9.1. The Hartree-Fock Approximation

The Hartree-Fock approximation is a variational approach to estimate the single-particle wavefunctions, and hence to find an approximate many body ground state wavefunction.

Consider the many body wavefunction given by the Slater determinant

$$\phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(1) & \cdots & \varphi_{\alpha_1}(N) \\ \vdots & \ddots & \vdots \\ \varphi_{\alpha_N}(1) & \cdots & \varphi_{\alpha_N}(N) \end{vmatrix} ,$$

Form the energy functional

$$\mathcal{E}[\phi] = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} ,$$

Choosing the normalization of $|\phi\rangle$ so that $\langle\phi|\phi\rangle = 1$, we desire to minimize $\mathcal{E}\{\phi\}$. Thus we minimize $\mathcal{E}[\phi] = \langle\phi|H|\phi\rangle$ subject to the constraint $\langle\phi|\phi\rangle = 1$.

Hence we will obtain an equation for the single particle states φ_α and $|\phi\rangle$ will be an approximation to the many body ground state. Let the Hamiltonian be a sum of one-body, T, and two-body, V, operators

$$H = T + V$$

where

$$T = \sum_{i=1}^{N} t(\vec{p}_i, i)$$

$$V = \frac{1}{2} \sum_{i,j=1}^{N} V(i,j) \quad .$$

Using our previous results, we find

$$\mathcal{E}[\phi] = \sum_{\alpha} \langle \varphi_\alpha | t | \varphi_\alpha \rangle + \frac{1}{2} \sum_{\alpha,\beta} \left[\langle \varphi_{\alpha,\beta} | V | \varphi_{\alpha,\beta} \rangle - \overline{\langle \varphi_{\alpha,\beta} | V | \varphi_{\beta,\alpha} \rangle} \right]$$

which recall is given by

$$\mathcal{E}\{\phi\} = \sum_{\alpha}{}' \int d^3r\, \varphi_\alpha^\dagger(\vec{r})\, t(\vec{p},\vec{r})\, \varphi_\alpha(\vec{r})$$

$$+\frac{1}{2}\sum_{\alpha,\beta}{}' \int d^3r\, d^3r'\, \varphi_\alpha^\dagger(\vec{r})\varphi_\beta^\dagger(\vec{r}')\, V(|\vec{r}-\vec{r}'|)\times$$

$$\times\left[\varphi_\alpha(\vec{r})\varphi_\beta(\vec{r}') - \varphi_\beta(\vec{r})\varphi_\alpha(\vec{r}')\right].$$

We treat φ_α & $\varphi_\alpha^\dagger$ as independent and perform the variations

$$\varphi_\alpha \to \varphi_\alpha + \delta\varphi_\alpha$$

$$\varphi_\alpha^\dagger \to \varphi_\alpha^\dagger + \delta\varphi_\alpha^\dagger\,.$$

Varying $\varphi_\alpha^\dagger$ $\Rightarrow$

$$\delta\mathcal{E}\{\phi\} = \sum_{\alpha}{}' \int d^3r\, \delta\varphi_\alpha^\dagger(\vec{r})\, t(\vec{p},\vec{r})\, \varphi_\alpha(\vec{r})$$

$$+\frac{1}{2}\sum_{\alpha,\beta}{}' \int d^3r\, d^3r' \left[\delta\varphi_\alpha^\dagger(\vec{r})\varphi_\beta^\dagger(\vec{r}') + \varphi_\alpha^\dagger(\vec{r})\,\delta\varphi_\beta^\dagger(\vec{r}')\right]\times$$

$$\times V(|\vec{r}-\vec{r}'|)\left[\varphi_\alpha(\vec{r})\varphi_\beta(\vec{r}') - \varphi_\beta(\vec{r})\varphi_\alpha(\vec{r}')\right].$$

