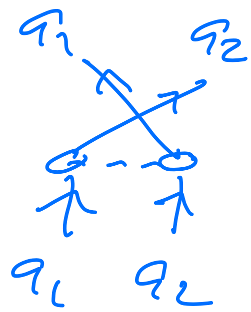
$$\longrightarrow$$



$$\langle a_1 | \hat{h}_0 | a_1 \rangle$$

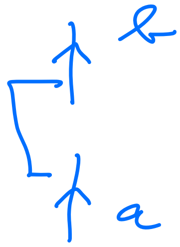
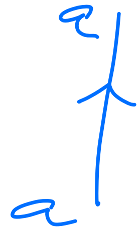
$$H_I = \frac{1}{4} \sum a_p^{\dagger} a_q^{\dagger} a_s a_r \langle pq | \hat{v} | rs \rangle_{AS}$$

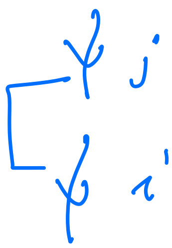
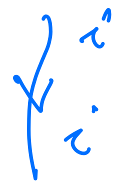


$=$  $+$ 

$$\langle a_1 a_2|\hat{v}|a_1 a_2\rangle - \langle a_2 a_1|\hat{v}|a_1 a_2\rangle$$

<u>Now</u>

$$a_b a_a^\dagger =$$  $=$  $= \delta_{ab}$

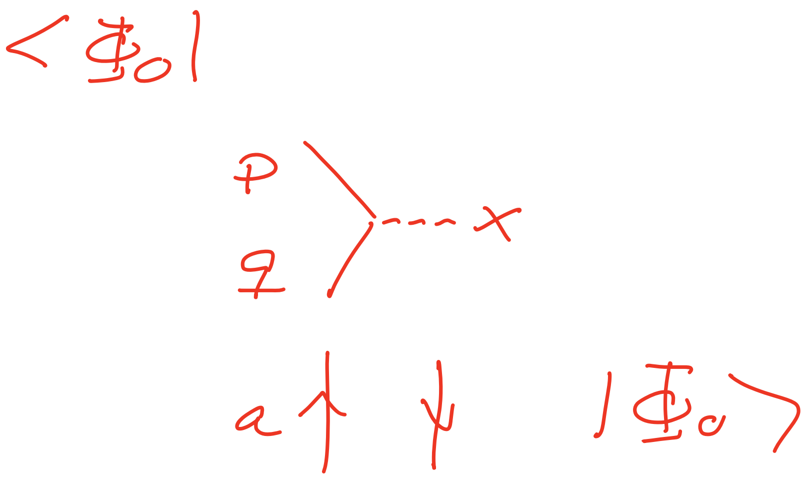
$$a_i^\dagger a_j =$$  $=$  $=$ 

$$= \delta_{ij}$$

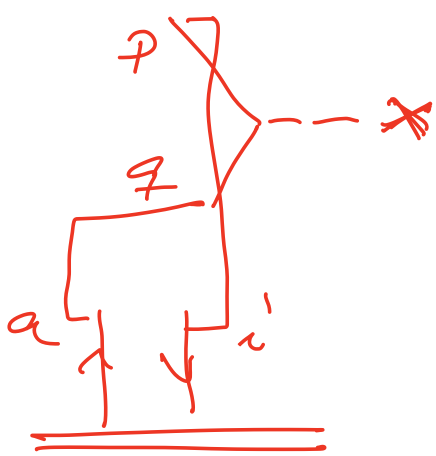
$$\langle \Phi_0 | H | \Phi_i^a \rangle \propto$$

$$\langle \Phi_0 | a_p^\dagger a_q a_a^\dagger a_i | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \underbrace{a_p^\dagger a_q^\dagger}_{=0} a_s a_r a_a^\dagger a_i | \Phi_0 \rangle$$

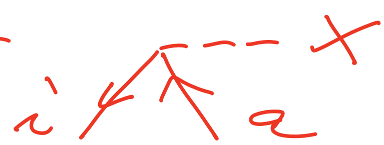


(Shavitt & Bartlett)



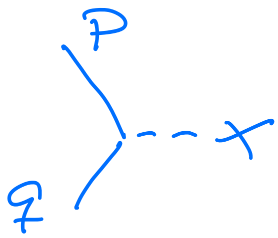
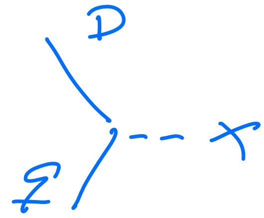
$= \langle i|f|a\rangle$

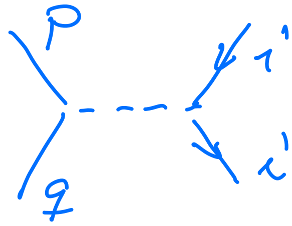
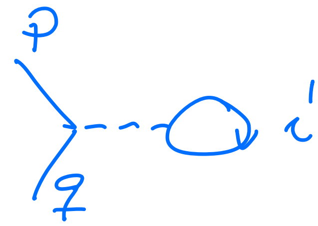
$=$

