Density Functional Theory

Chapter 1

The Hohenberg-Kohn Theorem

The Hohenberg-Kohn Theorem allows for the systematic formulation of a many body problem (interacting electrons in an external potential) in terms of the electon density as the basic variable. Let us emphasize would it be advantage of this approach over "direct" approach of solving the Schrödinger equation and then extracting physical quantities in which we are interested in.

Consider the Schródinger equation for N interacting electrons. This is a differential equation for a complex quantity, the wavefunction, which in three dimensions is a function of $3N$ variables This large number makes it impractical to solve even for just the ground-state wavefunction, which will generallay be insufficient, as we need informationabout the excited states. Moreover, the physical quantities in which we are interested have to be extracted from the wavefunction - this in itself may be techniqually very difficult,

It is clear that if we can instead work with just the electron density as the basic variable, this will lead to an enormous simplification, since the density of a three-dimensional system is a scalar field of only three variables. What is so remarkable is that, as we shall see, that all physical properties of the system can in principle be determined with knowledge only of the ground state density! This ia precisely the staement of the Hohenberg Kohn theorem.

1.1 Proof of the Hohenberg-Kohn Theorem (Nondegenerate Ground Sate)

Let

$$\mathcal{H} = T + V_{ext} + V \tag{1.1}$$

be the nonrelativistic, time-independent Hamiltonian of a system of N electrons. Here, T is the kinetic energy, V_{ext} is an external potential which couples to the density, and V is thetwo-body electron-electron interaction.

The Hohenberg-Kohn theorem states that the expectation value O of any operator is a unique functional (function of a function) $O[n_0(\mathbf{r})]$ of the ground-state density $[n_0(\mathbf{r})]$, by which we mean that the value of O depends on the value of $n_0(\mathbf{r})$ at all points $\mathbf{r}$.

We know that we could solve the Schródinger equation for the Hamiltonian $\mathcal{H}$ and find all the many-body eigenstates Ψ_α , we could then calculate the expectation value of any operator, and, in particular, the Hamiltonian determines the ground-state density. Note that since the kinetic energy operator T and th einteration V are the same for all non-relativistic interacting systems, it is really only the external potential that distinguishes and so characterises the Hamiltonian, and thus the eigenstates and the ground-state density. The Hohenberg-Kohn theorem states that this mapping from external potential to ground-state density is **invertible**. Given any density $n(\mathbf{r})$, which is specified by the ground-state density for some $N-$electron system, the Hamiltonian of that system uniquely determined, and so are all the eigenstates and the expectation value of any operator. So knowledge of only the ground-state density determines *everything* about that system.

The proof is actually quite simple.

Theorem 1.1.1 Proof of the Hohenberg-Kohn Theorem: *Two different, nondegenerate ground states necessarily lead to two different ground-state densities.*

Part (a)

We first show that two potentials, V_{ext} and V'_{ext} that differ by more than a trivial constant, neccesarily give rise to different ground states Ψ_0 and Ψ'_0. The Schrödinger equationss for Ψ_0 and Ψ'_0 are

$$\mathcal{H}\Psi_0 \equiv (T + V + V_{ext})\Psi_0 = \mathcal{E}_0\Psi_0 \tag{1.2}$$
$$\mathcal{H}'\Psi'_0 \equiv (T + V + V'_{ext})\Psi'_0 = \mathcal{E}'_0\Psi'_0 \tag{1.3}$$

where $\mathcal{E}_0$ and $\mathcal{E}'_0$ are the respective ground-state energies. We prove the first part of the theorem by contradiction. Suppose now that Ψ_0 and Ψ'_0 are the same. we then subtract (1.2) from (1.2) to obtain

$$(V_{ext} - V'_{ext})\Psi_0 = (\mathcal{E}_0 - \mathcal{E}'_0)\Psi_0$$

But $\mathcal{E}_0$ and $\mathcal{E}'_0$ are real numbers, which means that the two potentials V_{ext} and V'_{ext} can differ only by a constant, in contraction to the hypothesis.

Before we move onto proving the next part of the theorem, we note the relation between $n_0(\mathbf{r})$, $V_{ext}(\mathbf{r})$, and $\langle\Psi_0|V_{ext}|\Psi_0\rangle$. We recall that

$$n_0(\mathbf{r}) = \int \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \dots) \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$$

which allows us to write

$$\begin{aligned}
\langle\Psi_0|V_{ext}|\Phi_0\rangle &= \int \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \dots) \sum_i^N V_{ext}(\mathbf{r}_i)\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \\
&= \int \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \dots) \sum_i^N \delta(\mathbf{r}_p - \mathbf{r}_i)V_{ext}(\mathbf{r}_p)\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{r}_p \\
&= \int n_0(\mathbf{r})V_{ext}(\mathbf{r}) d\mathbf{r}. \qquad (1.4)
\end{aligned}$$

Part (b)

Now we can prove that if $V_{ext} \neq V'_{ext}$ (so $\Psi_0 \neq \Psi'_0$, as we have already proved), then we must have $n_0(\mathbf{r}) \neq n'_0(\mathbf{r})$. Again, we prove the assertion by contraction. In the following we will assume that $n_0(\mathbf{r}) = n'_0(\mathbf{r})$ and obtain a contradiction. According to the Rayleigh-Ritz variational principal (see appendix A for proof), we have

$$\mathcal{E}_0 = \langle\Psi_0|\mathcal{H}|\Psi_0\rangle < \langle\Psi'_0|\mathcal{H}|\Psi'_0\rangle,$$

and

$$\begin{aligned}
\langle\Psi'_0|\mathcal{H}|\Psi'_0\rangle &= \langle\Psi'_0|\mathcal{H}' + V_{ext} - V'_{ext}|\Psi'_0\rangle \\
&= \mathcal{E}'_0 + \int n'_0(\mathbf{r})[V_{ext}(\mathbf{r}) - V'_{ext}(\mathbf{r})] d\mathbf{r}, \qquad (1.5)
\end{aligned}$$

so that

$$\mathcal{E}_0 < \mathcal{E}'_0 + \int n'_0(\mathbf{r})[V_{ext}(\mathbf{r}) - V'_{ext}(\mathbf{r})] d\mathbf{r}. \qquad (1.6)$$

Reversing the primed and unprimed quantities in th eabove argument, yields

$$\mathcal{E}_0' < \mathcal{E}_0 + \int n_0(\mathbf{r})[V_{ext}'(\mathbf{r}) - V_{ext}(\mathbf{r})]d\mathbf{r}. \tag{1.7}$$

Adding (1.6) and (1.7), and using our assumption that $n_0(\mathbf{r}) = n_0'(\mathbf{r})$ we obtain the contradiction,

$$\mathcal{E}_0 + \mathcal{E}_0' < \mathcal{E}_0 + \mathcal{E}_0'.$$

We have completed the proof.

