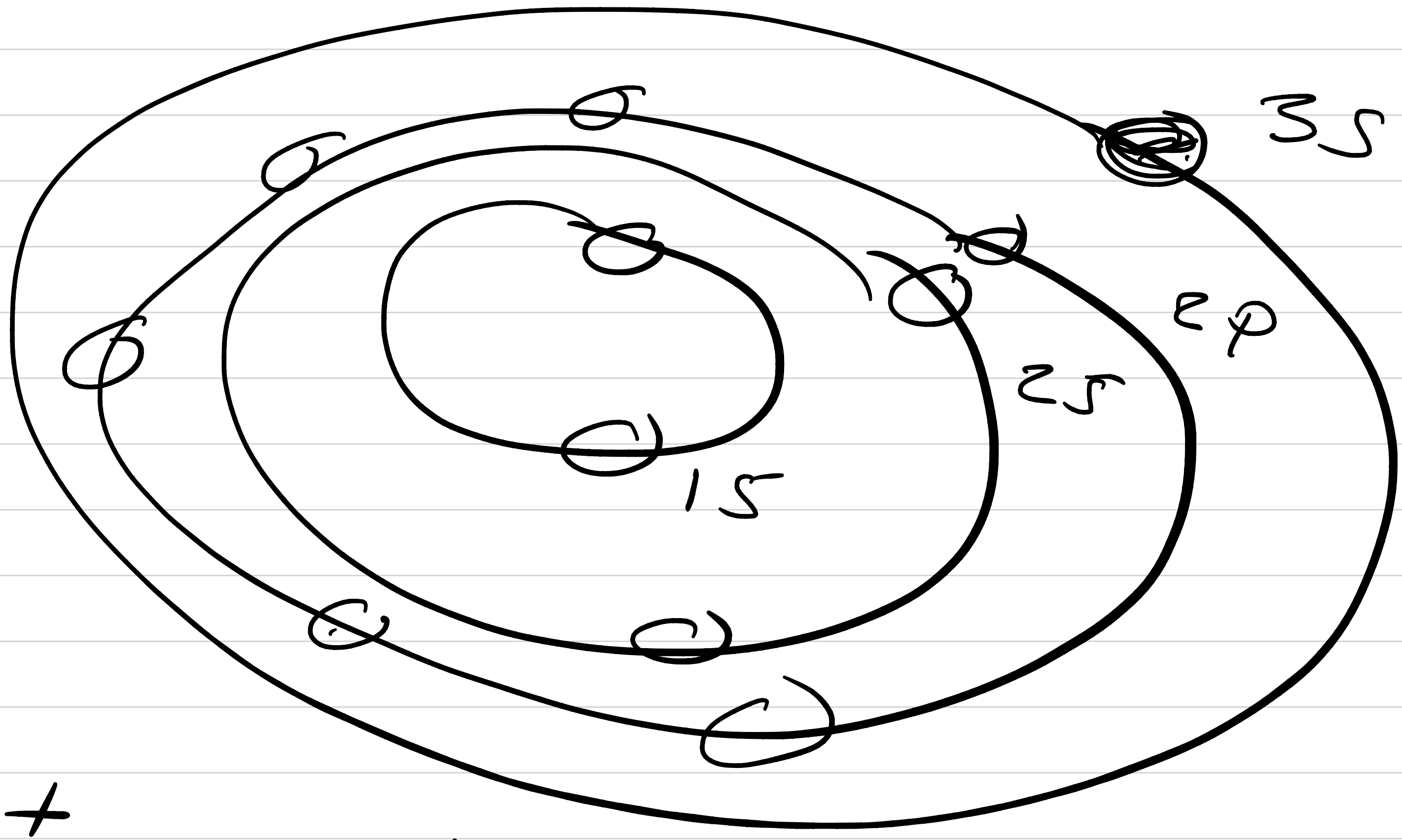
Lecture Fys4480, October 12, 2023

Koopman's theorem

Na : 11 electron
11 protons



Na^+ taken out 3s electron

Stability of HF

$$|\Phi_0^{HF}\rangle = |c\rangle = \prod_{i=1}^{N} a_i^\dagger |0\rangle$$

Thouless' theorem

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

assumption $\langle c' | c \rangle \neq 0$

Taylor expand

$$|c'\rangle = |c\rangle + \left\{ \sum_{ai} \underbrace{c_i^a}_{\delta c_i^a} \, a_a^\dagger a_i + \frac{1}{2} \sum_{\substack{ai \\ bj}} c_i^a c_j^b (a_a^\dagger a_i)(a_b^\dagger a_j) + \dots \right\} |c\rangle$$

$$C_i^a \to \delta C_i^a$$

$$|c'\rangle \simeq \boxed{|c\rangle + \underbrace{\sum_{ai} \delta C_i^a a_a^\dagger a_i |c\rangle}_{|\delta c\rangle}}$$

