Lecture 3

Energy bands in solids

In this lecture we will go beyond the free electron gas approximation by considering that in a real material electrons live inside the lattice formed by the ions (Fig. 3.1).

3.1 Bloch theorem

In this section we consider the case of 1D crystals since the maths are easy to handle; the key concepts remain valid also in 3D. With reference to Fig. 3.1, we can make the general observation that in a crystal the electrons experience a periodic potential:

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

(3.1)

where, in the case of crystals with one atom per unit cell, \( a \) is the interatomic distance. The Schrödinger equation for the electrons in the crystal is

\[ -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x). \]  

(3.2)

Can we say anything about the wavefunctions \( \psi \) based on the general observation that the potential in Eq. (3.1) is periodic? Certainly we can say that if \( \psi(x) \) is a solution, then also \( \psi(x + a) \) will be, and for the same eigenvalue. In fact if we replace \( x \) by \( x + a \) in Eq. (3.2) we find:

\[ -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial(x + a)^2} \psi(x + a) + V(x + a)\psi(x + a) = E\psi(x + a), \]  

(3.3)

\[ -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial x^2} \psi(x + a) + V(x)\psi(x + a) = E\psi(x + a), \]  

(3.4)

because the derivative is insensitive to translations and \( V(x + a) = V(x) \). Since \( \psi(x) \) and \( \psi(x + a) \) solve the same Schrödinger equation for the same eigenvalue, they must be
the same function up to a complex constant (indeed if \( \psi \) is a solution, also \( C\psi \) will be one). As a result we have the following condition:

\[
\psi(x + a) = C\psi(x). \tag{3.6}
\]

At this point we may observe that the electron density \( |\psi|^2 \) must be periodic: in a perfectly periodic crystal every unit cell behaves in exactly the same way (this property is called translational invariance). This implies that \(|C| = 1\), hence \( C = e^{i\theta} \) with \( \theta \) a real number.

\[
\psi(x + a) = e^{i\theta} \psi(x). \tag{3.7}
\]

In order to proceed further it is convenient to expand the wavefunction using the continuous Fourier transform:

\[
\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dq c(q)e^{iqx}, \tag{3.8}
\]

\[
c(q) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \psi(x)e^{-iqx}. \tag{3.9}
\]

By replacing Eq. (3.8) in Eq. (3.7) we find:

\[
\int_{-\infty}^{\infty} dq c(q)e^{iqx}e^{iqa} = e^{i\theta} \int_{-\infty}^{\infty} dq c(q)e^{iqa} \tag{3.10}
\]

\[
\int_{-\infty}^{\infty} dq e^{iqx} \left[ c(q) \left( e^{iqa} - e^{i\theta} \right) \right] = 0. \tag{3.11}
\]

The previous equality must hold for every \( x \), therefore we are left with two possibilities:

\[
\begin{cases}
  c(q) = 0, & \text{or} \\
  c(q) \neq 0 \text{ and } q = \frac{2\pi}{a} n + \frac{\theta}{a}, n = 0, \pm 1, \pm 2, \ldots
\end{cases} \tag{3.12}
\]
In practice only discrete values of $q$ are allowed in the Fourier expansion of $\psi$ and we can rewrite Eq. (3.8) as:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c(q_n)e^{\frac{2\pi i nx}{a}}e^{\theta x}.$$  \hspace{1cm} (3.13)

The function $\frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c(q_n)e^{\frac{2\pi i nx}{a}}$ is periodic with period $a$. Let call this function $u(x)$. In addition let us rename $\theta/a$ as $k$. The last equation can now be rewritten as:

$$\psi(x) = u(x)e^{ikx}, \text{ with } u(x+a) = u(x).$$  \hspace{1cm} (3.14)

This equation is one of the possible formulations of the Bloch theorem. In simple words this result means that electrons in a periodic potential have a “free-electron gas” component, $\exp(ikx)$, and a component associated with the shape of the potential, $u(x)$, see Fig. 3.2. Another possible formulation of the Bloch theorem, which follows from Eq. (3.14), is

$$\psi(x+a) = \psi(x)e^{ika}.$$  \hspace{1cm} (3.15)

The quantity $k$ is called the Bloch wavevector of the state $\psi$.

