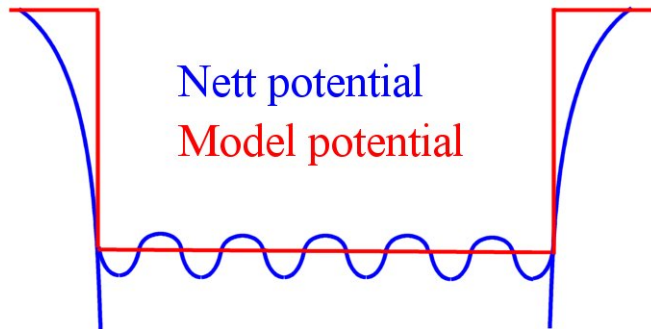# Solid State Physics

BEYOND THE FREE ELECTRON MODEL
Lecture 18

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7 Electrons in Periodic Structures

So far we have *completely* ignored the details of the potential seen by the electrons.

Nett potential
Model potential

The key point is that this is a *periodic* potential. Two consequences:
- restricts the form of the wavefunction;
- suggests Fourier analysis might be useful.

7.1 Bloch's theorem

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}),$$

with

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$$

where $\mathbf{R}$ is a lattice vector. Also, the probability density for the electrons must be a periodic function, so that it is the same in every unit cell, so

$$|\psi(\mathbf{r} + \mathbf{R})|^2 = |\psi(\mathbf{r})|^2$$

from which it follows that ψ only varies by a phase factor from cell to cell:

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\phi}\psi(\mathbf{r}).$$

Take a one-dimensional example: if the lattice spacing is a

$$\psi(x + a) = e^{i\phi}\psi(x),$$

so

$$\psi(x + Na) = e^{iN\phi}\psi(x).$$

But if we impose periodic boundary conditions for a system with N unit cells

$$\psi(x + Na) = e^{iN\phi}\psi(x) = \psi(x),$$

so

$$\phi = \frac{2n\pi}{N},$$

where n is an integer. This corresponds to

$$\phi = ka,$$

where

$$k = \frac{2n\pi}{Na}$$

is one of the allowed wavevectors in the system of length Na.

Now write the wavefunction in the form

$$\psi_k(x) = u_k(x)e^{ikx},$$

which satisfies

$$\psi_k(x+a) = e^{i\phi}\psi_k(x)$$

if

$$u(x+a) = u(x).$$

In other words, we have *Bloch's theorem*: the wavefunction for an electron in a periodic potential can be written as a phase factor e^{ikx} times a function with the same periodicity as the potential.

7.2 The Nearly Free Electron model

7.2.1 Basic ideas

In one dimension, consider the two free electron wavefunctions

$$\psi_+(x) = L^{-1/2}e^{i\pi x/a} \quad \text{and} \quad \psi_-(x) = L^{-1/2}e^{-i\pi x/a}$$

where the $L^{-1/2}$ normalizes over the length of the crystal, L: these both give constant electron densities $1/L$. But consider the combinations:

$$\psi_e(x) = \frac{1}{\sqrt{2}}(\psi_+(x) + \psi_-(x)) = \sqrt{\frac{2}{L}}\cos(\pi x/a))$$
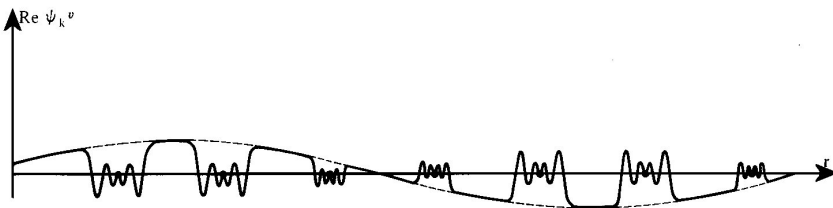
$$\psi_o(x) = \frac{1}{\sqrt{2}}(\psi_+(x) - \psi_-(x)) = \sqrt{\frac{2}{L}}\sin(\pi x/a)).$$

The new states are standing waves, not travelling waves.

