FYS 4480, OCT 7, 2022

Hartree-Fock theory

$$\psi_p = \sum_{\lambda=0}^{\alpha} C_{p\lambda} \varphi_\lambda$$

$$\langle \varphi_\lambda | \varphi_\sigma \rangle = \delta_{\lambda\sigma} \Rightarrow$$

$$\langle \psi_p | \psi_q \rangle = \delta_{pq}$$

$$\hat{h}_0 \varphi_\lambda = \varepsilon_\lambda \varphi_\lambda$$

$$\hat{h}^{HF} \psi_p^{HF} = \varepsilon_p^{HF} \psi_p^{HF}$$

$$\Phi_0 = \frac{1}{\sqrt{N!}} \sum_P (-)^P \hat{P} \varphi_{\lambda_1} \varphi_{\lambda_2} \cdots \varphi_{\lambda_N}$$

$$\Psi_0^{HF} = \frac{1}{\sqrt{N!}} \sum_P (-)^P \hat{P} \psi_{p_1}^{HF} \psi_{p_2}^{HF} \cdots \psi_{p_N}^{HF}$$

$$\langle \Phi_0 | H | \Phi_0 \rangle = \sum_{\mu=1}^{N} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu\nu} \langle \mu\nu | \hat{v} | \mu\nu \rangle_{AS}$$

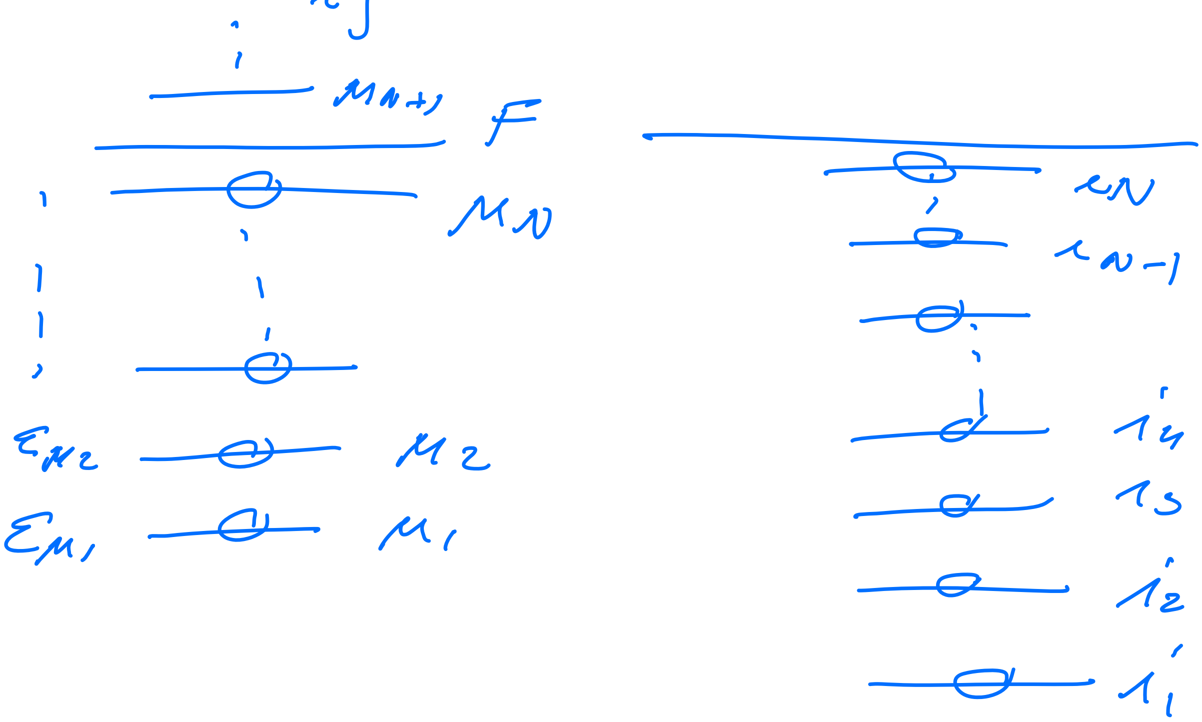
$$\sum_{\mu<\nu}$$

$$= \sum_{\mu=1}^{N} \varepsilon_\mu + \frac{1}{2}\sum_{\mu\nu}\langle \mu\nu|\hat{v}|\mu\nu\rangle_{AS}$$

