Periodic crystalline solids

If we’re interested in electron motion in solids, we can make the most headway considering the practical problem of crystalline solids. First, consider basic crystal structure:

Terms:

• **Lattice**: set of points in space which form a periodic structure. Each point sees the same environment as all others.

• **Basis**: building block of atoms attached to each lattice point to yield the crystal structure.

Thus: Lattice + Basis = Crystal Structure

Any lattice point can be described by one lattice vector plus integer lattice translation vectors:

\[
\vec{R}' = \vec{R} + \vec{r}_s
\]

\[
\vec{r}_s = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3
\]

Vectors \(\vec{a}_1, \vec{a}_2, \vec{a}_3\) are considered primitive if they describe a cell of the smallest possible volume.
Types of 3-D crystal lattices

There are seven crystal systems, and among them, 14 Bravais lattices are possible:

- Cubic \((a=b=c, \alpha=\beta=\gamma=90^\circ)\) [simple, body-centered, face-centered]
- Tetragonal \((a=b\neq c, \alpha=\beta=\gamma=90^\circ)\) [simple, centered]
- Orthorhombic \((a\neq b\neq c, \alpha=\beta=\gamma=90^\circ)\) [simple, base centered, body-centered, face-centered]
- Monoclinic \((a\neq b\neq c, \alpha=\gamma=90^\circ\neq \beta)\) [simple, centered]
- Triclinic \((a\neq b\neq c, \alpha\neq \beta\neq \gamma)\)
- Trigonal \((a=b=c, \alpha=\beta=\gamma<120^\circ \neq 90^\circ)\)
- Hexagonal \((a=b\neq c, \alpha=\beta=90^\circ, \gamma=120^\circ)\)

Each Bravais lattice can be described by primitive vectors:

- *e.g.* body-centered cubic

\[
\bar{a}_1 = a\bar{e}_x \\
\bar{a}_2 = a\bar{e}_y \\
\bar{a}_3 = \frac{a}{2}(\bar{e}_x + \bar{e}_y + \bar{e}_z) \\
\bar{a}_1 = \frac{a}{2}(\bar{e}_y + \bar{e}_z - \bar{e}_x) \\
\bar{a}_2 = \frac{a}{2}(\bar{e}_z + \bar{e}_x - \bar{e}_y) \\
\bar{a}_3 = \frac{a}{2}(\bar{e}_x + \bar{e}_y - \bar{e}_z)
\]
Face centered cubic lattice

The FCC Bravais lattice is the most important structure for electronic materials (=most important for nanomechanics)

- FCC lattice with two basis atoms, at (0,0,0) and (a/4)(1,1,1)
- Like two interpenetrating FCC lattices
- Si, Ge, C (group IV’s)
  (III-V’s are Zinc-Blende, e.g. GaAs, AlAs, InP)

\[
\overline{a}_1 = \frac{a}{2} \left( \overline{e}_y + \overline{e}_z \right)
\]
\[
\overline{a}_2 = \frac{a}{2} \left( \overline{e}_z + \overline{e}_x \right)
\]
\[
\overline{a}_3 = \frac{a}{2} \left( \overline{e}_x + \overline{e}_y \right)
\]
Reciprocal lattices

Every Bravais lattice has a reciprocal lattice (units of 1/length). Useful for X-ray diffraction, motion of electrons.

Will be useful later...for now, just consider it a mapping...

Primitives of the reciprocal lattice:

\[
\begin{align*}
\vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\
\vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\
\vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}
\end{align*}
\]

Then a general reciprocal lattice vector is:

\[
\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3
\]

So, for example, the reciprocal lattice of the FCC lattice is:

Note that:

\[
V = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = \frac{a^3}{4}
\]

Then:

\[
\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a} (\vec{e}_y + \vec{e}_z - \vec{e}_x) \\
\vec{b}_2 &= \frac{2\pi}{a} (\vec{e}_z + \vec{e}_x - \vec{e}_y) \\
\vec{b}_3 &= \frac{2\pi}{a} (\vec{e}_x + \vec{e}_y - \vec{e}_z)
\end{align*}
\]

Observation: the reciprocal lattice to the FCC lattice is the BCC lattice!
The motion of an electron in a crystalline solid can now be reduced to the problem of an electron in a periodic potential.

The underlying Bravais lattice determines the form of the potential:

$$V(\vec{r} + \vec{r}_s) = V(\vec{r}) \quad \text{for any Bravais lattice vector } \vec{r}_s$$

Now seek to solve:

$$-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})$$

**Bloch’s Theorem:**

$$\psi_{nk}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u_{nk}(\vec{r})$$

where \( u_{nk}(\vec{r} + \vec{r}_s) = u_{nk}(\vec{r}) \)
Comments on Bloch’s Theorem

1. The wave vector $k$ introduced in Bloch’s theorem has exactly the same role as the wave vector $k$ introduced in solving the Schrodinger equation in free space, except that the momentum can not be written as $\hbar k$, because with a spatially varying potential, $k$ is no longer an eigenvalue of the momentum operator.

2. The wave vector $k$ can always be reduced to a small value residing in the “first Brillouin zone”, since $k$ can be written as a base vector $k'$ plus a reciprocal lattice vector $G$.