□

Since the expectation value of any operaator O of a system is a unique functional of the ground-state density $n_0(\mathbf{r})$, this in particular appliess to the ground-state energy. We write this functional as

$$\mathcal{E}[n] \equiv \langle \Psi_0[n]|T + V_{ext} + V|\Psi_0[n]\rangle, \tag{1.8}$$

where V_{ext} is the specfific external potetntial of a system with ground -state energy uniquely determined by $n_0(\mathbf{r})$, the Rayleigh-Ritz principle establishes that

$$\mathcal{E}_0 < \mathcal{E}[n] \quad \text{for } n \neq n_0.$$

As it turns out, this is a very useful property. The ground-state energy can be found by varying the density to minimise the energy, provided we know the form of th efunctional $\mathcal{E}[n]$, or at least have a very good approximation for it. In fact we can write the ground-state energy functional as

$$\mathcal{E}[n] = F_{HK}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}, \tag{1.9}$$

where $F_{HK}[n] = \langle \Psi_0[n]|T + V|\Psi_0[n]\rangle$ is a unique functional. By which we mean that $F_{HK}[n]$ is the same functional of the density $n(\mathbf{r})$ for **all** interacting $N-$electron systems. We thus need to determine it only once, and can apply it to all systems.

Note on degenarate ground state

If there are more than one wavefunction corresponding to the ground-state energy for the system, one can no longer talk about the uniqueness of the ground-state expectation value of operators. In particular, one cannot prove part (a) of the theorem.

The theroem can be extended to include the case of degenerate ground states, which is formally very important.

Chapter 2

The Kohn-Sham Formulation

The Hohenberg-Kohn theorem establishes that we may use the density, and the density alone, to find the ground-state energy of an $N-$electron problem, i.e. the grounstate energy can be considred as a functional of the density. However, the Hohenberg-Kohn theorem does not provide us with any useful computational scheme.

A scheme is provided by the Kohn-Sham formalism. The idea is to map the problem of the system of interacting electrons onto a fictitious noninteracting system and to look for an external potential V_s such that the noninteracting system has the same ground-state density as the real, interacting system.

Once we have found this density, we can use it in the energy functional (1.8) or some approximation of it. The ground-state of a noninteraction system i=of N electrons is given by a Slater determinant (see appedix B) of the N lowest-lying single particle states. Since we can much more easily solve for these, the Kohn-Sham scheme allows for practical calculations to be performed. However, things are not so simple, the equations have to be solved self-consistently.

Question: Can we determine the form that V_s must take in order for the noninteracting system to have the same ground-state density as the ineteracting system in the external potential V_{ext}?

The effective potential will turn out to depend on the electron density. One typically starts by assuming an initial density. The strategy is then to repeat the following steps

(i) solve for the density using the auxilary noninteracting system, and then

(ii) insert this density (which by construction is the same as that for the interacting system) into an appropriate expression for the total energy of the interacting system

until self-consistency is obtained, that is, until the input and output density are sufficiently close to one another.

Various schemes have be developed to efficiently perform for self-efficient calculations.

We start by considering a noninteracting $N-$electron system in an external potential V_s. The Hamiltonian $\mathcal{H}_s$ of this sytem is given by

$$\mathcal{H}_s = T + V_s$$

We then apply the Hohenberg-Kohn theorem to this system.

$$\mathcal{E}_s[n] = T[n] + \int V_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \tag{2.1}$$

The ground-state density of this system is easily obtained. It is simply

$$n_s(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2, \tag{2.2}$$

where we have occupied the N single-particle states, that satsify the Schródinger-like equation

$$\left[\frac{-\hbar^2}{2m} + V_s(\mathbf{r})\right] \phi_i(\mathbf{r}) = \mathcal{E}_i \phi_i(\mathbf{r}), \qquad \mathcal{E}_1 \leq \mathcal{E}_2 \leq \cdots \tag{2.3}$$

and we have the N lowest eigenvalues $\mathcal{E}_i$.

The first step in this process is to write the energy functional $\mathcal{E}[n]$ of the interacting system, which was given in (1.8), as

$$\begin{aligned}
\mathcal{E}[n] &= T[n] + V[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \\
&= T_s[n] + \left\{ T[n] - T_s[n] + V[n] - \frac{e^2}{2} \int\int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} d\mathbf{r} d\mathbf{r}' \\
&\quad + \frac{e^2}{2} \int\int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \\
&\equiv T_s + \frac{e^2}{2} \int\int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \mathcal{E}_{ex}[n].
\end{aligned} \tag{2.4}$$

Here we have added and subtracted both the kinetic energy functional $T_s[n]$ of a noninteracting system and the direct, or Hartree. term in the electrostatic energy. We have then defined the sum of the terms in the braces to be the exchange-correlation energy functional $\mathcal{E}_{ex}[n]$.

$$\frac{\mathcal{E}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{ext}(\mathbf{r}) + v_{ec}[n(\mathbf{r})] = 0. \tag{2.5}$$

where we have defined the exchange-correlation potential as

$$v_{xc}[n(\mathbf{r})] := \frac{\delta \mathcal{E}_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$

We now use the fictitious noninteracting system and its Scrödinger equation, from which we can similarly show that

$$\frac{T_s[n]}{\delta n(\mathbf{r})} + V_(\mathbf{r}) = 0.$$

By comparing this result with (2.5) we see that this effective potential $V_s(\mathbf{r})$ must satisfy

$$V_(\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}). \tag{2.6}$$

Appendix A

Proof of the Rayleigh-Ritz Variational Principle

Theorem A.0.2 *Let $\mathcal{H}$ be a Hamiltonian acting on a Hilbert space $\mathscr{H}$ which has a discrete spectrum and ground-state energy $\mathcal{E}_0$. Let $|\Psi\rangle \in \mathscr{H}$ be any pure quantum state, then*

$$\langle \mathcal{H} \rangle \equiv \langle \Psi | \mathcal{H} | \Psi \rangle \geq \mathcal{E}_0. \tag{A.1}$$

Proof:

Let $\{|n\rangle\}$ be the set of state vectors corresponding to eigenstates of the Hamiltonian $\mathcal{H}$ Since these form an orthonormal basis of $\mathscr{H}$, we can write $|\psi\rangle$ as the expression $\sum_n \psi_n |n\rangle$, and it then follows

$$\begin{aligned} \langle \mathcal{H} \rangle - \mathcal{E}_0 &= \langle \Psi | (\mathcal{H} - \mathcal{E}_0) | \Psi \rangle \\ &= \sum_{m,n} \psi_m^* \psi_n \langle m | (\mathcal{H} - \mathcal{E}_0) | n \rangle \\ &= \sum_{m,n} \psi_m^* \psi_n \langle m | n \rangle (\mathcal{E}_n - \mathcal{E}_0) \\ &= \sum_n |\psi_n|^2 \underbrace{(\mathcal{E}_n - \mathcal{E}_0)}_{\geq 0} \geq 0. \end{aligned} \tag{A.2}$$

□

Proof:

