Hartree-Fock approximation

variational method

$H|\psi\rangle = \varepsilon|\psi\rangle$ can be derived by

minimizing $E[\psi] = \langle\psi|H|\psi\rangle$ under the constraint

$\langle\psi|\psi\rangle = 1$

i.e. $$\frac{\delta}{\delta\psi^*(\bar{r})}\Big[\langle\psi|H|\psi\rangle - \lambda(\langle\psi|\psi\rangle - 1)\Big] = 0$$

Lagrange multiplier

$\rightarrow$ $H\psi(\bar{r}) = \lambda\psi(\bar{r})$, $(\therefore \lambda \text{ is } \varepsilon)$

- manybody generalization

$$\Psi(\bar{r}_1, s_1 \cdots \bar{r}_N, s_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\bar{r}_1, s_1) & \psi_1(\bar{r}_1, s_2) & \cdots & \psi_1(\bar{r}_N, s_N) \\ \psi_2(\bar{r}_1, s_1) & \psi_2(\bar{r}_2, s_2) & \cdots & \psi_2(\bar{r}_N, s_N) \\ \vdots & & & \\ \psi_N(\bar{r}_1, s_1) & \cdots & & \psi_N(\bar{r}_N, s_N) \end{vmatrix}$$

where $\psi_1 \cdots \psi_N$ are filled by electrons (in ground state)

one-electron wave fn : $\langle \bar{r}_1 \underset{\hat{s}_1}{|} \psi_{p_1}\rangle = \phi_{p_1}(\bar{r}_1)\chi_{p_1}(1)$

orbital $\times$ spinor

$$H = \sum_i \left(\frac{p_i^2}{2m} + U(\bar{r}_i)\right) + \frac{1}{2}\sum_{\substack{ij \\ (i\neq j)}} \frac{e^2}{|\bar{r}_i - \bar{r}_j|} \equiv H_1 + H_2$$

compact form of Ψ :

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_{\text{all } p} (-1)^p |\psi_{p1}\rangle|\psi_{p2}\rangle \cdots |\psi_{pN}\rangle$$

where $p : (1, 2 \cdots N) \to (p1, p2 \cdots pN)$

$$(-1)^p = \begin{cases} +1 & \text{for even permutation} \\ -1 & \text{" odd "} \end{cases}$$

- $\langle \Psi | H_1 | \Psi \rangle$

$$= \sum_i \langle \Psi | \frac{p_i^2}{2m} + U(\bar{r}_i) | \Psi \rangle$$

$$= N \langle \Psi | \frac{p_1^2}{2m} + U(\bar{r}_1) | \Psi \rangle \quad \leftarrow \text{identical particles}$$

$$= \frac{N}{N!} \sum_{pp'} (-1)^p (-1)^{p'} \langle \psi_{p1} | \cdots \langle \psi_{pN} | \underline{\frac{p_1^2}{2m} + U(\bar{r}_1)} | \underline{\psi_{p'1}} \rangle \cdots | \psi_{p'N} \rangle$$

operate on

the other $|\psi_i\rangle$'s are unaffected.

use $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ to get $p' = p$

$\langle \Psi | H_1 | \Psi \rangle$

$$= \frac{N}{N!} \sum_p \langle \psi_{p1} | \frac{p_1^2}{2m} + U(\bar{r}_1) | \psi_{p1} \rangle \langle \psi_{p2} | \psi_{p2} \rangle \cdots \langle \psi_{pN} | \psi_{pN} \rangle$$

particle 1 at state ψ_{p1}

the other states allow $(N-1)!$ permutations

$$= \underbrace{\frac{N(N-1)!}{N!}}_{1} \sum_{p1=1}^{N} \langle \psi_{p1} | \frac{p_1^2}{2m} + U(\bar{r}_1) | \psi_{p1} \rangle \qquad (1)$$

$$H_2 = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\bar{r}_i-\bar{r}_j|}$$

again because of identical particles

- $$\langle\Psi|H_2|\Psi\rangle = \frac{N(N-1)}{2}\langle\Psi|\frac{e^2}{|\bar{r}_1-\bar{r}_2|}|\Psi\rangle$$

$$\langle\Psi|\frac{e^2}{|\bar{r}_1-\bar{r}_2|}|\Psi\rangle = \frac{1}{N!}\sum_{PP'}(-1)^P(-1)^{P'}$$

$$\times\underline{\langle\psi_{P_1}|\langle\psi_{P_2}|\frac{e^2}{|\bar{r}_1-\bar{r}_2|}|\psi_{P_1'}\rangle|\psi_{P_2'}\rangle}\langle\psi_{P_3}|\psi_{P_3'}\rangle\cdots$$

$\uparrow$

$P_1 = P_1'$, $P_2 = P_2'$

or $P_1 = P_2'$, $P_2 = P_1'$

the others allow $(N-2)!$ permutations

$$\therefore \langle\Psi|\frac{e^2}{|\bar{r}_1-\bar{r}_2|}|\Psi\rangle = \frac{1}{N(N-1)}\sum_{P_1P_2}\Big(\langle\psi_{P_1}|\langle\psi_{P_2}|\frac{e^2}{|\bar{r}_1-\bar{r}_2|}|\psi_{P_1}\rangle|\psi_{P_2}\rangle$$

$$-\langle\psi_{P_1}|\langle\psi_{P_2}|\frac{e^2}{|\bar{r}_1-\bar{r}_2|}|\psi_{P_2}\rangle|\psi_{P_1}\rangle\Big)$$

$$\rightarrow \langle\Psi|H_2|\Psi\rangle = \frac{1}{2}\sum_{P_1P_2}\big(\qquad\qquad '' \qquad\qquad\big) \quad ②$$

