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

$$\phi = \frac{1}{\sqrt{N!}} \left| \begin{array}{c} \psi_1(1) \cdots \psi_1(N) \\
\vdots \\
\psi_N(1) \cdots \psi_N(N) \end{array} \right| .$$

Form the energy functional

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

Choosing the normalization of $|\phi\rangle$ so that $\langle \phi | \phi \rangle = 1$, we desire to minimize $E[\phi]$. Thus we minimize $E[\phi] = \langle \phi | H | \phi \rangle$ subject to the constraint $\langle \phi | \phi \rangle = 1.$
Hence we will obtain an equation for the single-particle state \( |\psi_0\rangle\) 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

\[
T = \sum_i T_i \equiv \sum_i \hat{p}_i \hat{c}_i
\]

\[
V = \frac{1}{2} \sum_{i,j} V(i,j)
\]

Using our previous results, we find

\[
\mathcal{E} \Phi = \sum_i \langle \psi_0 | \hat{c}_i | \psi_0 \rangle + \frac{1}{2} \sum_{i,j} \left[ \langle \psi_{\alpha,\beta} | V | \psi_{\alpha,\beta} \rangle \langle \psi_{\alpha,\beta} | \right] - \langle \psi_{\alpha,\beta} | V | \psi_{\alpha,\beta} \rangle
\]

which recall is given by
\[ S \Phi = \sum \int d^3r \left[ \psi_\alpha^\dagger (\vec{r}) \psi_\alpha (\vec{r}) + \left( \bar{\psi}_\alpha (\vec{r}) \right) \bar{\psi}_\alpha (\vec{r}) \right] \\
+ \frac{i}{2} \sum_{\alpha, \beta} \int d^3r \int d^3r' \left[ \psi_\alpha^\dagger (\vec{r}) \psi_\beta^\dagger (\vec{r'}) V(\vec{r} - \vec{r'}) \left( \bar{\psi}_\beta^\dagger (\vec{r'}) \bar{\psi}_\alpha (\vec{r}) \right) \right] \\
\times \left[ \psi_\alpha^\dagger (\vec{r}) \bar{\psi}_\beta (\vec{r'}) - \bar{\psi}_\beta (\vec{r'}) \psi_\alpha (\vec{r}) \right]. \]

We treat \( \psi_\alpha^\dagger \psi_\alpha \) as independent and perform the variations

\[ \psi_\alpha \rightarrow \psi_\alpha + \delta \psi_\alpha \]
\[ \psi_\alpha^\dagger \rightarrow \psi_\alpha^\dagger + \delta \psi_\alpha^\dagger \]

Varying \( \psi_\alpha \) gives

\[ \delta S \Phi = \sum \int d^3r \left[ \delta \psi_\alpha^\dagger (\vec{r}) \right] \psi_\alpha (\vec{r}) \]

\[ + \frac{i}{2} \sum_{\alpha, \beta} \int d^3r \int d^3r' \left[ \delta \psi_\alpha^\dagger (\vec{r}) \psi_\alpha^\dagger (\vec{r'}) \left( \bar{\psi}_\beta (\vec{r'}) \bar{\psi}_\beta (\vec{r}) \right) \right] \\
\times V(\vec{r} - \vec{r'}) \left[ \psi_\alpha^\dagger (\vec{r}) \bar{\psi}_\beta (\vec{r'}) - \bar{\psi}_\beta (\vec{r'}) \psi_\alpha (\vec{r}) \right]. \]
But $V\left(|F^\perp\psi^\perp\right) = V\left(|F^\perp\psi^\perp\right)$, so changing the dummy variable $F^\perp \rightarrow F^\perp$, $\omega \rightarrow \beta$, the $\delta\phi^+_\alpha (F^\perp) \delta\phi^+_\beta (F^\perp)$ term equals the $\delta\phi^+_\alpha (F^\perp) \delta\phi^+_\beta (F^\perp)$ term, cancelling the $\Xi$. So

$$\delta\Xi = \frac{1}{\Xi} \int \prod_{\alpha} d^3\mathbf{r} \delta\phi^+_\alpha (F^\perp) \Xi (F^\perp) \phi^+_\alpha (F^\perp)$$

$$+ \sum_{\alpha, \beta} \int \prod_{\alpha, \beta} d^3\mathbf{r} \delta\phi^+_\alpha (F^\perp) \delta\phi^+_\beta (F^\perp) V (F^\perp F^\perp') \phi^+_\alpha (F^\perp') \phi^+_\beta (F^\perp')$$

$$- \sum_{\alpha, \beta} \int \prod_{\alpha, \beta} d^3\mathbf{r} \delta\phi^+_\alpha (F^\perp) \delta\phi^+_\beta (F^\perp) V (F^\perp F^\perp') \phi^+_\beta (F^\perp') \phi^+_\alpha (F^\perp')$$

