PH 557 (Class - 3)

$$h(\bar{r}_1)\psi_k(\bar{r}_1) + V_{eff}(\bar{r}_1)\psi_k(\bar{r}_1) = \epsilon_k\psi_k(\bar{r}_1)$$

$$\Rightarrow \left[h(\bar{r}_1) + V_{eff}(\bar{r}_1)\right]\psi_k(\bar{r}_1) = \epsilon_k\psi_k(\bar{r}_1)$$

where,

$$V_{eff}(\bar{r}_1) = \int d\bar{r}' \left(\sum_j |\psi_j(\bar{r}')|^2\right) \frac{(-e)(-e)}{4\pi\epsilon_0|\bar{r}_1 - \bar{r}'|}$$

$$= \int d\bar{r}' \underbrace{\left(-e\sum_j |\psi_j(\bar{r}')|^2\right)}_{\rho(\bar{r}')} \frac{(-e)}{4\pi\epsilon_0|\bar{r}_1 - \bar{r}'|}$$

$$= \int d\bar{r}' \frac{(-e)\rho(\bar{r}')}{4\pi\epsilon_0|\bar{r}_1 - \bar{r}'|} \quad \text{--- (26)}$$

Electron sees an effective charge distribution $\rho(\bar{r}')$, produced by other electrons.

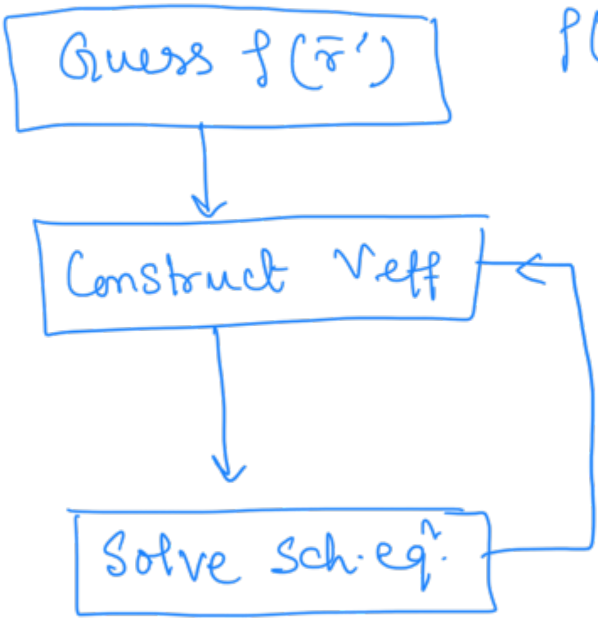
This is called mean-field approach.

Note that to know V_{eff}, we need to

know the wave funct^{n}s., which can be obtained by solving the Sch. eq^n. Solving the Sch. eq^n, however, requires the knowledge of V_{eff}.

Sol^n:

$$\rho(\bar{r}') = -\sum_j e|\psi_j(\bar{r}')|^2$$



Self consistent mean-field approx. method

Hartree-Fock method:

In the previous case, we start with a single-particle wave funct^n:

$$\phi(\bar{r}_1, \ldots \bar{r}_n) = \psi_1(\bar{r}_1)\psi_2(\bar{r}_2)\ldots\psi_n(\bar{r}_n)$$

If we have a system with 2 electrons,

$$\phi(\bar{r}_1, \bar{r}_2) = \psi_1(\bar{r}_1)\psi_2(\bar{r}_2)$$

$$\therefore \quad \phi(\bar{r}_2, \bar{r}_1) = \psi_1(\bar{r}_2)\psi_2(\bar{r}_1)$$

So the wave funct^n is neither sym. nor anti-sym.

However, electrons are fermions and hence the wave funct^n should be anti-sym.

$$\phi(\bar{r}_1, \bar{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_1(\bar{r}_1)\psi_2(\bar{r}_2) - \psi_1(\bar{r}_2)\psi_2(\bar{r}_1)\right]$$

$$\therefore \phi(\bar{r}_2, \bar{r}_1) = \frac{1}{\sqrt{2}}\left[\psi_1(\bar{r}_2)\psi_2(\bar{r}_1) - \psi_1(\bar{r}_1)\psi_2(\bar{r}_2)\right]$$

$$= -\phi(\bar{r}_1, \bar{r}_2)$$

We can write $\phi(\bar{r}_1, \bar{r}_2)$ in a more compact form as Slater determinant.

