5.62 Physical Chemistry II
Spring 2008

Band Theory of Solids

In the free electron theory we ignored all effects of the nuclei in the lattice, utilizing a particle-in-the-box approach <u>sans</u> a potential. In the band theory of solids considered here, we include a very simple potential representing the nuclei that leads to "bands" of potentially occupied states that are separated by gaps. The forces on the electrons are the regularly spaced, positively charged, essentially stationary nuclei and they are represented by delta functions.

Dirac Comb Potential: The simple periodic structure depicted below reproduces many interesting aspects of the band theory of metals. It is referred to as a *Dirac comb*, whereas a more sophisticated model, the Kronig-Penny model, employs a comb of rectangular shapes. The actual shape is not so important for our purposes.
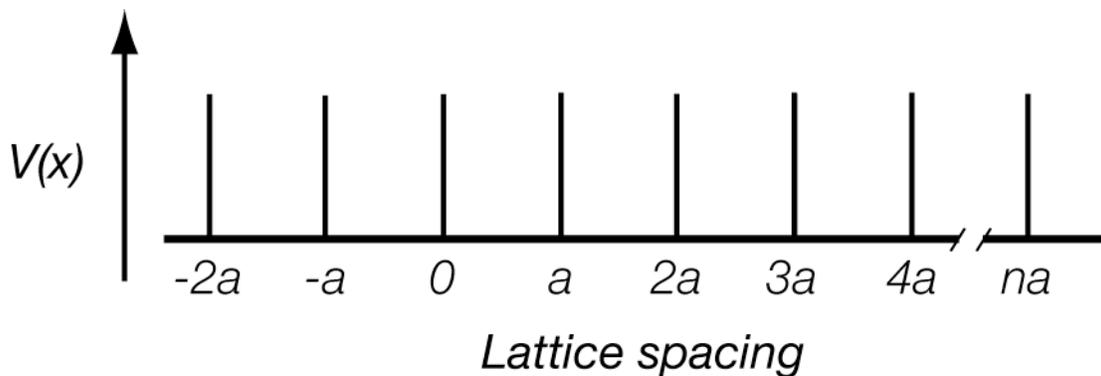
Lattice spacing

The potential periodic repeats itself after some distance a (the lattice spacing) so that we can write the potential as

$$V(x) = V(x + a)$$

This is the same idea that we used previously (the approach of *Born and von Kármán*) in our treatment of Debye solids and in the free electron theory of metals.

Bloch's Theorem – Felix Bloch [*Z. Physik* **52**, 555 (1928)] suggested an ingenious approach to treating this problem that is today know as Bloch's theorem. For the potential like the periodic comb above, the solution to the time independent Schrödinger equation (TISE)

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)\psi = E\psi$$

can be taken to satisfy the condition

$$\psi(x+a)=e^{iKa}\psi(x)$$

for some constant K. K could depend on E, but is generally independent of x.

We assume we have an operator $\hat{D}$ that moves us along the chain for "**a**" units such that

$$\hat{D}f(x)=f(x+a)$$

For a periodic potential, $\hat{D}$ commutes with $\hat{H}$ -- $\left[\hat{D},\hat{H}\right]=0$. Therefore, we can choose eigenfunctions of $\hat{H}$ that are simultaneously eigenfunctions $\hat{D}$.

$$D\psi = \lambda\psi$$

or

$$\psi(x+a)=\lambda\psi(x)$$

Therefore

$$\lambda = e^{iKa}$$

We will see below that K is real.

For a macroscopic crystal (containing N_a = Avogodro's number of sites) we can neglect the edge effect, and use the *Born-von Kármán* method to impose the boundary condition

$$\psi(x)=\psi(x+Na)$$

Therefore it follows that

$$\psi(x+Na)=e^{iNKa}\psi(x)$$

Since

$$e^{iNKa}=1=\cos(NKa)+i\sin(NKa)$$

and therefore

$$NKa=2\pi n \qquad \text{and} \qquad K=\left(\frac{2\pi n}{Na}\right) \qquad \left[n=0,\pm1,\pm2,.....\right]$$

Thus, K is real and we need to solve the TISE within a single cell (for example, for the interval $0 \leq x \leq a$.