In 3D:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}).$$
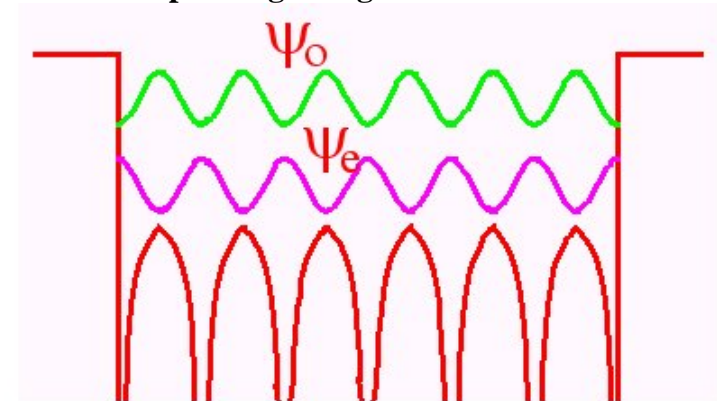
This gives the sort of wave we sketched before:

a periodic function *modulated* by a travelling wave.
The wave-vector, k, is significant whether we have free electrons ($u_{\mathbf{k}}(\mathbf{r}) = constant$) or not.

See what the corresponding charge densities are like:

It is clear that the even function has more charge density near the nuclei than the odd function, so we expect it to have lower energy.
The crystal potential has split the degeneracy of the states with $k = -\pi/a$ and $k = \pi/a$ – there is an *energy gap* between them.
As $(\pi/a) - (-\pi/a) = 2\pi/a = G$, a reciprocal lattice vector, we can imagine a wave with $k = \pi/a$ being Bragg reflected by interacting with the potential to give a wave with $k = -\pi/a$.

7.2.2 Perturbation theory

The idea of perturbation theory is to start with the solution to a problem, such as the free electron model, and assume that the difference between that model and the real problem (in our case, the periodic potential) is in some sense small.

That is, given a solution $\psi^{(0)}$ to the free electron Hamiltonian $\mathcal{H}^{(0)}$ with energy $E^{(0)}$, assume that the real hamiltonian is $\mathcal{H} = \mathcal{H}^{(0)} + \lambda\mathcal{H}'$, for some small parameter λ, and that the energy and the wavefunction may be written

$$\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots$$

and

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

so that

$$(\mathcal{H}^{(0)} + \lambda\mathcal{H}')(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots) = (E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots)$$
$$\times (\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots).$$

Expanding, and collecting the powers of λ, we find the λ-independent term

$$\mathcal{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)},$$

our original equation. The terms linear in λ give

$$\mathcal{H}^{(0)}\psi^{(1)} + \mathcal{H}'\psi^{(0)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}.$$

If we multiply through by $\psi^{(0)}$ and integrate, using the notation

$$\int \phi(x)\mathcal{H}\xi(x)\mathrm{d}x = \langle\phi|\mathcal{H}|\xi\rangle,$$

we find

$$\langle\psi^{(0)}|\mathcal{H}^{(0)}|\psi^{(1)}\rangle + \langle\psi^{(0)}|\mathcal{H}'|\psi^{(0)}\rangle = \langle\psi^{(0)}|E^{(0)}|\psi^{(1)}\rangle + \langle\psi^{(0)}|E^{(1)}|\psi^{(0)}\rangle,$$

but

$$\mathcal{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

means that (because the Hamiltonian is Hermitian) the first term

$$\langle\psi^{(0)}|\mathcal{H}^{(0)}|\psi^{(1)}\rangle = \langle\psi^{(1)}|\mathcal{H}^{(0)}|\psi^{(0)}\rangle^* = E^{(0)}\langle\psi^{(0)}|\psi^{(1)}\rangle$$

so

$$E^{(1)} = \langle\psi^{(0)}|\mathcal{H}'|\psi^{(0)}\rangle,$$

assuming normalised wavefunctions. This is first order perturbation theory.