$$\phi(\bar{r}_1, \bar{r}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(\bar{r}_1) & \psi_2(\bar{r}_1) \\ \psi_1(\bar{r}_2) & \psi_2(\bar{r}_2) \end{vmatrix}$$

For a general case,

$$\phi(\bar{r}_1, \cdots \bar{r}_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_1(\bar{r}_1) & \psi_2(\bar{r}_1) & \cdots & \psi_n(\bar{r}_1) \\ \vdots & \vdots & & \vdots \\ \psi_1(\bar{r}_n) & \psi_2(\bar{r}_n) & & \psi_n(\bar{r}_n) \end{vmatrix}$$

Including also the spin d.o.f.,

$$\phi(x_1, \cdots x_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \tilde{\psi}_1(x_1) & \tilde{\psi}_2(x_1) & \cdots & \tilde{\psi}_n(x_1) \\ \vdots & \vdots & & \vdots \end{vmatrix}$$

$$\begin{vmatrix} \tilde{\psi}_1(x_n) & \tilde{\psi}_2(x_n) & \tilde{\psi}_n(x_n) \end{vmatrix}$$

where $\tilde{\psi}_1(x_1) = \psi_1(\bar{r}_1)\, \chi_\sigma(\varsigma)$ — (27)

ς and σ are respectively the spin variable & spin quantum no. For spin $\frac{1}{2}$ particle, $\varsigma = \pm 1$ and $\sigma = \pm \frac{1}{2}$

For H-atom, $\psi_i(\bar{r}_1) \equiv \psi_{nlm}(r, \theta, \phi)$

$$= R_n(r)\, Y_{lm}(\theta, \phi)$$

Denoting (n, l, m) indices by a combined index α;

$$x \equiv (\bar{r}, \varsigma)$$
$$i \equiv (\alpha, \sigma)$$

We want to find the extremum value of $\langle \Phi | H | \Phi \rangle$ with the constraint $\langle \tilde{\psi}_i | \tilde{\psi}_j \rangle = \delta_{ij}$

This is called Hartree-Fock method.

The procedure is the same as described for the Hartree method.

To calculate $\langle \Phi | H | \Phi \rangle$, we consider a 2-particle system.

$$H_e = -\frac{\hbar^2}{2m}\sum_{i=1}^{2} \nabla_i^2 + \sum_{i=1}^{2} V_{ext}(\bar{r}_i)$$
$$+ \frac{1}{2}\sum_{\substack{i=1 \\ i\neq j}}^{2}\sum_{j=1}^{2} \frac{e^2}{4\pi\epsilon_0 |\bar{r}_i - \bar{r}_j|}$$

$$\Rightarrow H_e = \sum_{i=1}^{2} h(\bar{r}_i) + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} V(\bar{r}_i, \bar{r}_j)$$

where $h(\bar{r}) = -\frac{\hbar^2}{2m}\nabla_i^2 + V_{ext}(\bar{r})$

and $\Phi(x_1, x_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \tilde{\varphi}_1(x_1) & \tilde{\varphi}_2(x_1) \\ \tilde{\varphi}_1(x_2) & \tilde{\varphi}_2(x_2) \end{vmatrix}$

We have to find,

$$\langle \Phi | H | \Phi \rangle = \iint dx_1 dx_2 \, \phi^*(x_1, x_2)$$
$$* \left[\sum_{i=1}^{2} h(\bar{r}_i) + \frac{1}{2}\sum_{\substack{i \\ i\neq j}}\sum_{j} V(\bar{r}_i, \bar{r}_j) \right] \Phi(x_1, x_2)$$

Now the first term

$$= \frac{1}{2} \iint dx_1 dx_2 \left[\tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2) - \tilde{\psi}_2^*(x_1) \tilde{\psi}_1^*(x_2) \right]$$
$$(h_1 + h_2) \left[\tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2) - \tilde{\psi}_2(x_1) \tilde{\psi}_1(x_2) \right]$$

$$= \frac{1}{2} \iint dx_1 dx_2 \Big[\Big\{ \tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2)\, h_1 \tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2)$$