But $V(|\vec{r}-\vec{r}'|) = V(|\vec{r}'-\vec{r}|)$, so changing the dummy variable $\vec{r} \leftrightarrow \vec{r}'$, $\alpha \leftrightarrow \beta$, the $\varphi^\dagger_\alpha(\vec{r})\,\delta\varphi^\dagger_\beta(\vec{r}')$ term equals the $\delta\varphi^\dagger_\alpha(\vec{r})\,\varphi^\dagger_\beta(\vec{r}')$ term, cancelling the $\frac{1}{2}$. So

$$\delta \mathcal{E}[\phi] = \sum_\alpha{}' \int d^3r\, \delta\varphi^\dagger_\alpha(\vec{r})\, t(\vec{p},\vec{r})\,\varphi_\alpha(\vec{r})$$

$$+ \sum_{\alpha,\beta}{}' \int d^3r\, d^3r'\, \delta\varphi^\dagger_\alpha(\vec{r})\, \varphi^\dagger_\beta(\vec{r}')\, V(|\vec{r}-\vec{r}'|)\, \varphi_\alpha(\vec{r})\,\varphi_\beta(\vec{r}')$$

$$- \sum_{\alpha,\beta}{}' \int d^3r\, d^3r'\, \delta\varphi^\dagger_\alpha(\vec{r})\, \varphi^\dagger_\beta(\vec{r}')\, V(|\vec{r}-\vec{r}'|)\, \varphi_\beta(\vec{r})\,\varphi_\alpha(\vec{r}')$$

In addition we must require that $\langle\phi|\phi\rangle = 1$, that is the single particle wavefunctions are normalized to 1

$$1 = \int d^3r\, \varphi^\dagger_\alpha(\vec{r})\,\varphi_\alpha(\vec{r}) \quad .$$

Varying this wrt $\delta\varphi^\dagger_\alpha(\vec{r}) \Rightarrow$

$$0 = \int d^3r\, \delta\varphi^\dagger_\alpha(\vec{r})\,\varphi_\alpha(\vec{r}) \quad .$$

(more correctly we need Lagrange multiplier for $\delta_{\alpha\beta} = \int d^3r\, \varphi^\dagger_\alpha \varphi_\beta$, see Messiah Vol. II page 776.)

In order to include this constraint on the wavefunctions in the variation of $\mathcal{E}\{\phi\}$, it is easiest to use a Lagrange multiplier ϵ_α term added to $\delta\mathcal{E}\{\phi\}$

$$\sum_{\alpha}{}' \epsilon_\alpha \int d^3r \, \delta\varphi_\alpha^\dagger(\vec{r})\varphi_\alpha(\vec{r})$$

and then vary $\delta\varphi_\alpha^\dagger(\vec{r})$ unrestrictedly. So we get

$$\delta\mathcal{E}\{\phi\} = \sum_{\alpha}{}' \int d^3r \, \delta\varphi_\alpha^\dagger(\vec{r})\Big\{ t(\vec{p},\vec{r})\varphi_\alpha(\vec{r})$$

$$+ \sum_{\beta}{}' \int d^3r' \Big[\Big(\varphi_\beta^\dagger(\vec{r}')V(|\vec{r}-\vec{r}'|)\varphi_\beta(\vec{r}')\Big)\varphi_\alpha(\vec{r})$$

$$- \Big(\varphi_\beta^\dagger(\vec{r}')V(|\vec{r}-\vec{r}'|)\varphi_\alpha(\vec{r}')\Big)\varphi_\beta(\vec{r})\Big]$$

$$- \epsilon_\alpha\varphi_\alpha(\vec{r})\Big\}$$

So the extremum of $\mathcal{E}\{\phi\}$ is given by its stationarity

$$\delta\mathcal{E}\{\phi\} = 0.$$

Thus we find an equation for each $\delta\varphi^\dagger_\alpha(\vec{r})$ coefficient $\Rightarrow$

$$\boxed{\begin{aligned} & t(\vec{p},\vec{r})\,\varphi_\alpha(\vec{r}) \\ & \quad + {\sum_\beta}' \int d^3r' \left[\varphi^\dagger_\beta(\vec{r}\,')\,V(|\vec{r}-\vec{r}\,'|)\,\varphi_\beta(\vec{r}\,')\right]\varphi_\alpha(\vec{r}) \\ & \quad - {\sum_\beta}' \int d^3r' \left[\varphi^\dagger_\beta(\vec{r}\,')\,V(|\vec{r}-\vec{r}\,'|)\,\varphi_\alpha(\vec{r}\,')\right]\varphi_\beta(\vec{r}) \\ & \qquad = \epsilon_\alpha\,\varphi_\alpha(\vec{r}) \end{aligned}}$$

These integro-differential equations are the <u>Hartree–Fock equations</u>. There is one equation for each α. The one-body term t includes the single particle KE as well as any external one-body potential (U). The first sum over β (called the direct term) also acts like an effective one-body potential. The second sum includes exchange effects (called the exchange term).

