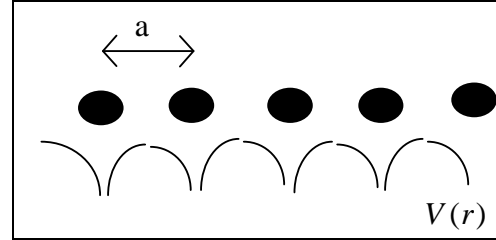


Beyond the free electron model

The effects of translational symmetry

The most serious omission in the free electron model is the entire neglect of the way the ions are arranged as a structure. If we are to include this, we need to discuss the Schrödinger equation with the potential due to the lattice included. The most important feature of the potential is that it



is *periodic*. The basic points can be made by considering a one-dimensional chain of atoms, equally spaced with separation a . The chain is either infinite in length or finite with periodic boundary conditions. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi = 0 \quad \text{Where } V(x) \text{ is periodic, i.e. } V(x+a) = V(x). \quad (1)$$

This is a one-dimensional lattice with one atom per unit cell and lattice parameter a .

The probability of finding an electron at a given point x is $|\psi(x)|^2$. But, from our discussion on the meaning of a unit cell, this probability must be the same at the same place in all unit cells. The *wavefunction* need not be the same in all cells provided that this condition is met, since the probability of finding an electron is an observable but the wavefunction is not. Thus, as we go from the first unit cell to the second cell in the chain, we can write $\psi(x+a) = C\psi(x)$ where C is a pure phase, so that

$|\psi(x+a)|^2 = |\psi(x)|^2$. Thus, for the p th cell, we have $\psi(x+pa) = C^p\psi(x)$. If the system is periodic, with N cells as the repeating block, we have the further condition that $\psi(x+Na) = \psi(x)$. This determines the constant C since $C^N = 1$. Hence C is one of the complex roots of unity; $C = \exp(2\pi i / N)$ and so the condition that the wavefunction must satisfy is

$$\psi(x+pa) = \psi(x)\exp(2\pi i p / N) \quad \text{where } p \text{ is an integer} \quad (2)$$

Let us write the wavefunction in the form $\psi(x) = u(x)\exp(2\pi i x / Na)$. Then, writing the wavefunction for the position $(x+pa)$, we have

$$\psi(x+pa) = u(x)\exp(2\pi i (x+pa) / Na) = u(x)\exp(2\pi i x / Na)\exp(2\pi i p / N) \quad (3)$$

This satisfies the condition (2) provided that $u(x+pa) = u(x)$. This, together with the form of the wavefunction suggested above, constitute *Bloch's theorem*. This argument closely resembles the arguments used when we were considering the displacement functions for lattice dynamics (except that there the displacements and not their squares are the observables). In other words the solutions we have found are travelling waves. As before, we can have a wavevector, $k = 2\pi p / Na$. Thus we can write the *Bloch wavefunction* as $\psi(x) = u(x)\exp(ikx)$. In three dimensions, this generalises to $\psi(\mathbf{r}) = u(\mathbf{r})\exp(i\mathbf{k} \cdot \mathbf{r})$. Also, as in the case of lattice dynamics, all the physically significant values of \mathbf{k} must lie in the (first) Brillouin zone (i.e. for $-\pi/a \leq k < \pi/a$ in the 1-d case). Using a Bloch wavefunction labelled by a k outside this region is equivalent to using one within it: the wavevector is defined modulo $k = 2\pi/a$.

The nearly-free electron model.

This theory assumes that the free electron model is quite a good approximation and that the ions make only a small perturbation. For the free electron model, we get standing

waves for the Bragg conditions $k = \pm\pi/a$. The (normalised) standing wave solutions are

$$\psi_S(+)=\frac{1}{\sqrt{2a}}(\exp(i\pi x/a)+\exp(-i\pi x/a)), \psi_S(-)=\frac{1}{\sqrt{2a}}(\exp(i\pi x/a)-\exp(-i\pi x/a));$$

which reduce to

$$\psi_S(+)=\sqrt{\frac{2}{a}}\cos(\pi x/a) \quad \psi_S(-)=i\sqrt{\frac{2}{a}}\sin(\pi x/a)$$

We can use first-order perturbation theory (see the note on perturbation theory at the end of the section) to calculate the effect the ionic potential provided that we can assume that the potential consists of a large, constant part (which the free electron model considers) and a small, periodically repeating bit, $V(x)$. For our one-dimensional chain, we can write this as a Fourier series,

$$V(x)=-\sum_{n=1}^{\infty}V_n\cos(2\pi nx/a)$$

Assuming that the lattice sites are at $x=la$, where l is an integer, then we would expect V_n to be strongly negative at that point (the electrons should be attracted to the ions) and have positive regions in between the sites. By first order perturbation theory, the energy change with respect to the unperturbed system is given by

