In the previous lecture, we started applying what we have learned to solids. We investigated a very simple model in which \( q \) electrons from each of \( N \) atoms in a solid of volume \( V \) are free. By applying boundary conditions (the wave function must be zero at the edges of the solid) and allowing only 2 electrons (\( \uparrow \) and \( \downarrow \)) in each state, because they are fermions, we arrived at the following results.
For a potential

\[ V(x, y, z) = \begin{cases} 0, & \text{inside } V; \\ \infty, & \text{otherwise.} \end{cases} \]

the allowed states occupy an octant in \( k \)-space and have energies

\[
E_{n_xn_yn_z} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)
\]

\[
= \frac{\hbar^2 k^2}{2m}.
\]

with a maximum \( k \) of

\[
k_F = (3\rho \pi^2)^{1/3}, \quad \rho \equiv \frac{Nq}{V}.
\]
The maximum energy (called Fermi energy) is

\[ E_F = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3} \]

At \( T = 0 \) all states up to the Fermi energy are filled and the states with higher energy are not filled:

\[ \rho(E) \begin{cases} \propto \sqrt{E} & \text{for } E < E_F, \\ = 0 & \text{for } E > E_F, \end{cases} \]

where \( \rho(E) \) is the density of states.
Notice that the electrons in the states with $E$ near $E_F$ can move into empty states when a small amount of energy is added. Therefore, this model would predict that all solids are conductors: the electrons whose energies are near $E_F$ can be accelerated easily, since slightly higher energy states are accessible to them.

We will now extend our model of the potential energy function to include a periodic potential (the exact shape of the potential doesn’t really matter much). This will lead to the prediction of bands of allowed energies in solids; the bands of allowed energies are separated by gaps that are forbidden.
In a conductor, $E_F$ falls inside an allowed band, called conduction band, as shown in the figure on the right. The electrons whose energies are near $E_F$ can then be accelerated easily, since the slightly high-energy states are accessible to them.

Example: conductor

\[ E \]

- partially filled band of allowed energies
- gap energies not allowed
- filled band of allowed energies

In an insulator, $E_F$ falls on the upper boundary of an allowed band, called the valence band. The electrons can be excited only by crossing the forbidden band, requiring an energy at least equal to $\Delta E$. 
So let’s see how these bands arise. (For an alternate treatment see, p. 1440–1446, Cohen-Tannoudji, Diu & Laloe, Vol. II.) Band structure arises when we consider a periodic potential, even in one dimension.

First consider a single particle subject to a periodic potential in one dimension:

\[ V(x + a) = V(x). \]

As an example, we will assume \( V(x) \) is a series of evenly spaced negative delta functions, spaced \( a \) units apart (\( a = \text{period} \)).

![Figure 5.5: The Dirac comb, Equation 5.57.](image)
Bloch’s Theorem:

If $V(x+a) = V(x)$, then the solution to the Schrödinger equation

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

can be taken to satisfy the condition

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

where $k$ is any constant (i.e. $K$ can be real or complex, but does not depend on $x$).
For a real solid, the potential energy function cannot really satisfy $V(x + a) = V(x)$ for all $x$ since the solid must be finite in size. Then Bloch’s theorem won’t apply. However, the following condition can ensure the periodicity for all $x$. Impose the ”boundary condition”:

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

where $N$ is the total # of atoms in the (one-dimensional) solid.

This is equivalent to ”wrapping” the $x$ axis around in a circle of circumference $Na$:
So now $V(x + a) = V(x)$ for all $x$. Then, since

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

by Bloch’s theorem, we can apply this $N$ times to get

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

But $\psi(x + Na) = \psi(x) \Rightarrow \psi(x) = e^{iNKa} \psi(x) \Rightarrow e^{iNKa} = 1$ or

$$NKa = 2\pi n,$$

where $n$ is an integer.

Thus,

$$K = \frac{2\pi n}{Na}, \quad n = 0, \pm 1, \pm 2, \ldots$$

and $K$ is necessarily real.
One might ask whether the assumption that $\psi(x + Na) = \psi(x)$ is justified. The only place it can make a difference is near the boundary. Since $N$ is such a large number generally, the assumption will have no effect in most of the volume of the solid.

\[ L \gg d \]

**FIGURE 8.7** Periodic potential that an electron sees in a one-dimensional crystalline solid.
So, now we only have to solve the T.I.S.E. within a single \textit{cell} (one period). Recursive application of \( \psi(x + a) = e^{iKa} \psi(a) \), \( K = \frac{2\pi n}{Na} \), will generate the solution everywhere else.

