FREE ELECTRON MODEL

Lecture 14

A.H. Harker
Physics and Astronomy
UCL

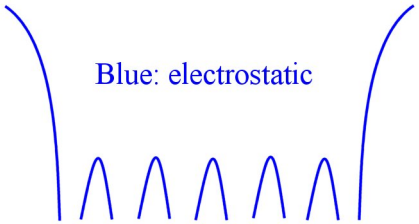
6 The Free Electron Model

6.1 Basic Assumptions

In the free electron model, we assume that the valence electrons can be treated as free, or at least moving in a region constant potential, and non-interacting. We'll examine the assumption of a constant potential first, and try to justify the neglect of interactions later.

6.1.1 Constant Potential

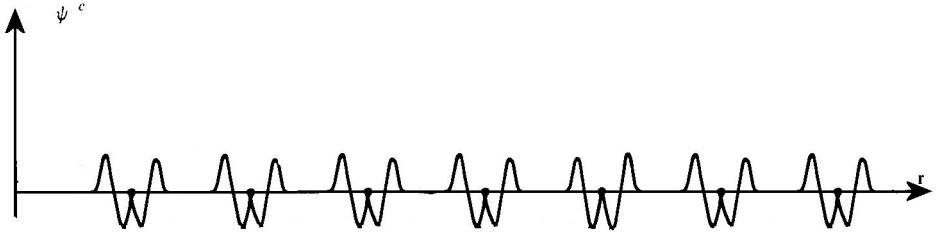
Imagine stripping the valence electrons from the atoms, and arranging the resulting ion cores on the aatomic positions in the crystal.



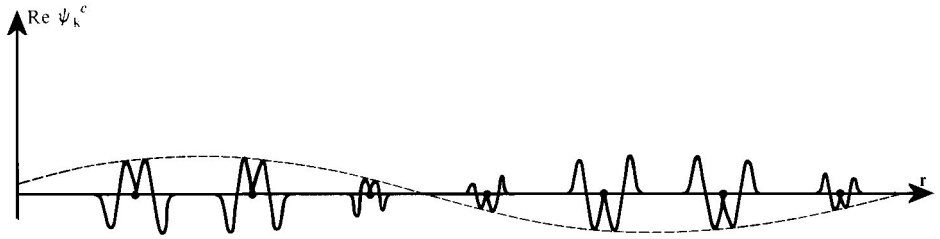
Resulting potential – periodic array of Coulombic attractions.

From atomic theory, we are used to the idea that different electronic functions must be orthogonal to each other (remember we used this idea in discussing the short-range repulsive part of interatomic potentials) i.e. if $\psi_c(\mathbf{r})$ is a core function and $\psi_v(\mathbf{r})$ is a valence function

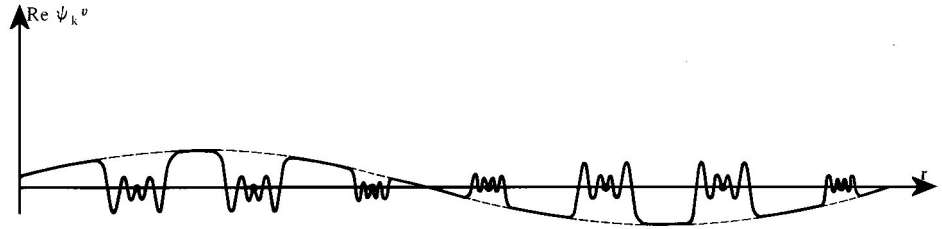
$$\int \psi_c(\mathbf{r})\psi_v(\mathbf{r})\mathrm{d}\mathbf{r} = 0.$$



Let's see how orthogonality might be achieved for a slowly-varying wave.

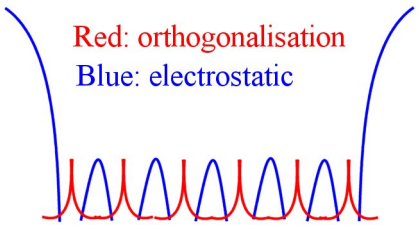


To achieve orthogonality:

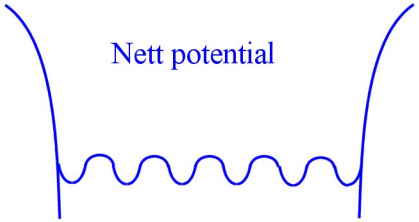


we need high spatial frequency (large k) components in the wave. Large $k \rightarrow$ large energy.