In addition we must require that $\langle \phi \phi \rangle = 1$, i.e. the single particle wavefunction are normalized to 1

$$1 = \int \prod_{\alpha} d^3\mathbf{r} \phi^+_\alpha (F^\perp) \phi^+_\alpha (F^\perp')$$

Varying this with $\delta\phi^+_\alpha (F^\perp)$:

$$0 = \int \prod_{\alpha} d^3\mathbf{r} \delta\phi^+_\alpha (F^\perp) \phi^+_\alpha (F^\perp')$$

(more correctly we need Lagrange multipliers for $\delta\phi^+_\alpha = \int \prod_{\alpha} d^3\mathbf{r} \phi^+_\alpha \phi^+_\beta$, see Messiah Vol. II page 77 (e))
In order to include this constraint on the wavefunction in the variation of \( E \phi^3 \), it is easiest to use a Lagrange multiplier \( E_x \) term added to \( E \phi^3 \):

\[
\sum_i \int d^3r \ E_x \phi^+ \phi \phi
\]

and then vary \( \phi^+ \phi \) unrestrictedly. So we get

\[
\delta E \phi^3 = \sum_i \int d^3r \ \delta \phi^+ \phi \left\{ + (E_x \phi) \phi \right\}
\]

\[
+ \sum_i \int d^3r \ \left[ (\phi^+ \phi) V(\mathbf{r} - \mathbf{r}') \phi \phi \right]
\]

\[
- (\phi^+ \phi) V(\mathbf{r} - \mathbf{r}') \phi \phi
\]

\[
- E_x \phi \phi
\]

So the extremum of \( E \phi^3 \) is given by its stationarity:

\[
\delta E \phi^3 = 0.
\]
Thus we find an equation for each $\Delta \Psi_\alpha (\vec{r})$

$$T (\vec{r}, \vec{r}') \Psi_\alpha (\vec{r}')$$

$$+ \sum_\beta \int d^3r \left[ \Psi_\beta (\vec{r}) V (\vec{r} - \vec{r}') \Psi_\beta (\vec{r}') \right] \Psi_\alpha (\vec{r}')$$

$$- \sum_\beta \int d^3r \left[ \Psi_+ \beta (\vec{r}') V (\vec{r} - \vec{r}') \Psi_\beta (\vec{r}') \right] \Psi_\alpha (\vec{r}')$$

$$= \epsilon_\alpha \Psi_\alpha (\vec{r})$$

These integro-differential equations are the Hartree-Fock equations. There is one equation for each $\alpha$. The one-body term $T$ includes the single-particle KE as well as any external one-body potential $U$. The first sum over $\beta$ (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 \( H - \Phi \) equations. We expect solutions only for certain eigenvalues \( E_\alpha \). Projecting the equations onto the \( \langle \Phi_\alpha | \rangle \) states (i.e., in coordinate space we act with \( \frac{\partial^2}{\partial \bar{\tau}^2} \Phi^+_\alpha (\bar{\tau}) \) on the equation) we find the \( H - \Phi \) equations for

\[
\langle \Phi_\alpha \pm i \Phi_\alpha \rangle + \sum_\beta \left[ \langle \Phi_\alpha, \beta | V | \Phi_\beta, \alpha \rangle \right.
\]

\[
- \langle \Phi_\alpha, \beta | V | \Phi_\beta, \alpha \rangle \left. \right] \right\}
\]

\[
= E_\alpha \langle \Phi_\alpha | \Phi_\alpha \rangle
\]

with

\[
\langle \Phi_\alpha, \beta | V | \Phi_\beta, \alpha \rangle = \int d^3x \, d^3\bar{x} \, (\Phi^+_\alpha (\bar{x}) \Phi^+_\beta (\bar{x}) V(x = \bar{x}) \Phi_\beta (x) \Phi_\alpha (\bar{x}))
\]

Now we have various general properties:

