FYS4480/9480 OCT 4

Stability of HF eqs.

$$|\Phi_0^{HF}\rangle = |c\rangle$$

$$\langle \delta c | H | c\rangle = 0 \wedge \langle c | H | \delta c\rangle = 0$$

$$|c'\rangle = |c\rangle + |\delta c\rangle$$

$$|c'\rangle = \exp\left\{ \sum_{ai} \delta c_i^a a_a^\dagger a_i \right\} |c\rangle$$

$$\frac{\langle c' | H | c'\rangle}{\langle c' | c'\rangle} \geq \langle c | H | c\rangle = E_0^{HF}$$

$$\langle c' | c' \rangle = ?$$

$$|c'\rangle = \Big\{ 1 + \sum_{ai'} \delta c_i^a \, a_a^\dagger a_{i'} + \frac{1}{2!} \sum_{ai'} \sum_{bj'} \delta c_i^a \delta c_j^b \, a_a^\dagger a_i \times a_b^\dagger a_{j'} - \ldots \Big\} |c\rangle$$

$$\langle c' | c' \rangle = 1 + \sum_{ai'} |\delta c_i^a|^2 + O((\delta c_i^a)^3)$$

$$\langle c' | c' \rangle \neq 1 \qquad \langle c' | c \rangle = \underline{1}$$

$$\langle c' | H | c' \rangle \simeq \underbrace{\langle c | H | c \rangle}_{E_c^{Ref}}$$

$$+ \sum_{ai}{}' \sum_{bj}{}' \delta c_i^{*a} \delta c_j^{b} \langle c | a_i^\dagger a_a H a_b^\dagger a_j | c \rangle$$

$$+ \frac{1}{2} \sum_{ai}{}' \sum_{bj}{}' \delta c_i^{a} \delta c_j^{b} \langle c | H a_a^\dagger a_i a_b^\dagger a_j | c \rangle$$

$$+ \frac{1}{2} \sum_{ai}{}' \sum_{bj}{}' \delta c_i^{*a} \delta c_j^{*b}$$

$$\times \langle c | a_j^\dagger a_b a_i^\dagger a_a H | c \rangle$$

$$\langle c | a_i^\dagger a_a \, H \, a_b^\dagger a_j | c \rangle$$

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

$$\delta_{ij} \, \delta_{ab} \, E_0^{Ref} +$$

$$\sum_{pq} \langle c | a_i^\dagger a_a \, a_p^\dagger a_q \, a_b^\dagger a_j | c \rangle \langle p | f | q \rangle$$

$$\delta_{ij} \, \delta_{pa} \, \delta_{qb}$$

$$\delta_{ab} \, \delta_{pj} \, \delta_{qi}$$

$$\left[\langle a | f | a \rangle - \langle i | f | i \rangle = \varepsilon_a^{HF} - \varepsilon_i^{HF} \right]$$

$$+\frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle_{AS} \quad \times$$

δ_{qj}

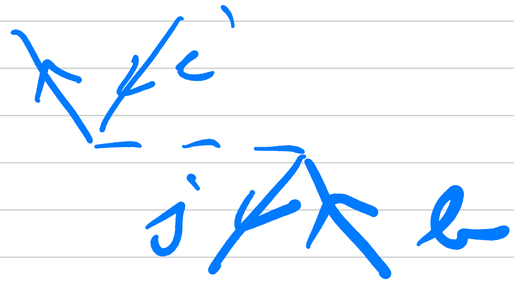
$$\times \langle c|\, a_i^{\dagger} a_a\, a_p^{\dagger} a_q^{\dagger} a_s a_r\, a_b^{\dagger} a_j \,|c\rangle$$