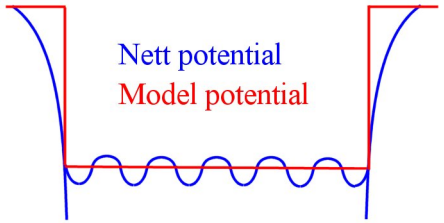
So the extra energy caused by the orthogonality partly cancels the Coulomb potential. This can be formalised in *pseudopotential theory*. The potential is weakened,



and the constant potential assumption is a reasonable one. The net result is that the effective potential seen by the electrons does not have very strong dependence on position.



So finally we assume that the attractive potential of the ion cores can be represented by a flat-bottomed potential.



We go further, and assume that the potential is deep enough that we can use a simple 'particle-in-a-box' model – the free electron model.

6.1.2 Free Electron Fermi Gas

For the particle in a box with potential $\mathcal{V}$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \mathcal{V}\psi = E'\psi,$$

or, with a shift of origin for energy, $E' - \mathcal{V} \to E$,

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi,$$

so that the wavefunctions have the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}\exp(i\mathbf{k}.\mathbf{r}),$$

where V is the volume of the material. These are travelling waves, with energies

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m},$$

dependent only on $k = |\mathbf{k}|$. Note that $E_{\mathbf{k}}$ depends only on the *magnitude* of $\mathbf{k}$, not its direction.

So we can use the result from section 4.4 (Lecture 10) that the number of states with modulus of wavevector between k and $k + \mathrm{d}k$ is

$$g(k)\mathrm{d}k = \frac{V}{8\pi^3}\ 4\pi k^2 \mathrm{d}k = \frac{V}{2\pi^2}\ k^2 \mathrm{d}k.$$

For electrons

$$\frac{\mathrm{d}E}{\mathrm{d}k} = \frac{\hbar^2 k}{m} = \frac{\hbar^2}{m}\sqrt{\frac{2mE}{\hbar^2}} = \frac{\hbar}{\sqrt{m}}\sqrt{2E}.$$

We also need to include a factor of 2 for spin up and spin down.

$$\begin{aligned} g(E) &= 2g(k)\frac{\mathrm{d}k}{\mathrm{d}E} \\ &= 2\frac{V}{2\pi^2}\ k^2\ \frac{\mathrm{d}k}{\mathrm{d}E} \\ &= 2\frac{V}{2\pi^2}\ \frac{2mE}{\hbar^2}\ \frac{\sqrt{m}}{\hbar\sqrt{2E}} \\ &= \frac{Vm}{\pi^2\hbar^3}\ \sqrt{2mE}. \end{aligned}$$

Note that as V increases, so does the density of states.

6.1.3 The Fermi Energy

Remember that the Fermi distribution function $n(E)$

$$n(E) = \frac{1}{\exp((E - E_F)/k_{\mathrm{B}}T) + 1}$$

at absolute zero is 1 up to the Fermi energy E_{F}. Suppose the volume V contains N_e electrons. Then we know

$$\begin{aligned} N_e &= \int_0^\infty g(E)n(E)\mathrm{d}E \\ &= \int_0^{E_{\mathrm{F}}} g(E)\mathrm{d}E \\ &= \frac{V\sqrt{2m^3}}{\pi^2\hbar^3}\int_0^{E_{\mathrm{F}}} \sqrt{E}\ \mathrm{d}E \\ &= \frac{V\sqrt{2m^3}}{\pi^2\hbar^3}\frac{2{E_{\mathrm{F}}}^{3/2}}{3} \end{aligned}$$

so

$$E_{\mathrm{F}} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N_e}{V}\right)^{2/3}.$$

We can define two related quantities:

- **Fermi temperature, T_{F},**

$$T_{\mathrm{F}} = E_{\mathrm{F}}/k_{\mathrm{B}}.$$

- **Fermi wavevector, k_{F}, the magnitude of the wavevector corresponding to k_{F},**

$$E_{\mathrm{F}} = \frac{\hbar^2 {k_{\mathrm{F}}}^2}{2m}$$

so

$$k_{\mathrm{F}} = \left(\frac{3\pi^2 N_e}{V}\right)^{1/3}.$$

6.1.4 Orders of magnitude

For a typical solid, the interatomic spacing is about 2.5×10^{-10} m. Assume each atom is in a cube with that dimension, and releases one valence electron, giving an electron density $N_e/V \approx 6 \times 10^{28}$ m^{-3}. Putting in the numbers, we find

- $E_\mathrm{F} \approx 9 \times 10^{-19}$ J $= 6$ eV**;**
- $T_\mathrm{F} \approx 70,000$ K**;**
- $k_\mathrm{F} \approx 1.2 \times 10^{10}$ m^{-1}**, comparable with the reciprocal lattice spacing** 2.5×10^{10} m^{-1}**;**