$$\langle \Psi_0^{HF}|H|\Psi_0^{HF}\rangle =$$

$$\sum_{i\le F}^{N}\langle i|h_0|i\rangle +$$

$$\frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle_{AS}$$



$$\det(\Psi_0^{HF}) = \det C \det \Phi_0$$

$$\langle \Psi_0^{HF}|H|\Psi_0^{HF}\rangle =$$

$$\sum_{i \le F}^{N} \sum_{\alpha\beta} C_{i\alpha}^{*} C_{i\beta} \boxed{\langle \alpha | h_0 | \beta \rangle} +$$

$$\frac{1}{2} \sum_{i,j \le F}^{N} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^{*} C_{j\beta}^{*} C_{i\gamma} C_{j\delta}$$

$$\times \boxed{\langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS}}$$

pre calculate and tabulate.

$$= E_0^{HF}$$

Functional to optimize

$$\frac{d}{dC_{i\alpha}^{*}} F[\Psi_0^{HF}]$$

$$F[\Psi_0^{HF}] = E_0^{HF} - \sum_{i=1}^{N} \lambda_i \sum_{\alpha} C_{i\alpha}^{*} \times C_{i\alpha}$$

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta}$$

For a specific $C_{i\alpha}^{*}$

$$\sum_{\beta} C_{i\beta} \langle \alpha | h_0 | \beta \rangle$$

$$+ \sum_{j \leq F} \sum_{\beta\gamma\delta} C^{*}_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS}$$

$$\beta \leftrightarrow \gamma$$

$$- \lambda_i C_{i\alpha}$$

$$\underline{h^{HF}_{\alpha\beta}} = \langle \alpha | h_0 | \beta \rangle + \sum_{j \leq F}^{N} \sum_{\gamma\delta}$$

$$\times C^{*}_{j\gamma} C_{j\delta} \langle \alpha\gamma | v | \beta\delta \rangle_{AS}$$

$$\sum_{\beta} C_{i\beta} h^{HF}_{\alpha\beta} = \lambda_i C_{i\alpha}$$

$$\hat{h}^{HF} C = \lambda C$$

$$\langle \alpha | h_0 | \beta \rangle = \varepsilon_\alpha \delta_{\alpha\beta}$$

Algorithm

- precalculate and tabulate
  $\langle \alpha | \hat{h}_0 | \beta \rangle$ and

  $\langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS}$

- Define Fermi level F
  and N

- Define $C_{i\alpha}^{(0)}$, typical choice $C_{i\alpha}^{(0)} = \delta_{i\alpha}$

$$h^{HF}\psi_p^{HF} = \varepsilon_p^{HF}\psi_p^{HF}$$

$$p : \{i_1, i_2 \ldots i_N, a_1 \ldots a_d\}$$

while convergence criterion not met $|\varepsilon_p^{HF}(n+1) - \varepsilon_p^{HF}(n)|$

calculate $h^{HF}(n)$

Diagonalize

$$h^{HF}(n)C(n) = \varepsilon^{HF}(n)C(n)$$

end while

<u>Koopman's theorem</u>

Assume we have removed a particle from a single-particle state below F

$$E^{HF}(N-1_k) = \sum_{\substack{i=1 \\ i\neq k}}^{N} \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{\substack{i,j \\ i\neq k \\ j\neq k}}$$

$$\times \left(\langle ij|\hat{v}|ij\rangle - \langle ji|v|ij\rangle \right)$$

$$= E^{HF}(N) - \langle k|\hat{h}_0|k\rangle - \frac{1}{2}\sum_{i=1}^{N} \langle ik|\hat{v}|ik\rangle_{AS} - \frac{1}{2}\sum_{j=1}^{N} \langle kj|\hat{v}|kj\rangle_{AS}$$

$$= E^{HF}(N) - \langle k|h_0|k\rangle - \sum_{i=1}^{N} \langle ik|\hat{v}|ik\rangle_{AS}$$

$$\left(h^{HF}_{pq} = \langle p|h_0|q\rangle + \sum_{j\le F} \langle pj|v|qj\rangle_{AS} \right)$$

$$\varepsilon^{HF}_k = \langle k|h_0|k\rangle + \sum_{i=1}^{N} \langle ki|v|ki\rangle_{AS}$$

$$E^{HF}(N-1_k) = E^{HF}(N) - \varepsilon^{HF}_k$$

$$\varepsilon^{HF}_k = E^{HF}(N) - E^{HF}(N-1_k)$$

Adding one particle

$$\varepsilon^{HF}_a = E^{HF}(N+1_a) - E^{H}(N)$$