FYS4480/9480, sept 25

GS (Ground state)

$$|\Phi_0\rangle = \left(\prod_{i\leq F} a_i^+\right)|0\rangle$$

1p1h

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

$$i \in |\Phi_0\rangle$$

$$a \notin |\Phi_0\rangle$$

2p2h

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

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

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

$$= \sum_{i \le F} \langle i | \hat{h}_0 | i \rangle$$

$$+ \frac{1}{2} \sum_{ij \le F} \langle ij | v | ij \rangle_{AS}$$

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

$$\langle p|\hat{f}|q\rangle = \langle p|\hat{h}_0|q\rangle$$

$$+ \sum_{j\le F} \langle pj|\hat{v}|qj\rangle_{AS}$$

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

From now and on, we drop $\{ - - \}$

and $\langle pq|v|rs\rangle_{AS} \longrightarrow$

$$\langle pq|v|rs\rangle$$

$$|\Psi_0\rangle = \sum_{\lambda=0}^{m} c_{0\lambda} |\Phi_\lambda\rangle$$

$$\left\{ \begin{array}{l} \langle \Phi_\lambda | \Phi_\delta \rangle = \delta_{\lambda\delta} \\ c_{0\lambda} = \langle \Psi_0 | \Phi_\lambda \rangle \end{array} \right\}$$

$$= \sum_{PH} C_H^P \underbrace{|\Phi_H^P\rangle}_{A_H^P |\Phi_0\rangle}$$

C_i^a 1p1h

$$a_a^\dagger a_i |\Phi_0\rangle$$

$$|\Psi_0\rangle = c_0 |\Phi_0\rangle \qquad \text{2p2h}$$

$$+ \underbrace{\sum_{ai} c_i^a |\Phi_i^a\rangle}_{\text{1p1h}} + \overbrace{\sum_{\substack{ab\\ij}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle}$$

$$+ \underset{\text{3p3h}}{-} \; \underset{\text{4p4h}}{-} \cdots + \underbrace{\sum_{\substack{NP\\NH}} c_{\underbrace{i_1 i_2 \ldots i_N}_{NH}}^{\overbrace{a_1 a_2 \ldots a_N}^{NP}} |\Phi_{NP}^{NH}\rangle}_{\text{NPNh}}$$

$$= (c_0 + \hat{C}) |\Phi_0\rangle$$

$$\hat{C} = \sum_{ai} c_i^a a_a^\dagger a_i + \sum_{\substack{ab\\ij}} c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \cdots$$

$c_0 \neq 0$. Normalization $|\Psi_0\rangle$ is at our disposal, we may then arbitrarily set $\boxed{c_0 = 1}$, which leads to corresponding proportional changes in all other coefficients c_H^P

$$\langle \Psi_0 | \underline{\Phi_0} \rangle = \langle \underline{\Phi_0} | \underline{\Phi_0} \rangle = c_0 = 1$$

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

CORRELATION OPERATOR

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$(\hat{H}-E_0)\sum_{PH} C_H^P|\Phi_H^P\rangle = 0$$

$$\langle\Psi_0| \times$$

$$\sum_{\substack{PH\\P'H'}} \langle\Phi_H^P|\hat{\mathcal{H}}-E_0|\Phi_{H'}^{P'}\rangle (C_H^P)^* C_{H'}^{P'} = 0$$

$$\Rightarrow \sum_{\substack{PH\\P'H'}} (C_H^P)^* C_{H'}^{P'} \langle\Phi_H^P|\hat{\mathcal{H}}|\Phi_{H'}^{P'}\rangle = E_0 \sum_{PH} |C_H^P|^2$$

equivalent to variational minimum

$$\langle \psi_0 | H | \psi_0 \rangle - \underbrace{\lambda}_{\text{Lagrangian multiplier}} \langle \psi_0 | \psi_0 \rangle$$

The minimization gives

$$\delta \left[\langle \psi_0 | H | \psi_0 \rangle - \lambda \langle \psi_0 | \psi_0 \rangle \right] = 0$$

$$\hat{\mathcal{H}} |\Psi_c\rangle = E_c |\Psi_c\rangle$$

$$\sum_{pH} C_H^p \hat{\mathcal{H}} |\Phi_H^p\rangle = E_c \sum_{pH} C_H^p |\Phi_H^p\rangle$$

$$\langle \Phi_0$$

$$\langle \Phi_n^q |$$

$$\vdots$$

$$\sum_{p'H'} \langle \Phi_{H'}^{p'} | (C_{H'}^{p'})^*$$

$$\sum_{PH} \underbrace{\langle \Phi_0 | \mathcal{H} | \Phi_H^P \rangle}_{} C_H^P = E_0 \sum_{PH} C_H^P \underbrace{\langle \Phi_0 | \Phi_H^P}_{}$$