1) Hermiticity properties
Since $E^+ = E \Rightarrow \langle \psi_8 | E^{+} | \psi_8 \rangle^* = \langle \psi_8 | E | \psi_8 \rangle$
and $V^+ = V \Rightarrow \langle \psi_8, s | V | \phi_{\alpha, \beta} \rangle^* = \langle \psi_8, s | V | \phi_{\alpha, \beta} \rangle$

Now we can use the $\overrightarrow{\rightarrow}$ symmetry of $V$
to find

\[
\langle \psi_{\alpha, \beta} | V | \psi_{s, s} \rangle = \int d^3r \int d^3r' \langle \psi_{\alpha}^+ (\mathbf{r}) | V (\mathbf{r} - \mathbf{r}') | \psi_{\beta}^+ (\mathbf{r}') \rangle \psi_s (\mathbf{r}') \psi_s (\mathbf{r})
\]

\[
\times V (\mathbf{r} - \mathbf{r}') \psi_s (\mathbf{r}') \psi_s (\mathbf{r})
\]

(lec $\overrightarrow{\rightarrow}$ $\overrightarrow{\rightarrow}$) \[
= \int d^3r \int d^3r' \langle \psi_{\alpha}^+ (\mathbf{r}) | V (\mathbf{r} - \mathbf{r}') | \psi_{\beta}^+ (\mathbf{r}') \rangle \psi_s (\mathbf{r}') \psi_s (\mathbf{r})
\]

\[
= \langle \psi_{\beta, \alpha} | V | \psi_{s, s} \rangle.
\]

2) $E_\alpha = E_\alpha^*$: Reality of the eigenvalues.

Let $\alpha = \gamma$ in the $H - \Phi$ equations $\Rightarrow$

\[
\langle \psi_\alpha | H | \psi_\alpha \rangle + \sum_{\beta} \left[ \langle \psi_{\alpha, \beta} | V | \psi_{\alpha, \beta} \rangle - \langle \psi_{\alpha, \beta} | V | \psi_{\beta, \alpha} \rangle \right]
\]

\[
= E_\alpha \langle \psi_\alpha | \psi_\alpha \rangle.
\]
Taking the complex conjugate and using the Hermiticity properties ⇒

\[ \langle \psi_\alpha | H | \psi_\alpha \rangle + \sum_\beta \left[ \langle \psi_\alpha | H | \psi_{\alpha, \beta} \rangle - \langle \psi_{\beta, \alpha} | H | \psi_{\alpha, \beta} \rangle \right] \]

\[ = \varepsilon_\alpha^* \langle \psi_\alpha | \psi_\alpha \rangle \]

but we had \[ \langle \psi_{\beta, \alpha} | H | \psi_{\alpha, \beta} \rangle = \langle \psi_{\alpha, \beta} | H | \psi_{\beta, \alpha} \rangle \]

⇒

\[ \langle \psi_\alpha | H | \psi_\alpha \rangle + \sum_\beta \left[ \langle \psi_{\alpha, \beta} | H | \psi_{\alpha, \beta} \rangle - \langle \psi_{\beta, \alpha} | H | \psi_{\alpha, \beta} \rangle \right] \]

\[ = \varepsilon_\alpha^* \langle \psi_\alpha | \psi_\alpha \rangle \]

So subtracting the 2 equations ⇒

\[ 0 = (\varepsilon_\alpha - \varepsilon_\alpha^*) \langle \psi_\alpha | \psi_\alpha \rangle \]

⇒ \[ \varepsilon_\alpha = \varepsilon_\alpha^* \]

3) Orthogonality of the $\psi_\alpha$'s.

The HSE equation

$$<\psi_\alpha|\pm|\psi_\alpha> + \sum_\beta \left[<\psi_\alpha,\beta|V|\psi_\beta,\alpha> - <\psi_\beta,\alpha|V|\psi_\beta,\alpha>\right]$$

$$= \epsilon_\alpha <\psi_\alpha|\psi_\alpha> \quad \text{becomes upon}$$

$\alpha \leftrightarrow \beta$ interchange

$$<\psi_\alpha|\pm|\psi_\alpha> + \sum_\beta \left[<\psi_\alpha,\beta|V|\psi_\beta,\beta> - <\psi_\beta,\beta|V|\psi_\beta,\beta>\right]$$

$$= \epsilon_\beta <\psi_\beta|\psi_\beta> \quad .$$

Taking the complex conjugate of this yields

$$<\psi_\beta|\pm|\psi_\alpha> + \sum_\beta \left[<\psi_\beta,\beta|V|\psi_\beta,\alpha> - <\psi_\beta,\alpha|V|\psi_\beta,\alpha>\right]$$

$$= \epsilon_\beta^* <\psi_\beta|\psi_\alpha>$$

$$= \epsilon_\beta$$
Subtracting the equations \( \Rightarrow \)

\[ 0 = (E_\alpha - E_\beta) \langle \psi_\alpha | \psi_\alpha \rangle. \]