$$+ \tilde{\psi}_2^*(x_1) \tilde{\psi}_1^*(x_2)\, h_1 \tilde{\psi}_2(x_1) \tilde{\psi}_1(x_2)$$
$$+ \tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2)\, h_2 \tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2)$$
$$+ \tilde{\psi}_2^*(x_1) \tilde{\psi}_1^*(x_2)\, h_2 \tilde{\psi}_2(x_1) \tilde{\psi}_1(x_2) \Big\}$$
$$- \Big\{ \tilde{\psi}_2^*(x_1) \tilde{\psi}_1^*(x_2)\, h_1 \tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2)$$
$$+ \tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2)\, h_1 \tilde{\psi}_2(x_1) \tilde{\psi}_1(x_2)$$
$$+ \tilde{\psi}_2^*(x_1) \tilde{\psi}_1^*(x_2)\, h_2 \tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2)$$
$$+ \tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2)\, h_2 \tilde{\psi}_2(x_1) \tilde{\psi}_1(x_2) \Big\} \Big]$$
$$= \iint dx_1 dx_2 \Big[\tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2)\, h_1 \tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2)$$
$$+ \tilde{\psi}_2^*(x_1) \tilde{\psi}_1^*(x_2)\, h_1 \tilde{\psi}_2(x_1) \tilde{\psi}_1(x_2) \Big]$$

[Since x_1 and x_2 are dummy indices we can interchange those and that is why the $1/2$ factor disappears]

$$= \int dx_1\, \tilde{\psi}_1^*(x_1)\, h_1 \tilde{\psi}_1(x_1) + \int dx_1\, \tilde{\psi}_2^*(x_1)\, h_1 \tilde{\psi}_2(x_1)$$

$$\therefore \langle \Phi | \sum_{i=1}^{2} h_i | \Phi \rangle = \langle \tilde{\varphi}_1 | h_1 | \tilde{\varphi}_1 \rangle + \langle \tilde{\varphi}_2 | h_1 | \tilde{\varphi}_2 \rangle$$

$$= \sum_{i=1}^{2} \langle \tilde{\psi}_i | h(\bar{r}) | \tilde{\psi}_i \rangle$$

Note that the sum over the position converted into sum over the quantum no.

In general,

$$\langle \Phi | \sum_{i=1}^{n} h(\bar{r}_i) | \Phi \rangle = \sum_{i=1}^{n} \langle \tilde{\psi}_i | h(\bar{r}) | \tilde{\psi}_i \rangle \quad \text{--- (28)}$$

Let's now consider the second term,

$$\langle \Phi | \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{2} \sum_{j=1}^{2} v(\bar{r}_i, \bar{r}_j) | \Phi \rangle$$

(Considering again 2-particle system)

$$= \frac{1}{2} \iint dx_1 \, dx_2 \left[\tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2) - \tilde{\psi}_1^*(x_2) \tilde{\psi}_2^*(x_1) \right]$$

$$\frac{1}{2}(v_{12} + v_{21}) \left[\tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2) - \tilde{\psi}_1(x_2) \tilde{\psi}_2(x_1) \right]$$

$$= \frac{1}{2} \iint dx_1 \, dx_2 \left[\left\{ \tilde{\psi}_1^*(x_1) \tilde{\psi}_2^*(x_2) v_{12} \tilde{\psi}_1(x_1) \tilde{\psi}_2(x_2) \right. \right.$$

$$+\tilde{\psi}_1^*(x_2)\,\tilde{\psi}_2^*(x_1)\,v_{12}\,\tilde{\psi}_1(x_2)\,\tilde{\psi}_2(x_1)\}$$

$$-\{\tilde{\psi}_1^*(x_2)\,\tilde{\psi}_2^*(x_1)\,v_{12}\,\tilde{\psi}_1(x_1)\,\tilde{\psi}_2(x_2)$$

$$+\tilde{\psi}_1^*(x_1)\,\tilde{\psi}_2^*(x_2)\,v_{12}\,\tilde{\psi}_1(x_2)\,\tilde{\psi}_2(x_1)\}\Big]$$

$$(\because v_{12} = v_{21})$$

$$= \langle \tilde{\psi}_1 \tilde{\psi}_2 | v_{12} | \tilde{\psi}_1 \tilde{\psi}_2 \rangle - \langle \tilde{\psi}_1 \tilde{\psi}_2 | v_{12} | \tilde{\psi}_2 \tilde{\psi}_1 \rangle$$

In general,

$$\langle \Phi | \sum_{i=1}^{n} \sum_{j=1}^{n} v_{ij} | \Phi \rangle = \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \langle \tilde{\psi}_i \tilde{\psi}_j | v_{12} | \tilde{\psi}_i \tilde{\psi}_j \rangle$$

$$- \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \langle \tilde{\psi}_i \tilde{\psi}_j | v_{12} | \tilde{\psi}_j \tilde{\psi}_i \rangle \qquad \text{--- (29)}$$

H.W.