3. The index $n$ appears in Bloch’s theorem since there is a whole spectrum of eigenstates that solve the Schrodinger equation.

4. The eigenvectors and eigenvalues can be written as periodic functions of wave vector:

$$\psi_{n(k+K)}(\vec{r}) = \psi_{nk}(\vec{r})$$

$$E_{n(k+K)} = E_{nk}$$

5. An electron can be shown to have a mean velocity:

$$v_n(k) = \frac{1}{\hbar} \nabla_k E_n(k)$$
Kronig-Penney Model

Simplest analytical model for electron in a periodic potential:

Solving:

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

Where, from the Bloch theorem:

\[\psi_k(x + (a + b)) = \exp(ik(a + b))\psi_k(x)\]

A solution is given by:

\[\psi(x) = \begin{cases} 
A \exp(i\beta x) + B \exp(-i\beta x), & -b < x < 0 \\
D \exp(i\alpha x) + F \exp(-i\alpha x), & 0 < x < a 
\end{cases}\]

\[\beta = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}\]

\[\alpha = \sqrt{\frac{2mE}{\hbar^2}}\]
Solving the Kronig-Penney Model

In the next period of the potential:

\[
\psi(x) = \exp(ik(a+b)) \left\{ \begin{array}{l}
A \exp(i\beta(x-(a+b))) + B \exp(-i\beta(x-(a+b))) \\
D \exp(i\alpha(x-(a+b))) + F \exp(-i\alpha(x-(a+b)))
\end{array} \right.
\]

Since the wave function and its derivatives must be continuous at \(x=0, x=a\), we get four equations for \(A, B, D, F\):

\[
\begin{align*}
A + B &= D + F \\
\beta(A - B) &= \alpha(D - F) \\
\exp(ik(a+b))(A \exp(-i\beta b) + B \exp(i\beta b)) &= D \exp(i\alpha a) + F \exp(-i\alpha a) \\
\beta \exp(ik(a+b))(A \exp(-i\beta b) - B \exp(i\beta b)) &= \alpha(D \exp(i\alpha a) - F \exp(-i\alpha a))
\end{align*}
\]

For non-trivial solutions the determinant of the corresponding matrix must vanish, which leads to the condition:

\[
\cos(k(a+b)) = \cos(a\alpha) \cosh(b\delta) - \frac{\alpha^2 - \delta^2}{2\alpha\delta} \sin(a\alpha) \sinh(b\delta), \quad 0 < E < V
\]

Where:

\[
\delta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}
\]
Solving the Kronig-Penney Model II

Look at only the limiting case:

\[ P = \lim_{b \to 0, \delta \to \infty} \frac{ab\delta^2}{2} \]

So \( k \) is allowed when:

\[ -1 \leq P \frac{\sin(a\alpha)}{a\alpha} + \cos(a\alpha) \leq +1 \]

Which is best solved graphically…

Main points:
- For a weak potential, get bands
- For a strong potential, get discrete values
The parameter $k$ is now referred to as the Bloch wave number. Observe that in one-dimension, with lattice constant $a$, any value of $k$ can be rewritten as:

$$K = \frac{2\pi n}{a} + k \quad \text{with} \quad -\frac{\pi}{a} < k < \frac{\pi}{a}$$

so that:

$$\psi_k = u_k(x) \exp(ikx) = u_k(x) \exp\left(\frac{2\pi ni}{a}\right) \exp(ik'x)$$

thus

$$\psi_{nk'} = u_{nk'}(x) \exp(ik'x)$$

where

$$u_{nk'}(x) = u_k(x) \exp\left(\frac{2\pi ni}{a}\right)$$

The range $[-\pi/a < k < \pi/a]$ is referred to as the first Brillouin zone.

Consider energies:

$$E = \frac{\hbar^2 k^2}{2m}$$
Energy bands in three dimensions

Combining concepts of Brillouin zone and 3-D reciprocal lattice for common materials, can make general comments about 3-D band structure: much more complicated!

• Shape of 1st Brillouin zone is Wigner-Seitz cell:

• Band diagram constructed with respect to symmetry points
General comments on 3-D bandstructure

- Set of valence bands, full at \( T=0 \), separated by band gap from set of conduction bands. Zero conventionally at valence band top

Basic chemical picture:

- Bottom of the conduction band: s-like
- Top of the valence band: p-like

- Different types of valence sub-bands: heavy and light

\( p_x \) orbital only

\( all \ p\)-type orbitals
3-D Bandstructure near $\Gamma$-point

- Near $k=0$, typical semiconductor bandstructure is approximated using the parabolic relations:

\[
E(k) \approx E_C + \frac{\hbar^2 k^2}{2m_0 m_e}, \quad \text{conduction band}
\]

\[
E(k) \approx E_V - \frac{\hbar^2 k^2}{2m_0 m_h}, \quad \text{hole subband}
\]

where $m_e$ and $m_h$ are effective masses of charge in each band

- This brings us back, essentially, to the free electron picture, where the charge carrier behavior is described using an effective mass
- Some optoelectronic devices based on vertical transitions of charge carriers in this picture
- Complication: not all materials have direct bandgaps (e.g. Si, AlAs)