Lecture 5

Recapping last lecture:

any operator in a many-electron system can be represented as:

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

Consider one-body operators:

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

As was shown in lecture 5, the matrix element $\langle n_1, n_2, \ldots | A | n_1', n_2', \ldots \rangle$ in this case is only nonvanishing when $|n_1, n_2, \ldots\rangle$ and $|n_1', n_2', \ldots\rangle$ differ by the occupation of not more than one state:

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

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

The matrix element in this case is simply equal to:

$$\langle n_1, n_2, \ldots | A | n_1', n_2', \ldots \rangle =$$

$$= \int d\vec{r}^{\,+} \, \psi^*_{k_i'}(\vec{r}^{\,+}) \, A(\vec{r}^{\,+}) \, \psi_{k_j'}(\vec{r}^{\,+}) = \langle k_i' | A | k_j' \rangle$$

Consider an arbitrary N-electron wavefunction:

$$|\Phi\rangle = \sum_{\{n_\gamma\}} C_{\{n_\gamma\}} |\{n_\gamma\}\rangle$$

$$A|\Phi\rangle = \sum_{\{n_\gamma\}\{n'_\gamma\}\{n''_\gamma\}} |\{n_\gamma\}\rangle \langle \{n_\gamma | A | \{n'_\gamma\}\rangle \cdot$$

$$\cdot \langle \{n'_\gamma | \{n''_\gamma\}\rangle C_{\{n''_\gamma\}} =$$

$$= \sum_{\{n_\gamma\}\{n'_\gamma\}} |\{n_\gamma\}\rangle \langle \{n_\gamma | A | \{n'_\gamma\}\rangle C_{\{n'_\gamma\}}$$

i.e. what A does it it takes Slater determinant $|\{n'_\gamma\}\rangle$ in the expansion of $|\Phi\rangle$ and replaces it with $|\{n_\gamma\}\rangle$, with the coefficient $\langle \{n_\gamma | A | \{n'_\gamma\}\rangle$.

Now we can write this in terms of creation-annihilation operators as:

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

Thus for kinetic energy we have:

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

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

Periodic potential:

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

Recall that momentum is closely related to translational invariance (homogeneity) of space.
Momentum is conserved when there is translational invariance $\Rightarrow$ this is reflected in the fact that the free noninteracting electron hamiltonian which only consists of kinetic energy T, is diagonal in momentum.

Any inhomogeneous potential, like the periodic crystal potential, breaks the translational invariance of free space $\Rightarrow$ momentum is no longer conserved. In other words, periodic potential scatters electrons between different momentum states.

So we now know how to write the single-particle part of the Hamiltonian in terms of creation-annihilation operators:

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

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

What remains is the interaction term. We could deal with it in the same way as with one-particle terms, but let's do it in a less figurny, but quicker way.

Introduce electron field operators:

$$\psi^+(\vec{r}) = \sum_k \psi_k^*(\vec{r}) C_k^+ = \frac{1}{\sqrt{V}} \sum_k e^{-i\vec{k}\cdot\vec{r}} C_k^+ =$$

$$= \sum_k \langle \vec{k} | \vec{r} \rangle C_k^+$$

$\psi^+(\vec{r})$ creates an electron at point $\vec{r}$.

Let rewrite H in terms of field operators.

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

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

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

$$H = \sum_{kk'} \int d\vec{r}\, d\vec{r}'\, \langle k|\vec{r}\rangle \langle \vec{r}|T+V|\vec{r}'\rangle\langle\vec{r}'|k'\rangle$$

$$\cdot\ C_k^\dagger C_{k'} = \int d\vec{r}\, d\vec{r}'\, \psi^+(\vec{r})\langle \vec{r}|T+V|\vec{r}'\rangle\psi(\vec{r}')$$

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

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

Thus we obtain:

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

This is why this formalism is often called second quantization: it looks just like an expectation value of a single-particle Hamiltonian:

$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$ in a state $\psi(\vec{r})$:

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

but with a wavefunction replaced by an operator.

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

$$\int d\vec{r}\, \rho(\vec{r}) = \int d\vec{r} \sum_{kk1} [illegible] \frac{1}{V} e^{-i(\vec{k}-\vec{k}1)\cdot\vec{r}} \quad C_k^+ C_{k1} =$$

$$= \sum_k C_k^+ C_k = \sum_k n_k = N \text{ - total particle number}$$

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

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

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

So finally we have:

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

$$+ \frac{1}{2} \int d\vec{r}\, d\vec{r}1 \sum_{\sigma\sigma1} \psi_\sigma^+(\vec{r})\, \psi_{\sigma1}^+(\vec{r}1)\, V(\vec{r}-\vec{r}1)\, \psi_{\sigma1}(\vec{r}1)\psi_\sigma(\vec{r})$$

$$V(\vec{r}-\vec{r}1) = \frac{e^2}{|\vec{r}-\vec{r}1|}$$