We can also estimate the electron velocity at the Fermi energy:

$$v_\mathrm{F} = \frac{\hbar k_\mathrm{F}}{m} \approx 1.4 \times 10^6 \mathrm{m\,s^{-1}},$$

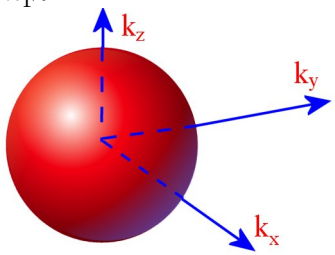
which is fast, but not relativistic.

$$\text{total energy of electrons} = \int_0^{E_\mathrm{F}} E\, g(E)\, \mathrm{d}E = \frac{3}{5} N_e E_\mathrm{F},$$

so that the average energy per electron is $\frac{3}{5}E_\mathrm{F}$.

6.1.5 The Fermi surface

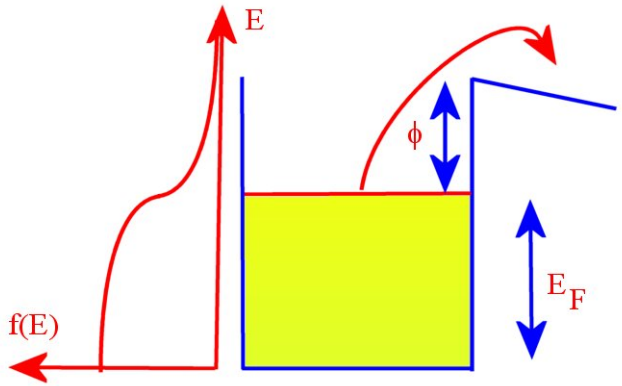
In later sections we shall talk a good deal about the Fermi surface. This is an constant-energy surface in reciprocal space (k-space) with energy corresponding to the Fermi energy. For the free electron gas, this is a sphere of radius k_F.



6.2 Some simple properties of the free electron gas

6.2.1 Thermionic emission

If the work function ϕ is small enough, if the material is heated the electrons may acquire enough thermal energy to escape the metal. A small electric field is used to draw them away.



The current

$$J = BT^2 \exp\left(-\frac{\phi}{k_\mathrm{B}T}\right),$$

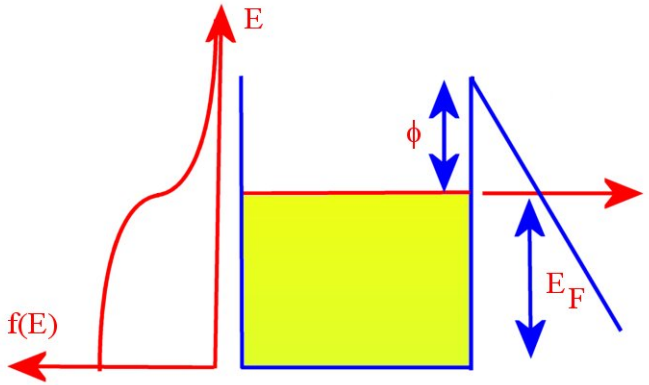
with a theoretical value

$$B = \frac{emk_\mathrm{B}{}^2}{\pi\hbar^2} = 1.2 \times 10^6 \ \mathrm{A\,m^{-2}\,K^{-2}}.$$

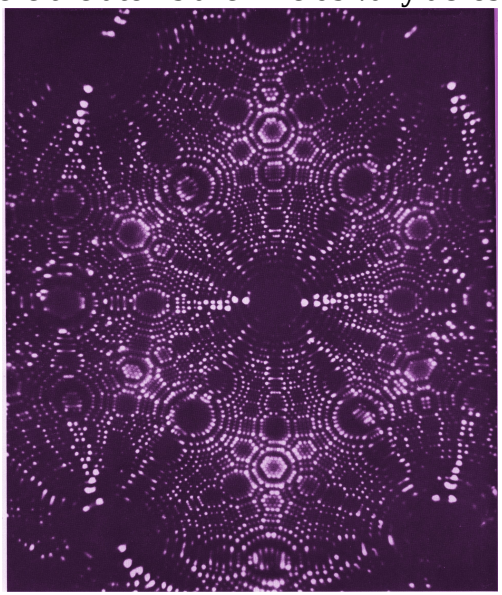
Experimentally the exponential dependence is confirmed, with similar values for B.

6.2.2 Field emission

A large applied field alters the potential outside the metal enough to allow electrons to *tunnel* out.



