Lecture 3

In lecture 2 we discussed the wavefunction and the ground state of free noninteracting electrons.
To learn how to deal with interactions we need to develop new notation – Slater determinants are too cumbersome to deal with directly.

Again, first recall some style-particle quantum mechanics.

Consider the wavefunctions of free electron in a box of volume V with periodic boundary conditions:

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$$

As you know, plane waves form a complete orthonormal set of states, i.e. any wavefunction, satisfying periodic boundary conditions, can be expanded in plane waves:

$$\Phi(\vec{r}) = \sum_{\vec{k}} C_k \psi_k(\vec{r})$$

~~$C_k = \int d\vec{r}\, \Phi(\vec{r})$~~

$$C_k = \int d\vec{r}\, \Phi(\vec{r})\, \psi_k^*(\vec{r}) = \frac{1}{\sqrt{V}} \int d\vec{r}\, \Phi(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}$$

Rewrite this in Dirac notation:

$$|\Phi\rangle = \sum_{\vec{k}} |\vec{k}\rangle\langle\vec{k}|\Phi\rangle$$

$$1 = \sum_{\vec{k}} |\vec{k}\rangle\langle\vec{k}|$$ - resolution of identity in terms of a complete set of states.

$$C_{\vec{k}} = \langle\vec{k}|\Phi\rangle$$

$$\langle\vec{r}|\Phi\rangle \equiv \Phi(\vec{r}) = \sum_{\vec{k}} \langle\vec{r}|\vec{k}\rangle\langle\vec{k}|\Phi\rangle$$

$$\langle\vec{r}|\vec{k}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

Now what about the states of N electrons in a box?

The analogs of plane waves in this case are Slater determinants:

$$\psi_{k_1,\dots,k_N}(\vec{r}_1,\dots,\vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \cdots & \psi_{k_1}(\vec{r}_N) \\ \vdots & & \vdots \\ \psi_{k_N}(\vec{r}_1) & \cdots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

$\vec{k}_1,\dots,\vec{k}_N$ are arbitrary (but distinct!) wavevectors from the set $\frac{2\pi}{L}(n_x, n_y, n_z)$ and I'm again

ignoring electron spin for brevity.

Any N-electron wavefunction can be expanded in terms of Slater determinants:

$$\Phi(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{k_1, \ldots, k_N} C_{k_1, \ldots, k_N} \Psi_{k_1, \ldots, k_N}(\vec{r}_1, \ldots, \vec{r}_N)$$

Calculating anything using this notation is extremely inconvenient. Need better notation!

Note the following property of Slater determinants: the only information contained in a Slater determinant is how many times a particular momentum label $\vec{k}_i$ appears in it: either never or once.
In other words, a Slater determinant is uniquely specified by the following list:

$$\vec{k}_1, \vec{k}_2, \ldots \vec{k}_N, \vec{k}_{N+1}, \ldots$$

$$n_1, n_2, \ldots, n_N, n_{N+1}, \ldots$$

where $n_i = 0, 1$.

Thus a Slater determinant can always be written as:

$$|n_1, n_2, \ldots, n_N, \ldots\rangle$$

This is called <u>occupation number representation</u>.

For example, consider a Slater determinant for 2 electrons

$$\Psi_{k_1,k_2}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_{k_1}(\vec{r}_1) & \Psi_{k_1}(\vec{r}_2) \\ \Psi_{k_2}(\vec{r}_1) & \Psi_{k_2}(\vec{r}_2) \end{vmatrix}$$

- Occupation number representation for this is:

$$|1,1,0,0,0,\ldots\rangle$$

Many-body quantum mechanics is most conveniently formulated in the occupation number representation.

- Operators acting on states in the occupation number representation increase or decrease particle numbers in different single-particle quantum states.
- Any operator can be built out of fundamental "building blocks" — creation and annihilation operators!

Creation operator:

$$C_{k_i}^{+} |n_1, n_2, \ldots, n_i, \ldots\rangle = |n_1, n_2, \ldots, n_i+1, \ldots\rangle$$

$C_{k_i}^{+}$ add one particle to state k_i.

It's hermitian conjugate is the annihilation operator:

$$C_{k_i} |n_1, n_2, \ldots, n_i, \ldots\rangle = |n_1, n_2, \ldots, n_i-1, \ldots\rangle$$

Due to Pauli principle, if $n_i=1$ then $C_{k_i}^{+}=0$ and if $n_i=0$, $C_{k_i}=0$.

It follows that $(C^+_{k_i})^2 = (C_{k_i})^2 = 0$.