① + ② :

$$\langle\Psi|H|\Psi\rangle = \sum_{i=1}^{N}\langle\psi_i|\frac{p^2}{2m}+U(\bar{r})|\psi_i\rangle$$

$$+\frac{1}{2}\sum_{ij}\Big(\langle\psi_i|\langle\psi_j|\frac{e^2}{|\vec{r}-\vec{r}'|}|\psi_i\rangle|\psi_j\rangle$$

$$-\langle\psi_i|\psi_j|\frac{e^2}{|\bar{r}-\bar{r}'|}|\psi_j\rangle|\psi_i\rangle\Big)$$

Hartree-Fock equation:

note: if $F[\psi] = \int d^3r' \psi^*(\bar{r}') \hat{O} \psi(\bar{r}')$

then $\dfrac{\delta F[\psi]}{\delta \psi^*(\bar{r})} = \hat{O} \psi(\bar{r})$

- non-interacting terms

$$\frac{\delta}{\delta \psi_\ell^*(\bar{r},s)} \sum_i \langle \psi_i | \frac{p^2}{2m} + U | \psi_i \rangle = \left(\frac{p^2}{2m} + U\right) \psi_\ell(\bar{r},s) \qquad (3)$$

bracket of ψ_i has $\bar{r}$-integration and spin summation

- Hartree term

$$\frac{\delta}{\delta \psi_\ell^*(\bar{r},s)} \sum_{ij} \underbrace{\langle \psi_i | \langle \psi_j | \frac{e^2}{|\bar{r}'-\bar{r}''|} | \psi_i \rangle | \psi_j \rangle}_{\sum_{s's''} \int d^3r' d^3r'' \psi_i^*(\bar{r}'s') \psi_j^*(\bar{r}''s'') \frac{e^2}{|\bar{r}'-\bar{r}''|} \psi_i(\bar{r}'s') \psi_j(\bar{r}''s'')}$$

$i=\ell \rightarrow \quad = \sum_j \sum_{s''} \int d^3r'' \psi_j^*(\bar{r}''s'') \dfrac{e^2}{|\bar{r}-\bar{r}''|} \psi_\ell(\bar{r},s) \psi_j(\bar{r}''s'')$

$j=\ell \rightarrow \quad + \sum_i \sum_{s'} \int d^3r' \psi_i^*(\bar{r}'s') \dfrac{e^2}{|\bar{r}'-\bar{r}|} \psi_i(\bar{r}'s') \psi_\ell(\bar{r},s)$

the same (4)

- Fock term

$$\frac{\delta}{\delta\psi_e^*(\vec r,s)} \sum_{ij} \underbrace{\langle\psi_i|\langle\psi_j|\frac{e^2}{|\vec r'-\vec r''|}|\psi_j\rangle|\psi_i\rangle}$$

$$\sum_{s's''}\int d^3r'\,d^3r''\;\underbrace{\psi_i^*(\vec r's')}_{\downarrow\;\chi_i^+}\,\psi_j^*(\vec r''s'')\,\frac{e^2}{|\vec r'-\vec r''|}\,\underbrace{\psi_j(\vec r's')}_{\downarrow\;\chi_j}\,\psi_i(\vec r''s'')$$

$\chi_i^+\chi_j=\delta_{ij}$, $\therefore$ the states χ_i, χ_j need to have the same spin.

$l=i$ $$= \sum_j\sum_{s''}\int d^3r''\,\psi_j^*(\vec r''s'')\,\frac{e^2}{|\vec r-\vec r''|}\,\psi_j(\vec r\,s)\,\psi_e(\vec r''s'')\,\delta_{ss''}$$

$l=j$ $$+\sum_i\sum_{s'}\int d^3r'\,\psi_i^*(\vec r's')\,\frac{e^2}{|\vec r'-\vec r|}\,\psi_e(\vec r's')\,\psi_i(\vec r,s)\,\delta_{ss'}$$

again this 2 terms are the same. (5)

$\therefore$ finally (3) + (4) + (5)

$$\left(\frac{p^2}{2m}+U\right)\psi_e(\vec r,s)+\sum_i\sum_{s'}\int d^3r'\,\psi_i^*(\vec r's')\,\frac{e^2}{|\vec r'-\vec r|}\,\psi_i(\vec r's')\,\psi_e(\vec r,s)$$

$$-\sum_i\sum_{s'}\int d^3r'\,\psi_i^*(\vec r's')\,\frac{e^2}{|\vec r'-\vec r|}\,\psi_e(\vec r's')\,\psi_i(\vec r,s)\,\delta_{ss'}$$

$$=\varepsilon_e\psi_e(\vec r,s)$$

$\uparrow$

from $\displaystyle\frac{\delta}{\delta\psi_e^*}\sum_i\varepsilon_i(\langle\psi_i|\psi_i\rangle-1)$