So if \( E_\alpha \neq E_\beta \Rightarrow \langle \psi_\alpha | \psi_\alpha \rangle = 0, \)

That is \( \int d^3r \, \psi^*_\alpha(r) \psi_\alpha (r) = 0. \)

Note: if \( E_\alpha \) is degenerate, we can use the Gram-Schmidt method to construct orthogonal wavefunctions in the degenerate subspaces. So combining this with our normalization we have

\[ \langle \psi_\alpha | \psi_\beta \rangle = \delta_{\alpha \beta}. \]

4) \( E_\alpha \) and the ground-state energy \( E. \)

Set \( \alpha = \gamma \) in the H-or equations to find

\[ \langle \psi_\alpha | t \psi_\alpha \rangle + \frac{2i}{\beta} \left[ \langle \psi_\alpha | V | \psi_\beta \rangle \langle \psi_\beta | V | \psi_\alpha \rangle - \langle \psi_\alpha | V | \psi_\beta \rangle \right] \]

\[ = E_\alpha \langle \psi_\alpha | \psi_\alpha \rangle = E_\alpha \]
Defining \[ E_\alpha = \langle \phi_\alpha | H | \phi_\alpha \rangle \]
\[ V_\alpha = \sum \left[ \langle \phi_\alpha | V | \phi_\beta \rangle - \langle \phi_\alpha | V | \phi_\beta, \alpha \rangle \right] \]

we have
\[ E_\alpha = E_\alpha + V_\alpha. \]

So from page -1308-, we see that the Hartree-Fock estimate of the ground state energy is just given by \[ E_\text{HF} = \text{E}\left| \begin{array}{c}
H - \delta
\delta \varepsilon = 0.
\end{array} \right. \]

\[ E = \sum \frac{1}{\alpha} E_\alpha + \frac{1}{2} \sum \frac{1}{\alpha} V_\alpha. \]

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 $\Omega$. To begin we take non-interacting fermions; so

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 \quad V = 0.$$ 

The $H\Phi$ equations simplify (page -132-)

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

where we let $\lambda = \uparrow \downarrow$ spin projection $\pm 1$, $\hbar \mathbf{k} = \text{momentum} = \text{Four}$.

The plane wave solution to this equation is given by

$$\Phi_{k\lambda}(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{A}}} e^{i \mathbf{k} \cdot \mathbf{r}} \chi_{\lambda},$$

with $\chi_{\uparrow} = (1)$ and $\chi_{\downarrow} = (i)$ and

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

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

$$k_{\xi} = \frac{2\pi}{L} n_{\xi} \quad ; \quad n_{\xi} = 0, 1, 2, \ldots$$

and $L^3 = \Omega$. 
The number of states in $d^3k$ is
$$d\mathcal{N} = d^3k \frac{\Omega}{(2\pi)^3} \cdot 2 \quad \text{spin} \uparrow \text{and } \downarrow \quad \text{degeneracy}.$$  

The many body ground state is obtained by filling up all single particle states with spin $\uparrow$ and $\downarrow$ until we reach the Fermi surface $k_F$. So the total number of particles ($\text{spin } \frac{1}{2} \text{ fermions}$) is
$$N = \frac{\Omega k_F^3}{2!} = \frac{2}{(2\pi)^3} \int d^3k = \frac{\Omega}{(2\pi)^3} \frac{4\pi}{3} k_F^3.$$  

So the particle density $n = \frac{N}{\Omega}$ is simply
$$n = \frac{k_F^3}{3\pi^2}.$$  

The total energy is
$$E = \sum_{\alpha} \frac{\hbar^2 k^2_{\alpha}}{2m} = \frac{\hbar^2}{2m} \frac{2}{(2\pi)^3} \int d^3k k^2$$  

$$= \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} N.$$
So the energy per particle is \( \frac{E}{N} \)

\[
\frac{E}{N} = \frac{3}{5} \frac{\hbar^2 k_{\text{F}}^2}{2m}
\]