We can study the general properties

of the H-ϕ equations, We expect solutions only for certain eigenvalues ϵ_α. Projecting the equations onto the $\langle \varphi_\gamma |$ state (i.e. in coordinate space we act with $\int d^3r\, \varphi_\gamma^\dagger(\vec{r})$ on the equation) we find the H-ϕ equations for

$$\langle \varphi_\gamma | t | \varphi_\alpha \rangle + \sum_\beta \Big[\langle \varphi_{\gamma,\beta} | V | \varphi_{\alpha,\beta} \rangle - \langle \varphi_{\gamma,\beta} | V | \varphi_{\beta,\alpha} \rangle \Big\} = \epsilon_\alpha \langle \varphi_\gamma | \varphi_\alpha \rangle$$

with

$$\langle \varphi_{\alpha,\beta} | V | \varphi_{\gamma,\delta} \rangle \equiv \int d^3r\, d^3r'\, \varphi_\alpha^\dagger(\vec{r})\, \varphi_\beta^\dagger(\vec{r}\,')\, V(|\vec{r}-\vec{r}\,'|)\, \varphi_\gamma(\vec{r})\, \varphi_\delta(\vec{r}\,') \, .$$

Now we have various general properties

1) Hermiticity properties

Since $t^\dagger = t \Rightarrow \langle\varphi_\gamma|t|\varphi_\alpha\rangle^* = \langle\varphi_\alpha|t|\varphi_\gamma\rangle$

and $V^\dagger = V \Rightarrow \langle\varphi_{\gamma,\delta}|V|\varphi_{\alpha,\beta}\rangle^* = \langle\varphi_{\alpha,\beta}|V|\varphi_{\gamma,\delta}\rangle$

Now we can use the $\vec{r} \leftrightarrow \vec{r}\,'$ symmetry of V to find

$$\langle\varphi_{\alpha,\beta}|V|\varphi_{\gamma,\delta}\rangle = \int d^3r\, d^3r'\, \varphi_\alpha^\dagger(\vec{r})\varphi_\beta^\dagger(\vec{r}\,') \times V(|\vec{r}-\vec{r}\,'|)\varphi_\gamma(\vec{r})\varphi_\delta(\vec{r}\,')$$

(let $\vec{r} \leftrightarrow \vec{r}\,'$) $$= \int d^3r\, d^3r'\, \varphi_\alpha^\dagger(\vec{r}\,')\varphi_\beta^\dagger(\vec{r})V(|\vec{r}-\vec{r}\,'|)\varphi_\gamma(\vec{r}\,')\varphi_\delta(\vec{r})$$

$$= \langle\varphi_{\beta,\alpha}|V|\varphi_{\delta,\gamma}\rangle \,.$$

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2) $\epsilon_\alpha = \epsilon_\alpha^*$, reality of the eigenvalues.

let $\alpha = \gamma$ in the H-ϕ equations $\Rightarrow$

$$\langle\varphi_\alpha|t|\varphi_\alpha\rangle + \sum_\beta{}' \left[\langle\varphi_{\alpha,\beta}|V|\varphi_{\alpha,\beta}\rangle - \langle\varphi_{\alpha,\beta}|V|\varphi_{\beta,\alpha}\rangle\right]$$

$$= \epsilon_\alpha\langle\varphi_\alpha|\varphi_\alpha\rangle \,.$$

Taking the complex conjugate and using the Hermiticity properties $\Rightarrow$

$$\langle \varphi_\alpha | t | \varphi_\alpha \rangle + \sum_\beta{}' \Big[\langle \varphi_{\alpha,\beta} | V | \varphi_{\alpha,\beta} \rangle - \langle \varphi_{\beta,\alpha} | V | \varphi_{\alpha,\beta} \rangle \Big] = \epsilon_\alpha^* \langle \varphi_\alpha | \varphi_\alpha \rangle$$

but we had $\langle \varphi_{\beta,\alpha} | V | \varphi_{\alpha,\beta} \rangle = \langle \varphi_{\alpha,\beta} | V | \varphi_{\beta,\alpha} \rangle$

$\Rightarrow$

$$\langle \varphi_\alpha | t | \varphi_\alpha \rangle + \sum_\beta{}' \Big[\langle \varphi_{\alpha,\beta} | V | \varphi_{\alpha,\beta} \rangle - \langle \varphi_{\alpha,\beta} | V | \varphi_{\beta,\alpha} \rangle \Big] = \epsilon_\alpha^* \langle \varphi_\alpha | \varphi_\alpha \rangle .$$

So subtracting the 2 equations $\Rightarrow$

$$0 = (\epsilon_\alpha - \epsilon_\alpha^*) \langle \varphi_\alpha | \varphi_\alpha \rangle$$

$$\Rightarrow \epsilon_\alpha = \epsilon_\alpha^* .$$

3) Orthogonality of the φ_α.

