Electrons in a crystal

When we discussed X-ray scattering we saw that the condition of constructive interference required that an incident wavevector \( \mathbf{k} \) could only scatter into wavevectors \( \mathbf{k}' = \mathbf{k} - \mathbf{R} \) where \( \mathbf{R} \) was in the R.L.

For electrons in a crystal we expect similar behavior since our argument depended only on the wave nature of the scattering.

So a free electron plane wave state \( e^{i \mathbf{k} \cdot \mathbf{r}} \) will get scattered into states \( e^{i \mathbf{k}' \cdot \mathbf{r}} \) with \( \mathbf{k}' = \mathbf{k} - \mathbf{R} \). We therefore expect the eigenstates of an electron in the periodic ionic potential of the crystal will be a mixture of these scattered states:

\[
\psi_k(\mathbf{r}) = \sum_k e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} c_{k-k} = e^{i \mathbf{k} \cdot \mathbf{r}} \sum_k e^{-i \mathbf{k}' \cdot \mathbf{r}} c_{k-k} = e^{i \mathbf{k} \cdot \mathbf{r}} u_k(\mathbf{r}) \quad \text{where} \quad u_k(\mathbf{r}) = \sum_{k} e^{-i \mathbf{k} \cdot \mathbf{r}} c_{k-k}
\]

\( u_k(\mathbf{r}) \) is periodic on the Bravais lattice:

\[
\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \sum_k e^{-i \mathbf{k} \cdot (\mathbf{r} + \mathbf{R})} c_{k-k} = \sum_k e^{-i \mathbf{k} \cdot \mathbf{r}} e^{-i \mathbf{k} \cdot \mathbf{R}} c_{k-k} = \sum_k e^{-i \mathbf{k} \cdot \mathbf{r}} c_{k-k} = u_k(\mathbf{r}) \quad \text{since} \quad e^{-i \mathbf{k} \cdot \mathbf{R}} = 1
\]

for all \( \mathbf{R} \) in R.L.
The then yields **Bloch's Theorem** which we prove more rigorously later.

The energy eigenstates of an electron in a potential with the periodicity of a Bravais lattice can be written in the form

\[ \psi_k(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} \psi_k(\mathbf{r}) \]

Where \( \psi_k(\mathbf{r}+\mathbf{R}) = \psi_k(r) \) is periodic on the B.L.

An equivalent alternative statement of Bloch's Theorem is

\[ \psi_k(\mathbf{r}+\mathbf{R}) = e^{i \mathbf{k} \cdot \mathbf{R}} \psi_k(\mathbf{r}) \]

If the wavevector \( \mathbf{k} \) lies exactly on the Bragg plane defined by R.L. vector \( \mathbf{R} \), then the two free electron plane wave states \( \mathbf{k} \) and \( \mathbf{k}' = \mathbf{k} - \mathbf{R} \) are degenerate in energy and so we expect they must mix equally in forming the new eigenstates in the presence of the periodic potential. Since we start with two states \( \mathbf{k}, \mathbf{k}' \) we should wind up with two new states. If they mix equally, their relative coefficients should just be a phase factor \( e^{i \phi} \). Hence we expect the two eigenstates to have the form

\[ \psi_1(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} + e^{i \mathbf{k}' \cdot \mathbf{r}} \]

\[ \psi_2(\mathbf{r}) = e^{-i \mathbf{k} \cdot \mathbf{r}} + e^{i \mathbf{k}' \cdot \mathbf{r}} \]
The new eigenstates \( \psi_i \) and \( \psi_2 \) should be orthogonal

\[
0 = \langle \psi_1 | \psi_2 \rangle = \int d^3r \, \psi_1^*(\vec{r}) \psi_2(\vec{r})
\]

\[
= \int d^3r \left[ e^{-i\vec{k}_1 \cdot \vec{r}} + e^{-i\vec{k}_1' \cdot \vec{r}} \right] \left[ e^{i\vec{k}_2 \cdot \vec{r}} + e^{i\vec{k}_2' \cdot \vec{r}} \right]
\]

\[
= \int d^3r \left[ 1 + e^{i(\vec{k}_2 - \vec{k}_1) \cdot \vec{r}} + e^{-i(\vec{k}_2' - \vec{k}_1') \cdot \vec{r}} + e^{i(\vec{k}_2' - \vec{k}_1') \cdot \vec{r}} \right]
\]

\[
= \int d^3r \left[ 1 + e^{i(\vec{k}_2 - \vec{k}_1) \cdot \vec{r}} \right]
\]

\[
= 0 \quad \text{only if} \quad \vec{k}_2 - \vec{k}_1 = \pi
\]

\[
\vec{k}' = \vec{k} - \vec{k}'
\]

\[
\text{write} \quad \vec{k}_c = \vec{k}_|| + \vec{k}_\perp
\]

\[
\text{then} \quad \vec{k}_c' = -\vec{k}_|| + \vec{k}_\perp
\]

