Distraction

Crystal structure was originally observed and mapped out using X-ray diffraction. The procedure is straightforward; emit an X-ray and observe it scatter off the crystal. The X-ray wave interacts only weakly with each plane of atoms but over a series of parallel planes in the crystal, a significant reflection can occur. The observed wave will, however, depend on certain conditions which are, in turn, dependent on the crystal structure.

If the wave $e^{i\mathbf{k}.\mathbf{r}}$ is reflected by some crystal quantity $n(\mathbf{r})$, it results in...
this $n(\vec{r})$ is the charge density which has the crystal periodicity $n(\vec{r}) = n(\vec{r} + \vec{K})$
then we can write the scattered amplitude as an integral over the entire crystal volume $V$ of the quantity $n(\vec{r})$ and the phase difference between incoming and outgoing wave

$$F = \int_V dV \, n(\vec{r}) \exp\left[ i (\vec{K} - \vec{K}') \cdot \vec{r} \right]$$

Using the Fourier series expansion

$$n(\vec{r}) = \sum G \, n_G \, e^{i \vec{G} \cdot \vec{r}}$$

we can write this scattering amplitude as

$$F = \sum G \int_V dV \, n_G \exp\left[ i \left( \vec{G} + \vec{K} - \vec{K}' \right) \cdot \vec{r} \right]$$

Using the property that $$\int dV \, \exp\left( i \vec{r} \cdot \vec{r} \right) = S(\vec{K})$$

we get

$$F = V \, n_G \, S(\vec{G} + \vec{K} - \vec{K}')$$
or

that reflection is only possible when
\[ k + \vec{G} = k'. \] Since we can assume this scattering is electric and \( \omega = \vec{k} \)
then \[ |\vec{k}| = |\vec{k}'| \Rightarrow k^2 = k'^2 \] so that
\[ (\vec{k} + \vec{G})^2 = k'^2 = k^2 \] or
\[ 2 \vec{k} \cdot \vec{G} = \vec{G}^2 \]

Dividing through by 4 we get
\[ \frac{k}{2} \vec{G} = \left( \frac{1}{2} \vec{G} \right)^2 \]

The planes bisecting the reciprocal space vectors \( \vec{G} \) are all the points satisfying this condition. The volume enclosed by these planes is called a Brillouin Zone.

There are infinitely many Brillouin Zones, one for each set of bisectors which completely enclose a space.
The 1st Brillouin Zone is the Wigner-Seitz primitive unit cell in reciprocal space. All this means is that most of the action we care about happens exactly in the smallest possible space in the reciprocal space. We will discuss the 1st BZ many times because any point in the crystal's reciprocal space can be represented by an equivalent point in the 1st BZ -- there is no need to consider wave-vectors outside the 1st BZ.

* Bloch Theorem:*

The wavefunction \( \psi(\vec{r}) \) in a periodic potential is not necessarily periodic \( \psi(\vec{r}) \neq \psi(\vec{r} + \vec{R}) \), but quantities like charge density \( n(\vec{r}) = \psi^* \psi(\vec{r}) \) are periodic: \( n(\vec{r}) = n(\vec{r} + \vec{R}) \).

How do we reconcile this? The wave function then has to be periodic up to a phase factor \( \exp(i\vec{k} \cdot \vec{R}) \) so that we have

\[
\psi(\vec{r} + \vec{R}) = \psi(\vec{r}) \exp(i\vec{k} \cdot \vec{R})
\]
This condition ensures \( n(\vec{r}) = n(\vec{r} + \vec{R}) \) is periodic

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

\[
= \psi(\vec{r}) e^{-i \vec{k} \cdot \vec{R}} \psi(\vec{r}) e^{i \vec{k} \cdot \vec{R}} = \psi(\vec{r}) \psi(\vec{r}) = \psi(\vec{r})
\]

Consequently, in a periodic potential, the wave function can be written as

\[
\psi_k(\vec{r}) = \psi(\vec{r}) \exp(i \vec{k} \cdot \vec{r})
\]

which is known as **Bloch Theorem**

and it states that a wave function in a periodic potential can be expressed as a product of a periodic function

\[
u_k(\vec{r}) = \psi_k(\vec{r} + \vec{R})
\]

and a plane wave \( \exp(i \vec{k} \cdot \vec{r}) \).

Check if this holds:

\[
\psi_k(\vec{r} + \vec{R}) = \psi_k(\vec{r} + \vec{R}) \exp(i \vec{k} \cdot (\vec{r} + \vec{R}))
\]

\[
= \psi_k(\vec{r}) \exp(i \vec{k} \cdot \vec{r}) \exp(i \vec{k} \cdot \vec{R})
\]

\[
= \psi(\vec{r}) \exp(i \vec{k} \cdot \vec{R})
\]
Born-von Kármán BCs

Even though the wave function is not periodic with period $R$, if we have a large crystal consisting of some large number $N$ of unit cells, the wave functions at the ends of the crystal have to be the same:

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

Using Bloch theorem

$$\Psi(x + Na) = \Psi(x) e^{i k N a}$$

Therefore we have $e^{i k N a} = 1$ and it follows that $k = \frac{2\pi n}{Na}$, where $n = 0, \pm 1, \pm 2, \ldots$ and $L = Na$ is the size of the crystal.