The H-ϕ equation

$$\langle \varphi_\gamma | t | \varphi_\alpha \rangle + \sum_\beta{}' \Big[\langle \varphi_{\gamma,\beta} | V | \varphi_{\alpha,\beta} \rangle - \langle \varphi_{\gamma,\beta} | V | \varphi_{\beta,\alpha} \rangle \Big]$$

$$= \epsilon_\alpha \langle \varphi_\gamma | \varphi_\alpha \rangle$$ becomes upon

$\alpha \Leftrightarrow \gamma$ interchange

$$\langle \varphi_\alpha | t | \varphi_\gamma \rangle + \sum_\beta{}' \Big[\langle \varphi_{\alpha,\beta} | V | \varphi_{\gamma,\beta} \rangle - \langle \varphi_{\alpha,\beta} | V | \varphi_{\beta,\gamma} \rangle \Big]$$

$$= \epsilon_\gamma \langle \varphi_\alpha | \varphi_\gamma \rangle .$$

Taking the complex conjugate of this yields

$$\langle \varphi_\gamma | t | \varphi_\alpha \rangle + \sum_\beta{}' \Big[\langle \varphi_{\gamma,\beta} | V | \varphi_{\alpha,\beta} \rangle - \underbrace{\langle \varphi_{\beta,\gamma} | V | \varphi_{\alpha,\beta} \rangle}_{= \langle \varphi_{\gamma,\beta} | V | \varphi_{\beta,\alpha} \rangle} \Big]$$

$$= \underbrace{\epsilon_\gamma^*}_{= \epsilon_\gamma} \langle \varphi_\gamma | \varphi_\alpha \rangle$$

Subtracting the 2 equations $\Rightarrow$

$$0 = (\epsilon_\alpha - \epsilon_\gamma)\langle\varphi_\gamma|\varphi_\alpha\rangle .$$

So if $\epsilon_\alpha \neq \epsilon_\gamma \Rightarrow \langle\varphi_\gamma|\varphi_\alpha\rangle = 0$,

that is $\int d^3r\, \varphi_\gamma^\dagger(\vec{r})\varphi_\alpha(\vec{r}) = 0$.

Note: if ϵ_α is degenerate we can use the Gram-Schmidt method to construct othogonal wavefunctions in the degenerate subspaces. So combining this with our normalization we have

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

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4) ϵ_α and the groundstate energy E.

Set $\alpha=\gamma$ in the H-ϕ equation to find

$$\langle\varphi_\alpha|t|\varphi_\alpha\rangle + \sum_\beta{}^{f}\Big[\langle\varphi_{\alpha,\beta}|V|\varphi_{\alpha,\beta}\rangle - \langle\varphi_{\alpha,\beta}|V|\varphi_{\beta,\alpha}\rangle\Big]$$

$$= \epsilon_\alpha \underbrace{\langle\varphi_\alpha|\varphi_\alpha\rangle}_{=1} = \epsilon_\alpha$$

Defining
$$t_\alpha \equiv \langle \varphi_\alpha | t | \varphi_\alpha \rangle$$
$$V_\alpha \equiv \sum_\beta{}' \left[\langle \varphi_{\alpha,\beta} | V | \varphi_{\alpha,\beta} \rangle - \langle \varphi_{\alpha,\beta} | V | \varphi_{\beta,\alpha} \rangle \right]$$

we have
$$\epsilon_\alpha = t_\alpha + V_\alpha \ .$$

So from page -1308-, we see that the Hartree-Fock estimate of the ground state energy is just given by $\mathcal{E}[\Phi]\Big|_{\substack{H-\phi \\ \delta\mathcal{E}=0.}} = E$

$$E = \sum_\alpha{}' t_\alpha + \frac{1}{2} \sum_\alpha{}' V_\alpha \ .$$

Example: Uniform Fermi Gas

(This is a model for
1) electrons in a metal
2) nucleons in nuclear matter
3) neutrons in a neutron star
4) electrons in a white dwarf star.)

