Lecture Fys4480, October 5, 2023

FCI

Ground state example

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

$$|\Psi_0\rangle = \sum_{i=0}^{\infty} C_{0i}|\Phi_i\rangle$$

$$\langle\Phi_i|\Phi_j\rangle = \delta_{ij}$$

$$\hat{H}_0|\Phi_i\rangle = \varepsilon_i|\Phi_i\rangle$$

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

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

$\Rightarrow$ matrix-problem, eigen value problem

$$HC = \lambda C$$

$$H = \begin{array}{c c} & \begin{array}{ccccc} 0p0h & 1p1h & 2p2h & 3p3h & \cdots \end{array} \\ \begin{array}{c} 0p0h \\ 1p1h \\ 2p2h \\ \vdots \\ \vdots \\ \vdots \end{array} & \begin{bmatrix} x & x & x & 0 & 0 \\ x & x & x & x & \\ x & x & x & x & x \\ 0 & x & x & x & x \\ \vdots & 0 & x & x & x \\ \vdots & \vdots & & x & x \end{bmatrix} \end{array}$$

H_{ij} ; example

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

1p1h

$$= \langle i | \hat{h}_0 | a \rangle + \sum_{j \leq F} \langle ij | \hat{v} | aj \rangle_{AS}$$

$$\hat{C} = \begin{bmatrix} C_0 \\ C_i^a \\ C_{ij}^{ab} \\ \vdots \\ C_{NH}^{NP} \end{bmatrix}$$

First approximation: Hartree-Fock theory, example of mean-field theory.

$$HC = \lambda C \; ; \quad UU^{+} = U^{+}U = \mathbb{1}$$

$$UHU^{+} = D = \begin{bmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_d \end{bmatrix}$$

in practice

$$U_M U_{M-1} \cdots U_1 H U_1^{+} U_2^{+} \cdots U_{M-1}^{+} U_M^{+}$$

$$= D$$

Perform M unitary transformations

We can view HF-theory as a particular unitary transform

1p1h-Block

$$H = \begin{bmatrix} \times & \times & \times & \cdots \\ \times & \times & \times & \cdots \\ \times & \times & \vdots & \\ 0 & \times & & \\ \vdots & \vdots & \vdots & \end{bmatrix}$$

$\langle 1p1h | H | \Phi_c \rangle$

$\langle 1p1h | H | 1p1h \rangle$

$$U_{HF} H U_{HF}^{\dagger} = \begin{bmatrix} \tilde{\times} & 0 & \tilde{\times} & 0 & \cdots \\ 0 & \tilde{\times} & & & \\ \tilde{\times} & \tilde{\times} & & & \\ 0 & \vdots & & & \\ \vdots & \vdots & & & \end{bmatrix}$$

$$\boxed{\langle 1p1h | H | \Phi_c \rangle = 0}$$

Derivation of HF equations

1st quantization

$$\Phi_0(x_1, x_2 \ldots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \ldots & \varphi_1(x_N) \\ \varphi_2(x_1) & & \vdots \\ \vdots & & \vdots \\ \varphi_N(x_1) & & \varphi_N(x_N) \end{vmatrix}$$

$$\int dx\, \varphi_i^*(x)\, \varphi_j(x) = \delta_{ij}$$

variational calculus

$$\varphi_i(x) \longrightarrow N_i\left(\varphi_i(x) + \delta\varphi_i(x)\right)$$

$$i \leq F$$

$$\delta\psi_i \longrightarrow \eta\, \varphi_a(x) \qquad a > F$$

Normalization factor

small constant

$$N_i^{-2} = \int dx \left(\varphi_i^*(x) + \eta^* \varphi_a^*(x) \right) \times \left(\varphi_i(x) + \eta \varphi_a(x) \right)$$

$$= 1 + |\eta|^2$$

$N_i \simeq 1$ at linear order in η

$$\Phi_0 \longrightarrow \Phi_{HF} + \eta \, \delta \Phi_{HF}$$

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

$$+ \left[\eta^* \langle \delta\Phi_{HF} | H | \Phi_{HF} \rangle \right.$$

$$\left. + \eta \langle \Phi_{HF} | H | \delta\Phi_{HF} \rangle \right]$$

$$+ |\eta|^2 \langle \delta\Phi_{HF} | H | \delta\Phi_{HF} \rangle$$

assumption is that η is an infinitesimal constant, we neglect $|\eta|^2$

$$\delta E_{HF} = \eta^* \langle \delta \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle$$

$$+ \eta \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle$$

$$= 0$$

(i) $\eta = \mathrm{Re}\,\eta + i\,\mathrm{Im}\,\eta$

(ii) H is hermitian

$$\mathrm{Re}\,\eta\ \mathrm{Re}\left(\langle \delta \Phi_{HF} | H | \Phi_{HF} \rangle \right)$$