Define

$$
\begin{aligned}
F(\alpha) &:= \frac{\langle \Psi_0 + \alpha\Phi | \mathcal{H} | \Psi_0 + \alpha\Phi \rangle}{\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle} \\
&= \frac{\mathcal{E}_0 + \alpha\mathcal{E}_0\langle\Phi|\Psi_0\rangle + \alpha\mathcal{E}_0\langle\Psi_0|\Phi\rangle + \alpha^2}{\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle}
\end{aligned} \tag{A.3}
$$

Then

$$
\begin{aligned}
\left.\frac{\partial F}{\partial \alpha}\right|_{\alpha=0} &= \frac{\mathcal{E}_0(\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle)(\langle\Psi_0|\Psi_0\rangle) - (\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle)(\mathcal{E}_0)}{(\langle\Psi_0|\Psi_0\rangle)^2} \\
&= 0.
\end{aligned} \tag{A.4}
$$

We wish to examine the second derivative at $\alpha = 0$. Now

$$
\begin{aligned}
\frac{\partial F}{\partial \alpha} &= \frac{\dfrac{\partial}{\partial\alpha}\langle \Psi_0 + \alpha\Phi | \mathcal{H} | \Psi_0 + \alpha\Phi \rangle - F(\alpha)\dfrac{\partial}{\partial\alpha}\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle}{\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle} \\
&= \frac{(\mathcal{E}_0 - F(\alpha))(\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle + 2\alpha)}{\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle}
\end{aligned} \tag{A.5}
$$

$$
\frac{\partial^2 F}{\partial \alpha^2} = \frac{\left(2\mathcal{E}_0 - 2F(\alpha) + \dfrac{\partial F}{\partial\alpha}(\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle + 2\alpha)\right) - (\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle + 2\alpha)^2}{\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle} \tag{A.6}
$$

$$
\begin{aligned}
\left.\frac{\partial^2 F}{\partial \alpha^2}\right|_{\alpha=0} &= \frac{\left(2\mathcal{E}_0 - F(\alpha) + \dfrac{\partial F}{\partial\alpha}(\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle\alpha)\right) - (\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle + 2\alpha)^2}{\langle \Psi_0 + \alpha\Phi | \Psi_0 + \alpha\Phi \rangle} \\
&= -\frac{(\langle\Phi|\Psi_0\rangle + \langle\Psi_0|\Phi\rangle)^2}{\langle\Psi_0|\Psi_0\rangle} \\
&= -4\frac{(\mathrm{Re}(\langle\Phi|\Psi_0\rangle))^2}{\langle\Psi_0|\Psi_0\rangle} \\
&\leq 0.
\end{aligned} \tag{A.7}
$$

Which proves that it is a local minimum.

In fact if we replace $|\Psi_0\rangle$ by any eigenstate of $\mathcal{H}$, $|\Psi_n\rangle$, (with eigenvalue $\mathcal{E}_n$) satisfies $\left.\dfrac{\partial F}{\partial \alpha}\right|_{\alpha=0} = 0$. Consider

$$F_n(\alpha) := \frac{\langle \Psi_n + \alpha\Phi | \mathcal{H} | \Psi_n + \alpha\Phi \rangle}{\langle \Psi_n + \alpha\Phi | \Psi_n + \alpha\Phi \rangle} \tag{A.8}$$

We have $F_n(0) = \mathcal{E}_n$, which by deinition $\mathcal{E}_0 \leq \mathcal{E}_1 \leq \cdots$.

□

Appendix B

Second Quantisation

B.1 Many Particle wavefunctions

As is well known in quantum mechanics, with a system of identical particles, there is no way of distinguishing the particles. Thus for any possible state Ψ of the system and for all observables B,

$$\int d^N x \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_k, \ldots, \mathbf{x}_N) \hat{B} \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_k, \ldots, \mathbf{x}_N)$$
$$\int d^N x \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_k, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) \hat{B} \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_k, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) \quad \text{(B.1)}$$

for all pairs (j, k). The coordinates $\mathbf{x} \equiv (\mathbf{r}, s)$ contain the space and spin degrees of freedon of the particales. We use the notation

$$\int dx \sum_s \int d^3 r \quad \text{and} \quad \int d^N x = \int dx_1 \int dx_2 \cdots \int dx_N.$$

B.1.1 Permutation Operators

As any permutation of P can be expressed as a sequence of two-particle interchanges, each permutation can be expressed as a product of transpositions P_{jk}:

$$P = \prod P_{jk}$$

The transpositions P_{jk} are expressed as operators with the action

$$\hat{P}_{jk}\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_k,\ldots,\mathbf{x}_N) := \Psi(\mathbf{x}_1,\ldots,\mathbf{x}_k,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_N)$$

on the many particle wavefunction. Applying the same permutation operator $\hat{P}_{jk}$ twice restores the original wavefunction. Hence, it follows that

$$\hat{P}_{jk}\hat{P}_{jk} = \mathrm{Id} = 1, \qquad \text{so } \hat{P}_{jk}^{-1} = \hat{P}_{jk}$$

By means of the transposition operators, (B.1) can be written

$$\begin{aligned}\langle\Psi|\hat{B}|\Psi\rangle &= \langle\hat{P}_{jk}\Psi|\hat{B}|\hat{P}_{jk}\Psi\rangle \\ &= \langle\Psi|\hat{P}_{jk}^{\dagger}\hat{B}\hat{P}_{jk}|\Psi\rangle \qquad \text{for all } (j,k).\end{aligned}$$

This equation can then be inserted into the RHS of the identity

$$\begin{aligned}\langle\Phi|\hat{B}|\Psi\rangle = \frac{1}{4}\Big(&\langle\Phi+\Psi|\hat{B}|\Phi+\Psi\rangle - \langle\Phi-\Psi|\hat{B}|\Phi-\Psi\rangle \\ &-i\langle\Phi+i\Psi|\hat{B}|\Phi+i\Psi\rangle + i\langle\Phi-i\Psi|\hat{B}|\Phi-i\Psi\rangle\Big)\end{aligned}$$

which yields

$$\langle\Phi|\hat{B}|\Psi\rangle = \langle\Phi|\hat{P}_{jk}^{\dagger}\hat{B}\hat{P}_{jk}|\Psi\rangle$$

for all (j,k) and for arbitrary wavefunctions Φ and Ψ in the Hilbert space. This implies the operator identity

$$\hat{B} = \hat{P}_{jk}^{\dagger}\hat{B}\hat{P}_{jk} \qquad \text{for all } (j,k). \tag{B.2}$$

In particular, if we take the $\hat{B}$ to be the identity operator, i.e., $\hat{B} = 1$, it follows that

$$1 = \hat{P}_{jk}^{\dagger}\hat{P}_{jk}.$$

Multiplication from the right by $\hat{P}_{jk}$ yields

$$\hat{P}_{jk} = \hat{P}_{jk}^{\dagger}$$

so finally we obtain

$$\hat{P}_{jk}^{-1} = \hat{P}_{jk} = \hat{P}_{jk}^{\dagger}.$$

Thus the transosition operators are self-adjoint and unitary (when operating in on the space of identical particles).