Consider the system to be placed in a box of volume Ω. To begin we take non-interacting fermions; so

$$t = -\frac{\hbar^2}{2m}\nabla^2 \;,\; V = 0.$$

The H-ϕ equations simplify (page -1312-)

$$-\frac{\hbar^2}{2m}\nabla^2 \varphi_{\vec{k}\lambda}(\vec{r}) = \epsilon_{\vec{k}\lambda}\,\varphi_{\vec{k}\lambda}(\vec{r}),$$

where we let $\alpha = \vec{k}\lambda$

$\hbar\vec{k}$ = momentum

spin projection ± 1, $= \uparrow$ or $\downarrow$

The plane wave solution to this equation is given by

$$\varphi_{\vec{k}\lambda}(\vec{r}) = \frac{1}{\sqrt{\Omega}}\, e^{i\vec{k}\cdot\vec{r}}\, \chi_\lambda$$

with $\chi_\uparrow = \begin{pmatrix}1\\0\end{pmatrix}$ and $\chi_\downarrow = \begin{pmatrix}0\\1\end{pmatrix}$ and

$$\epsilon_{\vec{k}\lambda} = \frac{\hbar^2 \vec{k}^2}{2m}.$$

Since the fermions are in a box, we impose periodic boundary conditions

$$k_i = \frac{2\pi}{L} n_i \quad ; \; n_i = 0, 1, 2, \ldots$$

$$\& \; L^3 = \Omega.$$

The number of states in d^3k is

$$dn = d^3k \frac{\Omega}{(2\pi)^3} \cdot 2 \leftarrow \text{spin } \uparrow \text{ or } \downarrow \text{ degeneracy.}$$

The many body ground state is obtained by filling up the single particle states for spin $\uparrow$ and $\downarrow$ until we reach wavenumber k_F. So the total number of particles (spin $\frac{1}{2}$ fermions) is

$$N = \sum_{\vec{k},\lambda}^{k_F} 1 = 2\frac{\Omega}{(2\pi)^3}\int_{k<k_F} d^3k = 2\frac{\Omega}{(2\pi)^3}\frac{4\pi}{3}k_F^3 .$$

So the particle density $n = \frac{N}{\Omega}$ is simply

$$n = \frac{k_F^3}{3\pi^2} .$$

The total energy is

$$E = \sum_\alpha t_\alpha = \sum_\alpha \langle \varphi_\alpha | t | \varphi_\alpha \rangle$$

$$= \sum_{\vec{k}\lambda}^{k_F} \frac{\hbar^2 \vec{k}^2}{2m} = \frac{\hbar^2}{2m} 2 \frac{\Omega}{(2\pi)^3}\int_{k<k_F} d^3k\, \vec{k}^2$$

$$= \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} N .$$

So the energy per particle is $\frac{E}{N}$

$$\frac{E}{N} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m}.$$

Next, we consider the fermions to interact via a two-body potential

$$V = \frac{1}{2}\sum_{i,j=1}^{N}{}' V(|\vec{r}_i - \vec{r}_j|).$$

The H-ϕ equations become

$$\boxed{\begin{aligned} &-\frac{\hbar^2}{2m}\nabla^2 \varphi_{\vec{k}\lambda}(\vec{r}) \\ &+\sum_{\vec{k}'\lambda'}{}' \int d^3r' \left[\varphi^{\dagger}_{\vec{k}'\lambda'}(\vec{r}')V(|\vec{r}-\vec{r}'|)\varphi_{\vec{k}'\lambda'}(\vec{r}')\right]\varphi_{\vec{k}\lambda}(\vec{r}) \\ &-\sum_{\vec{k}'\lambda'}{}' \int d^3r' \left[\varphi^{\dagger}_{\vec{k}'\lambda'}(\vec{r}')V(|\vec{r}-\vec{r}'|)\varphi_{\vec{k}\lambda}(\vec{r}')\right]\varphi_{\vec{k}'\lambda'}(\vec{r}) \\ &= \epsilon_{\vec{k}\lambda}\varphi_{\vec{k}\lambda}(\vec{r}) \end{aligned}}$$

Since the potential is translationally invariant, we can try to solve

The H-ϕ equations by means of plane waves again.