$|p|$ h

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

if E_0^{HF} is the "best" minimum

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

$H|\Phi_0^{HF}\rangle$

$\neq E_0|\Phi_0^{HF}\rangle$

$$\langle c' | H | c' \rangle = \underbrace{\langle c | H | c \rangle}_{= E_0^{HF}}$$

$$+ \underbrace{\langle \delta c | H | c \rangle}_{= 0} + \underbrace{\langle c | H | \delta c \rangle}_{\langle 0p0h | H | 1p1h \rangle = 0}$$

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

$$+ \langle c | H | (\delta c)^2 \rangle + \langle (\delta c)^2 | H | c \rangle$$

$$\underset{\text{ipin}}{\langle \delta c} | H | \underset{\text{open}}{c \rangle} =$$

$$\sum_{ai} \delta c_i^{*a} \langle c | a_i^\dagger a_a H | c \rangle = 0$$

(i) $\langle c | a_i^\dagger a_a a_p^\dagger a_q | c \rangle$

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

(ii) $\langle c | a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r | c \rangle$

+ other contractions $= 0$

$\Rightarrow \langle a | \hat{f} | i \rangle = 0$

$$\langle a|\hat{f}|i\rangle = \langle a|\hat{h}_0|i\rangle + \sum_j \langle aj||v||ij\rangle_{A}$$

$$\hat{f} \Rightarrow \hat{h}^{HF}$$

$$\boxed{\begin{aligned} \hat{h}^{HF}|i\rangle &= \varepsilon_i^{HF}|i\rangle \\ \hat{h}^{HF}|a\rangle &= \varepsilon_a^{HF}|a\rangle \end{aligned}}$$

$$\boxed{\langle a|\hat{f}|i\rangle = 0} = \varepsilon_i^{HF}\delta_{ai} = 0$$

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

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

(i) $$\langle c|\, a_i^\dagger a_a\, a_p^\dagger a_q\, a_b^\dagger a_j \,|c\rangle$$

$$\delta_{ij}\, \delta_{ab}\, \langle a|\hat{f}|b\rangle$$

$$= \delta_{ij}\, \delta_{ab}\, \varepsilon_a^{HF}$$

(ii) $$\langle c|\, a_i^\dagger a_a\, a_p^\dagger a_q\, a_b^\dagger a_j \,|c\rangle$$

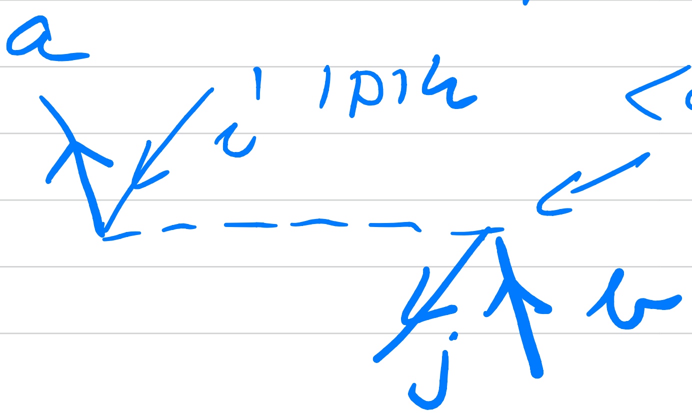
$$-\delta_{ij}\, \delta_{ab}\, \varepsilon_i^{HF}$$

(iii') $\langle c | a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j | c \rangle$

$$= -\frac{1}{4} \delta_{ap} \delta_{si} \delta_{qj} \delta_{rb} \langle pq | v | rs \rangle_{AS}$$

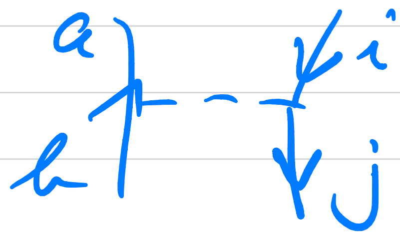
$$= -\frac{1}{4} \langle aj | v | bi \rangle_{AS}$$