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

\[
V = \frac{1}{2} \sum_{i<j}^N V(|\vec{r}_i - \vec{r}_j|)
\]

The \( H - \phi \) equations became

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi_{\ell \chi}(\vec{r})
\]

\[
+ \sum_i^N \int d^3r' \left[ \phi_{\ell' \chi'}^+(\vec{r}') V(|\vec{r}-\vec{r}'|) \phi_{\ell \chi}(\vec{r}) \right] \Psi_{\ell \chi}(\vec{r})
\]

\[
- \sum_i^N \int d^3r' \left[ \phi_{\ell' \chi'}^+(\vec{r}') V(|\vec{r}-\vec{r}'|) \phi_{\ell \chi}(\vec{r}) \right] \Psi_{\ell' \chi'}(\vec{r}')
\]

\[
= \epsilon_{\ell \chi} \Psi_{\ell \chi}(\vec{r})
\]

Since the potential is translationally invariant, we can try to solve
The $H-\Phi$ equations by means of plane waves again. The first sum is the direct term

$$V_d(\bar{r}) = \sum \int d^3r' \Phi^+_{h',\chi'}(\bar{r}') V(\bar{r}-\bar{r}') \Phi_{h,\chi}(\bar{r})$$

$$= \sum \int d^3r' \frac{1}{\sqrt{2\Omega}} e^{i\frac{h'r'}{\Omega}} \frac{1}{\sqrt{2\Omega}} e^{-i\frac{h'r}{\Omega}} \chi' \chi$$

Now $\chi', \chi = 1$, so this gives

$$V_d(\bar{r}) = \frac{1}{2\Omega} \sum \int d^3r' V(\bar{r}-\bar{r}')$$

$$= \frac{N}{2\Omega} \int d^3r'' V(\bar{r}''\bar{r})$$

So

$$V_d(\bar{r}) = N \int d^3r'' V(\bar{r}''\bar{r})$$

independent of $\bar{r}$. The second sum is the exchange term.
\[ \sum \int d^3r \int \frac{d^3r'}{(2\pi)^3} \left[ \psi_\alpha^+(r') V(12-1'2') \psi_\beta(r') \right] \psi_\beta^+(r) \]

\[ = \sum \int d^3r \int \frac{d^3r'}{(2\pi)^3} \left[ \frac{1}{\sqrt{2}} e^{i \frac{t_2}{\Omega}} X'_\alpha V(12-1'2') \frac{1}{\sqrt{2}} e^{i \frac{t_1}{\Omega}} X_\beta \right] \]

\[ \times \frac{1}{\sqrt{2 \Omega}} e^{i \frac{t_2}{\Omega}} X' \]

Again \( X'_\alpha X_\beta = \delta \alpha \beta \), so this becomes

\[ = \sum \frac{1}{\sqrt{2 \Omega}} \delta \alpha \beta \int d^3r \int d^3r' \left[ \frac{1}{\sqrt{2}} e^{i \frac{t_2}{\Omega}} V(12-1'2') \right] \]

\[ \times \frac{1}{\sqrt{2 \Omega}} e^{i \frac{t_1}{\Omega}} X' \]

let \( \tau'' = \tau - \tau' \), and this yields

\[ = \sum \frac{1}{\sqrt{2 \Omega}} \delta \alpha \beta \int d^3r'' \left[ \frac{1}{\sqrt{2}} e^{i \frac{t_2}{\Omega}} V(12-1'2') \right] \]

\[ \times \frac{1}{\sqrt{2 \Omega}} e^{i \frac{t_1}{\Omega}} X' \]

pulling out the \( e^{i \frac{t_2}{\Omega}} e^{i \frac{t_1}{\Omega}} = e^{i \frac{t}{\Omega}} \) we finally get
\[ -\frac{\hbar^2}{2m} \nabla^2 + V_d(l) - V_E(l) \psi_{l\alpha}(l) = \epsilon_{l\alpha} \psi_{l\alpha}(l) \]

which is roughly the Fourier transform of the potential.