If we multilply (B.2) from the left with $\hat{P}_{jk}$, we obtain

$$\left[\hat{P}_{jk}, \hat{B}\right] = 0 \quad \text{for all } (j,k). \tag{B.3}$$

We now calculate the eigenvalues of of the transposition operators. Let Ψ be an eigenfunction of $\hat{P}_{jk}$ with eigenvalue $\lambda_{(j,k)}$:

$$\hat{P}_{jk}\Psi = \lambda_{(j,k)}\Psi,$$

It follows that

$$\Psi = \hat{P}_{jk}^2\Psi = \lambda_{(j,k)}^2\Psi$$

implying that $\lambda_{(j,k)}^2 = 1$. So $\lambda_{(j,k)} = \pm 1$.

It is easy to prove that if a function Ψ is an eigenfunction of all $\hat{P}_{jk}$, the eigenvalues of all the $\hat{P}_{jk}$ must be identitcal:

$$\hat{P}_{jk}\Psi = a_{(1,2)}\Psi \qquad \text{for all } (j,k)$$

We prove by writing the transposition $\hat{P}_{jk}$ as

$$\hat{P}_{jk} = \hat{P}_{1j}\hat{P}_{2k}\hat{P}_{12}\hat{P}_{2k}\hat{P}_{1j}$$

so that

$$\hat{P}_{jk}\Psi = \lambda_{(1j)}^2\lambda_{(2k)}^2\lambda_{(12)} = \lambda_{(12)}\Psi$$

for all (j,k). A wavefunction satisfying

(i) $\hat{P}_{jk}\Psi = +\Psi$ for all (j,k) is said to be symmetric

(ii) $\hat{P}_{jk}\Psi = +\Psi$ for all (j,k) is said to be antisymmetric.

If Ψ_S is symmetric and Ψ_A is antisymmetric, it is obvious that for an permutation $\hat{P}$ we have

$$\hat{P}\Psi_S = +\Psi_S, \qquad \hat{P}\Psi_A = \mathrm{sgn}(P)\cdot\Psi_A$$

where $\mathrm{sgn}(P) = +1$ if $\hat{P}$ is comprised of an even number of transpositions, and $\mathrm{sgn}(P) = -1$ if $\hat{P}$ is comprised of an odd number of transpositions.

Defining symmetric functions by

$$\Psi_S(x_1,\ldots,x_N) := \sum_{P\in S_N}\hat{P}f(x_1,\ldots,x_N)$$

where $f\Psi_S(x_1,\ldots,x_N)$ is an arbtrary function of N variables, and the sum runs over all elments P of the permutation group S_N.

Defining antisymmetric functions by

$$\Psi_S(x_1,\ldots,x_N) := \sum_{P\in S_N}\mathrm{sgn}(P)\hat{P}f(x_1,\ldots,x_N)$$

where $f\Psi_S(x_1,\ldots,x_N)$ is an arbtrary function of N variables.

We have

$$\hat{P}_{jk}\sum_{P\in S_N}\hat{P} = \sum_{P\in S_N}\left(\hat{P}_{jk}\hat{P}\right) = \sum_{P\in S_N}P$$

and

$$\begin{aligned}\hat{P}_{jk}\sum_{P\in S_N}\mathrm{agn}(P)\hat{P} &= \sum_{P\in S_N}\mathrm{sgn}(P)\left(\hat{P}_{jk}\hat{P}\right)\\ &= \sum_{P\in S_N}\left[-\mathrm{sgn}(P_{jk}P)\right]\left(\hat{P}_{jk}\hat{P}\right)\\ &= \sum_{P\in S_N}\left[-\mathrm{sgn}(P)\right]P\end{aligned}$$

and thus

$$\begin{aligned}\hat{P}_{jk}\Psi_S &= \Psi_S \\ \hat{P}_{jk}\Psi_A &= \Psi_A\end{aligned}$$

for all (j,k).

B.1.2 Symmetric Wavefunctions and Slater Determinants

$$\Phi^{(S)} = \frac{1}{\sqrt{N!}\sqrt{\prod_{k=1}^{K} n_k!}} \sum_{P\in S_N} P\left[\phi_{\nu_1}(x_1)\phi_{\nu_2}(x_2)\cdots\phi_{\nu_N}(x_N)\right] \tag{B.4}$$

$$\begin{aligned}\Phi^{(A)} &= \frac{1}{\sqrt{N!}} \sum_{P\in S_N} \mathrm{sgn}(P) P\left[\phi_{\nu_1}(x_1)\phi_{\nu_2}(x_2)\cdots\phi_{\nu_N}(x_N)\right] \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\nu_1}(x_1) & \cdots & \phi_{\nu_1}(x_N) \\ \vdots & & \vdots \\ \phi_{\nu_N}(x_1) & \cdots & \phi_{\nu_N}(x_N) \end{vmatrix}\end{aligned} \tag{B.5}$$

Thus the Slater determinant can be written in either of the two ways:

$$\begin{aligned}\Phi_c^{(A)}(x_1,\ldots,x_N) &= \frac{1}{\sqrt{N!}} \sum_{P\in S_N} \mathrm{sgn}(P)\phi_{c_1}(x_{P(1)})\cdots\phi_{c_N}(x_{P(N)}) \\ &= \frac{1}{\sqrt{N!}} \sum_{P\in S_N} \mathrm{sgn}(P)\phi_{c_{P(1)}}(x_1)\cdots\phi_{c_{P(N)}}(x_N)\end{aligned}$$

B.1.3 Orthonomality and Completeness of Symmetric and Antisymmetric Wavefunctions

For any observable B of a system of identical particles, we have

$$\int d^N x \Phi_b^* \hat{B} \Phi_c = \frac{\sqrt{N!}}{\sqrt{\prod_{k=1}^{K} n_k^{(c)}!}} \int d^N x \Phi_b^* \hat{B} \phi_{c_1}(x_1)\cdots\phi_{c_N}(x_N) \tag{B.6}$$

for both $\Phi = \Phi^{(S)}$ and for $\Phi^{(A)}$ (in the latter case, $\sqrt{\prod_{k=1}^{K} n_k^{(c)}!} = 1$.)