Show that the above equality holds for the 2-particle system.

The cost funct^n. in this case is,

$$F[\tilde{\psi}_i^*, \tilde{\psi}_j] = \langle \Phi | H | \Phi \rangle - \sum_{ij} \lambda_{ij} [\langle \tilde{\psi}_i | \tilde{\psi}_j \rangle - \delta_{ij}]$$

$$= \sum_{i=1}^{n} \langle \tilde{\psi}_i | h_i | \tilde{\psi}_i \rangle + \frac{1}{2} \sum_{\substack{i \\ i \neq j}} \sum_{j} \langle \tilde{\psi}_i \tilde{\psi}_j | v_{12} | \tilde{\psi}_i \tilde{\psi}_j \rangle$$

$$-\frac{1}{2}\sum_{i}\sum_{\substack{j \\ i\neq j}} \langle \tilde{\varphi}_i \tilde{\varphi}_j | v_{12} | \tilde{\varphi}_j \tilde{\varphi}_i \rangle$$

$$-\sum_{ij} \lambda_{ij} \left[\langle \tilde{\varphi}_i | \tilde{\varphi}_j \rangle - \delta_{ij} \right]$$

$$\frac{\delta F}{\delta \tilde{\varphi}_k^*(x)} = 0$$

$$\Rightarrow \frac{\delta}{\delta \tilde{\varphi}_k^*(x)} \left[\sum_i \int \tilde{\varphi}_i^*(x_1)\, h_1\, \tilde{\varphi}_i(x_1)\, dx_1 \right.$$

$$+\frac{1}{2}\sum_{\substack{ij \\ i\neq j}} \int \tilde{\varphi}_i^*(x_1)\, \tilde{\varphi}_j^*(x_2)\, v_{12}\, \tilde{\varphi}_i(x_1)\, \tilde{\varphi}_j(x_2)\, dx_1 dx_2$$

$$-\frac{1}{2}\sum_{\substack{ij \\ i\neq j}} \int \tilde{\varphi}_i^*(x_1)\, \tilde{\varphi}_j^*(x_2)\, v_{12}\, \tilde{\varphi}_j(x_1)\, \tilde{\varphi}_i(x_2)\, dx_1 dx_2$$

$$\left. -\sum_{ij} \lambda_{ij} \left\{ \int \tilde{\varphi}_i^*(x_1)\, \tilde{\varphi}_j(x_1)\, dx_1 - \delta_{ij} \right\} \right] = 0$$

$$\Rightarrow \sum_i \int dx_1 \frac{\delta \tilde{\varphi}_i^*(x_1)}{\delta \tilde{\varphi}_k^*(x)}\, h_1\, \tilde{\varphi}_i(x_1)\, dx_1$$

$$+\frac{1}{2}\sum_{\substack{ij \\ i\neq j}} \int \left[\frac{\delta \tilde{\varphi}_i^*(x_1)}{\delta \tilde{\varphi}_k^*(x)}\, \tilde{\varphi}_j^*(x_2)\, v_{12}\, \tilde{\varphi}_i(x_1)\, \tilde{\varphi}_j(x_2)\, dx_1 dx_2 \right.$$

$$+ \tilde{\psi}_i^*(x_1) \frac{\delta \tilde{\psi}_j^*(x_2)}{\delta \tilde{\psi}_k^*(x)} v_{12} \tilde{\psi}_i(x_1) \tilde{\psi}_j(x_2) dx_1 dx_2 \Big]$$

$$- \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \int \Big[\frac{\delta \tilde{\psi}_i^*(x_1)}{\delta \tilde{\psi}_k^*(x)} \tilde{\psi}_j^*(x_2) v_{12} \tilde{\psi}_j(x_1) \tilde{\psi}_i(x_2) dx_1 dx_2$$