$$\langle \Phi_0 | \mathcal{H} | \Phi_{1P1H} \rangle$$

$$\underbrace{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle}_{\mathcal{H}_{00}} C_0 + \sum_{ai} \langle \Phi_0 | \mathcal{H} | \Phi_i^a \rangle C_i^a$$

$$+ \sum_{\substack{ab\\ij}} \underbrace{\langle \Phi_0 | \mathcal{H} | \Phi_{ij}^{ab} \rangle}_{} C_{ij}^{ab} + - \,.\,.\,.\, \sum_{\substack{NP\\NH}} - \,-\,-$$

$$= E_0 C_0$$

$$= \mathcal{H}_{00} C_0 + \underbrace{\mathcal{H}_{01} C_1}_{\langle \Phi_0 | \mathcal{H} | \Phi_{1P1H} \rangle C_{1P1H}} + \overset{\langle \Phi_0 | \mathcal{H} | \Phi_{2P2H} \rangle}{\mathcal{H}_{02}} \underbrace{C_2}_{C_{2P2H}} +$$

$$+ H_{03} C_3 + \cdots H_{0N} C_N = E_0 C_0$$

$\langle 1p1h |$ $\quad \langle 1$

$$H_{10} C_0 + H_{11} C_1 + \cdots H_{1N} C_N = E_0 C_1$$

$\langle 2p2h |$

$$H_{20} C_0 + H_{21} C_1 + H_{22} C_2 + \cdots$$

$$H_{2N} C_N = E_0 C_2$$

$$\sum_{j=0p0h}^{NpNh} H_{ij} C_j = E_i C_i$$

$$\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle \qquad \langle \Phi_0 | \mathcal{H} | \Phi_{2H}^{2P} \rangle$$

$$\begin{bmatrix} \mathcal{H}_{00} & \mathcal{H}_{01} & \mathcal{H}_{02} & - - - & \mathcal{H}_{0N} \\ \mathcal{H}_{10} & \mathcal{H}_{11} & - & - - & \mathcal{H}_{1N} \\ \vdots & & & & \\ \mathcal{H}_{N0} & - & & - - & \mathcal{H}_{NN} \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix}$$

$$\mathcal{H}_{ij} = \langle \underset{NPNH}{\Phi_i} | \mathcal{H} | \underset{NPNH}{\Phi_j} \rangle$$

$$= E_0 \begin{bmatrix} c_0 \\ c_1 \\ \vdots \\ \vdots \\ | \\ c_N \end{bmatrix}$$

$$\Rightarrow \boxed{\mathcal{H} c = \lambda c}$$

$$\mathcal{H}_{00} = \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle$$

$$= \sum_{i \leq F} \langle i | \hat{h}_0 | i \rangle +$$

$$\frac{1}{2} \sum_{ij \leq F} \langle ij | v | ij \rangle$$

$$\mathcal{H}_{01} = \langle \Phi_0 | \mathcal{H} | \Phi_{1h}^{1p} \rangle$$

$$= \langle \Phi_0 | \mathcal{H} | \Phi_i^a \rangle$$

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

$$\mathcal{H}_{02} = \langle \Phi_0 | \mathcal{H} | \Phi_{2H}^{2P} \rangle$$

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

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

$$\mathcal{H}_{03} = \langle \Phi_0 | \underbrace{\mathcal{H}}_{\text{at most twobody}} | \Phi_{3H}^{3P} \rangle = 0$$

$$\mathcal{H}_{04} = 0 = \mathcal{H}_{05} = \dots = \mathcal{H}_{0\,NPNH}$$

$$\mathcal{H}_{11} = \langle \Phi_{1H}^{1P} | \mathcal{H} | \Phi_{1H'}^{1P'} \rangle$$

$$\langle \Phi_{i}^{a} | \mathcal{H} | \Phi_{j}^{b} \rangle \neq 0$$

$$\mathcal{H}_{14} = \langle \Phi_{1H}^{1P} | \mathcal{H} | \Phi_{4H}^{4P} \rangle$$

$$\langle \Phi_{i}^{a} | \mathcal{H} | \Phi_{klmn}^{bcde} \rangle = 0$$

$$
\begin{array}{c|cccccccc|}
 & 00 & 01 & 02 & 03 & - & - & \cdot & 0N \\
00 & X & X & X & 0 & 0 & - & \cdot & 0 \\
10 & X & X & X & X & 0 & - & - & 0 \\
20 & X & X & X & x & X & 0 & - \cdot & 0 \\
 & 0 & X & X & & & & & 0 \\
\vert & 0 & 0 & X & & & & & \\
\vert & & 0 & 0 & & & & & \\
\vert & \vert & \vert & \vert & & & & & \\
 & & \vert & \vert & & 0 & & & \\
N0 & 0 & 0 & \vert & & & & &
\end{array}
\overset{c}{\begin{bmatrix} x \\ x \\ \vert \\ \vert \\ \vert \\ \vert \\ x \end{bmatrix}}
= \lambda
\overset{c}{\begin{bmatrix} x \\ \vert \\ \vert \\ \vert \\ \vert \\ x \end{bmatrix}}
$$