Orthonomality of Antisymmetric Wavefunctions

We will prove

$$\int d^N x \Phi_b^* \hat{B} \Phi_c = \int d^N x \Phi_b^* \hat{B} \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \mathrm{sgn}(P) \cdot P \left[\varphi_{c_1}(x_1), \cdots, \varphi_{c_N}(x_N) \right]. \tag{B.7}$$

Since we have $\hat{B}\hat{P} = \hat{P}\hat{B}$ for observables of the system, this expression becomes

$$\begin{aligned} &\int d^N x \Phi_b^* \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \mathrm{sgn}(P) \cdot P \left[\hat{B} \varphi_{c_1}(x_1) \cdots \varphi_{c_N}(x_N) \right] \\ &= \int d^N x \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \mathrm{sgn}(P) \cdot P \left(P^{-1} \Phi_b^* \right) \hat{B} \varphi_{c_1}(x_1) \cdots \varphi_{c_N}(x_N) \end{aligned}$$

As $P^{-1}\Phi_b^* = \mathrm{sgn}(P^{-1}) \cdot \Phi_b^* = \mathrm{sgn}(P) \cdot \Phi_b^*$, we may write this as

$$\frac{1}{\sqrt{N!}} \sum_{P \in S_N} \mathrm{sgn}^2(P) \cdot P \int d^N x \Phi_b^* \hat{B} \varphi_{c_1}(x_1) \cdots \varphi_{c_N}(x_N).$$

Since the integral remains unchanged if we interchange the integration variables $x_i \to x_{P(i)}$, we therefore obtain the same value for each permutation (of which there are $N!$), and so we arrive at the expression

$$\sqrt{N!} \int d^N x \Phi_b^*(x_1, \ldots, x_N) \hat{B} \varphi_{c_1}(x_1) \cdots \varphi_{c_N}(x_N).$$

We can now prove that

$$\int d^N x \Phi_b^* \Phi_c = \delta_{b,c}. \tag{B.8}$$

When $b = c$ we have

$$
\begin{aligned}
&\int d^N x \Phi_c^* \Phi_c \\
&= \sqrt{N!} \int d^N x \Phi_b^* \varphi_{c_1}(x_1) \cdots \varphi_{c_N}(x_N) \\
&= \sqrt{N!} \int d^N x \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \mathrm{sgn}(P) \varphi^*_{c_{P(1)}}(x_1) \cdots \varphi^*_{c_{P(N)}}(x_N) \varphi_{c_1}(x_1) \cdots \varphi_{c_N}(x_N) \\
&= \sum_{P \in S_N} \int dx_1 \varphi^*_{c_{P(1)}}(x_1) \varphi_{c_1}(x_1) \times \cdots \times \int dx_N \varphi^*_{c_{P(N)}}(x_N) \varphi_{c_N}(x_N) \\
&= 1
\end{aligned}
$$

as the products of integrals are non-zero only for the identity permutation as we assumed that the $\{\phi_i\}$ are orthonormal and as $P(\mathrm{Id}) = 1$. If $b \neq c$, there exists at least one index b_j which is not contained in c. It follows that at least one factor in the product of integrals (in the analagous expression for $\int d^N x \Phi_b^* \Phi_c$) vanishes in every term in the sum over permutations.

Completeness of Symmetric and Antisymmetric Wavefunctions

To prove the result, we start by showing that an arbitrary many particle wavefunction can be expanded in products of single-particle functions. We fix the last $N-1$ coordinates at $x_i^{(0)}$ for $i = 2, 3, \ldots, N$, and expand the wavefunction with respect to thhhe forst coordinate:

$$
\Psi(x_1, x_2^{(0)}, \ldots, x_N^{(0)}) = \sum_{\nu_1} a_{\nu_1} \phi_{\nu_1}(x_1).
$$

The expansion coefficients are functions of the fixed coordinates:

$$
a_{\nu_1} = a_{\nu_1}\left(x_2^{(0)}, \ldots, x_N^{(0)}\right)
$$

so that

$$
\Psi(x_1, x_2, \ldots, x_N) = \sum_{\nu_1} a_{\nu_1}(x_2, \ldots, x_N) \phi_{\nu_1}(x_1).
$$

If we apply the same reasoning to $a_{\nu_1}(x_2, \ldots, x_N)$ we obtain

$$
a_{\nu_1}(x_2, \ldots, x_N) = \sum_{\nu_2} a_{\nu_1, \nu_2}(x_3, \ldots, x_N) \phi_{\nu_2}(x_2)
$$

and so on, we obtain

$$\Psi(x_1, x_2, \ldots, x_N) = \sum_{\nu_1,\ldots,\nu_N} a_{\nu_1,\ldots,\nu_N} \phi_{\nu_1}(x_1) \cdots \phi_{\nu_N}(x_N).$$

If the functions Ψ have a definite symmetries $\hat{P}_{jk}\Psi = \pm\Psi$ with $+$ for bosons, and a $-$ for fermions, we can conclude that the expansion coefficients $a_{\nu_1,\ldots,\nu_N}$ have the same symmetry:

$$\begin{aligned}
&\sum_{\nu_1,\ldots,\nu_N} \pm a_{\nu_1,\ldots\nu_j,\ldots,\nu_k,\ldots,\nu_N} \phi_{\nu_1}(x_1) \cdot \cdots \cdot \phi_{\nu_j}(x_j) \cdots \phi_{\nu_k}(x_k) \cdots \phi_{\nu_N}(x_N) \\
&\qquad = \pm\Psi(x_1, \ldots, x_j, \ldots x_k, \ldots, x_N) \\
&\qquad = \hat{P}_{jk}\Psi(x_1, \ldots, x_j, \ldots x_k, \ldots, x_N) \\
&\qquad = \Psi(x_1, \ldots, x_k, \ldots x_j, \ldots, x_N) \\
= &\sum_{\nu_1,\ldots,\nu_N} a_{\nu_1,\ldots,\nu_j,\ldots,\nu_k,\ldots,\nu_N} \phi_{\nu_1}(x_1) \cdot \cdots \cdot \phi_{\nu_j}(x_k) \cdots \phi_{\nu_k}(x_j) \cdots \phi_{\nu_N}(x_N) \\
= &\sum_{\nu_1,\ldots,\nu_N} a_{\nu_1,\ldots,\nu_k,\ldots,\nu_j,\ldots,\nu_N} \phi_{\nu_1}(x_1) \cdot \cdots \cdot \phi_{\nu_k}(x_k) \cdots \phi_{\nu_j}(x_j) \cdots \phi_{\nu_N}(x_N)
\end{aligned}$$

It follows from the linear independence of the product functions that

$$\pm a_{\nu_1,\ldots,\nu_j,\ldots,\nu_k,\ldots,\nu_N} = a_{\nu_1,\ldots,\nu_k,\ldots,\nu_j,\ldots,\nu_N} = P_{jk} a_{\nu_1,\ldots,\nu_j,\ldots,\nu_k,\ldots,\nu_N}.$$