δ_{ap} $\qquad$ δ_{rb}

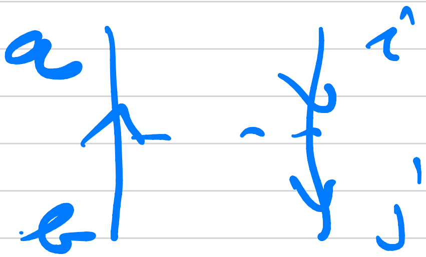
δ_{is}

$$\Big[\; -\frac{1}{4}\langle aj|v|bi\rangle_{AS}$$

$$= +\frac{1}{4}\langle aj||ib\rangle_{AS}$$



$+$



$\Big]$

collecting:

$$\delta_{ij'}\delta_{ab}\, E_0^{HF}\, |\delta C_i^a|^2$$

$$+\sum_{ai'}\left(\varepsilon_a^H - \varepsilon_i^{HF}\right)|\delta C_i^a|^2\delta_{ij'}\delta_{ab}$$

$$+\sum_{ai'}\sum_{bj'}\delta C_i^{*a}\,\delta C_j^b\,\langle aj'|v|ik\rangle_{AS}$$

$$\langle c|H|a_a^+ a_i\, a_b^+ a_j|c\rangle$$

$$\underbrace{E_0^{ref}}_{=0} + \langle c|a_p^+ a_q\, a_a^+ a_i a_b^+ a_j|c\rangle$$

$$\Big[\ \langle c|\, a_p^\dagger a_q \underbrace{a_a^\dagger a_i\, a_b^\dagger a_j}_{} \,|c\rangle$$

$$2p2h \approx 0$$

$$+\ \langle c|\, a_p^\dagger a_q^\dagger a_s a_r\, a_a^\dagger a_i\, a_b^\dagger a_j \,|c\rangle$$

$$-\frac{1}{4}\langle ji|v|ab\rangle_{AS}$$

$$= \frac{1}{4}\langle ij|v|ab\rangle_{AS}$$

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

$$\langle c | a_j^\dagger a_b \, a_i^\dagger a_a \; H | c \rangle$$

$$\langle a | A | b \rangle = \langle b | A^\dagger | a \rangle^*$$

$$\langle c | a_j^\dagger a_b \, a_i^\dagger a_a \, H | c \rangle = \langle ab \| ij \rangle_{AS}$$

$$= \langle ij \| ab \rangle^*_{AS}$$

$$\langle c' | H | c' \rangle = \langle c | H | c \rangle \Big(1 + \sum_{ai} |\delta c_i^a|^2 \Big)$$

$$+ \sum_{ai} |\delta c_i^a|^2 \left(\varepsilon_a^{HF} - \varepsilon_i^{HF} \right)$$

$$+ \sum_{ai} \sum_{bj} \delta^* c_i^a \, \delta c_j^b \langle aj \| ib \rangle_{AS}$$

$$+ \frac{1}{2} \sum_{a i} \sum_{b j} \delta c_i^a \, \delta c_j^b \langle ij | v | ab \rangle_{AS}$$

$$+ \frac{1}{2} \sum_{a i} \sum_{b j} \delta c_i^{*a} \, \delta c_j^{*b} \langle ab | v | ij \rangle_{AS}$$

$$= \left(1 + \sum_{a i} |\delta c_i^a|^2\right) E_0^{HF}$$

$$+ \Delta E + O\left((\delta c_i^a)^3\right)$$

denominator $1 + |\delta c^2|$

$$\frac{\langle c' | H | c' \rangle}{\langle c' | c' \rangle} \simeq E_0^{HF} + \frac{\Delta E}{1 + \sum_{a i} |\delta c_i^a|^2}$$

$$\Delta E \geq 0$$

$$\frac{\langle c' | H | c' \rangle}{\langle c' | c' \rangle} \geq E_0^{HF}$$

$$\langle \delta c | H | \delta c \rangle =$$

$$\sum_{\substack{ab \\ ij}} \delta^* c_i^a \, \delta c_j^b \left\{ \left[\varepsilon_a^{HF} \delta_{ab} \delta_{ij} - \varepsilon_i^{HF} \delta_{ab} \delta_{ij} \right] + \langle aj | v | ib \rangle_{AS} \right\}$$

$$I = \{ai\} \qquad J = \{bj\}$$

$$\langle aj \| v \| ib \rangle = A_{ai,bj} = A_{IJ}$$

$$\delta^* C_i^a = \delta^* C_I \qquad \delta C_j^b = \delta C_J$$

$$\Delta E_{IJ} = (\varepsilon_a^{HF} - \varepsilon_i^{HF})\,\delta_{ab}\,\delta_{ij}$$