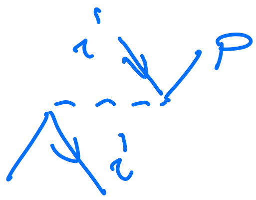


$$\hat{F} = \sum_{pq} \langle p|h_0|q\rangle\, a_p^{\dagger} a_q$$

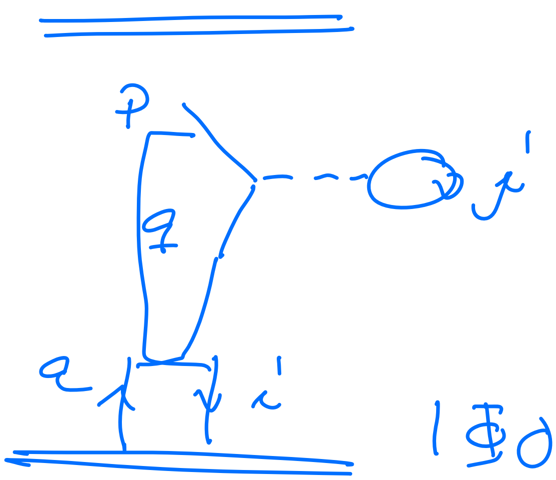
$$+ \sum_{pqi} \langle pi|\hat{v}|qi\rangle_{AS}\, a_p^\dagger a_q$$

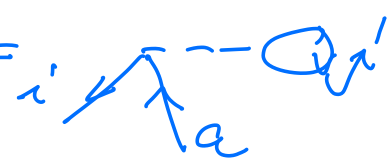
$\sum_{pq}$  $=$ 

$\sum_{i}$  $=$ 

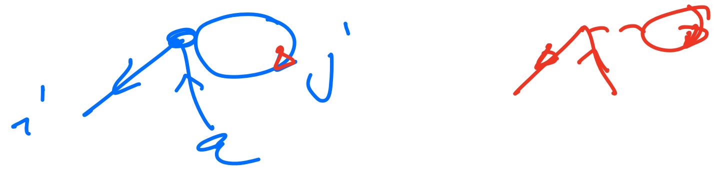
$\sum_{iq}$  $=$ 

$\langle\Phi_0|$

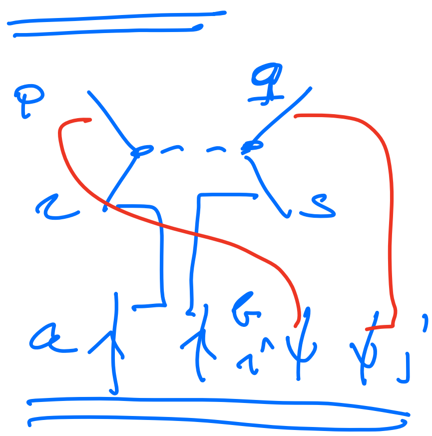


$|\Phi_0\rangle$ $=$ 

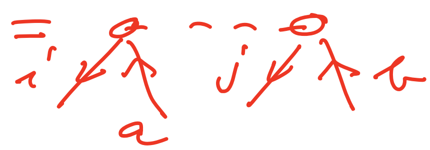
$$\langle i|\hat{f}|a\rangle =$$ 



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



2p2h

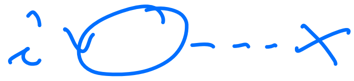


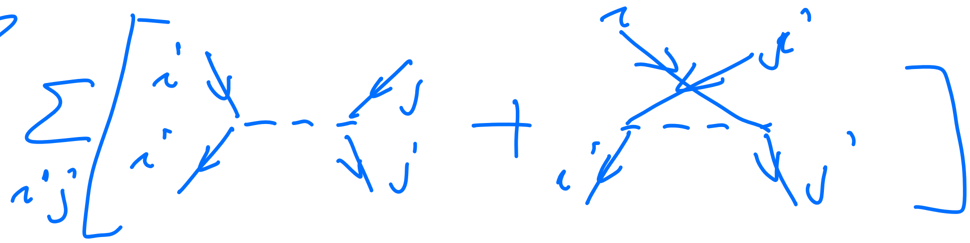
$$= \langle ij | v | ab \rangle$$

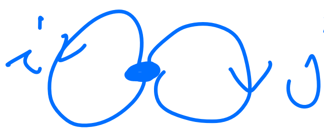
$$\langle \Phi_0 | H | \Phi_0 \rangle = E_0^{Ref}$$

$$= \sum_i \langle i | h_0 | i \rangle + \frac{1}{2} \sum_{ij} \left\{ \langle ij | v | ij \rangle - \langle ji | v | ij \rangle \right\}$$