So,

\[
\psi_i(\vec{r}) = e^{i\Phi_i/2} e^{i\vec{k}_|| \cdot \vec{r}} \left( e^{-i\Phi_i/2} e^{i\vec{k}_\perp \cdot \vec{r}} + \epsilon \right)
\]

\[
= e^{i\Phi_i/2} e^{i\vec{k}_c \cdot \vec{r}} \times \cos (\vec{k}_c \cdot \vec{r} - \Phi_i/2)
\]

Similarly,

\[
\psi_2(\vec{r}) = e^{i\Phi_2/2} e^{i\vec{k}_c' \cdot \vec{r}} \times \cos (\vec{k}_c' \cdot \vec{r} - \Phi_2/2)
\]

\[
= e^{i\Phi_2/2} e^{i\vec{k}_c \cdot \vec{r}} \times \cos (\vec{k}_c \cdot \vec{r} - \Phi_2/2 - \pi)
\]

\[
= e^{i\Phi_2/2} e^{-i\vec{k}_c \cdot \vec{r}} \times \cos (\vec{k}_c \cdot \vec{r} - \Phi_2/2 - \pi)
\]
\[ |\psi_1(\vec{r})|^2 \sim \cos^2(\vec{k}_\parallel \cdot \vec{r} - \phi/2) \]
\[ |\psi_2(\vec{r})|^2 \sim \sin^2(\vec{k}_\parallel \cdot \vec{r} - \phi/2) \]

probability density

reflection from Bragg plane gives standing waves in direction \( \vec{k} \)

Since \( \vec{k}_\parallel = \frac{\vec{k}}{2} \) we have \( \vec{k}_\parallel \cdot \vec{R} = \frac{\vec{k} \cdot \vec{R}}{2} = \pi n \)

where \( n \) is an integer

\[ \Rightarrow |\psi_1(\vec{r})|^2 + |\psi_2(\vec{r})|^2 \text{ have the periodicity of the B.L.} \]
\[ = |\psi(\vec{r} + \vec{R})|^2 = \cos^2(\vec{k}_\parallel \cdot (\vec{r} + \vec{R}) - \phi/2) = \cos^2(\vec{k}_\parallel \cdot \vec{r} - \phi/2) \]
\[ = |\psi(\vec{r})|^2 \]

The only difference between \( \psi_1 \) and \( \psi_2 \) is their relative phase shift of \( \pi/2 \), which shifts the location of the peaks of \( |\psi_1|^2 \) and \( |\psi_2|^2 \) relative to the positions of the ions. By symmetry, we expect one of these, say \( \psi_1 \), will have its peaks positioned at the same sites as the ions, while the other, \( \psi_2 \), will have its peaks positioned in between the sites of the ions. For example, if \( \vec{R} \) is the smallest non-zero B.L. vector, \( |\vec{R}| = \frac{2\pi}{d} \) with \( d \) = separation between ions, we expect...
The spatial periodicity of \( \Phi_1 \) and \( \Phi_2 \) is \( \lambda = \frac{2\pi}{k_1} = \frac{2\pi}{(k/\ell)} \). The spatial periodicity of \( 1411^2 \) and \( 14_1^2 \) is therefore \( \frac{1}{2} \lambda = a \). Since \( 14_1^2 \) and \( 4_2^2 \) are \( \frac{\pi}{2} \) out of phase, then \( 14_1^2 \) and \( 14_1^2 \) are \( \pi \) out of phase, hence their relative peaks are separated by \( a/2 \) as in the diagram above.

Now when one turns on the attractive ionic potential, the state \( \Phi_1 \) will have a lower energy than the state \( \Phi_2 \). Since \( \Phi_1 \) has its peaks located at the ions, where the interaction is strongest, while \( \Phi_2 \) has its peaks in the middle between the ions, where the interaction is weakest.

Hence we expect that the two states, \( \Phi_1 \) and \( \Phi_2 \), which were degenerate in energy before turning on the ionic potential, now split in energy, with a finite energy gap between them, \( E_1 < E_2 \).