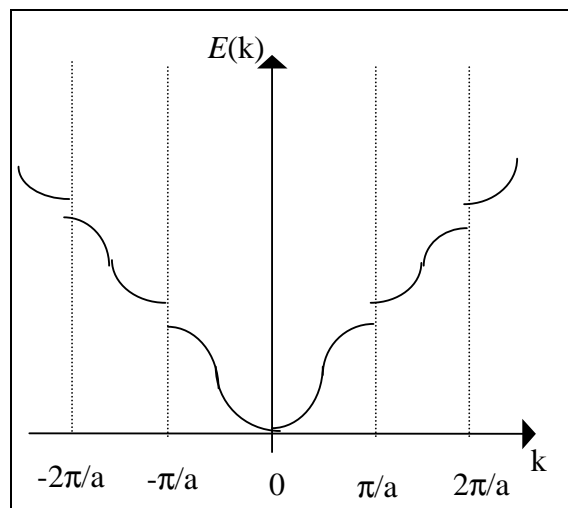
$$E' = \langle \Psi^0 | H' | \Psi^0 \rangle$$

The wavefunctions Ψ^0 we need are the standing wave states for the free-electron model $\psi_S(+)$ and $\psi_S(-)$. These are orthogonal to each other and normalised. Also, they look physically reasonable since the first function peaks at the lattice sites and the second peaks between them for $k = \pi/a$, so the energy of the two wavefunctions should be different. Putting in the wavefunctions and the potential, the perturbation on the energy can now be calculated. This is given by

$$E'(+)=\frac{2}{a}\int_0^a\cos^2(\pi x/a)\left(-\sum_{n=1}^{\infty}V_n\cos(2\pi nx/a)\right)dx$$

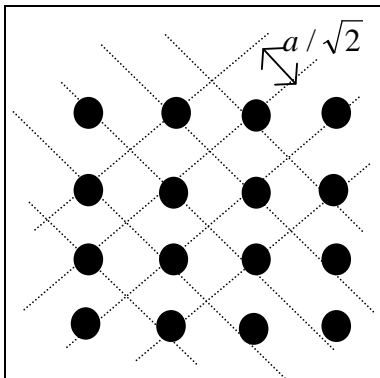
$$E'(-)=-\frac{2}{a}\int_0^a\sin^2(\pi x/a)\left(-\sum_{n=1}^{\infty}V_n\cos(2\pi nx/a)\right)dx$$

This is a somewhat messy calculation, requiring the use of the standard trigonometrical integrals. All terms in the summation give zero except for $n=1$. The final result is $E'(\pm) = \mp V_1/2$. In this case, E^0 is the free electron result $E(k) = \hbar^2 k^2 / 2m \pm V_n / 2$ and we can add E' to the free-electron parabola; at $k = \pm\pi/a$. This gives the same kind of effect that we saw when, in the lattice dynamics case, we considered the system with two different masses (although the physics is completely different); see diagram on the right). As before, the

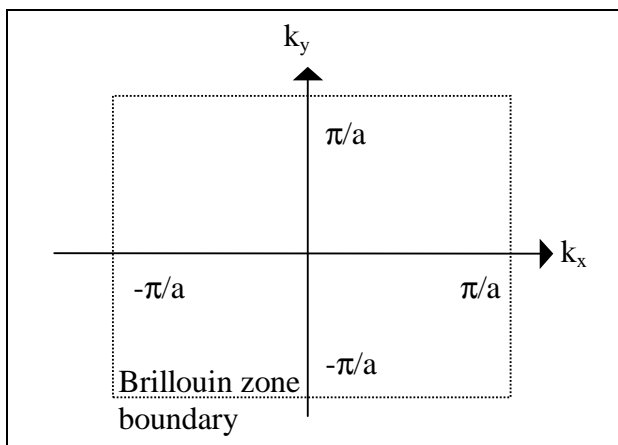


states with $k = \pm\pi / a$ are standing waves, and a *band gap* has opened up at the zone boundary. The basic physical point is that the *band gaps arise because of the ionic structure*. One should be careful how this is interpreted. The way we have derived it, it seems that the gaps come because of translational symmetry. This is not true. Amorphous solids have band gaps. That said, the band gaps we shall consider for the time being *are* tightly linked to the translational symmetry of the lattice.