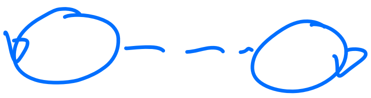
V

$=$ 



$=$ 

$(-1)^{n_e + n_h}$



FCI = Full configuration interaction theory.

$$|\Phi_c\rangle = \prod_{i=1}^{N} a_i^\dagger |0\rangle$$

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle$$

$$\langle \Phi_i^a | \Phi_j^b \rangle = \delta_{ab}\,\delta_{ij}$$

General states $|\Phi_\alpha\rangle$, $|\Phi_\lambda\rangle$

$$\langle \Phi_\lambda | \Phi_\alpha \rangle = \delta_{\lambda\alpha}$$

$$|\Psi_0\rangle = \sum_\lambda C_{\lambda 0} |\Phi_\lambda\rangle$$

$$= \underbrace{C_{00}}_{C_0} |\Phi_0\rangle + \sum_{ai} C_i^a |\Phi_i^a\rangle$$

$$+ \sum_{\substack{ab\\ij}} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots ,$$

$$\sum_{\substack{a_1 a_2 \dots a_N\\ i_1 i_2 \dots i_N}} C_{i_1 i_2 \dots i_N}^{a_1 a_2 \dots a_N} |\Phi_{i_1 \dots}^{a_1 \dots}\rangle$$

$$= (C_0 + \hat{C}) |\Phi_0\rangle$$

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

$\hat{C}$ = correlation operator,

$$|\Psi_0\rangle = \sum_{PH} C_H^P |\Phi_H^P\rangle$$

$$E = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

$$= \sum_{\substack{PH \\ P'H'}} (C_H^P)^* C_{H'}^{P'} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle$$

$$E = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

$$\frac{\partial E}{\partial (C_H^P)^*} = 0$$

$$\sum_{P'H'} \Big[\langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'} - E\, C_{H'}^{P'} \langle \Phi_H^P | \Phi_{H'}^{P'} \rangle \Big] = 0$$

$$(PH) \to i \qquad (P'H') \to j$$

$$\langle \Phi_H^{P} | \hat{H} | \Phi_{H'}^{P'} \rangle = H_{ij}'$$

$$C_{H'}^{P'} \rightarrow C_j$$

$$\langle \Phi_{H'}^{P'} | \Phi_H^{P} \rangle = S_{ij}'$$

$$\frac{\partial E}{\partial c_i^*} = \sum_j c_j \left(H_{ij}' - E S_{ij}' \right) = 0$$

$$S_{ij}' = \delta_{ij}'$$

$$\sum_j c_j H_{ij}' = c_i E$$

$$\mathbf{H} \mathbf{C} = E \mathbf{C}$$

$$\begin{array}{c|cccccc|}
 & \text{0p0h} & \text{1p1h} & \text{2p2h} & & \text{NPNH} \\
 & |\Phi_0\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle & \cdots & |\Phi_{ij\ldots}^{ab\ldots}\rangle \\
\hline
\langle \Phi_0 | & & & & & \\
\langle \Phi_i^a | & & & & & \\
\langle \Phi_{ij}^{ab} | & & & & & \\
\text{3p3h} & & & & &
\end{array}$$

$$
\begin{array}{l|c|}
4p4h & \\
\vdots & \\
NpNh & \\
\hline
\end{array}
$$

$$
\times \begin{bmatrix} c_0 \\ c(1p1h) \\ c(2p2h) \\ \vdots \\ c(NpNh) \end{bmatrix} = E \begin{bmatrix} c_0 \\ c(1p1h) \\ \vdots \\ c(NpNh) \end{bmatrix}
$$

$$
\det(H - ES) = 0
$$

$$
\mathbb{H} = \begin{array}{l} \\ 0p0h \\ 1p1h \\ 2p2h \\ 3p3h \\ \vdots \\ \vdots \\ NpNh \end{array}
\begin{array}{c}
\begin{array}{cccccccc} 0p0h & 1p1h & 2p2h & 3p3h & - & - & - & - \end{array} \\
\begin{bmatrix}
\times & \times & \times & 0 & - & - & 0 \\
\times & \times & \times & \times & 0 & - & - \\
\times & \times & \times & \times & \times & 0 & - \\
0 & \times & \times & & & & \\
0 & 0 & \times & & & & \\
\vdots & \vdots & 0 & & & & \\
0 & 0 & 0 & & & &
\end{bmatrix}
\end{array}
$$

two-body operator

$$
\langle \Phi_0 | H | \Phi_{ijk}^{abc} \rangle = 0
$$

$$
\langle \Phi_0 | H | \Phi_0 \rangle = E_0^{ref}
$$

$$\langle \Phi_0 | H | \Phi_i^a \rangle = \langle i | f | a \rangle$$

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