The first sum is the <u>direct</u> <u>term</u>

$$V_D(\vec{r}) = \sum_{\vec{k}'\lambda'}{}' \int d^3r'\, \varphi^{\dagger}_{\vec{k}'\lambda'}(\vec{r}')\, V(|\vec{r}-\vec{r}'|)\, \varphi_{\vec{k}'\lambda'}(\vec{r}')$$

$$= \sum_{\vec{k}'\lambda'}{}' \int d^3r' \frac{1}{\sqrt{\Omega}} e^{-i\vec{k}'\cdot\vec{r}'} \chi^{\dagger}_{\lambda'} V(|\vec{r}-\vec{r}'|) \times \frac{1}{\sqrt{\Omega}} e^{+i\vec{k}'\cdot\vec{r}'} \chi_{\lambda'}$$

Now $\chi^{\dagger}_{\lambda'} \chi_{\lambda'} = 1$, so this gives

$$V_D(\vec{r}) = \frac{1}{\Omega} \underbrace{\sum_{\vec{k}'\lambda'}{}'}_{=N} \int d^3r'\, V(|\vec{r}-\vec{r}'|)$$

$$= \frac{N}{\Omega} \int d^3r''\, V(|\vec{r}''|) \, .$$

So $\boxed{V_D(\vec{r}) = n \int d^3r''\, V(|\vec{r}''|)}$ independent of $\vec{r}$.

The second sum is the <u>exchange</u> <u>term</u>

$$\sum_{\vec{k}'\lambda'}' \int d^3r' \left[\varphi^{\dagger}_{\vec{k}'\lambda'}(\vec{r}\,')V(|\vec{r}-\vec{r}\,'|)\varphi_{\vec{k}\lambda}(\vec{r}\,')\right]\varphi_{\vec{k}'\lambda'}(\vec{r})$$

$$= \sum_{\vec{k}'\lambda'}' \int d^3r' \left[\frac{1}{\sqrt{\Omega}} e^{-i\vec{k}'\cdot\vec{r}\,'}\chi^{\dagger}_{\lambda'} V(|\vec{r}-\vec{r}\,'|)\frac{1}{\sqrt{\Omega}} e^{+i\vec{k}\cdot\vec{r}\,'}\chi_{\lambda}\right]$$

$$\times \frac{1}{\sqrt{\Omega}} e^{i\vec{k}'\cdot\vec{r}}\chi_{\lambda'}$$

Again $\chi^{\dagger}_{\lambda'}\chi_{\lambda} = \delta_{\lambda\lambda'}$, so this becomes

$$= \sum_{\vec{k}'\lambda'}' \frac{1}{\Omega}\delta_{\lambda\lambda'}\int d^3r' e^{i(\vec{k}-\vec{k}')\cdot\vec{r}\,'} V(|\vec{r}-\vec{r}\,'|) \times$$

$$\times \frac{1}{\sqrt{\Omega}} e^{+i\vec{k}'\cdot\vec{r}} \underbrace{\chi_{\lambda'}}_{=\chi_{\lambda} \text{ due to } \delta_{\lambda\lambda'}}$$

let $\vec{r}\,'' = \vec{r}-\vec{r}\,'$, and this yields

$$= \sum_{\vec{k}'\lambda'}' \frac{1}{\Omega}\delta_{\lambda'\lambda}\int d^3r'' e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}\,'')} V(|\vec{r}\,''|) \times$$

$$\times \frac{1}{\sqrt{\Omega}} e^{i\vec{k}'\cdot\vec{r}}\chi_{\lambda}$$

pulling out the $e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} e^{i\vec{k}'\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}}$

we finally get

$$= \sum_{\vec{k}'\lambda'} \frac{1}{\Omega} \delta_{\lambda\lambda'} \int d^3r'' \, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}''} V(|\vec{r}''|) \times$$

$$\times \underbrace{\frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} \chi_\lambda}_{= \varphi_{\vec{k}\lambda}(\vec{r})}$$

$$\equiv \tilde{V}_E(\vec{k}) \varphi_{\vec{k}\lambda}(\vec{r})$$

with

$$\tilde{V}_E(\vec{k}) = \sum_{\vec{k}'\lambda'} \frac{1}{\Omega} \delta_{\lambda\lambda'} \int d^3r'' \, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}''} V(|\vec{r}''|)$$

which is roughly the Fourier transform of the potential.