$$- \mathrm{Im}\,\eta\ \mathrm{Im}\left(\langle \delta \Phi_{HF} | H | \Phi_{HF} \rangle \right)$$

$$= 0$$

η is arbitrarily small

$$\mathrm{Re}\left[\langle \delta\Phi_{HF} | \hat{H} | \Phi_{HF} \rangle\right]$$

$$= \mathrm{Im}\left[\langle \delta\Phi_{HF} | \hat{H} | \Phi_{HF} \rangle\right]$$

$$\Rightarrow \quad \langle \delta\Phi_{HF} | \hat{H} | \Phi_{HF} \rangle = 0$$

(in slides derivation in 1st quantization)

in second quantization

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

we have a variation

$$|\delta\Phi_{HF}\rangle = \eta a_a^{\dagger} a_i |\Phi_{HF}\rangle$$

$$\langle \delta\Phi_{HF} | \hat{H} | \Phi_{HF}\rangle = 0$$

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

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

$$+ E_0^{ref}$$

$$E_0^{ref} = \sum_i \langle i|h_0|i\rangle + \frac{1}{2}\sum_{ij} \langle ij|v|ij\rangle_{AS}$$

$$\langle \Phi_{HF} | a_r^\dagger a_a \hat{H} | \Phi_{HF} \rangle$$

$$\{a_r^\dagger a_a\}\{a_p^\dagger a_q\}$$

For $\hat{F}_N$ gives $\langle a | \hat{f} | r \rangle$

For $\hat{V}_N$ gives $= 0$

$$\{a_r^\dagger a_a\}\{a_p^\dagger a_q^\dagger a_s a_r\} = 0$$

$$\langle \Phi_{HF} | a_r^\dagger a_a E_0^{ref} | \Phi_{HF} \rangle = 0$$

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

$$= \langle a | h_c | i \rangle + \sum_{j \leq F} \langle a j | \hat{v} | i j \rangle_{AS}$$

Back to FCI

$1p1h$

$2p2h$

$$\begin{array}{c|c}
 & \begin{array}{ccccc} |\Phi_0\rangle & |\Phi_i^a\rangle & |\Phi_{ij}^{ab}\rangle & - & \cdots \end{array} \\
\begin{array}{c} \langle\Phi_0| \\ \langle\Phi_i^a| \\ \langle\Phi_{ij}^{ab}| \\ \vdots \\ \vdots \end{array} &
\begin{bmatrix}
\times & \langle i|\hat{f}|a\rangle = 0 & \langle ij|v|ab\rangle & \\
\langle a|\hat{f}|i\rangle = 0 & \times & \times & \\
\langle ab|v|ij\rangle_{AS} & \times & \times & \\
 & & \vdots & \\
 & & &
\end{bmatrix}
\end{array}$$

$$U_{HF}\hat{H}U_{HF}^{\dagger}$$

$$= \begin{bmatrix} \tilde{x} & 0 & \tilde{x} & \cdots \\ 0 & \tilde{x} & \tilde{x} & \\ \tilde{x} & \tilde{x} & & \\ 0 & 0 & & \\ \vdots & \vdots & & \\ 0 & & & \end{bmatrix}$$

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

one way to solve this equation (standard HF)

$$\langle p | \hat{f} | q \rangle = \lambda_p \delta_{pq}$$

$$p = a \qquad q = i$$

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

$$\langle i | \hat{h}_0 | i \rangle + \sum_j \langle ij | v | ij \rangle_{AS}$$

$$= \lambda_i = \varepsilon_i^{HF} \qquad i \leq F$$

$$\langle a | \hat{h}_0 | a \rangle + \sum_j \langle aj | v | aj \rangle_{AS} = \varepsilon_a^{HF}$$

$$a > F$$

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

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

$$\langle q|h^{HF}|p\rangle = \varepsilon_p^{HF}\langle q|p\rangle = \varepsilon_p^{HF}\delta_{pq}$$

$$\hat{h}^{HF} = \sum_p \varepsilon_p^{HF} a_p^\dagger a_p$$

$$\langle\Phi_{HF}|\hat{H}|\Phi_{HF}\rangle =$$

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

$$= \sum_i \Big\{ \langle i|h_0|i\rangle + \frac{1}{2}\sum_j \langle ij|\hat{v}|ij\rangle_{AS} + \frac{1}{2}\sum_j \langle ij|\hat{v}|ij\rangle - \frac{1}{2}\sum_j \langle ij|\hat{v}|ij\rangle \Big\}$$

$$= \sum_i \varepsilon_i^{HF} - \frac{1}{2} \sum_{ij} \langle ij | v | ij \rangle_{AS}$$