Lecture 4

Continuing the properties of ~~[illegible]~~ creation-annihilation operators.

Consider a Slater determinant state:

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

Let's remove a particle ~~[illegible]~~ from state k_1 and add a particle to state $\vec{k}_{N+1}$, keeping the total number of particles N. This can be done 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:

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

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

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

Thus we obtain the following commutation relation:

$$\{ C_{k_1}, C^+_{k_2} \} = 0 \text{ , since } C^+_{k_2} C_{k_1} = - C_{k_1} C^+_{k_2}.$$

Finally, let's consider combinations of the type:

$C^+_{k_i} C_{k_i}$ and $C_{k_i} C^+_{k_i}$.

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:

$C^+_{k_i} C_{k_i} |0\rangle = 0$ since $C_{k_i} |0\rangle = 0$

$C_{k_i} C^+_{k_i} |1\rangle = 0$ since $C^+_{k_i} |1\rangle = 0$

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

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

It follows that:

$C_{k_i} C^+_{k_i} |0\rangle = |0\rangle$ and $C^+_{k_i} C_{k_i} |1\rangle = |1\rangle$

This can be written as:

$$C_{k_i} C^+_{k_i} + C^+_{k_i} C_{k_i} = 1 \text{ or } \{ C_{k_i}, C^+_{k_i} \} = 1$$

Thus we finally get the following set of 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:

$$n_i = C^{+}_{ki} C_{ki} \quad \text{- number operator.}$$

The last piece of formalism we need to learn is how to write down quantum mechanical operators in terms of creation and annihilation operators.

Recall single-particle quantum mechanics of electron in a box again:

Any operator can be written as:

$$A = \sum_{\vec{k}, \vec{k}'} |\vec{k}\rangle \langle \vec{k} | A | \vec{k}' \rangle \langle \vec{k}' |$$

$$\langle \vec{k} | A | \vec{k}' \rangle = \frac{1}{V} \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} A e^{i\vec{k}'\cdot\vec{r}}$$

For example, kinetic energy operator:

$$\langle \vec{k} | T | \vec{k}' \rangle = \frac{1}{V} \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \left(-\frac{\hbar^2}{2m} \nabla^2 \right) e^{i\vec{k}'\cdot\vec{r}} =$$

$$= \frac{1}{V} \int d\vec{r}\, \frac{\hbar^2 k'^2}{2m} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} = \frac{\hbar^2 k^2}{2m} \delta_{kk'}$$

Periodic crystal potential:

$$\langle \vec{k} | V | \vec{k}' \rangle = \frac{1}{V} \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, V(\vec{r})\, e^{i\vec{k}'\cdot\vec{r}} =$$

$$= \frac{1}{V} \int d\vec{r}\, V(\vec{r})\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} = V(k-\vec{k}')$$

In an N-electron system, we can represent operators in terms of Slater determinants:

$$A = \sum_{n_1,n_2,\ldots,n_N} \sum_{n_1',n_2',\ldots,n_N'} | n_1, n_2, \ldots, n_N \ldots \rangle \langle n_1, n_2, \ldots, n_N | A |$$

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

Consider an example with $N=3$ electrons.

$$| n_1, n_2, n_3, \ldots \rangle = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \psi_{k_1}(\vec{r}_2) & \psi_{k_1}(\vec{r}_3) \\ \psi_{k_2}(\vec{r}_1) & \psi_{k_2}(\vec{r}_2) & \psi_{k_2}(\vec{r}_3) \\ \psi_{k_3}(\vec{r}_1) & \psi_{k_3}(\vec{r}_2) & \psi_{k_3}(\vec{r}_3) \end{vmatrix} =$$

$$= \frac{1}{\sqrt{3!}} \Big[\psi_{k_1}(\vec{r}_1)\psi_{k_2}(\vec{r}_2)\psi_{k_3}(\vec{r}_3) - \psi_{k_1}(\vec{r}_1)\psi_{k_2}(\vec{r}_3)\psi_{k_3}(\vec{r}_2)$$

$$- \psi_{k_1}(\vec{r}_2)\psi_{k_2}(\vec{r}_1)\psi_{k_3}(\vec{r}_3) + \psi_{k_1}(\vec{r}_2)\psi_{k_2}(\vec{r}_3)\psi_{k_3}(\vec{r}_1) +$$

$$+ \psi_{k_1}(\vec{r}_3)\psi_{k_2}(\vec{r}_1)\psi_{k_3}(\vec{r}_2) - \psi_{k_1}(\vec{r}_3)\psi_{k_2}(\vec{r}_2)\psi_{k_3}(\vec{r}_1) \Big]$$