So the H-ϕ equation becomes

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V_D(\vec{r}) - \tilde{V}_E(\vec{k})\right]\varphi_{\vec{k}\lambda}(\vec{r}) = \epsilon_{\vec{k}\lambda}\varphi_{\vec{k}\lambda}(\vec{r})}$$

For plane waves $\varphi_{\vec{k}\lambda}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} \chi_\lambda$
this reduces to

$$\epsilon_{\vec{k}\lambda} = \frac{\hbar^2 \vec{k}^2}{2m} + \overset{=\frac{N}{\Omega} = \frac{1}{\Omega}\sum'_{\vec{k}'\lambda'} 1}{n} \int d^3r' \, V(|\vec{r}'|)$$

$$- \sum'_{\vec{k}'\lambda'} \frac{1}{\Omega} \delta_{\lambda\lambda'} \int d^3r' \, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}'} V(|\vec{r}'|)$$

That is

$$\boxed{\epsilon_{\vec{k}\lambda} = \frac{\hbar^2 \vec{k}^2}{2m} + \sum'^{k_F}_{\vec{k}'\lambda'} \frac{1}{\Omega} \int d^3r \, V(|\vec{r}|) \times \Big[\underset{\text{Direct term}}{1} - \underbrace{\delta_{\lambda\lambda'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}}_{\text{exchange term}} \Big]}$$

So we find that indeed the plane wave is a solution to the H-F equation for translationally invariant systems.

Note that the exchange term contributes <u>only when</u> $\lambda' = \lambda$, for a spin independent potential

Although possible, as we have seen the use of many body wavefunctions is somewhat cumbersome, if not tedious. An alternate and much more compact formalism is to use creation and annihilation operators to form the N-particle states from the no-particle or ground state.

Thus the fermion many body states will be given by creation operators $c_\alpha^\dagger$ operating on the no-particle (vacuum) state $|0\rangle$ so that

$$|\varphi_\alpha\rangle \equiv c_\alpha^\dagger |0\rangle$$

$$|\varphi_{\alpha,\beta}\rangle \equiv c_\alpha^\dagger |\varphi_\beta\rangle = c_\alpha^\dagger c_\beta^\dagger |0\rangle$$

$$\vdots$$

$$|\varphi_{\alpha_1 \cdots \alpha_N}\rangle = c_{\alpha_1}^\dagger \cdots c_{\alpha_N}^\dagger |0\rangle .$$

Since these states are antisymmetric under interchange of identical particles

$$|\varphi_{\alpha,\beta}\rangle = -|\varphi_{\beta,\alpha}\rangle$$

$$\Rightarrow \quad c_\alpha^\dagger c_\beta^\dagger = -c_\beta^\dagger c_\alpha^\dagger$$

or taking the hermitian conjugate ⇒

$$\{c_\alpha, c_\beta\} = 0 = \{c_\alpha^\dagger, c_\beta^\dagger\}$$

The creation operators, $c_\alpha^\dagger$, and the annihilation operators, c_α, separately anti-commute. This is a reflection of the Pauli-Exclusion Principle.

In addition the single particle states are normalized

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

hence $\langle 0 | c_\alpha c_\beta^\dagger | 0 \rangle = \delta_{\alpha\beta}$

This suggests that $\{c_\alpha, c_\beta^\dagger\} = \delta_{\alpha\beta}$

and $c_\alpha |0\rangle = 0$. This is proved by considering

$$\langle \varphi_{\alpha\alpha_1\cdots\alpha_N} | c_\alpha^\dagger | \varphi_{\alpha_1\cdots\alpha_N} \rangle$$

$$= \langle \varphi_{\alpha\alpha_1\cdots\alpha_N} | \varphi_{\alpha\alpha_1\cdots\alpha_N} \rangle = 1$$

further $\langle \varphi_{\alpha_1\cdots\alpha_N} | c_\alpha^\dagger | \varphi_{\beta_1\cdots\beta_M} \rangle = 0$

if $\langle \varphi_{\alpha_1\cdots\alpha_N} | \varphi_{\alpha\beta_1\cdots\beta_M} \rangle = 0$.

and by the Pauli Exclusion principle

$$C_\alpha^+ |\varphi_{\alpha\alpha_1\cdots\alpha_N}\rangle = 0 .$$

Hence we have

$$\langle\varphi_{\alpha_1\cdots\alpha_N}|C_\alpha|\varphi_{\alpha\alpha_1\cdots\alpha_N}\rangle = 1$$

$$\langle\varphi_{\alpha_1\cdots\alpha_N}|C_\alpha|\varphi_{\beta_1\cdots\beta_M}\rangle = 0$$

if $\langle\varphi_{\beta_1\cdots\beta_M}|\varphi_{\alpha\alpha_1\cdots\alpha_N}\rangle = 0$

and $\langle\varphi_{\alpha\alpha_1\cdots\alpha_N}|C_\alpha|\varphi_{\beta_1\cdots\beta_M}\rangle = 0.$