\( \Rightarrow \) Ionic potential cause a gap to appear in the energy dispersion relation \( E(k) \) whenever \( k \) crosses a Bragg plane. Since the Brillouin zones are formed by the intersections of Bragg planes, gaps in \( E(k) \) open as \( k \) crosses the boundary of any Brillouin zone.
For a 1-dimensional square B.L. of lattice constant $a$,

$$R = n a, \quad m \text{ integers},$$

$$K = m b, \quad b = \frac{2\pi}{a}, \quad n \text{ integers}$$

gap open in $E(k)$
every time $k$ crosses the boundary of

the Brillouin zone

Bragg planes are at

$$\frac{K}{2} = \left( \frac{2\pi n}{a} \right) \frac{1}{2} = \frac{\pi n}{a}$$

for $n$ integers

For a 2-dimensional square B.L. of lattice constant $a$,

Bragg planes divide $k$-space into Brillouin zones

1st BZ

2nd BZ

3rd BZ

Whenever $k$ crosses the surface of a BZ, there
then is a discrete jump in the energy $E(k)$

Each BZ is a primitive cell of the B.L.
Each $\mathbf{k}$ in $k$-space can be written as $\mathbf{k} = \mathbf{\bar{k}} + \mathbf{K}$ with $\mathbf{\bar{k}}$ a R.L. vector and $\mathbf{\bar{k}}$ a vector in the 1st B.Z. $\mathbf{\bar{k}}$ is unique.

⇒ each $n^{th}$ B.Z. may be mapped onto the 1st B.Z. by translating its pieces by appropriate R.L. vectors $\mathbf{K}$.

It is customary to label the eigenstates and eigenvalues by the $\mathbf{\bar{k}}$ ad by discrete index $n$. $\mathbf{\bar{k}}$ is called the "crystal momentum" ad $n$ the "band index." The state $(\mathbf{\bar{k}}, n)$ corresponds to the free electron state in the $n^{th}$ B.Z. with wave vector $\mathbf{\bar{k}} = \mathbf{\bar{k}} + \mathbf{K}$ ($\mathbf{\bar{k}}$ is the R.L. vector that translates $\mathbf{\bar{k}}$ into the $n^{th}$ B.Z.)

The wave functions $\Psi_{\bar{k},n}$ and energies $E_n(\mathbf{\bar{k}})$ are called the band structure.
Born-\textendash{}von \textit{K}arman boundary conditions

and Fourier transforms for a Bravais lattice

We generalize the idea of periodic (or Born-\textit{K}arman)
boundary conditions to electron states on a Bravais lattice.

\( \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \)
\( n_1, n_2, n_3 \) integers.

For a BL of finite size we have \( 0 \leq n_i \leq N_i \)
\( N = N_1 N_2 N_3 \) is total number of points in the BL.

Total volume of the finite BL is
\[
V = \frac{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}{\text{volume of primitive cell}} N
\]

We want our electron wave functions to be periodic
on such a finite BL

\[
\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r})
\]

As we saw earlier for free electrons, this imposes
a constraint on the wave vectors \( \mathbf{k} \) that can
appear in the Fourier transform of \( \psi(\mathbf{r}) \).

Write \( \psi(\mathbf{r}) \) in terms of its Fourier transform

\[
\psi(\mathbf{r}) = \sum_k c_k e^{i \mathbf{k} \cdot \mathbf{r}}
\]
(\( c_k \) \( \mathbf{k} \) Fourier coefficients for \( \psi(\mathbf{r}) \))
Then
\[ \psi(\mathbf{r} + N_i \mathbf{a}_i) = \sum_k e^{i \mathbf{k} \cdot (\mathbf{r} + N_i \mathbf{a}_i)} \psi_k \]
\[ = e^{i N_i \mathbf{k} \cdot \mathbf{a}_i} \sum_k e^{i \mathbf{k} \cdot \mathbf{r}} \psi_k \]
\[ = e^{i N_i \mathbf{k} \cdot \mathbf{a}_i} \psi(\mathbf{r}) \]

\( \Rightarrow \) must have \( e^{i N_i \mathbf{k} \cdot \mathbf{a}_i} = 1 \) for all \( \mathbf{k} \)
that appear in Fourier transform of \( \psi(\mathbf{r}) \)

Write \( \mathbf{k} \) in terms of the primitive vectors \( b_i \) of the RL

\[ \mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3 \]
\( x_i \) are not \( m_i \) general integers

Then \( e^{i N_i \mathbf{k} \cdot \mathbf{a}_i} = e^{i N_i 2\pi x_i} = 1 \)

\( \Rightarrow \) \( x_i N_i = m_i \) integer
\[ x_i = \frac{m_i}{N_i} \]

So the allowed wavevectors are

\[ \mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 \]

where \( m_1, m_2, m_3 \) are integers.

This is the Born-von Karman boundary conditions.