So the H-\( \phi \) equation becomes
For plane waves, 
\[ \psi_{\mathbf{p}} (\mathbf{r}) = \frac{1}{\sqrt{2\pi}} e^{i \mathbf{p} \cdot \mathbf{r}} \]
This reduces to:
\[ \frac{\mathbf{p}}{\hbar} = \frac{n}{2} = \frac{1}{2} \mathbf{\alpha} \cdot \mathbf{\alpha} \]
\[ E_{\mathbf{p}} = \frac{\hbar^2 \mathbf{p}^2}{2m} + n \int d^3r' \sqrt{(1\pm\mathbf{\alpha}) \cdot \mathbf{p}' \mathbf{p}'^{-1}} \]
\[ -\sum_i \frac{1}{2} \delta_{XX} \int d^3r' e^{-i(\mathbf{r}-\mathbf{r}') \cdot \mathbf{p}'} V(\mathbf{r}'\mathbf{r}) \]
That is:
\[ E_{\mathbf{p}} = \frac{\hbar^2 \mathbf{p}^2}{2m} + \sum_i \frac{1}{2} \frac{1}{\hbar \mathbf{p}'} \int d^3r' V(\mathbf{r}'\mathbf{r}) \]
\[ \times \left[ 1 - \delta_{XX} e^{-i(\mathbf{r}-\mathbf{r}') \cdot \mathbf{p}'} \right] \]
\[ \text{Direct term} \]
\[ \text{Exchange term} \]
So we find that indeed the plane wave is a solution to the \( H \) equation for translationally invariant systems.
Note that the exchange term contributes only when \( \mathbf{r}' = \mathbf{r} \), 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 state from the no-particle or ground state.

Thus the fermion many-body state will be given by creation operators $c_i^+$ operating on the no-particle (vacuum) state $|0\rangle$. So that:

$$|\psi_\alpha\rangle \equiv c_\alpha^+ |0\rangle$$

$$|\psi_\alpha,\beta\rangle \equiv c_\alpha^+ |\psi_\beta\rangle = c_\alpha^+ c_\beta^+ |0\rangle$$

$$|\psi_{\alpha_1,\alpha_2,\ldots,\alpha_N}\rangle = c_{\alpha_1}^+ \cdots c_{\alpha_N}^+ |0\rangle$$.

Since these states are antisymmetric under interchange of identical particles

$$|\psi_\alpha,\beta\rangle = -|\psi_\beta,\alpha\rangle$$

$$\Rightarrow c_\alpha^+ c_\beta^+ = -c_\beta^+ c_\alpha^+$$
Taking the hermitian conjugate:
\[ \{ C_\alpha, C_\beta^\dagger \} = 0 = \{ C_\alpha^\dagger, C_\beta \} \]

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

In addition, the single-particle states are normalized:
\[ \langle \psi_{\alpha} | \psi_{\beta} \rangle = \delta_{\alpha \beta} \]

Hence, \[ \langle 0 | C_\alpha C_\beta^\dagger 10 \rangle = \delta_{\alpha \beta} \]

This suggests that \( \{ C_\alpha, C_\beta^\dagger \} = \delta_{\alpha \beta} \) and \( C_\alpha 10 \rangle = 0 \). This is proved by considering:
\[ \langle \psi_{\alpha_1 \ldots \alpha_n} | C_\alpha^\dagger | \psi_{\beta_1 \ldots \beta_m} \rangle \]
\[ = \langle \psi_{\alpha_1 \ldots \alpha_n} | \psi_{\alpha_1 \ldots \alpha_n} \rangle = 1 \]

Further:
\[ \langle \psi_{\alpha_1 \ldots \alpha_n} | C_\alpha^\dagger | \psi_{\beta_1 \ldots \beta_m} \rangle = 0 \]
\[ \text{if } \langle \psi_{\alpha_1 \ldots \alpha_n} | \psi_{\beta_1 \ldots \beta_m} \rangle = 0 \].

and by Pauli Exclusion principle

\[ C_\alpha |\Psi_{\alpha_1...\alpha_n}\rangle = 0. \]

Hence we have

\[ \langle \Psi_{\alpha_1...\alpha_n} | C_\alpha |\Psi_{\alpha_1...\alpha_n}\rangle = 1 \]

\[ \langle \Psi_{\alpha_1...\alpha_n} | C_\alpha |\Psi_{\beta_1...\beta_m}\rangle = 0. \]

If \[ \langle \Psi_{\beta_1...\beta_m} |\Psi_{\alpha_1...\alpha_n}\rangle = 0 \]

and \[ \langle \Psi_{\alpha_1...\alpha_n} | C_\alpha |\Psi_{\beta_1...\beta_m}\rangle = 0. \]