For the series of negative delta functions, we have

\[
V(x) = -\alpha \sum_{j=0}^{\infty} \delta(x - ja).
\]

The wells represent the electrical attraction between the electrons and the nuclei in the lattice.
In the region $0 < x < a$ the potential is zero, so

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \Rightarrow \quad \frac{d^2\psi}{dx^2} = -k^2 \psi \quad \text{with} \quad k \equiv \frac{\sqrt{2mE}}{\hbar},$$

as usual.

General solution:

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

Now we will use Bloch’s theorem to write the wave function immediately to the left of the origin and then apply the boundary conditions at $x = 0$. 
Bloch’s theorem $\Rightarrow \psi(x + a) = e^{+iKa}\psi(x)$.

For $-a < x < 0$,

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

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

I merely made the substitution $x \rightarrow x + a$ in the general solution for $0 < x + a < a \Rightarrow -a < x < 0$.

So we have

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

$$\psi(x) = e^{-iKa} \left[ A \sin k(x + a) + B \cos k(x + a) \right], \ -a < x < 0.$$
\psi \text{ must be continuous at } x = 0 \Rightarrow B = e^{-iKa}[A \sin ka + B \cos ka].

The derivative of \psi encounters a discontinuity proportional to the strength of the delta function:

\[ \Delta \left( \frac{d\psi}{dx} \right)\bigg|_{x=0} = -\frac{2m\alpha}{\hbar^2}\psi(0) \]

when \( V(x) = -\alpha \delta(x) \) [eq. 2.125, p. 72 in Griffith].

\[
\begin{align*}
\frac{d\psi}{dx}\bigg|_{x^+} &= k(A \cos kx - B \sin kx)\bigg|_{x=0} = Ak \\
\frac{d\psi}{dx}\bigg|_{x^-} &= e^{-iKa}k[A \cos k(x+a) - B \sin(x+a)]\bigg|_{x=0} = e^{-iKa}k[A \cos ka - B \sin ka]
\end{align*}
\]

Also, \( \psi(0^+) = B \). Thus, the boundary condition is

\[ kA - e^{-iKa}k[A \cos ka - B \sin ka] = -\frac{2m\alpha}{\hbar^2}B. \]
Solving the first boundary condition for $A \sin ka$ yields

$$A \sin ka = [e^{iK_a} - \cos ka] B.$$  

The second boundary condition can be written as

$$e^{-iK_a} k A[e^{iK_a} - \cos ka] + B e^{-iK_a} k \sin ka = -\frac{2m\alpha}{\hbar^2}B.$$ 

Multiply by $\frac{\sin ka}{k}$:

$$e^{-iK_a} A \sin ka[e^{iK_a} - \cos ka] + B e^{iK_a} \sin^2 ka = -\frac{2m\alpha}{\hbar^2 k}B \sin ka$$

Substitute expression on top of this page

$$e^{-iK_a} B \left[e^{iK_a} - \cos ka\right]^2 + B e^{-iK_a} \sin^2 ka = -\frac{2m\alpha}{\hbar^2 k}B \sin ka.$$
\[ e^{-iKa} \left[ e^{i2Ka} - 2e^{iKa} \cos ka + \cos^2 ka \right] + e^{-iKa} \sin^2 ka = -\frac{2m\alpha}{\hbar^2 k} \sin ka \]

\[ \frac{e^{iK_a} + e^{-iK_a}}{2 \cos K_a} - 2 \cos ka = -\frac{2m\alpha}{\hbar^2 k} \sin ka \]

\[ \cos Ka - \cos ka = -\frac{m\alpha}{\hbar^2 k} \sin ka \]

Recall that \( K = \frac{2\pi n}{Na}, \ n = 0, \pm 1, \pm 2, \ldots \) [from boundary condition \( \psi(x + Na) = \psi(x) \)], and \( k = \frac{\sqrt{2mE}}{\hbar} \). Therefore, the above equation defines the allowed values of \( k \) and therefore \( E \).
Write the equation as

\[ \cos Ka = \cos ka - \frac{m\alpha}{\hbar^2 k} \sin ka. \]

To simplify the notation, define the dimensionless variable \( z \equiv ka \) (we want to find allowed values of \( z \)) and the dimensionless number \( \beta \equiv \frac{m\alpha a}{\hbar^2} \), which is related to the strength and the spacing of the potential.