It follows that if

$$(\nu'_1, \nu'_2, \ldots, \nu'_N) = P\,(\nu_1, \nu_2, \ldots, \nu_N)$$

then

$$a_{\nu'_1,\ldots,\nu'_N} = \begin{pmatrix} + \\ \mathrm{sgn}(P) \end{pmatrix} a_{\nu_1,\ldots,\nu_N}$$

with $+$ for bosons and $\mathrm{sgn}(P)$ for fermions. In the last part of the proof, we replace the multiple sum over all indices in

$$\Psi(x_1, \ldots, x_N) = \sum_{\nu_1,\ldots,\nu_N} a_{\nu_1,\ldots,\nu_N} \phi_{\nu_1}(x_1) \cdots \phi_{\nu_N}(x_N)$$

by an (infinite) sum over all ordered combinations $c = (\nu_1, \ldots, \nu_N)$, together with a sum over all permutations $P(\nu_1, \ldots, \nu_N)$ of these combinations, with the result

$$\Psi(x_1, \ldots, x_N) = \sum_{c=(\nu_1,\ldots,\nu_N)} \sum_{P(c)=P(\nu_1,\ldots,\nu_N)} P\left[a_{\nu_1,\ldots,\nu_N}\phi_{\nu_1}(x_1)\cdots\phi_{\nu_N}(x_N)\right].$$

By using the above result

$$a_{P(\nu_1,\ldots,\nu_N)} = a_{P(c)} = \binom{+}{\mathrm{sgn}(P)} a_c$$

it follows that

$$\begin{aligned}\Psi(x_1, \ldots, x_N) &= \sum_c a_c \sum_{P\in S_N} \binom{+}{\mathrm{sgn}(P)} P\left[\phi_{\nu_1}(x_1)\cdots\phi_{\nu_N}(x_N)\right] \\ &\equiv \sum_c f_c \Phi_c^{(S/A)}(x_1, \ldots, x_N).\end{aligned}$$

This concludes the proof.

B.2 Creation and Annihilation Operators

We define annihilation and creation operators. These operators are mappings between the many-particle Hilbert spaces of different particle numbers:

$$\hat{c}_k : \mathscr{H}(N) \to \mathscr{H}(N-1) \tag{B.9}$$
$$\hat{c}_k^\dagger : \mathscr{H}(N-1) \to \mathscr{H}(N) \tag{B.10}$$

We the previous section we establisge that Slater determinants $\Phi(x_1, \ldots, x_N)$ form a basis in the $N-$fermion Hilbert space.

B.2.1 The annihilation operator

We define the action of $\hat{c}_k$ on this basis as

$$\hat{c}_k \Phi_{(c_1,\ldots,c_N)}(x_1, \ldots, x_N) = 0, \quad \text{if } k \neq \{c_1, \ldots, c_N\}$$

and if $k = c_j$

$$\begin{aligned}
&\hat{c}_k \Phi_{(c_1,\ldots,c_N)}(x_1,\ldots,x_N) = (-1)^{j-1}\Phi_{(c_1,\ldots,c_{j-1},c_{j+1},\ldots,c_N)}(x_1,\ldots,x_{N=1}) \\
= \quad & \frac{(-1)^{j-1}}{\sqrt{(N-1)!}} \sum_{P\in S_{n-1}} \mathrm{sgn}(P) P(\phi_{c_1}(x_1)\cdots\phi_{c_{j-1}}(x_{j-1})\phi_{c_{j+1}}(x_{j+1})\cdots\phi_{c_{N-1}}(x_{N-1})).
\end{aligned}$$

The action of the annihilation operator on a Slater determinant can be understood as carryindg out the following steps:

(i) interchange the row with $c_j = k$ with each row until it is at the top of the determinant, which gives the prefactor $(-1)^{j-1}$;

(ii) cross out the first row and the last column of the determinant;

(iii) normalise the new determinant.

Explicitly,

$$\hat{c}_k \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{c_1}(x_1) & \cdots & \varphi_{c_1}(x_N) \\ \vdots & & \vdots \\ \varphi_{c_j}(x_1) & \cdots & \varphi_{c_j}(x_N) \\ \vdots & & \vdots \\ \varphi_{c_N}(x_1) & \cdots & \varphi_{c_N}(x_N) \end{vmatrix} = \frac{(-1)^{j-1}}{\sqrt{(N-1)!}} \begin{vmatrix} \varphi_{c_1}(x_1) & \cdots & \varphi_{c_1}(x_{N-1}) \\ \vdots & & \vdots \\ \varphi_{c_{j-1}}(x_1) & \cdots & \varphi_{c_{j-1}}(x_{N-1}) \\ \varphi_{c_{j+1}}(x_1) & \cdots & \varphi_{c_{j+1}}(x_{N-1}) \\ \vdots & & \vdots \\ \varphi_{c_N}(x_1) & \cdots & \varphi_{c_N}(x_{N-1}) \end{vmatrix}$$

The operators are define as linear opartors on the Hilbert space $\mathscr{H}(N)$. The action of $\hat{c}_k$ on a general many-particle wavefunction Ψ is then completely determined by the expansion of Ψ in terms of Slater detrminants, $\Psi = \sum_c f_c \Phi_c$:

$$\hat{c}_k \Psi = \hat{c}_k \left(\sum_c f_c \Phi_c \right) = \sum_c f_c (\hat{c}_k \Phi_c).$$

B.2.2 The creation operator

We define the creation opertor $\hat{c}_k^\dagger$ as the adjoint of $\hat{c}_k$.

$$\begin{aligned}
\langle \hat{c}_k^\dagger \Phi_c | \Phi_b \rangle &= \langle \Phi_c | \hat{c}_k \Phi_b \rangle \\
&= \begin{cases} (-1)^{\ell-1} \langle \Phi_c | \Phi_{b-\{k\}} \rangle \\ 0 \qquad\qquad \text{otherwise} \end{cases}
\end{aligned} \tag{B.11}$$

This result clearly means (if $c_\ell < k < c_{\ell+1}$)

$$\hat{c}_k^\dagger \frac{1}{\sqrt{(N+1)!}} \begin{vmatrix} \varphi_{c_1}(x_1) & \cdots & \varphi_{c_1}(x_N) \\ \vdots & & \vdots \\ \varphi_{c_\ell}(x_1) & \cdots & \varphi_{c_\ell}(x_N) \\ \vdots & & \vdots \\ \varphi_{c_N}(x_1) & \cdots & \varphi_{c_N}(x_N) \end{vmatrix} = \frac{(-1)^\ell}{\sqrt{(N-1)!}} \begin{vmatrix} \varphi_{c_1}(x_1) & \cdots & \varphi_{c_1}(x_{N+1}) \\ \vdots & & \vdots \\ \varphi_{c_\ell}(x_1) & \cdots & \varphi_{c_\ell}(x_{N+1}) \\ \varphi_k(x_1) & \cdots & \varphi_k(x_{N+1}) \\ \varphi_{c_{\ell+1}}(x_1) & \cdots & \varphi_{c_{\ell+1}}(x_{N+1}) \\ \vdots & & \vdots \\ \varphi_{c_N}(x_1) & \cdots & \varphi_{c_N}(x_{N+1}) \end{vmatrix}$$

As with $\hat{c}_k$, the action of $\hat{c}_k^\dagger$ on an arbitrary many-particle state $\Psi = \sum_c f_c \Phi_c$

$$\hat{c}_k^\dagger \Psi = \hat{c}_k^\dagger \left(\sum_c f_c \Phi_c \right) = \sum_c f_c \left(\hat{c}_k^\dagger \Phi_c \right).$$