Suppose A is a one-body operator, like kinetic energy or periodic potential:

$$A = \sum_{i=1}^{N} A(\vec{r}_i)$$

$$T = \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2$$

$$V = \sum_{i=1}^{N} V(\vec{r}_i)$$

$$\langle n_1, n_2, n_3, \ldots | A | n_1', n_2', n_3', \ldots \rangle = \frac{1}{3!}\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \cdot$$

$$\cdot \Big[-\psi_{k_1}^*(\vec{r}_1)\psi_{k_2}^*(\vec{r}_2)\psi_{k_3}^*(\vec{r}_3) \sum_{i=1}^{3} A(\vec{r}_i)\, \psi_{k_1'}(\vec{r}_2)\psi_{k_2'}(\vec{r}_1) \cdot$$

$$\cdot \psi_{k_3'}(\vec{r}_3) + \ldots \Big]$$

We see that for one-body operators, the Slater determinants $|n_1, n_2, \ldots, n_N, \ldots\rangle$ and $|n_1', n_2', \ldots, n_N', \ldots\rangle$ can differ by the occupation of not more than one state:

$$|n_1, n_2, \ldots, n_i = 1, \ldots, n_j = 0, \ldots\rangle$$

$$|n_1', n_2', \ldots\rangle = |n_1, n_2, \ldots, n_i = 0, \ldots, n_j = 1, \ldots\rangle$$

In terms of creation-annihilation operators this can be written as:

$$A = \sum_{\vec{k}, \vec{k}'} \langle \vec{k} | A | \vec{k}' \rangle C_k^+ C_{k'} =$$

$$= \sum_{kk'} A_{kk'} C_k^+ C_{k'}$$

Thus for kinetic energy we have:

$$T = \sum_{kk'} \frac{\hbar^2 k^2}{2m} \delta_{kk'} C_k^+ C_{k'} = \sum_k \frac{\hbar^2 k^2}{2m} C_k^+ C_k =$$

$$= \sum_k \frac{\hbar^2 k^2}{2m} n_k$$ - simply counts total energy of all occupied momentum states.

Periodic potential:

$$V = \sum_{kk'} V(\vec{k} - \vec{k}') C_k^+ C_{k'}$$

Recall that momentum is closely related to translational invariance (homogeneity) of space. Momentum is conserved when there is translational invariance (like in free space).

Any inhomogeneous potential breaks translational invariance $\Rightarrow$ $\Rightarrow$ momentum is no longer conserved. In other words, potential scatters particles from one momentum state to the other.

So, we know how to write the single-particle part of the Hamiltonian in terms of creation-annihilation operators (this is often called second-quantized representation).

$$H = \sum_{k} \varepsilon_k C_k^{+} C_k + \sum_{kk'} V(\vec{k}-\vec{k}') C_k^{+} C_{k'}$$

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

What remains is the interaction term:

Introduce electron field operators:

$$\psi^{+}(\vec{r}) = \sum_{k} \psi_k^{*}(\vec{r}) C_k^{+} = \sum_{\vec{k}} \langle \vec{k} | \vec{r} \rangle C_k^{+}$$

If C_k^{+} creates an electron in a state with definite momentum $\vec{k}$, $\psi^{+}(\vec{r})$ creates an electron at point $\vec{r}$.