Potential V(x) – We assume that V(x) consists of a long string of delta function spikes (the Dirac comb) depicted above. This is represented algebraically as

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$$

Thus, the x-axis of the comb has been "wrapped around" so the Nth spike occurs at x= -a.

$\underline{0 < x < a}$: In this region the potential is zero so

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad\qquad \frac{d^2\psi}{dx^2} = -k^2\psi \qquad\qquad \text{where} \qquad\qquad k = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$$

per usual. And the general solution is

$$\psi(x) = A\sin(kx) + B\cos(kx) \qquad 0 < x < a$$

$\underline{-a < x < 0}$:   In the cell immediately to the left of the origin

$$\psi(x) = e^{-iKa}\left[A\sin k(x+a) + B\cos k(x+a)\right] \quad -a < x < 0$$

At x=0, $\psi(x)$ must be continuous and therefore

$$B = e^{-iKa}\left[A\sin(ka) + B\cos(ka)\right]$$

Rearranging the expression yields

$$A\sin(ka) = B\left[e^{-iKa} - \cos(ka)\right] \tag{1}$$

At the boundary between the cells the derivative of $\psi(x)$ exhibits a discontinuity the intensity being proportional to α the amplitude of the delta function.

To deal with this situation we integrate the TISE from $-\varepsilon$ to $+\varepsilon$ (around zero) and take the limit as $\varepsilon \to 0$.

$$-\frac{\hbar^2}{2m}\int_{-\varepsilon}^{+\varepsilon}\frac{d^2\psi(x)}{dx^2}dx + \int_{-\varepsilon}^{+\varepsilon}V(x)\psi(x)dx = \underbrace{E\int_{-\varepsilon}^{+\varepsilon}\psi(x)dx}_{\substack{vanishing\\width}}$$

which yields

$$-\frac{\hbar^2}{2m}\frac{d\psi(x)}{dx}\bigg|_{-\varepsilon}^{+\varepsilon} + \int_{-\varepsilon}^{+\varepsilon}V(x)\psi(x)dx = 0$$

rearranging we obtain

$$\Delta\left(\frac{d\psi}{dx}\right) = \frac{\partial\psi}{\partial x}\bigg|_{+\varepsilon} - \frac{\partial\psi}{\partial x}\bigg|_{-\varepsilon} = \left(\frac{2m}{\hbar^2}\right)\underset{\varepsilon\to 0}{\text{limit}}\int_{-\varepsilon}^{+\varepsilon}V(x)\psi(x)dx$$

Usually the limit on the RHS vanishes and therefore $(\partial\psi(x)/\partial x)$ is continuous. However when V(x) is a delta function, this argument fails. In the case considered here $V(x) = \alpha \cdot \delta(x)$ and we obtain

$$\Delta\left(\frac{d\psi}{dx}\right) = \left(\frac{2m\alpha}{\hbar^2}\right)\psi(0) = \left(\frac{2m\alpha}{\hbar^2}\right)B$$

Next we evaluate the two derivatives $(\partial\psi/\partial x)_{+\varepsilon}$ and $(\partial\psi/\partial x)_{-\varepsilon}$ and take there difference at x=0 to obtain

$$Ak - e^{-iKa}k\left[A\cos(ka) - B\sin(ka)\right] = \left(\frac{2m\alpha}{\hbar^2}\right)B \tag{2}$$