B.2.3 Fock space

The creation and annihilation operators map Hilberts spaces with fixed particle numbers onto each other, (B.9) and (B.10). However, the formalism of second quantisation is especially suited for problems with variable particle numbers. Therefore, it is more appropriate to form the product of Hilbert space

$$\mathcal{F} \equiv \bigotimes_{N=0}^{\infty} \mathscr{H}(N)$$

from the Hilbert spaces $(\mathscr{H}(N), \langle \cdot | \cdot \rangle$ of antisymmetric wavefunctions of N particles. We define the scalar product on $\mathcal{F}$ to be the natural scalar product

$$\left\langle \bigotimes_{N=0}^{\infty} \phi_N \middle| \bigotimes_{N=0}^{\infty} \tilde{\phi}_N \right\rangle \equiv \sum_{N=0}^{\infty} \langle \phi_N | \tilde{\phi}_N \rangle_N \,.$$

We can then regard $\hat{c}_k$ and $\hat{c}_k^\dagger$ as operators on the space $\mathcal{F}$, the well know Fock-space, instead of collections of operators which map between different Hilbert spaces $\mathscr{H}(N)$ onto one another.

In single-particlre quantum mechanics the states are usually represented by quantum numbers in Dirac notation $\langle \mathbf{r} | n\ell n \rangle$. We can characterise the Slater determinants in an

analogous way by their associated $N-$tuples of indicies: $|c\rangle$ with the position-spin representation $\langle \mathbf{x}_1, \ldots, \mathbf{x}_N | c \rangle = \Phi_c(\mathbf{x}_1, \ldots, \mathbf{x}_N)$.

Another equivalent representation is the so-called **occupation-number representation**:

$$|c\rangle \equiv |n_1, n_2, n_3, \ldots \rangle$$

with $n_i = 0$ if $i \notin \{c_1, \ldots, c_N\}$

and $n_i = 1$ if $i \in \{c_1, \ldots, c_N\}$.

We should keep in mind that the position-spin representation of an abstract state vector is simply a Slater determinant. However, by using the occupation-number representation allows you to write the action of the creation and annihilation operators more compactly:

$$\begin{aligned} \hat{c}_k |n_1, \ldots, 1_k, \ldots \rangle &= (-1)^{\sum_{j<k}} |n_1, \ldots, 0_k, \ldots \rangle \\ \hat{c}_k |n_1, \ldots, 0_k, \ldots \rangle &= 0 \end{aligned} \tag{B.12}$$

or

$$\hat{c}_k |n_1, \ldots, 0_k, \ldots \rangle = \theta_k n_k |n_1, \ldots, 0_k, \ldots \rangle$$

where

$$\theta_k \equiv (-1)^{\sum_{j<k}}.$$

Similarly, we have

$$\begin{aligned} \hat{c}_k^\dagger |n_1, \ldots, 0_k, \ldots \rangle &= \theta_k |n_1, \ldots, 0_k, \ldots \rangle \\ \hat{c}_k^\dagger |n_1, \ldots, 1_k, \ldots \rangle &= 0 \end{aligned} \tag{B.13}$$

and hence

$$\hat{c}_k^\dagger |n_1, \ldots, n_k, \ldots \rangle = \theta_k (1 - n_k) |n_1, \ldots, 1_k, \ldots \rangle$$

We define the vacuum state, denoted $|0\rangle$, to be the state that gives zero when actted upon by any annihilation operator:

$$\hat{c}_k|0\rangle = 0 \qquad \text{for all } k \in \mathbb{N}.$$

By applying the creation operators to the vacuum state, we can generate every possible $N-$particle state. We obtaion the basis functions via

$$\begin{aligned} |c_1, c_2, \ldots, c_N\rangle &= \hat{c}^\dagger_{c1}\hat{c}^\dagger_{c2}\cdots\hat{c}^\dagger_{c_N}|0\rangle \\ &= \prod_{k=1}^{\infty}\left(\hat{c}^\dagger_k\right)^{n_k}|0\rangle \end{aligned} \tag{B.14}$$

.

B.2.4 Anticommutation Relations

We now arrive at the most important property of fermion creation and annihilation operators

$$\begin{aligned} \{\hat{c}_{c_\ell}, \hat{c}_{c_k}\} &= 0, \\ \{\hat{c}^\dagger_{c_\ell}, \hat{c}^\dagger_{c_k}\} &= 0, \\ \{\hat{c}^\dagger_{c_\ell}, \hat{c}_{c_k}\} &= \delta_{\ell.k}. \end{aligned} \tag{B.15}$$

The proof of the anticommutation relations is as follows:

$$\begin{aligned} \hat{c}_k\hat{c}_\ell|n_1, \ldots, n_k, \ldots, n_\ell, \ldots\rangle &= \theta_\ell n_\ell \hat{c}_k|n_1, \ldots, n_k, \ldots, 0_\ell, \ldots\rangle \\ &= \theta_\ell\theta_k n_\ell n_k|n_1, \ldots, 0_k, \ldots, 0_\ell, \ldots\rangle \\ \\ \hat{c}_\ell\hat{c}_k|n_1, \ldots, n_k, \ldots, n_\ell, \ldots\rangle &= \theta_k n_k \hat{c}_\ell|n_1, \ldots, 0_k, \ldots, n_\ell, \ldots\rangle \\ &= \theta_k(-1\cdot\theta_\ell)n_k n_\ell|n_1, \ldots, 0_k, \ldots, 0_\ell, \ldots\rangle \end{aligned} \tag{B.16}$$

Note that if we have $n_k = 0$ the entire expression vanishes. Hence we can write the last expression as

$$-\theta_k\theta_\ell n_k n_\ell|n_1, \ldots, 0_k, \ldots, 0_\ell, \ldots\rangle$$

Thus, we have $(\hat{c}_k\hat{c}_\ell + \hat{c}_\ell\hat{c}_k)|n_1, \ldots, n_k, \ldots\rangle = 0$ for any arbitrary Slater determinant, proving the first anticommutation relations.