For $|\varphi_{\beta_1\cdots\beta_M}\rangle = |0\rangle \Rightarrow \langle\varphi_{\alpha_1\cdots\alpha_N}|C_\alpha|0\rangle = 0$

$\Rightarrow C_\alpha|0\rangle$ is $\perp$ to all vectors in which $\alpha_i \neq \alpha$.

As well $\langle\varphi_{\alpha\alpha_1\cdots\alpha_N}|C_\alpha|0\rangle = 0 \Rightarrow$

$C_\alpha|0\rangle$ is $\perp$ to all vectors in which α is occupied.

$$\Rightarrow \quad C_\alpha|0\rangle = 0.$$

Further then we have that

$C_\alpha|\alpha\rangle = |0\rangle$ and so on.

So we find that the creation and annihilation operators obey the CAR

$$\{C_\alpha, C_\beta^\dagger\} = \delta_{\alpha\beta}$$

$$\{C_\alpha, C_\beta\} = 0 = \{C_\alpha^\dagger, C_\beta^\dagger\}$$

Hence the number operator for the α-type particle state is $N_\alpha = C_\alpha^\dagger C_\alpha$ and the total # operator is

$$N = \sum_\alpha C_\alpha^\dagger C_\alpha \quad .$$

The wavefunctions are given by

$$\varphi_\alpha(\vec{r}) = \langle \vec{r} | \varphi_\alpha \rangle = \langle \vec{r} | C_\alpha^\dagger | 0 \rangle$$

and so on. We can define <u>second quantized</u> operators in coordinate space by expanding the C_α in terms of $\varphi_\alpha(\vec{r})$ i.e.

$$\psi(\vec{r}) \equiv \sum_\alpha \varphi_\alpha(\vec{r}) C_\alpha$$

$$\psi^\dagger(\vec{r}) = \sum_\alpha \varphi_\alpha^\dagger(\vec{r}) C_\alpha^\dagger \quad .$$

The completeness of the $\varphi_\alpha(\vec{r})$ single particle wave functions and the CAR $\Rightarrow$

$$\{\psi(\vec{x}), \psi^\dagger(\vec{y})\}$$

$$= \sum_\alpha{}' \sum_\beta{}' \varphi_\alpha(\vec{x})\varphi_\beta^\dagger(\vec{y}) \underbrace{\{C_\alpha, C_\beta^\dagger\}}_{=\delta_{\alpha\beta}}$$

$$= \sum_\alpha{}' \varphi_\alpha(\vec{x})\varphi_\alpha^\dagger(\vec{y})$$

$$= \delta^3(\vec{x}-\vec{y})$$

and $\psi^\dagger(\vec{r})\psi(\vec{r})$ is the <u>number density</u> operator so

$$N = \int d^3r\, \psi^\dagger(\vec{r})\psi(\vec{r}) .$$

The Hamiltonian can then be written in second quantized form as

$$H = \sum_\alpha{}' \sum_\beta{}' \langle \varphi_\alpha | t | \varphi_\beta \rangle C_\alpha^\dagger C_\beta$$

$$+ \frac{1}{2}\sum_\alpha{}' \sum_\beta{}' \langle \varphi_{\alpha,\beta} | V | \varphi_{\alpha,\beta} \rangle C_\alpha^\dagger C_\alpha C_\beta^\dagger C_\beta$$

One can directly verify that the many body matrix elements of this operator reproduces the matrix elements we found earlier.

$$\langle \varphi_{\alpha_1 \cdots \alpha_N} | H | \varphi_{\alpha_1 \cdots \alpha_N} \rangle$$

$$= \langle 0 | C_{\alpha_N} \cdots C_{\alpha_1} H C^{+}_{\alpha_1} \cdots C^{+}_{\alpha_N} | 0 \rangle$$

$$= \langle H \rangle$$ (page -1302- to -1306-).

The utility of this <u>second quantized</u> approach becomes apparent when working through specific examples encountered in Many-Body Physics (i.ex. BCS theory). It becomes a necessity when dealing with relativistic quantum field theory, since the Number operator is no longer conserved.
