Physics 460/560 Lecture 10

Electrons in metals

Many physical properties of metals can be understood by considering the conduction electrons to form a free Fermi gas. The simplest metals are the alkali metals—lithium, sodium, potassium, cesium, and rubidium. These atoms have one s-electron outside a noble-gas shell. In the metal, this s-orbital hybridizes to form a conduction band. The ionic core has a filled electronic shell and is inert, but has a net charge $+e$. In sodium, the

ionic cores occupy only 15%
of the volume of the crystal.

The free-electron model of metals was developed even before the advent of quantum mechanics. The classical theory had several successes, such as the derivation of Ohm's law and the relation of thermal + electrical conductivity. However, it failed to explain the heat capacity and magnetic susceptibility of metals — this was a failing not of the free electron model, but of classical statistical mechanics.

At first sight, the free-electron model seems to be a crude approx.:

i) After all, even if the ionic core is small, as in sodium, it is still positively charged, and will scatter electrons. However, an electron is not scattered by a <u>periodic lattice</u> of ions because matter waves propagate freely in a periodic structure.

ii) Electrons should also interact strongly with other electrons via Coulomb interactions. However, the Pauli principle blocks most scattering processes at low temperatures. In a very pure specimen at low temperatures, an electron may have a mean free up to 10^8 interatomic spacings (> 1 cm)!

path up to 10^8 interatomic spacings (> 1 cm)!

Fermions

We showed that bosonic particles, like phonons, can be described in terms of creation and annihilation operators a_k^+ + a_k, which satisfy an algebra:

$$[a_k, a_{k'}^+] = \delta_{kk'},$$

$$[a_k, a_{k'}] = [a_k^+, a_{k'}^+] = 0.$$

The operator which "counts" how many bosons are in a mode k is

$$\hat{n}_k = a_k^+ a_k.$$

There is another possible algebra to describe a system of identical particles. The fact that $[a_k^+, a_{k'}^+] = 0$ means that the many-phonon wavefunction is <u>symmetric</u> under interchange of particles.

<u>Fermions</u> are particles for which the many-body wavefunction is <u>antisymmetric</u> under interchange of particles. This feature can be built in using an algebra based on the <u>anticommutator</u>

$$[a, b]_+ = ab + ba.$$

Let c_k^+ be the creation operator for an electron in state k, and c_k an annihilation operator for the same state. Assume that these operators obey the following algebra:

$$[c_k, c_{k'}^+]_+ = \delta_{kk'}$$

$$[c_k, c_{k'}]_+ = [c_k^+, c_{k'}^+]_+ = 0$$

Also, let $\hat{n}_k = c_k^+ c_k$ and let the state with no fermions present be denoted $|0\rangle$.

Consider a state $|\psi\rangle$ which is an eigenstate of $\hat{n}_k$

with eigenvalue n_k:

$$\hat{n}_k |\psi\rangle = n_k |\psi\rangle .$$

What is the state $c_k |\psi\rangle$?

$$\hat{n}_k c_k |\psi\rangle = c_k^\dagger c_k c_k |\psi\rangle$$

$$= \left[1 - c_k c_k^\dagger\right] c_k |\psi\rangle$$

$$= c_k (1 - \hat{n}_k) |\psi\rangle$$

$$= (1 - n_k) c_k |\psi\rangle$$

However, we also have

$$[c_k, c_k]_+ = 2 c_k c_k = 0 , \text{ so}$$

$$\hat{n}_k c_k |\psi\rangle = c_k^\dagger c_k c_k |\psi\rangle = 0 .$$

Thus, there are only two possibilities: either $n_k = 1$ or $c_k |\psi\rangle = 0$.

But if $c_k|\psi\rangle = 0$ then

$c_k^\dagger c_k |\psi\rangle = \hat{n}_k |\psi\rangle = 0$.

Thus $\hat{n}_k$ can have only two eigenvalues, 0 and 1.

Next consider the state

$c_k^\dagger |\psi\rangle$:

$$\hat{n}_k c_k^\dagger |\psi\rangle = c_k^\dagger c_k c_k^\dagger |\psi\rangle$$
$$= c_k^\dagger [1 - c_k^\dagger c_k] |\psi\rangle$$
$$= (1 - n_k) c_k^\dagger |\psi\rangle$$

If $n_k = 0$, then $c_k^\dagger |\psi\rangle$ is an eigenstate of $\hat{n}_k$ with eigenvalue 1; $c_k^\dagger$ creates a Fermion in the state k.

- $c_k^\dagger \, | n_k = 0 \rangle = \alpha | n_k = 1 \rangle$

$\langle n_k = 0 | \, c_k \, c_k^\dagger \, | n_k = 0 \rangle = |\alpha|^2 \langle n_k = 1 | n_k = 1 \rangle$

$\langle n_k = 0 | (1 - \hat{n}_k) | n_k = 0 \rangle = |\alpha|^2$

$1 = |\alpha|^2$

α may be chosen to be 1.