Figure 3.2: Schematic representation of the Bloch theorem. The electronic wavefunctions in a periodic potential (i.e. in a crystalline solid) can be written as the product between a plane wave $\exp(ikx)$ which is not periodic, and a periodic function $u(x)$, which has the same periodicity $a$ of the lattice: $\psi(x) = u(x)\exp(ikx)$. The plane wave gives the “free-electron gas” component of $\psi(x)$, while the periodic part $u(x)$ describes the atomistic aspects associated with the detailed arrangement of the atoms in the unit cell.

### 3.2 Krönig-Penny model

The 1D Krönig-Penny model is among the simplest possible models to describe electrons in periodic lattices. The maths are a bit involved but this model will allow us to discuss qualitatively several important concepts. In the previous section we discovered something very general about electron wavefunctions in a periodic potential, but we did
not specify the shape of the potential $V(x)$. In this section we will assign a shape to this potential, and in particular the simplest possible shape: a rectangular periodic function, as in Fig. 3.3.

With reference to Fig. 3.3 we want to solve the usual Schrödinger equation. A simple way of doing this is to observe that, due to the Bloch theorem Eq. (3.15), we only need to solve our equation for $x$ between 0 and $a$. Then we can generate the entire function using Eq. (3.15). In Fig. 3.3 we have two regions, the ceiling of the potential for $x$ between 0 and $t$ (region I), and the floor of the potential for $x$ between $t$ and $a$ (region II).

**Solution for region I**

The Schrödinger equation in region I reads:

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi_I(x) + V_0\psi_I(x) = E\psi_I(x).$$

(3.16)

Let us take $E$ between 0 and $V_0$ for simplicity. In this case we can define

$$\beta^2 = \frac{2m_e(V_0 - E)}{\hbar^2} > 0,$$

(3.17)

and rewrite Eq. (3.16) as

$$\frac{\partial^2}{\partial x^2}\psi_I(x) = \beta^2\psi_I(x).$$

(3.18)

The solution of this equation is a combination of exponential functions:

$$\psi_I(x) = Ae^{\beta x} + Be^{-\beta x}, \text{ for } 0 < x < t.$$

(3.19)

**Solution for region II**

The Schrödinger equation in region II reads:

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi_{II}(x) = E\psi_{II}(x).$$

(3.20)

If we define

$$\alpha^2 = \frac{2m_eE}{\hbar^2} > 0,$$

(3.21)

we can rewrite Eq. (3.20) as

$$\frac{\partial^2}{\partial x^2}\psi_{II}(x) = -\alpha^2\psi_{II}(x).$$

(3.22)

In this case the solution is given by a combination of complex exponential functions (or equivalently sin and cos functions):

$$\psi_{II}(x) = Ce^{i\alpha x} + De^{-i\alpha x}, \text{ for } t < x < a.$$

(3.23)
Krönig-Penny model

Figure 3.3: The potential $V(x)$ in the Krönig-Penny model. The periodic unit cell extends from $x = 0$ to $a$. We need to solve the Schrödinger equation for the electrons in regions I and II separately and then match the solutions using the boundary conditions of continuous wavefunction and its derivative at $x = t$ and $x = a$.

At this point we need to match the two solutions by imposing the boundary conditions. We have 4 unknowns $(A, B, C, D)$ therefore we need 4 equations. We impose the continuity of the wavefunction and its derivative at $x = 0$ and $x = t$. The need for a continuous wavefunction is self-evident. The condition on the derivative means that the electronic current is continuous, i.e. electrons cannot disappear all of a sudden.

$$
\begin{align*}
\psi_I(t^-) &= \psi_{II}(t^+)
\frac{\partial}{\partial x}\psi_I(t^-) &= \frac{\partial}{\partial x}\psi_{II}(t^+)
\psi_{II}(a^-) &= \psi_I(a^+)
\frac{\partial}{\partial x}\psi_{II}(a^-) &= \frac{\partial}{\partial x}\psi_I(a^+)
\end{align*}
$$