All states in the occupation number representation can be built from one special state — the vacuum state:

$$|0\rangle \equiv |0, 0, 0, \dots\rangle$$

$$|n_1, n_2, \dots, n_N, \dots\rangle = (C^+_{k_1})^{n_1} (C^+_{k_2})^{n_2} \dots |0\rangle$$

Consider $|1, 1, 1, \dots, \underset{N}{1}, 0, \dots\rangle =$

$$= C^+_{k_1} C^+_{k_2} \dots C^+_{k_N} |0\rangle =$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \dots & \psi_{k_1}(\vec{r}_N) \\ \vdots & & \vdots \\ \psi_{k_N}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

Clearly, the order of the creation operators is important:

$$C^+_{k_2} C^+_{k_1} \dots C^+_{k_N} |0\rangle = - C^+_{k_1} C^+_{k_2} \dots C^+_{k_N} |0\rangle$$

Thus creation operators anticommute:

$$C^+_{k_1} C^+_{k_2} = - C^+_{k_2} C^+_{k_1}$$

or, introducing the anticommutator notation:

$$\{c^+_{k_1}, c^+_{k_2}\} = c^+_{k_1} c^+_{k_2} + c^+_{k_2} c^+_{k_1} = 0$$

From here it also follows that $(c^+_{k_1})^2 = 0$, as mentioned above.

Consider:

$$c^+_{k_1} \dots c^+_{k_N} |0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \dots & \psi_{k_1}(\vec{r}_N) \\ \vdots & & \\ \psi_{k_N}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

Let's remove a particle from state $\vec{k}_1$ and add a particle in state $\vec{k}_{N+1}$, keeping the total number of particles N. We can do this in two different ways:

$$c^+_{k_{N+1}} c_{k_1} c^+_{k_1} \dots c^+_{k_N} |0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_{N+1}}(\vec{r}_1) & \dots & \psi_{k_{N+1}}(\vec{r}_N) \\ \psi_{k_2}(\vec{r}_1) & \dots & \psi_{k_2}(\vec{r}_N) \\ \vdots & & \\ \psi_{k_N}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

or:

$$c_{k_1} c^+_{k_{N+1}} c^+_{k_1} \dots c^+_{k_N} |0\rangle =$$

$$= - c_{k_1} c^+_{k_1} c^+_{k_{N+1}} \dots c^+_{k_N} |0\rangle =$$

$$= - \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_{N+1}}(\vec{r}_1) & \dots & \psi_{k_{N+1}}(\vec{r}_N) \\ \vdots & & \\ \psi_{k_N}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

Thus we see that:

$$\{C_{k_1}, C^\dagger_{k_2}\} = 0$$

By taking a Hermitian conjugate of $\{C^\dagger_{k_1}, C^\dagger_{k_2}\} = 0$ we can also see that:

$$\{C_{k_1}, C_{k_2}\} = 0.$$

What remains is to consider combinations of the type: $C^\dagger_{k_i} C_{k_i}$ and $C_{k_i} C^\dagger_{k_i}$.

Consider two states:

$$|0\rangle = |n_1, n_2, \ldots, \underset{i}{0}, \ldots\rangle$$
$$|1\rangle = |n_1, n_2, \ldots, \underset{i}{1}, \ldots\rangle$$

Clearly, the following relations are true:

$C^\dagger_{k_i} C_{k_i} |0\rangle = 0$, since $C_{k_i}|0\rangle = 0$

$C_{k_i} C^\dagger_{k_i} |1\rangle = 0$, since $C^\dagger_{k_i}|1\rangle = 0$

$C^\dagger_{k_i}|0\rangle = 1$

$C_{k_i}|1\rangle = 0$

It follows that $C_{k_i} C^\dagger_{k_i}|0\rangle = |0\rangle$ and $C^\dagger_{k_i} C_{k_i}|1\rangle = |1\rangle$.

This can be written as:

$$C_{ki} C_{ki}^{+} + C_{ki}^{+} C_{ki} = 1 \quad \text{or} \quad \{C_{ki}, C_{ki}^{+}\} = 1.$$

Thus we finally have the following commutation relations for electron creation–annihilation operators:

$$\{C_{ki}, C_{kj}^{+}\} = \delta_{ij}$$

$$\{C_{ki}^{+}, C_{kj}^{+}\} = 0$$

$$\{C_{ki}, C_{kj}\} = 0.$$

Since $C_{ki}^{+} C_{ki} |0\rangle = 0 = 0 \cdot |0\rangle$

$$C_{ki}^{+} C_{ki} |1\rangle = 1 \cdot |1\rangle,$$

we can think of this operator as measuring the number of particles in state k_i:

$$n_i = C_{ki}^{+} C_{ki} \text{ – number operator.}$$