$$(\mathcal{H} - E_0) \sum_{PH} C_H^P |\Phi_H^P\rangle = 0$$

1st row is given by multiplying from the left with $\langle\Phi_0|$

And use $c_0 = 1$

$$\langle \Phi_0 | \hat{\mathcal{H}} - E_0 | \Phi_0 \rangle +$$

$$\sum_{ai} \langle \Phi_0 | \hat{\mathcal{H}} - E_0 | \Phi_i^a \rangle c_i^a +$$

$$+ \sum_{\substack{ab \\ ij}} \langle \Phi_0 | \mathcal{H} - E_0 | \Phi_{ij}^{ab} \rangle c_{ij}^{ab} = 0$$

$$\Rightarrow \underbrace{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle}_{E_0^{ref}} - \langle \Phi_0 | \Phi_0 \rangle \underbrace{E_0}_{exact}$$

$$+ \sum_{ai} \overbrace{\langle \Phi_0 | \mathcal{H} | \Phi_i^a \rangle}^{\langle i | f | a \rangle} c_i^a$$

$$+ \sum_{\substack{ab \\ ij}} \overset{\langle ij | v | ab \rangle_{AS}}{\langle \Phi_0 | \mathcal{H} | \Phi_{ij}^{ab} \rangle} c_{ij}^{ab}$$

$$= 0$$

$$\underbrace{\Delta E_0}_{\text{correlation energy}} = E_0 - E_0^{Ref}$$

$$= \sum_{ia} \langle i|f|a\rangle \boxed{c_i^a} + \sum_{\substack{ab\\ i'j'}} \langle i'j'|v|ab\rangle \boxed{c_{i'j'}^{ab}}$$

known from diagonalization

Hartree-Fock $\langle i|f|a\rangle = 0$

Mean-Field methods

For the Hamiltonian matrix

$$\begin{bmatrix} x^2 & 0 & x^2 & 0 & 0 & - & - & 0 \\ 0 & x^2 & x^2 & x^2 & & & 0 & \\ x^2 & x^2 & & & & & & \\ 0 & x^2 & & & & & & \\ | & & x^2 & & & & & \\ | & 0 & & & & & & \end{bmatrix}$$

$$u^+ u = u u^+ = \underline{\mathbb{1}} \qquad u^+ = u^{-1}$$

$$u \,\Big|\, \mathcal{H} c = \lambda c$$

$$u \mathcal{H} \underset{\overset{\uparrow}{\underline{\mathbb{1}}}}{\,} c = \lambda u c$$

$$\underbrace{u \mathcal{H} u^+}_{D} \underbrace{u c}_{b} = \lambda \underbrace{u c}_{b}$$

$$D = \begin{bmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_N \end{bmatrix}$$

$$D = U_M U_{M-1} \cdots U_1 \mathcal{H} U_1^{\dagger} U_2^{\dagger} \cdots U_M^{\dagger}$$

$\langle \Phi_c | \mathcal{H} | \Phi_i^q \rangle = 0$, correspond to a specific U_i which zeros out a subblock of the Hamiltonian matrix

$$\langle \Phi_r^a | (\mathcal{H} - E_0) \sum_{pH} C_H^p | \Phi_H^p \rangle = 0$$

$$\underbrace{\langle \Phi_r^a | \mathcal{H} | \Phi_0 \rangle}_{\langle a|f|i\rangle} - E_0 \underbrace{\langle \Phi_r^a | \Phi_0 \rangle}_{=\boxed{0}}$$

$$+ \sum_{bj} \langle \Phi_r^a | \mathcal{H} - E_0 | \Phi_j^b \rangle C_j^b$$

$$+ \sum_{\substack{bc \\ jk}} \langle \Phi_r^a | \mathcal{H} - E_0 | \Phi_{jk}^{bc} \rangle C_{jk}^{bc}$$

$$+ \sum_{\substack{bcd \\ jkl}} \langle \Phi_r^a | \mathcal{H} - E_0 | \Phi_{jkl}^{bcd} \rangle C_{jkl}^{bcd}$$

$$= 0$$

$$\langle a|f|i\rangle + \langle \Phi_i^a | H - E_0 | \Phi_i^a \rangle c_i^a$$

$$+ \sum_{\substack{bj \\ \neq ai}} \langle \Phi_i^a | H | \Phi_j^b \rangle c_j^b$$

$$+ \text{ two more } = 0$$

$$\langle a|f|i\rangle + \langle \Phi_i^a | H | \Phi_i^a \rangle c_i^a$$

$$= E_0 \, c_i^a$$

$$\langle a|f|i\rangle = (\varepsilon_i - \varepsilon_a) c_i^a$$

$$\Rightarrow \quad c_i^a = \boxed{\langle a|f|i\rangle / \varepsilon_i - \varepsilon_a}$$