Solving (1) for A, substituting into (2), and canceling a factor *kB* yields

$$\left[e^{iKa} - \cos(ka)\right]\left[1 - e^{-iKa}\cos(ka)\right] + e^{-iKa}\sin^2(ka) = \left(\frac{2m\alpha}{\hbar^2 k}\right)\sin(ka)$$

and this simplifies after some algebra to

$$\cos(Ka) = \cos(ka) + \left(\frac{m\alpha}{\hbar^2 k}\right)\sin(ka) \tag{3}$$

This equation determines the possible values of k and therefore the permitted energies. To place it into a more transparent form we let

$$z \equiv ka \qquad \text{and} \qquad \beta \equiv \left(\frac{m\alpha a}{\hbar^2}\right)$$

then we can write

$$\boxed{f(z) \equiv \cos(z) + \beta\frac{\sin(z)}{z}}$$

This function has two parts

$\cos(z)$: this term simply oscillates with z=ka *ad infinitum.*

$\beta\dfrac{\sin(z)}{z}$: This is a sinc function scaled by β . It is localized around z=0

and oscillates, decaying to zero as $z \rightarrow \infty$.

Note that in (3) above $\cos(Ka) = \pm 1$ and outside these limits there is not a solution to the equation since $|\cos(Ka)|$ cannot be ›1. These regions, which arise from the sinc term, correspond to "gaps" and are forbidden energies. These are separated by "bands" which are allowed energies. Within a band any energy is allowed since

$$Ka = \left(\frac{2\pi n}{N}\right)$$

recall that N is a very large number and n = an integer.

The figure below illustrates the bands and gaps. The oscillating function descends from on high (β=10 in this example) and decays to a constant cos (ka). The shaded regions between ±1 correspond to the bands and the unshaded to the gaps.

Bands

Gaps
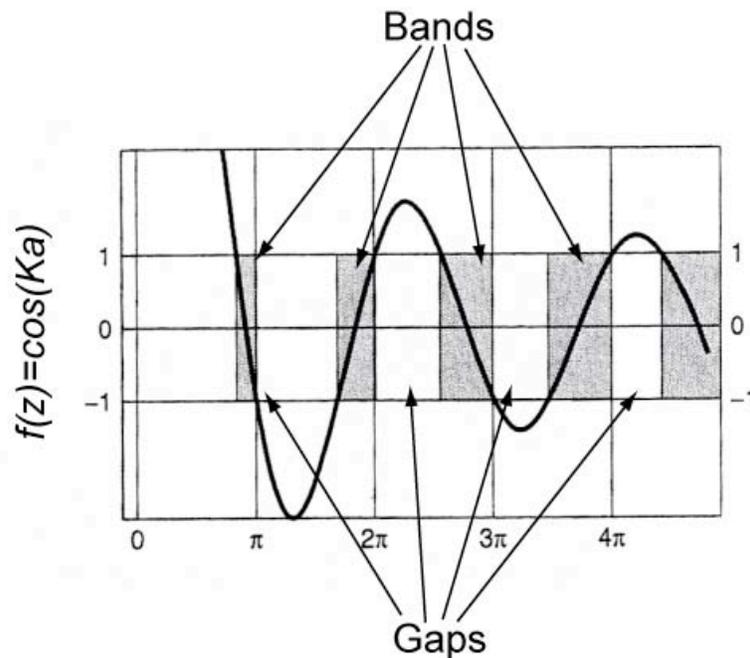
For a filled band (with q=2) it takes a large energy to excite an electron across the gap to the conduction band – this is an *insulator !*

However, if the band is partially filled it generally takes less energy to excite an electron and this material is typically a *conductor*.

If we dope an insulator with a few atoms with either larger or smaller q, then we place extra electrons into the next high band or create holes in the previously filled band. This permits weak currents to flow and the materials are referred to as <u>semiconductors</u>.

<u>Summary:</u> In the free electron theory all solids are conductors because there are no gaps in the energy level scheme. It takes the periodic potential of band theory to account for the factors of $\sim 10^{30}$ that are observed experimentally in resistivity/conductivity.