- Thus $c_k^\dagger \, | n_k = 0 \rangle = | n_k = 1 \rangle$.

What is $c_k^\dagger \, | n_k = 1 \rangle$?

$c_k^\dagger \, | n_k = 1 \rangle = c_k^\dagger \, c_k^\dagger \, | n_k = 0 \rangle = 0.$

$c_k^\dagger \, c_k^\dagger = 0$

$\Rightarrow$ Pauli exclusion principle prevents two Fermions from occupying the same state.

Summarizing:

$$c^\dagger|0\rangle = |1\rangle$$

$$c^\dagger|1\rangle = |0\rangle$$

$$c|1\rangle = |0\rangle$$

$$c|0\rangle = 0$$

Consider the following states, which form a basis for the many-fermion Hilbert space:

$$|\Psi\rangle = \prod_k c_k^+ |0\rangle, \quad (\star)$$

where all k's must be distinct.

Let $|k\,k'\rangle = c_k^+ c_{k'}^+ |0\rangle$.

$$|k'k\rangle = c_{k'}^+ c_k^+ |0\rangle$$

$$= -c_k^+ c_{k'}^+ |0\rangle$$

$$= -|k\,k'\rangle.$$

In general, any state of the form $(\star)$ is antisymmetric under interchange of particles.

Let k be a wavevector in one dimension and $|k\rangle = c_k^\dagger |0\rangle$.

Then $\langle x|k\rangle = \langle x| c_k^\dagger |0\rangle = \frac{1}{\sqrt{L}} e^{ikx}$

$= \psi_k(x)$.

What is $\langle x, x' | k k' \rangle$?

Up to a phase factor, it must be

$\langle x, x' | k k' \rangle = \langle x, x' | c_k^\dagger c_{k'}^\dagger | 0 \rangle$

$= \frac{\psi_k(x)\psi_{k'}(x') - \psi_{k'}(x)\psi_k(x')}{\sqrt{2}}$

since it is antisymmetric under interchange of particles. In general, a many-fermion basis wavefunction may be expressed as a sister

determinant:

$$\langle x_1 x_2 x_3 \cdots x_N | \prod_{k=k_1}^{k_N} c_k^\dagger | 0 \rangle$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(x_1) & \psi_{k_1}(x_2) & \cdots & \psi_{k_1}(x_N) \\ \psi_{k_2}(x_1) & \psi_{k_2}(x_2) & \cdots & \psi_{k_2}(x_N) \\ \vdots & & & \vdots \\ \psi_{k_N}(x_1) & \cdots & & \psi_{k_N}(x_N) \end{vmatrix}$$

By the definition of the determinant, the wavefunction is antisymmetric under interchange of any two particles.

If the state k has energy ε_k, then the energy of this wavefunction is

- $E = \sum_{k=k_1}^{k_N} \varepsilon_k$.

Clearly the operator

$H = \sum_k \varepsilon_k \hat{n}_k$ has this

eigenvalue:

- $H|\psi\rangle = H \prod_{k=k_1}^{k_N} c_k^+ |0\rangle$

$= \sum_p \varepsilon_p \hat{n}_p \prod_{k=k_1}^{k_N} c_k^+ |0\rangle$

What is $\hat{n}_p c_k^+$?

$\hat{n}_p c_k^+ = c_p^+ c_p c_k^+ = c_p^+ (\delta_{pk} - c_k^+ c_p)$

$= \delta_{pk} c_k^+ + c_k^+ c_p^+ c_p$.

So $[\hat{n}_p, c_k^+] = \delta_{pk} c_k^+$

$$H|\psi\rangle = \sum_p \varepsilon_p \left[\hat{n}_p, \prod_{k=k_1}^{k_N} c_k^+\right]|0\rangle$$

This equality follows since the second term in the commutator is zero since $\hat{n}_p|0\rangle = 0$. If $p \notin \{k_1, \ldots k_N\}$, then $\left[\hat{n}_p, \prod_k c_k^+\right] = 0$. If $p \in \{k_1, \ldots k_N\}$ then

$$\left[\hat{n}_p, \prod_{k=k_1}^{k_N} c_k^+\right] = \prod_{k=k_1}^{k_N} c_k^+ .$$

Thus $H|\psi\rangle = \sum_{k=k_1}^{k_N} \varepsilon_k |\psi\rangle$.

A big advantage of writing the Hamiltonian as $H = \sum_k c_k^+ c_k \varepsilon_k$

Typically, the Hamiltonian for a system of fermions has the form:

$$H = \sum_i \left[\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{x}_i) \right] + \frac{1}{2} \sum_{i \neq j} V(\vec{x}_i - \vec{x}_j)$$

Just as for bosons, one can introduce fermion field operators

$$\hat{\psi}(\vec{x}) = \sum_k \psi_k(\vec{x})\, c_k$$

$$\hat{\psi}^\dagger(\vec{x}) = \sum_k \psi_k^*(\vec{x})\, c_k^\dagger ,$$

where the sum runs over a complete set of basis states.