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



1p1h $\langle aj | v | ib \rangle$ $- \langle aj | v | bi \rangle$

1p1h



+ 3 more similar contractions

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

$$+ \frac{1}{4} \langle ja | v | bi \rangle_{AS}$$

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

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

$$= \sum_{\substack{ai \\ bj}} \delta c_i^{a*} \, \delta c_j^b \Big\{ \Big[\varepsilon_a^{HF} \delta_{ab} \delta_{ji} - \varepsilon_i^{HF} \delta_{ab} \delta_{ij} \Big] +$$

$$+ \langle aj \| v \| ib \rangle_{AS}$$

$$I = (\text{ph-config}) \{ai\}$$

$$J = \{bj\}$$

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

δC contains all δc_i^a

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

$$a \quad i = I$$

$$2 \langle (ai^{-1}) | v | (bj^{-1}) \rangle \quad j \quad b = J$$

$1p1h$

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

$$= \sum_{IJ} \delta c_I^* \, \delta c_J \left[\Delta \varepsilon_{IJ} \, \delta_{IJ} + A_{IJ} \right]$$

$$\left[x^T A x = \sum_{ij} x_i \, a_{ij} \, x_j \right]$$

$$\delta c^* \begin{bmatrix} \Delta\varepsilon_{11} + A_{11} & A_{12} & \cdots & A_{1\,PH} \\ \vdots & \Delta\varepsilon_{22} + A_{22} & & \\ & & \ddots & \\ A_{PH\,1} & & & \Delta\varepsilon_{PH} + A_{PHPH} \end{bmatrix} \delta c$$

$$\langle c | H | (\delta c)^2 \rangle$$

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

(i) $\langle c | \{a_p^\dagger a_q\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\} | c \rangle$

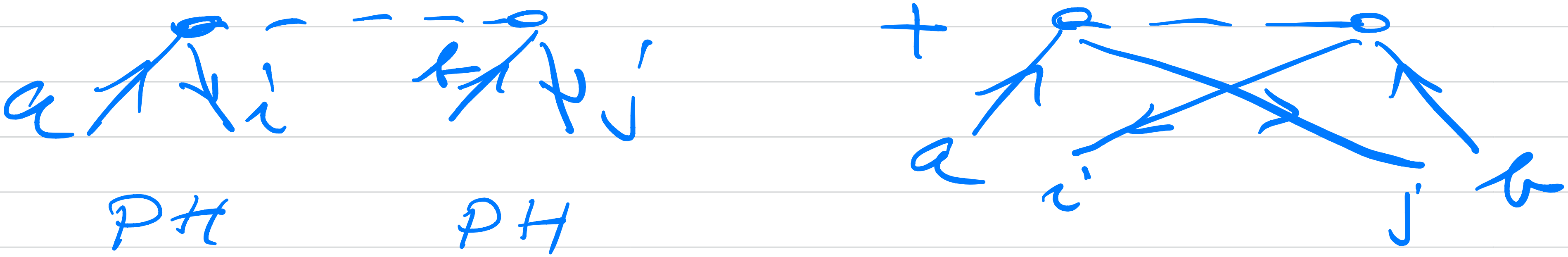
$$\langle 1p1h | 2p2h \rangle = 0$$

(ii) $\langle c | a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j | c \rangle$

$$= \frac{1}{4} \langle j i | v | a b \rangle_{AS} = \frac{1}{4} \langle ij | H | ab \rangle$$

+ 3 more

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



$$\langle (\delta c)^2|H|c\rangle = \langle ab|v|ij\rangle_{AS}$$

$$B_{ai\,bj} = B_{IJ} = \langle ij|v|ab\rangle$$

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

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

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

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

$$\begin{bmatrix} \delta c^\dagger & \delta c^{*\dagger} \end{bmatrix} \begin{bmatrix} \Delta\varepsilon + A & B \\ B^* & \Delta\varepsilon + A^* \end{bmatrix} \times \begin{bmatrix} \delta c \\ \delta c^* \end{bmatrix}$$

$$= \frac{1}{2}\left\{ \boxed{\delta c^\dagger (\Delta\varepsilon + A)\, \delta c} + \delta c^{*\dagger} B^* \delta c + \delta c^\dagger B\, \delta c^* + \boxed{\delta c^{*\dagger} (\Delta\varepsilon + A)^* \delta c^*} \right\} \frac{1}{2}$$

$$\frac{1}{2} \sum_{ij} \delta c_i \, \Delta\varepsilon_{ij} \, \delta c_j^* + \sum_{ij} \delta c_i A_{ij} \, \delta c_j^* + \frac{1}{2}$$

$A^*_{ij} = A_{ji}$

$\Delta E \geq 0 \Rightarrow$

M has to be semi-positive definite; eigenvalues of M are ≥ 0

A necessary condition: diagonal elements ≥ 0

$$\varepsilon_a^{HF} - \varepsilon_i^{HF} + \langle aj \| ib \rangle_{AS}$$

$$\geq 0$$