In order to obtain $\psi_I$ and its derivative at $x = a^+$ we can now use the Bloch theorem through Eq. (3.15):

$$
\psi_I(a^+) = \psi_I(0^+) e^{ika}.
$$

Note that we have not specified the Bloch wavevector $k$ yet. Our job now is to find out which combinations of $(E, k)$ lead to wavefunctions which are solutions of our original Schrödinger equation. We can combine together Eqs. (3.19),(3.23),(3.24),(3.25), to obtain:

$$
\begin{align*}
A e^{\beta t} + B e^{-\beta t} &= C e^{\iota at} + D e^{-\iota at} \\
\beta A e^{\beta t} - \beta B e^{-\beta t} &= i\alpha C e^{\iota at} - i\alpha D e^{-\iota at} \\
C e^{\iota a a} + D e^{-\iota a a} &= A e^{ika} + B e^{ika} \\
i\alpha C e^{\iota a a} - i\alpha D e^{-\iota a a} &= \beta A e^{ika} - \beta B e^{ika}
\end{align*}
$$

(3.26)
The above expression can be rewritten using matrix notation:

\[
\begin{bmatrix}
    e^{\beta t} & e^{-\beta t} & -e^{i\alpha t} & -e^{-i\alpha t} \\
    \beta e^{\beta t} & -\beta e^{-\beta t} & -i\alpha e^{i\alpha t} & i\alpha e^{-i\alpha t} \\
    e^{ika} & e^{ika} & -e^{i\alpha a} & -e^{-i\alpha a} \\
    \beta e^{ika} & -\beta e^{ika} & -i\alpha e^{i\alpha a} & i\alpha e^{-i\alpha a}
\end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}
\] (3.27)

This matrix equation admits nontrivial solutions only if the determinant vanishes (secular equation). The calculation of this determinant is rather involved. If you feel brave and motivated you can try and calculate it using symbolic solvers, such as e.g. Mathematica. Note: The derivation of the secular equation Eq. (3.28) is not examinable.

According to Fig. 3.4 the secular equation is:

\[
\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh(\beta t) \sin[\alpha(a - t)] + \cosh(\beta t) \cos[\alpha(a - t)] = \cos(ka).
\] (3.28)

Since this result is still quite complicated we make the following simplification: we take \( t \to 0 \) and \( V_0 \to \infty \) in such a way that \( V_0 t = S \), \( S \) being a finite constant. In practice this means that we replace the rectangular potential barrier in Fig. (3.3) by a "Dirac
delta function”, $S \delta(x)$, in such a way that the area under the barrier is preserved. This approximation allows us to simplify the maths while leaving the physics essentially unchanged. From Eq. (3.17) we have then
\[ \beta^2 t^2 = \frac{2m_e}{\hbar^2} \left( St - E t^2 \right) \rightarrow 0, \quad (3.29) \]
and from Eq. (3.21) we have
\[ \alpha^2 t^2 = \frac{2m_e E}{\hbar^2} t^2 \rightarrow 0. \quad (3.30) \]
We can now rewrite Eq. (3.28) as
\[ \frac{\beta^2 - \alpha^2}{2\alpha \beta} \beta t \sin(\alpha a) + \cos(\alpha a) = \cos(ka). \quad (3.31) \]
By using Eqs. (3.17) and (3.21) we find:
\[ \frac{\beta^2 - \alpha^2}{2\alpha \beta} \beta t = \frac{2m_e V_0 - 2E}{2\sqrt{E} t} \rightarrow \frac{2m_e}{\hbar^2} \frac{V_0}{2\sqrt{E} t} t \quad (3.32) \]
\[ \frac{\beta^2 - \alpha^2}{2\alpha \beta} \beta t \rightarrow \frac{2m_e}{\hbar^2} \frac{V_0}{2\sqrt{E} t} = \frac{m_e a S}{\hbar^2} \frac{1}{\alpha a}. \quad (3.33) \]
The quantity
\[ \mu = \frac{m_e a S}{\hbar^2} \quad (3.34) \]
is dimensionless and is a measure of the strength of the potential barrier. If we also define $\eta = \alpha a$ we can rewrite the simplified secular equation Eq. (3.31) as
\[ \mu \frac{\sin \eta}{\eta} + \cos \eta = \cos ka. \quad (3.35) \]
Let us recall that our initial goal was to establish whether there exist couples $(E, k)$ leading to nontrivial solution of the secular equation (3.35). It is therefore useful to write down the relation between $\eta$ and the energy eigenvalue $E$ using Eq. (3.21):
\[ E = \frac{\hbar^2 \eta^2}{2m_e a^2}. \quad (3.36) \]
This equation tells us that we need to check whether, for a given value of $\mu$ (given by the shape of our potential) and for a given Bloch wavevector $k$, there is at least one value of $\eta$ which solves Eq. (3.35). If that is the case, then we have a solution of the Kröning-Penny model for the potential $\mu$ and the Bloch wavevector $k$. By sweeping $\mu$ from 0 to $\infty$ we discover 4 qualitatively different situations.
Case $\mu = 0$: free electron gas