$$+ \tilde{\psi}_i^*(x_1) \frac{\delta \tilde{\psi}_j^*(x_2)}{\delta \tilde{\psi}_k^*(x)} v_{12} \tilde{\psi}_j(x_1) \tilde{\psi}_i(x_2) dx_1 dx_2 \Big]$$

$$- \sum_{ij} \lambda_{ij} \left\{ \int \frac{\delta \tilde{\psi}_i^*(x_1)}{\delta \tilde{\psi}_k^*(x)} \tilde{\psi}_j(x_1) dx_1 \right\} = 0$$

$$\Rightarrow \sum_i \int dx_1 \, \delta_{ik} \, \delta(x - x_1) h_1 \tilde{\psi}_i(x_1) dx_1$$

$$+ \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \int \Big[\delta_{ik} \, \delta(x - x_1) \tilde{\psi}_j^*(x_2) v_{12} \tilde{\psi}_i(x_1) \tilde{\psi}_j(x_2) dx_1 dx_2$$

$$+ \tilde{\psi}_i^*(x_1) \delta_{jk} \, \delta(x - x_2) v_{12} \tilde{\psi}_i(x_1) \tilde{\psi}_j(x_2) dx_1 dx_2 \Big]$$

$$- \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \int \Big[\delta_{ik} \, \delta(x - x_1) \tilde{\psi}_j^*(x_2) v_{12} \tilde{\psi}_j(x_1) \tilde{\psi}_i(x_2) dx_1 dx_2$$

$$+ \tilde{\psi}_i^*(x_1) \delta_{jk} \, \delta(x - x_2) v_{12} \tilde{\psi}_j(x_1) \tilde{\psi}_i(x_2) dx_1 dx_2 \Big]$$

$$- \sum_{ij} \lambda_{ij} \int \delta_{ik} \, \delta(x - x_1) \tilde{\psi}_j(x_1) dx_1 = 0$$

$$\Rightarrow h(x) \tilde{\psi}_k(x) + \frac{1}{2} \Big[\sum_{\substack{j \\ j \neq i}} \int \tilde{\psi}_j^*(x_2) v_{12} \tilde{\psi}_k(x) \tilde{\psi}_j(x_2) dx_2$$

$$+ \sum_{\substack{i \\ i\neq j}} \int \tilde{\varphi}_i^*(x_1)\, v_{12}\, \tilde{\varphi}_i(x_1)\, \tilde{\varphi}_k(x)\, dx_1 \Big]$$

$$- \frac{1}{2}\Big[\sum_{\substack{j \\ j\neq i}} \int \tilde{\varphi}_j^*(x_2)\, v_{12}\, \tilde{\varphi}_j(x)\, \tilde{\varphi}_k(x_2)\, dx_2$$

$$+ \sum_{\substack{i \\ i\neq j}} \int \tilde{\varphi}_i^*(x_1)\, v_{12}\, \tilde{\varphi}_k(x_1)\, \tilde{\varphi}_i(x)\, dx_1 \Big]$$

$$- \sum_j \lambda_{kj}\, \tilde{\varphi}_j(x) = 0$$

$$\Rightarrow h(x)\, \tilde{\varphi}_k(x) + \left[\sum_{\substack{j \\ j\neq i}} \int \frac{\tilde{\varphi}_j^*(x_2)\tilde{\varphi}_j(x_2)\, e^2}{4\pi\epsilon_0 |x - x_2|}\, dx_2 \right] \tilde{\varphi}_k(x)$$

$$- \sum_{\substack{j \\ j\neq i}} \int \tilde{\varphi}_j^*(x_2)\, v_{12}\, \tilde{\varphi}_j(x)\, \tilde{\varphi}_k(x_2)\, dx_2$$

$$- \sum_j \epsilon_k\, \delta_{jk}\, \tilde{\varphi}_j(x) \quad \text{--- (30)}$$