Rewrite H in terms of field operators.

$$H = \sum_{kk'} \langle \vec{k} | T | \vec{k}' \rangle C_k^{+} C_{k'} +$$

$$+ \sum_{kk'} \langle \vec{k} | V | \vec{k}' \rangle C_k^{+} C_{k'}$$

Insert identity resolutions using states with definite $\vec{r}$:

$$1 = \int d\vec{r}\, |\vec{r}\rangle\langle\vec{r}|$$

$$\mathcal{H} = \sum_{kk'} \int d\vec{r}\, d\vec{r}\,' \langle\vec{k}|\vec{r}\rangle\langle\vec{r}|T|\vec{r}\,'\rangle\langle\vec{r}\,'|\vec{k}'\rangle \cdot C_k^\dagger C_{k'} + \sum_{kk'} \int d\vec{r}\, d\vec{r}\,' \langle\vec{k}|\vec{r}\rangle \langle\vec{r}|V|\vec{r}\,'\rangle \cdot \langle\vec{r}\,'|\vec{k}'\rangle C_k^\dagger C_{k'} =$$

$$= \int d\vec{r}\, d\vec{r}\,' \,\Psi^\dagger(\vec{r}) \langle\vec{r}|T|\vec{r}\,'\rangle \Psi(\vec{r}\,') +$$

$$+ \int d\vec{r}\, d\vec{r}\,' \,\Psi^\dagger(\vec{r}) \langle\vec{r}|V|\vec{r}\,'\rangle \Psi(\vec{r}\,')$$

$$\langle\vec{r}|T|\vec{r}\,'\rangle = -\frac{\hbar^2}{2m}\nabla^2 \delta(\vec{r}-\vec{r}\,')$$

$$\langle\vec{r}|V|\vec{r}\,'\rangle = V(\vec{r})\,\delta(\vec{r}-\vec{r}\,')$$

$$\mathcal{H} = \int d\vec{r}\, \Psi^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \Psi(\vec{r}) +$$

$$+ \int d\vec{r}\, \Psi^\dagger(\vec{r})\, V(\vec{r})\, \Psi(\vec{r})$$

This should remind you expectation value of a Hamiltonian in a state $\psi(\vec{r})$:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

$$\langle\psi|H|\psi\rangle = \int d\vec{r}\, \psi^*(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r})$$

This is why the creation-annihilation operator formalism is sometimes called second quantization: it looks as if wavefunction becomes an operator.

$$\rho(\vec{r}) = \psi^+(\vec{r})\psi(\vec{r}) \text{ - density operator.}$$

$$\int d\vec{r}\, \rho(\vec{r}) = \int d\vec{r} \sum_{kk'} \psi^*_k(\vec{r})\, \psi_{k'}(\vec{r})\, C^+_k C_{k'} =$$

$$= \int d\vec{r} \sum_{kk'} \frac{1}{V} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}\, C^+_k C_{k'} =$$

$$= \sum_k C^+_k C_k = \sum_k n_k = N$$

Electron-electron interaction term in the Hamiltonian can then be written as:

$$H_{int} = \frac{1}{2}\int d\vec{r}\, d\vec{r}'\, \rho(\vec{r}) \frac{e^2}{|\vec{r}-\vec{r}'|} \rho(\vec{r}') =$$

$$= \frac{1}{2}\int d\vec{r}\, d\vec{r}'\, \psi^+(\vec{r})\psi(\vec{r}) \frac{e^2}{|\vec{r}-\vec{r}'|} \psi^+(\vec{r}')\psi(\vec{r}')$$

Thus the full Hamiltonian can be witten as:

$$\mathcal{H} = \int d\vec{r}\, \psi^{+}(\vec{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) +$$

$$+ \frac{1}{2} \int d\vec{r}\, d\vec{r}\,' \, \psi^{+}(\vec{r})\, \psi^{+}(\vec{r}\,')\, V(\vec{r}-\vec{r}\,')\, \psi(\vec{r}\,')\, \psi(\vec{r})$$

Add spin index:

$$\mathcal{H} = \int d\vec{r} \sum_{\sigma} \psi_{\sigma}^{+}(\vec{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi_{\sigma}(\vec{r}) +$$

$$+ \frac{1}{2} \int d\vec{r}\, d\vec{r}\,' \sum_{\sigma\sigma'} \psi_{\sigma}^{+}(\vec{r})\, \psi_{\sigma'}^{+}(\vec{r}\,')\, V(\vec{r}-\vec{r}\,')\, \psi_{\sigma'}(\vec{r}\,')\, \psi_{\sigma}(\vec{r})$$