In our model, we know that the physically significant values of k lie in the range $k = \pm\pi / a$ and that, for a lattice with N primitive unit cells, the allowed values of k are equally spaced and separated by $2\pi / Na = 2\pi / L$. Thus there are N values of k and, since we must also consider spin, $2N$ possible states for electrons to occupy. (This is generally true). Thus, for a monatomic element (Na, K for example) the band is half-filled. However, we have apparently concluded that diatomic elements have filled bands, i.e. that Mg is an insulator. This is an embarrassing conclusion to come to since Mg is a metal.



Our one-dimensional model is too simple. We must consider filling bands in all spatial directions simultaneously. Let us consider the situation in two dimensions, and try to map out the Brillouin zone boundary. Along [10] and [01] it is obviously at $k = \pm\pi / a$. In the [11] direction, the planes are separated by $a / \sqrt{2}$. Hence Bragg reflection will occur at $k = \pm\pi\sqrt{2} / a$. The Brillouin zone is a square with the vertices at $k = \pm\pi / a$ along the k_x, k_y axes. Moreover, the effect of the perturbation due to the lattice is different in different directions. Thus we



have, along the [10] direction,

$$E = \hbar^2 k_{10}^2 / 2m \pm V_n ([10]) / 2 .$$

Along the [11] direction, on the other hand, we have

$$E = \hbar^2 k_{11}^2 / 2m \pm V_n ([11]) / 2 .$$

Thus, the question arises, do we finish filling the first band before we start filling the second? If we do, then there will be a gap in the density of states and we have an insulator. If we do not, there may be a dip in the density of states,

but no gap and we still have a metal. The second is the case in Mg.

Summary of nearly free electron model

Successes

1. We have a physical explanation of why gaps appear.
2. We have an explanation of why a periodic lattice does not scatter electrons.

Problems

1. The explanation is so tightly linked to the idea of translational symmetry that it obviously cannot explain why glass has a band gap.

A note on perturbation theory

There are many cases where we do not know the answer for the system we are considering, but we do know the answer for a simple case that is, in some sense, 'close' to it. In this situation we can use the techniques of perturbation theory. I give here a simple, non-rigorous derivation of the argument. Those who want to see the job done better should consult a standard text on quantum mechanics; Schiff for example. Those who really want to see the job done should start with Dirac's text.

Consider a reference system with a Hamiltonian H^0 and wavefunctions $|\Psi^0\rangle$ i.e. the Schrodinger equation for this case is $H^0|\Psi^0\rangle = E^0|\Psi^0\rangle$. Now consider a *perturbed system* with Hamiltonian $H = H^0 + \lambda H'$ where H' is in some sense small and λ is the 'knob' (varying from zero to unity) that turns on the perturbation. As λ is varied, we assume that the wavefunctions and energies vary smoothly as

$$|\Psi\rangle = |\Psi^0\rangle + \lambda|\Psi^1\rangle + \dots \text{ and } E = E^0 + \lambda E^1 + \dots \text{ such that } \langle\Psi^0|\Psi^1\rangle = 0.$$

We can therefore expand the Schrodinger equation for the perturbed system as

$$(H^0 + \lambda H' + \dots)(|\Psi^0\rangle + \lambda|\Psi^1\rangle + \dots) = (E^0 + \lambda E^1 + \dots)(|\Psi^0\rangle + \lambda|\Psi^1\rangle + \dots)$$

Collecting terms to first order in λ , we obtain

$$H^0|\Psi^0\rangle = E^0|\Psi^0\rangle \quad \lambda(H^0|\Psi^1\rangle + H'|\Psi^0\rangle) = \lambda(E^0|\Psi^1\rangle + E^1|\Psi^0\rangle)$$

The first equation is simply the Schrodinger equation for the unperturbed system.

Rearranging the second equation we get

$$(H^0 - E^0)|\Psi^1\rangle = (E^1 - H')|\Psi^0\rangle$$

Premultiplying from the left by $\langle\Psi^0|$, we get

$$\langle\Psi^0|H^0|\Psi^1\rangle - E^0\langle\Psi^0|\Psi^1\rangle = \langle\Psi^0|\Psi^0\rangle E^1 - \langle\Psi^0|H'|\Psi^0\rangle$$

The terms on the left hand side vanish because $\langle\Psi^0|\Psi^1\rangle = 0$ (after using Schrodinger's equation for the unperturbed system on the first term). This gives our result

$$E^1 = \langle\Psi^0|H'|\Psi^0\rangle$$

This assumes that $|\Psi^0\rangle$ is normalised; if it is not, we must divide the right-hand side by $\langle\Psi^0|\Psi^0\rangle$.