Then the right-hand side of the defining equation can be written

\[ f(z) = \cos z - \beta \frac{\sin z}{z}. \]

Typical values for the dimensionless number \( \beta \) are \( \mathcal{O}(1) \) (see next page).
\[
\beta = \frac{m \alpha a}{\hbar^2}
\]

\[
m = \text{electron mass} = 0.51 \text{ MeV}/c^2
\]

\[
\hbar = 6.6 \times 10^{-22} \text{ MeV s}
\]

\[
[\alpha] = \text{energy} \times \text{length}
\]

\[
[\alpha a] = \text{energy} \times \text{length}^2
\]

The only length scale in the problem is the inter atom spacing, which is typically a few \( \AA = 10^{-10} \text{m} \).

The only energy scale is the binding energies, which are typically \( \mathcal{O}(\text{a few eV}) \).

Thus, \( \beta \) is of the order

\[
\frac{0.51 \text{ Mev}}{(3 \times 10^8 \text{ ms}^{-1})^2} \times \frac{5 \times 10^{-6} \text{ MeV} \cdot (2 \times 10^{-10}m)^2}{(6.6 \times 10^{-22} \text{ MeV s})^2} \sim 1
\]
The following figure is plotted for the case $\beta = 1$; i.e.,

$$f(z) = \cos z - \frac{\sin z}{z}. \quad \text{[\textit{f(z) is an even function of } z.]}$$

$$\lim_{z \to 0} \frac{\sin z}{z} = 1 \implies f(0) = 0$$

Note, that $f(z)$ can be greater than 1 and less than $-1$. But the left-hand side of the defining equation is $\cos Ka = \cos \frac{2\pi n}{N}$.

Since $|\cos(Ka)| \leq 1$, the only allowed values of $z$ (and therefore $k = \frac{z}{a}$ and $E = \frac{\hbar^2 k^2}{2m}$) are those for which $|f(z)| \leq 1$, indicated as the 1st band, 2nd band, etc., in the above figure.
Within a given band, any value of \( z \) for which \( f(z) = \cos \frac{2\pi n}{N} \) where \( n = 0, \pm 1, \pm 2, \ldots \) and \( N \) is a huge number, is allowed.

Imagine drawing \( N \) horizontal lines on the figure, at values of \( \cos \frac{2\pi n}{N}, n = 0, \pm 1, \pm 2, \ldots \) Positive and negative values of \( n \) give the same result.

\[
\begin{align*}
n = 0 & \Rightarrow \cos \frac{2\pi n}{N} = +1 \\
0 < n < \frac{N}{2} & \Rightarrow +1 > \cos \frac{2\pi n}{N} > -1 \\
\frac{N}{2} < n < N & \Rightarrow -1 < \cos \frac{2\pi n}{N} < +1
\end{align*}
\]

As \( n \) goes from 0 to \( N - 1 \), the Bloch factor \( e^{iKa} = e^{i\left(\frac{2\pi n}{N}\right)} \) takes on all the allowed values between \( e^{i0} = 1 \) and \( e^{i2\pi\frac{N-1}{N}} \). When \( n = N \), we get \( e^{i2\pi} = 1 \) again. Therefore, letting \( n \) go from 0 to \( N - 1 \) generates all the unique solutions.
The intersection of each of these horizontal lines with $f(z)$ yields an allowed energy. Therefore, there are $\frac{N}{2} \left\{ n \in \left[ \frac{N}{4}, \frac{3N}{4} \right] \right\}$ positive-$z$ (or $k$) states in the first band (and $\frac{N}{2}$ negative-$z$ (or $k$) states) and $N$ allowed energies in all other bands. Since $N$ is so large, the allowed energies are so closely spaced that we can regard them as forming a continuum.
The total \# of electrons will be \( Nq \) where \( q \) is the \# of free electrons per atom. Because of the Pauli exclusion principle, only two electrons can occupy a given spatial state.

Therefore, if \( q = 1 \), the \( Nq \) electrons will occupy \( \frac{N}{2} \) different states:

If \( q = 1 \), the \( N \) electrons will just fill the first band.

If \( q = 2 \), the electrons will half fill the second band. If \( q = 3 \), they completely fill the second band and so on.

Therefore, if \( q = 2, 4, 6, \ldots \) the solid will behave like a conductor; if \( q = 1, 3, 5, \ldots \) the solid will behave like an insulator.
Of course, this is just a 1-dimensional model and the details don’t correspond to a three-dimensional solid.

If we dope an insulator with a few atoms of larger (or smaller) \( q \), the extra electrons will go into the next higher energy band (or holes will be created in the otherwise filled band). In this case, weak electrical currents can flow and the material is called a semi-conductor.

Typical band gaps in semiconductors are \( \sim \) eV.

Example:

Silicon — band gap = 1.1 eV,
Diamond — band gap = 5.5 eV.