The proof of the remaining relations can be proved similarly.

$$\begin{aligned}
\hat{c}_k\hat{c}_k^\dagger|n_1,\ldots,n_k,\ldots\rangle &= \theta_\ell\hat{c}_k(1-n_k)|n_1,\ldots,1_k,\ldots\rangle \\
&= \theta_k\theta_k(1-n_k)|n_1,\ldots,0_k,\ldots\rangle \\
&= (1-n_k)|n_1,\ldots,0_k,\ldots\rangle
\end{aligned}$$

$$\begin{aligned}
\hat{c}_k^\dagger\hat{c}_k|n_1,\ldots,n_k,\ldots\rangle &= \hat{c}_k^\dagger\theta_k n_k|n_1,\ldots,0_k,\ldots\rangle \\
&= \theta_k\theta_k n_k(1-0)|n_1,\ldots,0_k,\ldots\ldots\rangle \\
&= n_k|n_1,\ldots,1_k,\ldots\ldots\rangle
\end{aligned}$$

B.2.5 Number operator

The property $\hat{c}_k^\dagger\hat{c}_k|n_1,n_2,\ldots\rangle = n_k|n_1,n_2,\ldots\rangle$, we can introduce the **number operator** $\hat{N}$ by

$$\hat{N} \equiv \sum_{k=1}^{\infty}\hat{c}_k^\dagger\hat{c}_k.$$

From this definition, it follows that

$$\hat{N}|n_1,\ldots,n_k,\ldots\rangle = \left(\sum_{k=1}^{\infty}n_k\right)|n_1,\ldots,n_k,\ldots\rangle = N|n_1,\ldots,n_k,\ldots\rangle$$

for Slater determinants.

If we expand an arbitrary many-particle state in Slater determinants, $|\Psi\rangle = \sum_c f_c|\Phi_c\rangle$, we obtain

$$\begin{aligned}
\hat{c}_\ell^\dagger\hat{c}_\ell|\Psi\rangle &= \sum_c f_c\hat{c}_\ell^\dagger\hat{c}_\ell|\Phi_c\rangle \\
&= \sum_c f_c\hat{c}_\ell^\dagger\hat{c}_\ell|\Phi_c\rangle
\end{aligned}$$

Thus the expectation value of the number of particles in the single-particle state ℓ in the state $|\Phi_c\rangle$ is

$$\begin{aligned}\langle n_\ell \rangle &\equiv \langle \Psi | \hat{c}_\ell^\dagger \hat{c}_\ell | \Psi \rangle \\ &= \sum_c \sum_{c'} f_{c'} f_c n_\ell^{(c)} \langle \Phi_{c'} | \Phi_c \rangle \\ &= \sum_c |f_c|^2 n_\ell^{(c)}.\end{aligned}$$

Since $\sum_c |f_c|^2 = 1$, it follows that

$$0 \leq \langle n_\ell \rangle \leq 1$$

for fermions ($n_\ell^{(c)} = 0$ or 1).

B.2.6 Hamiltonian In terms of Creation and Anihhilation Operators

(i) For single particle operators

$$\hat{\mathscr{H}}_0 = \sum_{i=1}^{N} \hat{h}(\mathbf{x}_i) = \sum_{i,j=1}^{\infty} \langle i|\hat{h}|j\rangle \hat{c}_i^\dagger \hat{c}_j \tag{B.17}$$

where $\langle i|\hat{h}|j\rangle = \int \phi_i^*(x)\phi_j(x)dx$; and

(ii) for local two-particle operators

$$\hat{V} = \frac{1}{2} \sum_{i,j=1(i\neq j)}^{N} \hat{v}(\mathbf{x}_i, \mathbf{x}_j) = \frac{1}{2} \sum_{i,j,k,\ell=1}^{\infty} \langle ij|\hat{v}|k\ell\rangle \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_\ell \hat{c}_k \tag{B.18}$$

where $\langle ij|\hat{v}|k\ell\rangle = \int\int \phi_i^*(x)\phi_j^*(x')v(x,x')\phi_k(x)\phi_\ell(x')dxdx'$.

B.3 Second Quantisation for Bosons

Second quantisation for bosons is analogous to second quantisation for fermions: the action of the creation and annihilation operators is defined on the complete system of symmetriseed functions

$$\Phi_c(\mathbf{x}_1,\ldots.\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\frac{1}{\sqrt{\prod_{k=1}^{\infty} n_k^{(c)}!}}\sum_{P\in S_N} P\left[\varphi_{c_1}(\mathbf{x}_1\cdots\varphi_{C_N}\mathbf{x}_N)\right]. \tag{B.19}$$

Again, we represent these states by the occupation numbers n_i in the Dirac notation. The occupation numbers declare that the single-particle state i appears n_i times in $(c_1,\ldots,c_N)$:

$$|c\rangle = |c_1,\ldots,c_N\rangle \equiv |n_1,n_2,n_3\ldots\rangle$$

with the position-spin represenation

$$\langle \mathbf{x}_1,\ldots,\mathbf{x}_N|n_1,\ldots\rangle = \Phi_c(\mathbf{x}_1,\ldots,\mathbf{x}_N).$$

In contrast to the case of the fermion wavefunctions, the occupation numbers are not restricted to only values 0 and 1.

$$\begin{aligned}\hat{b}_k|\ldots,n_k,\ldots\rangle &\equiv \sqrt{n_k}|\ldots,(n_k-1),\ldots\rangle\\ \hat{b}_k^\dagger|\ldots,n_k,\ldots\rangle &\equiv \sqrt{n_k+1}|\ldots,(n_k+1),\ldots\rangle\end{aligned}$$

The square roots in these definitions are chosen so that we can introduce the number operator just as in the case of the fermions

$$\hat{N} \equiv \sum_{k=1}^{\infty} b_k^\dagger b_k$$

since we then have

$$\begin{aligned}b_k^\dagger b_k|\ldots,n_k,\ldots\rangle &= \sqrt{n_i}b_k^\dagger|\ldots,(n_k-1),\ldots\rangle\\ &= n_k|\ldots,n_k,\ldots\rangle\end{aligned}$$

By applying the creation operators on the vacuum, we can generate all the basis functions of the type in equation (B.19):

$$|n_1,n_2,n_3,\ldots\rangle = \prod_{k=1}^{\infty}\frac{\left(\hat{b}_k^\dagger\right)^{n_k}}{\sqrt{n_k!}}|0\rangle.$$

Furthermore, $\hat{b}_k$ and $\hat{b}_k^\dagger$ are the adjoints of one another, and the following commutation relations hold:

$$\begin{aligned}\left[\hat{b}_\ell, \hat{b}_k\right] &= 0, \\ \left[\hat{b}_\ell^\dagger, \hat{b}_k^\dagger\right] &= 0, \\ \left[\hat{b}_\ell, \hat{b}_k^\dagger\right] &= \delta_{\ell,k}.\end{aligned}$$

The representations of single-particle and two-particle operators for bosons are identcal to the representations of the fermion operators:

$$\hat{\mathscr{H}}_0 = \sum_{i=1}^{N} \hat{h}(\mathbf{x}_i) = \sum_{i,j=1}^{\infty} \langle i|\hat{h}|j\rangle \hat{b}_i^\dagger \hat{b}_j \tag{B.20}$$

and

$$\hat{V} = \frac{1}{2}\sum_{i,j=1}^{N} \hat{v}(\mathbf{x}_i, \mathbf{x}_j) = \frac{1}{2}\sum_{i,j,k,\ell=1}^{\infty} \langle ij|\hat{v}|k\ell\rangle \hat{b}_i^\dagger \hat{b}_j^\dagger \hat{b}_\ell \hat{b}_k \tag{B.21}$$