Now let us consider,

$$\tilde{\varphi}_k(x) = \psi_\alpha(\bar{r})\, \chi_\sigma(\xi)$$

$$\tilde{\varphi}_j(x) = \psi_\beta(\bar{r})\, \chi_{\sigma'}(\xi)$$

Substituting this in Eq^n (30) we get,

$$h(\bar{r})\,\psi_\alpha(\bar{r})\,\chi_\sigma(\xi)+\left[2\sum_\beta\int d\bar{r}'\,\frac{\psi_\beta^*(\bar{r}')\,\psi_\beta(\bar{r}')e^2}{4\pi\epsilon_0|\bar{r}-\bar{r}'|}\right]*\psi_\alpha(\bar{r})\,\chi_\sigma(\xi)$$

$$-\sum_{\beta,\sigma'}\int\psi_\beta^*(\bar{r}')\,V_{\bar{r},\bar{r}'}\psi_\alpha(\bar{r}')\,d\bar{r}'\,\delta_{\sigma\sigma'}\,\psi_\beta(\bar{r})\,\chi_{\sigma'}(\xi)$$

$$=\epsilon_k\,\psi_\alpha(\bar{r})\,\chi_\sigma(\xi) \quad \text{--- (31)}$$

where we have used,

$$\sum_{\sigma\sigma'}\chi_{\sigma'}^*(\xi)\,\chi_\sigma(\xi)=\delta_{\sigma\sigma'}$$

Note that actually there is a factor of 2 as each state is occupied by 2 electrons.

$\therefore$ From Eq. (31),

$$h(\bar{r})\,\psi_\alpha(\bar{r})\,\chi_\sigma(\xi)+\left[2\sum_\beta\int d\bar{r}'\,\frac{\psi_\beta^*(\bar{r}')\,\psi_\beta(\bar{r}')e^2}{4\pi\epsilon_0|\bar{r}-\bar{r}'|}\right]*\psi_\alpha(\bar{r})\,\chi_\sigma(\xi)$$

$$-\sum_\beta{}'\int\psi_\beta^*(\bar{r}')\,V_{\bar{r},\bar{r}'}\psi_\alpha(\bar{r}')\,d\bar{r}'\,\psi_\beta(\bar{r})\,\chi_\sigma(\xi)$$

$$=\epsilon_k\,\psi_\alpha(\bar{r})\,\chi_\sigma(\xi)$$

[$\sum'$ indicates sum over parallel spins]

$$\Rightarrow h(\bar{r})\,\psi_\alpha(\bar{r})+\left[2\sum_\beta\int d\bar{r}'\,\frac{\psi_\beta^*(\bar{r}')\,\psi_\beta(\bar{r}')e^2}{4\pi\epsilon_0|\bar{r}-\bar{r}'|}\right]\psi_\alpha(\bar{r})$$

$$-\left[\sum_\beta{}'\int\psi_\beta^*(\bar{r}')\,V_{\bar{r},\bar{r}'}\psi_\alpha(\bar{r}')\,d\bar{r}'\right]\psi_\beta(\bar{r})=\epsilon_k\,\psi_\alpha(\bar{r}) \quad \text{--- (32)}$$

If we have two electrons with quantum no.s (α, σ) and (β, σ') respectively, there are 2 possibilities $\sigma = \sigma'$ and $\sigma \neq \sigma'$

When $\sigma = \sigma'$, both 2nd and 3rd terms in Eq.ⁿ 32 would contribute, while for $\sigma \neq \sigma'$ only the 2nd term will be non-zero. The second term is called the Hartree term, which we discussed earlier. The third term can be rewritten as,

$$\left[\sum_{\beta}{}' \int d\bar{r}' \psi_\beta^*(\bar{r}') V_{\bar{r},\bar{r}'} \psi_\alpha(\bar{r}')\right] \psi_\beta(\bar{r})$$

$$= \int d\bar{r}' V_{\bar{r},\bar{r}'} \left(\sum_{\beta}{}' \psi_\beta^*(\bar{r}') \psi_\beta(\bar{r})\right) \psi_\alpha(\bar{r}')$$

$$= \int d\bar{r}' \underbrace{V_{\bar{r},\bar{r}'} \rho_{\text{non-local}}(\bar{r},\bar{r}')} \psi_\alpha(\bar{r}')$$

$$= \int d\bar{r}' V_{\text{non-local}}(\bar{r},\bar{r}') \psi_\alpha(\bar{r}')$$

$\therefore$ Using the above identity from Eq.ⁿ 32 we get,

$$h(\bar{r})\psi_\alpha(\bar{r}) + V_H(\bar{r})\psi_\alpha(\bar{r}) - \int d\bar{r}'\, V_{\text{non-local}}(\bar{r},\bar{r}')\,\psi_\alpha(\bar{r}') = \epsilon_k \psi_\alpha(\bar{r})$$