In this case the secular equation Eq. (3.35) becomes

$$\cos \eta = \cos ka,$$  

(3.37)

therefore for each $k$ we have the solutions $\eta = ka + 2\pi n$, $n$ integer. For $n = 0$ the energy eigenvalues read

$$E = \frac{\hbar^2 k^2}{2m_e},$$

(3.38)

therefore we are back to the free electron gas (the cases $n \neq 0$ are essentially equivalent to this). This result was to be expected because $\mu = 0$ means that there is no potential barrier (flat potential = free electron gas).

Case $\mu = \infty$: atomic limit

In this case the secular equation Eq. (3.35) becomes

$$\sin \eta = 0,$$  

(3.39)

therefore for each $k$ we have the solutions $\eta = n\pi$, $n$ integer, and the energy eigenvalues read

$$E = \frac{\hbar^2 \pi^2}{2m_e a^2 n^2}.$$  

(3.40)

This situation corresponds to the case of an isolated atom with discrete energy levels (infinite potential well).

Case $0 < \mu < 1$: nearly free electron gas

In this case we need to solve Eq. (3.35) numerically. We have solutions whenever $\mu|\sin \eta/\eta + \cos \eta| < 1$ because in the rhs of Eq. (3.35) there is a cosine. Figure 3.5(a) shows the allowed $\eta$ values for $\mu = 0.1$ for several wavevectors $k$.

Case $\mu > 1$: tight-binding

In this case Eq. (3.35) also needs to be solved numerically. Figure 3.5(b) shows the allowed $\eta$ values for $\mu = 0.1$ for several wavevectors $k$. 
Figure 3.5: Solutions of the secular Eq. (3.35) for the Krönig-Penny model (for \( a = 2 \text{ Å} \)).

(a) The case \( \mu = 0.5 \). Solutions exist only when \( \mu \sin \eta / \eta + \cos \eta \) falls between -1 and 1 (hatched regions). In order to find a solution, we decide the wavevector \( k \) (in the example \( k = \pi / 2a \)) and we look for the intersections between \( \mu \sin \eta / \eta + \cos \eta \) and \( \cos(ka) \). This procedure allows us to determine the allowed energy values \( E(k) \) for each Bloch wavevector \( k \). The energy eigenvalues cluster into regions called energy bands (hatched). Outside of these bands the Schrödinger equation does not admit solutions and we call these no-solution regions band gaps. In the case \( \mu < 1 \) we have wide bands and narrow band gaps, and this situation can be described within the nearly-free electron gas approximation. (b) The case \( \mu = 10 \). In this case we have rather narrow bands and large band gaps. This situation is best described within the tight-binding approximation.
Figure 3.6: Electron band structures in the Kröning-Penny model (for $a = 2 \text{ Å}$). A band structure is a plot of electron energy ($E$) vs. wavevector ($k$) in a solid. $k$ is typically restricted to the first Brillouin zone $[-\pi/a, \pi/a]$ because the $E$ vs. $k$ dispersion relation is periodic in $k$. In (a) we have the solution for $\mu = 0.5$, with wide bands and narrow gaps (nearly-free electron gas regime). In (b) we have the solution for $\mu = 10$, with narrow bands and large gaps (tight-binding regime).