For \[ |\Psi_{\beta_1...\beta_m}\rangle = |0\rangle \Rightarrow \langle \Psi_{\alpha_1...\alpha_n} | C_\alpha |0\rangle = 0 \]

\[ \Rightarrow C_\alpha |0\rangle \text{ is } \perp \text{ for all vectors in which } \alpha \neq \alpha. \]

As well \[ \langle \Psi_{\alpha_1...\alpha_n} | C_\alpha |0\rangle = 0 \Rightarrow \]

\[ C_\alpha |0\rangle \text{ is } \perp \text{ to all vectors in which } \alpha \text{ is occupied.} \]

\[ \Rightarrow C_\alpha |0\rangle = 0. \]

Further then we have that \[ C_\alpha |\Psi_{\alpha_1...\alpha_n}\rangle = |0\rangle \text{ and so on.} \]
So we find that the creation and annihilation operators obey the CAR
\[ \Sigma C_\alpha, C_\beta^+ \delta_{\alpha\beta} = \delta_{\alpha\beta} \]
\[ \Sigma C_\alpha, C_\beta^+ = 0 = \Sigma C_\alpha^+, C_\beta^+ \]

Hence the number operator for the \( \alpha \)-type particle state is \( \hat{N}_\alpha = C_\alpha^+ C_\alpha \)
and the total number operator is
\[ \hat{N} = \sum_\alpha \hat{N}_\alpha \]

The wavefunctions are given by
\[ \psi_\alpha(\vec{r}) = \langle \vec{r} | \psi_\alpha \rangle = \langle \vec{r} | C_\alpha^+ \mid 0 \rangle \]
and so on. We can define second quantized operators in coordinate space by expanding the \( \hat{C}_\alpha \) in terms of \( \psi_\alpha(\vec{r}) \), i.e.
\[ \hat{C}_\alpha(\vec{r}) \equiv \sum_\alpha \psi_\alpha(\vec{r}) C_\alpha \]
\[ \hat{C}_\alpha^+(\vec{r}) \equiv \sum_\alpha \psi_\alpha^+(\vec{r}) C_\alpha^+ \]
The complement of the $|\Psi\rangle$ single particle wave function and the CAR

\[\varepsilon_\alpha \psi_\alpha(x), \varepsilon_\beta \psi_\beta(y)\]  
\[= \sum_\alpha \sum_\beta \varepsilon_\alpha \psi_\alpha(x) \varepsilon_\beta \psi_\beta(y) \varepsilon_\alpha^{+} \varepsilon_\beta^{+} \delta_{\alpha \beta}\]  
\[= \sum_\alpha \varepsilon_\alpha \psi_\alpha(x) \varepsilon_\alpha^{+} \psi_\alpha(y)\]  
\[= \delta^3(x-y)\]

and $\varepsilon_\alpha^{+} \psi_\alpha(x)$ is the number density operator so

\[N = \int d^3r \varepsilon_\alpha^{+} \psi_\alpha(x) \psi_\alpha(x)\].

The Hamiltonian can then be written in second quantized form as

\[H = \sum_\alpha \sum_\beta \varepsilon_\alpha \varepsilon_\beta^{+} \langle \psi_\alpha \mid 1 \mid \psi_\beta^{+} \rangle \varepsilon_\alpha^{+} \varepsilon_\beta\]

\[+ \frac{1}{2} \sum_\alpha \sum_\beta \varepsilon_\alpha \varepsilon_\beta^{+} \langle \psi_\alpha \mid W \mid \psi_\beta \rangle \varepsilon_\alpha^{+} \varepsilon_\beta^{+} \varepsilon_\alpha \varepsilon_\beta\]
One can directly verify that the many-body matrix elements of this operator reproduce the matrix elements we found earlier.

\[ \langle \psi_{k_1 ... k_n} | H | \psi_{k_1 ... k_n} \rangle \]
\[ = \langle 0 | C_{k_1} ... C_{k_n} H C_{k_1}^{+} ... C_{k_n}^{+} | 0 \rangle \]
\[ = \langle H \rangle \quad (\text{page 1302-6-1306}) \]

The utility of this second quantized approach becomes apparent when working through specific examples encountered in Many-Body Physics (e.g., BCS theory). It becomes necessary when dealing with relativistic Quantum Field Theory since the number operator is no longer conserved.