7.2.3 Fourier Analysis

The one-dimensional periodic potential $V(x)$ may be expanded as a Fourier series. As usual, for a function with period a we expand in exponentials of $2n\pi x/a$. But $2\pi/a$ is a primitive reciprocal lattice vector. Generalizing to three dimensions:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}}.$$

7.2.4 The Energy Gap

In one dimension, the periodic potential is

$$V(x) = \sum_n (V_n e^{2\pi inx/a} + V_{-n} e^{-2\pi inx/a}),$$

and if we assume V is symmetrical about $x = 0$ this is

$$V(x) = 2\sum_n V_n \cos(2\pi nx/a).$$

Now, using perturbation theory, the energy difference between the $\sin$ and $\cos$ functions will be

$$E_o - E_e = \int_0^L 2\sum_n V_n \cos(2\pi nx/a)\frac{2}{L}(\sin^2(\pi x/a) - \cos^2(\pi x/a))\mathrm{d}x$$

$$= -\frac{4}{L}\sum_n V_n \int_0^L \cos(2\pi nx/a)\cos(2\pi x/a)\mathrm{d}x$$

and we know that only the $n = 1$ term in the integral will survive, integrating up to $L/2$, so

$$E_o - E_e = -2V_1.$$

The states at $k = \pi/a$ are separated by an amount equal to twice the lowest Fourier component of the potential. Note: strictly speaking, we should be using degenerate perturbation theory, but we have side-stepped this by 'spotting' the correct combinations of degenerate states (the $\cos$ and $\sin$ functions).
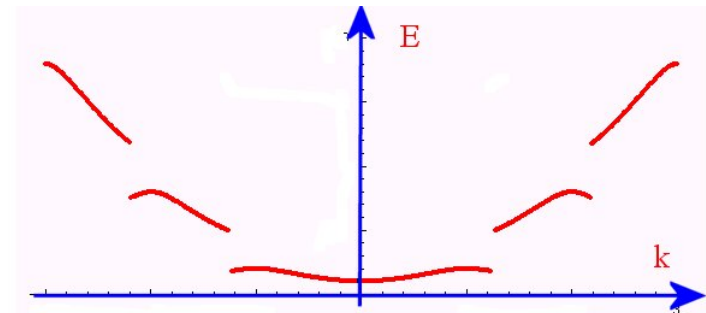
7.3 An exactly-soluble model

We know from second-year quantum mechanics that square well potentials are quite easy to deal with. The Kronig-Penney model is based on this.
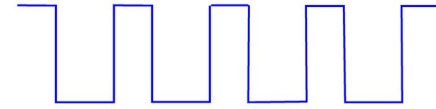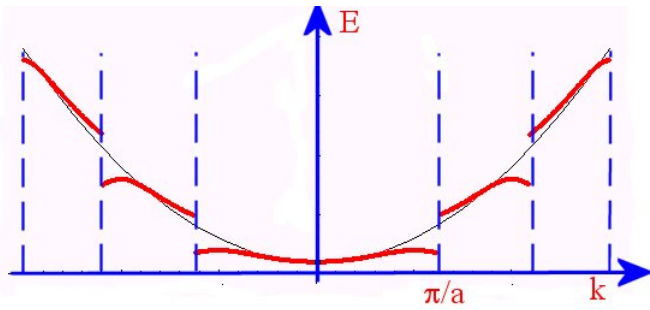

For details of the calculation, see for example Kittel *Introduction to Solid State Physics*.

We can seen the gaps in the energy spectrum – regions of energy in which there are no allowed states.

The free electron approximation remains a good approximation well away from the edges of the Brillouin zone – only wave-vectors close to a multiple of π/a are mixed together and have their energies altered by the periodic potential.

Translational symmetry is not essential for producing a band gap – amorphous solids also have band gaps.