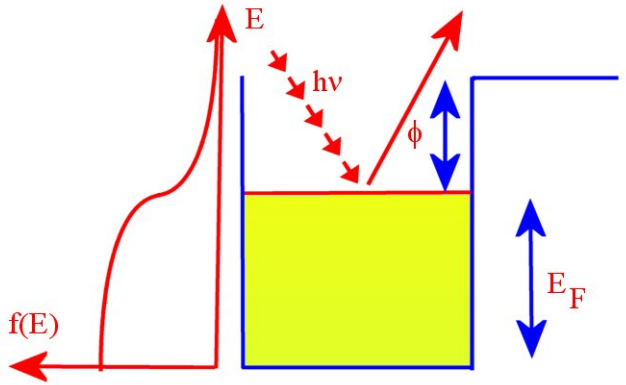
Very large fields are needed, but a sharp metal tip can give an image which shows where the atoms are – fields vary across the atoms.



More detail from newer scanning probe microscopes.

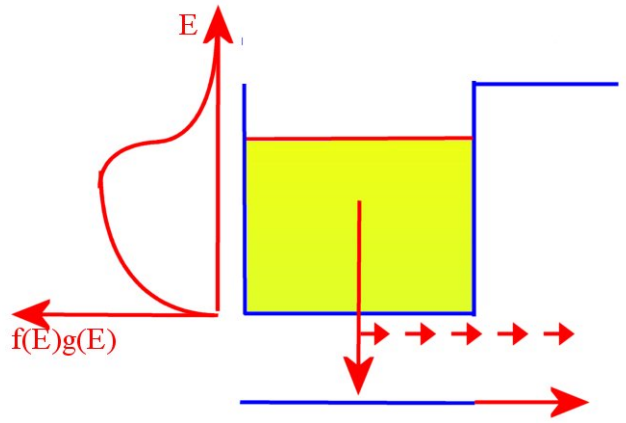
6.2.3 Photoemission

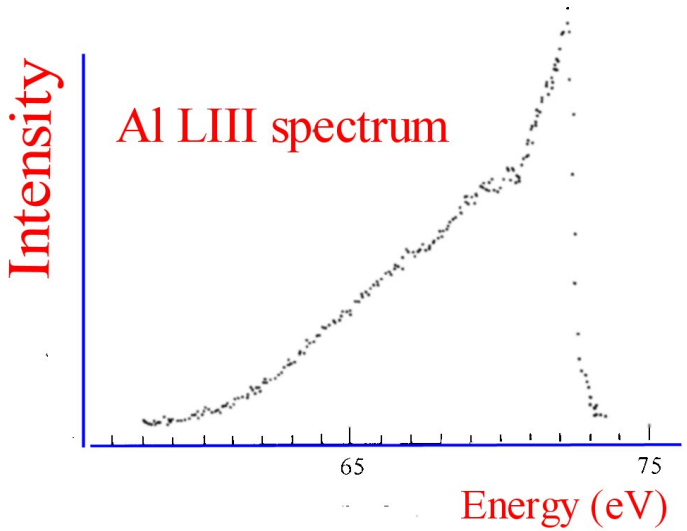
A photon with energy greater than the work function can eject an electron from the metal.



6.2.4 X-ray emission (Auger spectroscopy)

A high-energy electron incident on a metal may knock out an electron from a core state (almost unchanged from the atomic state). An alectron from the band can fall into the empty state, emitting an x-ray.

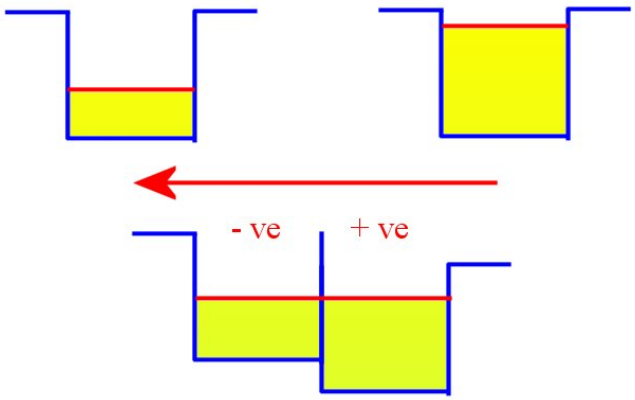




A typical soft X-ray spectrum for a simple metal. (After Aita and Sagawa (1969).)

6.2.5 Contact potential

If two metals with different Fermi energies are brought into contact, electrons will move so as to equalize the Fermi levels. As a result, one becomes positively charged and the other negatively charged, creating a potential difference which prevents further electron flow.



Summary

- **Justification for neglecting details of crystal potential.**
- **Fermi energy – several eV**
- **Fermi surface – comparable with size of Brillouin zone**
- **Simple properties**