$\hat{\psi}$ and $\hat{\psi}^+$ obey anticommutation relations

$$\left[\hat{\psi}(\vec{x}), \hat{\psi}^+(\vec{y})\right]_+ = \delta(\vec{x}-\vec{y})$$

$$\left[\hat{\psi}(\vec{x}), \hat{\psi}(\vec{y})\right]_+ = 0$$

$$\left[\hat{\psi}^+(\vec{x}), \hat{\psi}^+(\vec{y})\right]_+ = 0$$

As for bosons, the Hamiltonian may be written

$$H = \int d^3x\, \hat{\psi}^+(\vec{x})\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{x})\right]\hat{\psi}(\vec{x})$$

$$+ \frac{1}{2}\int d^3x \int d^3y\, \hat{\psi}^+(\vec{x})\,\hat{\psi}^+(\vec{y})\,V(\vec{x}-\vec{y})\,\hat{\psi}(\vec{y})\,\hat{\psi}(\vec{x})$$

or, in a general basis as

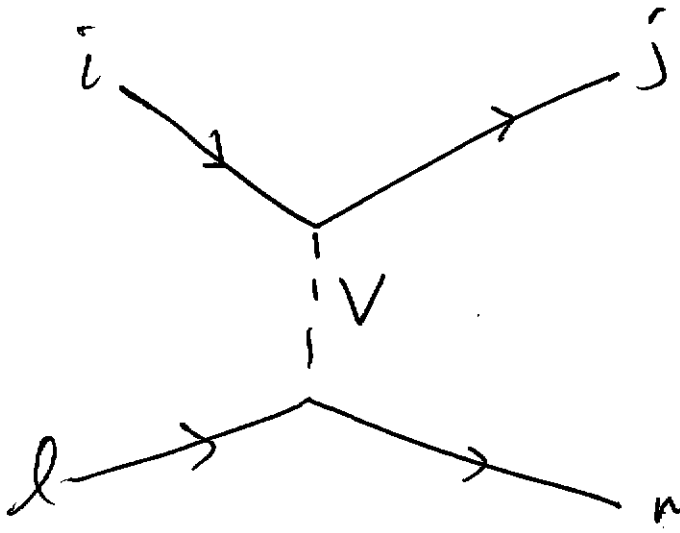
$$H = \sum_{ij} H^{(1)}_{ij} c_i^+ c_j + \frac{1}{2} \sum_{ijlm} V_{ijlm} c_j^+ c_m^+ c_l c_i$$

where

$$H^{(1)}_{ij} = \int d^3x \, \psi_i^*(\vec{x}) \left[\frac{-\hbar^2}{2m} \nabla^2 + U(\vec{x}) \right] \psi_j(\vec{x})$$

and

$$V_{ijlm} = \int d^3x \int d^3y \, \psi_j^*(\vec{x}) \psi_i(\vec{x}) V(\vec{x}-\vec{y}) \psi_m^*(\vec{y}) \psi_l(\vec{y})$$



is that one doesn't need to know how many particles there are in advance!

- Ground state for N independent fermions

$$|\psi_0\rangle = \prod_{|k| \le k_F} c_k^\dagger |0\rangle ,$$

where the product is over all distinct wavevectors of magnitude less than k_F, which is to be determined as a function of the number of particles and the size of the system.

Consider a 1D system of length L, with periodic boundary conditions:

$$\psi_k(x+L) = \psi_k(x)$$

$$\frac{1}{\sqrt{L}} e^{ik(x+L)} = \frac{1}{\sqrt{L}} e^{ikx}$$

$$\Rightarrow e^{ikL} = 1$$

$$k = \frac{2\pi n}{L}, \quad n \in \mathbb{Z}$$

If there are a total of N particles and we neglect spin, we have

$$-\frac{\pi N}{L} < k \leq \frac{\pi N}{L} = k_F$$

If we include spin, then for spin-1/2 electrons each k state may be occupied by one ↑ and one ↓

$$|\psi_0\rangle = \prod_{\sigma=\uparrow,\downarrow} \prod_{|k|\le k_F} c^{+}_{k\sigma}|0\rangle$$

$$-\frac{\pi N}{2L} < k \le \frac{\pi N}{2L} = k_F$$

This wavevector k_F is called the Fermi wavevector. The energy of the highest occupied state is called

the Fermi energy

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}.$$

The total energy of the ground state is

$$E_0 = \sum_{|k| \le k_F} \frac{\hbar^2 k^2}{2m}$$

$$= \underset{L\to\infty}{2} \frac{L}{2\pi} \int_{-k_F}^{k_F} dk \; \frac{\hbar^2 k^2}{2m}$$

↑ spin

$$= 2\frac{L}{\pi} \; \frac{\hbar^2}{2m} \; \frac{k_F^3}{3}$$

$$= \frac{\hbar^2 k_F^2}{2m} \; \frac{2L}{3\pi} \; \frac{\pi N}{2L} = \frac{N}{3}\varepsilon_F$$