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

$$B^*_{IJ} = \langle ij \| v \| ab \rangle_{AS}$$

$$\langle \delta c | H | \delta c \rangle = \sum_{IJ} \delta c_I^* \delta c_J$$

$$\times \left[\Delta \varepsilon_{IJ} \delta_{IJ} + A_{IJ} \right]$$

$$\left(x^T A x = \sum_{i,j} x_i a_{ij} x_j \right)$$

$$\delta c^* \cdot \Delta \varepsilon \, \delta c + \delta^* c A \delta c$$

$$\Delta E = \frac{1}{2} \langle X | M | X \rangle$$

$$X = \begin{bmatrix} \delta c \\ \delta_c^* \end{bmatrix}$$

$$M = \begin{bmatrix} \Delta\varepsilon + A & B \\ B^* & \Delta\varepsilon + A^* \end{bmatrix}$$

$\Delta\varepsilon \geq 0$, then M has to be semi-positive definite, i.e. $\lambda_i \geq 0$

A necessary (but not sufficient) condition is that

$$\varepsilon_a^{HF} - \varepsilon_i^{HF} + \langle ai \| ia \rangle_{AS} \geq 0$$

<u>FCI</u>

$$\begin{bmatrix} \langle \Phi_0 | H | \Phi_0 \rangle & \cancel{\langle \Phi_0 | H | 1p1h \rangle} & \langle \Phi_0 | H | 2p2h \rangle & \cdots \\ \cancel{\langle 1p1h | H | \Phi_0 \rangle} & \langle 1p1h | H | 1p1h \rangle & \cdots & \cdots \\ \langle 2p2h | H | \Phi_0 \rangle & \vdots & & \\ \vdots & \vdots & & \end{bmatrix}$$

$$\langle \delta\Phi_0 | H | \Phi_0 \rangle = 0 \Rightarrow$$

$$\langle i | f | a \rangle = 0 \wedge \langle a | f | i \rangle = 0$$

classical solution

$$h^{HF} = f \Rightarrow h^{HF} | p \rangle = \varepsilon_p^{HF} | p \rangle$$

$$\langle i | f | a \rangle = \langle i | h^{HF} | a \rangle = 0$$

$$\langle i | h^{HF} | i \rangle = \varepsilon_i^{HF}$$

$$\langle a | h^{HF} | a \rangle = \varepsilon_a^{HF}$$

HEG $\langle a | h^{HF} | a \rangle = 0$

TDA (Tamm-Dancoff approximation)

$$\langle a|f|i\rangle = 0 \quad \text{if HF}$$

$$\Delta E = E_0 - E_0^{ref} = \sum_{ai} c_i^a \langle i|f|a\rangle + \sum_{\substack{ab \\ ij}} c_{ij}^{ab} \times \langle ab|v|ij\rangle_{AS}$$

$$E_0 - E_0^{ref} \;\rightarrow\; \langle \Phi_0|H|\Phi_0\rangle$$

$$\langle \Phi_i^a | H | \Phi_j^b \rangle c_j^b =$$

$$E_0^{ref} c_i^a \delta_{ij} \delta_{ab} + (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab}$$

$$\times c_i^a + \sum_{jb} \langle aj \| bi \rangle_{AS} c_j^b$$

(Neglected $\langle \Phi_i^a | H - X | \Phi_0 \rangle$

$$\sum_{jb} \langle \Phi_i^a | H - X | \Phi_j^b \rangle c_j^b = 0$$

$$c_{ij}^{ab} = c_{ijk}^{abc} = 0$$

$$A_{ij}^{ab} = \langle aj' | v | i'b \rangle_{AS} = A_{IJ}$$

$$I = \{ai\} \quad J = \{bj\}$$

$$\Delta \varepsilon_{IJ} =$$

$$(\varepsilon_a - \varepsilon_i)\, \delta_{ij'}\, \delta_{ab}$$

$$\Delta E = \lambda - E_0^{Ref}$$

$$\sum \Big(\overbrace{\Delta \varepsilon_{IJ} + A_{IJ}}^{H_{IJ}} \Big) C_J =$$

$$\Delta E \; C_I$$

$$\sum_{J} H_{IJ} C_J = \Delta E \, C_I$$

corresponds to the eigenvalues of the spin states.