Therefore the $k$ in the Bloch theorem is called crystal momentum as it resembles the momentum of a free electron and is almost continuous when $L$ is large compared to $a$. 
König–Penney Model

Consider a simple rectangular potential

\[ U(x) = \begin{cases} 0, & 0 < x < a \\ U_0, & a < x < 2a \\ -U_0, & -b < x < 0 \end{cases} \]

with the periodicity \( U(x+a+b) = U(x) \)

Solve the Schrödinger Equation

\[ \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (U-E)\psi = 0 \]

for this potential

\[ \psi(x) = \begin{cases} A e^{ikx} + Be^{-ikx}, & 0 < x < a \\ Ce^{Qx} + De^{-Qx}, & -b < x < 0 \end{cases} \]

with energy given by

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

and \( U_0 - E = \frac{\hbar^2 Q^2}{2m} \)
Using continuity at $y$ and its derivative $\frac{dy}{dx}$ at point $x=0$, we have $A+B = C+D$ and
\[ iK(A-B) = 2(C-D) \]

Because $y(0) = \begin{cases} A+B, & 0 < x < a \\ C+D, & -b < x < 0 \end{cases}$
\[ \frac{dy}{dx}(0) = \begin{cases} iKA - iKB, & 0 < x < a \\ CA - DA, & -b < x < 0 \end{cases} \]

We have 4 unknowns, so we need another set of BCs at $x=a$. This requires that we know $y$ in the region $a < x < a+b$ which can be determined from $y$ in $-b < x < 0$ by the Bloch theorem:

\[ y(x+a+b) = y(x) \exp \left[ iK(a+b) \right] \]

Therefore at $x=a$ we get the following:

\[ A e^{iKa} + B e^{-iKa} = (C e^{2Qb} + D e^{2Qb}) e^{ik(a+b)} \]
\[ iK (A e^{iKa} - B e^{-iKa}) = 2 (C e^{-Qb} + D e^{Qb}) iK(a+b) \]
This set of 4 equations can be expressed as a matrix

\[
\begin{pmatrix}
1 & 1 & -1 & 1 \\
\text{ik} & -\text{ik} & -\text{Q} & \text{ik}(	ext{Q}+\text{ik}) \\
\text{e}^{-\text{ik}a} & \text{e}^{-\text{ik}a} & -\text{e}^{-\text{ik}b} & \text{e}^{-\text{ik}b} \\
\text{e}^{-\text{ik}a} & \text{e}^{-\text{ik}a} & -\text{e}^{-\text{ik}b} & \text{e}^{-\text{ik}b}
\end{pmatrix}
\begin{pmatrix}
\text{A} \\
\text{B} \\
\text{C} \\
\text{D}
\end{pmatrix} = 0
\]

The determinant is zero when

\[
\frac{\text{Q}^2-\text{K}^2}{2\text{KQ}} \text{ sinh } (\text{Qb}) \text{ sin } (\text{Ka}) + \cosh (\text{Qb}) \cos (\text{ka}) = \cos [(\text{K}+\text{Q})a]
\]

where \( \text{KQ} = \sqrt{2mE} \) and \( \text{Q} = \sqrt{\frac{2m(E_{\text{g.s.}})}{\hbar^2}} \).

So this equation defines a relationship between \( E \) and \( K \). This relationship \( E(K) \) is called "dispersion" or "electronic structure".

We can simplify somewhat if we let \( b \to 0 \), \( b \to \infty \) but keep \( \frac{\text{Q}^2 \text{KQ}}{2} = \rho \) a constant, \( \rho = \text{constant} \).

Then \( \text{sinh } (\text{Qb}) \propto \text{Qb} \) and \( \cosh (\text{Qb}) \approx 1 \).
and the above equation reduces to a simpler form
\[
\frac{P \sin (Ka)}{Ka} + \frac{P}{\sqrt{\frac{2mE}{\hbar^2}}} \sin \left( \sqrt{\frac{2mE}{\hbar^2}} a \right) + \cos \left( \sqrt{\frac{2mE}{\hbar^2}} a \right) = \cos (ka)
\]

Q. What happens to the solution if we add \(2\pi/a\) to \(k\)?

\[
\cos \left[ \left( k + \frac{2\pi}{a} \right) a \right] = \cos (ka + 2\pi) = \cos (ka)
\]

The solution does not change!

Then \(E(k)\) is periodic with period \(\frac{2\pi}{a}\).

The 2nd important point is that the LHS of the equation can be greater than 1, while the RHS cannot. This means there will be some values of \(E\) which are not allowed, regardless of the choice of \(k\). This is the energy gap which characterizes all semi conductors.
Metals have periodic structure but they do not have a gap. Is this possible?

On the contrary: metals can have energy gaps, but they just happen to be in a range which is not important for transport.

- Why do we get $E(k + \vec{g}) = E(\vec{k})$ from $\psi_+ (\vec{r}) = e^{i \vec{k} \cdot \vec{r}} u_+ (\vec{r})$?

  Plug in: $\psi_{\vec{k} + \vec{g}} (\vec{r}) = e^{i (\vec{k} + \vec{g}) \cdot \vec{r}} u_{\vec{k} + \vec{g}} (\vec{r})$

  $\psi_{\vec{k} + \vec{g}} (\vec{r}) = e^{i \vec{g} \cdot \vec{r}} \psi_\vec{k} (\vec{r})$

  $\psi_{\vec{k}} (\vec{r}) = e^{i \vec{g} \cdot \vec{r}} \psi_{\vec{k} + \vec{g}} (\vec{r})$

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