Lecture 6 – Bloch’s theorem

Reading
Ashcroft & Mermin, Ch. 8, pp. 132 – 145.

Content
- Periodic potentials
- Bloch’s theorem
- Born – von Karman boundary condition
- Crystal momentum
- Band index
- Group velocity, external force
- Fermi surface
- Band gap
- Density of states
- van Hove singularities

Central concepts
- Periodic potentials
  A periodic potential appears because the ions are arranged with a periodicity of their Bravais lattice, given by lattice vectors $\mathbf{R}$.
  \[ U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \]
  This potential enters into the Schrödinger equation
  \[ \hat{H}\psi = \left( -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \right)\psi = \epsilon\psi \]
  The electrons are no longer free electrons, but are now called Bloch electrons.
- Bloch’s theorem
  **Theorem:** The eigenstates $\psi$ of the Hamiltonian $\hat{H}$ above can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice:
  \[ \psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{nk}(\mathbf{r}) \]
  where
  \[ u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r}) \]
  The quantum number $n$ is called the *band index* and takes numbers $n = 1, 2, 3, \ldots$. This quantum number corresponds to the appearance of independent eigenstates of different energies but with the same $\mathbf{k}$, as will be shown later.
  An alternative formulation of Bloch’s theorem is that the eigenstates of $\hat{H}$ can be chosen so that associated with each $\psi$ is a wave vector $\mathbf{k}$ such that
  \[ \psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}) \]
• Born – von Karman boundary condition

Apply boundary condition of macroscopic periodicity. Generalize to volume commensurate with underlying Bravais lattice:

\[ \psi(r + N_i a_i) = \psi(r), \quad i = 1, 2, 3 \]

where \( a_i \) are the primitive vectors and \( N_i \) are integers of order \( N^{1/3} \) where \( N = N_1 N_2 N_3 \) is the total number of primitive cells in the crystal. The quantum number \( k \) can be composed from the reciprocal lattice vectors with (non-integer) coefficients \( x_i \),

\[ k = \sum_{i=1}^{3} m_i \frac{b_i}{N_i} \]

with \( m_i \) integers. For a simple cubic Bravais lattice, the allowed wave vector components reduce to the earlier \( k_x = \frac{2\pi m_x}{L} \) etc., since \( N_i = L/a \) and \( b_i = (2\pi/a) \hat{b} \) etc.

As for the free electron case, the volume \( \Delta k \) per allowed \( k \) is given by

\[ \Delta k = \frac{(2\pi)^3}{V} \]

• Crystal momentum

For Bloch electrons, \( \psi_{nk} \) is no longer a momentum eigenstate, i.e., \( \hat{p} \psi_{nk} \neq \hbar k \psi_{nk} \). The relation \( p = \hbar k \) is no longer valid. Some similarities remain, however, and \( \hbar k \) is called the crystal momentum.

• Band index

Any value of \( k \) that is outside the first Brillouin zone can be reduced to the first zone, since all wave vectors \( k' = k + G \) are associated with the same eigenstate \( \psi \), as follows from the alternative formulation of Bloch’s theorem. Allowing \( k \) to range outside the first Brillouin zone thus gives a redundant description. For a given \( k \), there are many solutions to the Schrödinger equation with different eigenvalues \( \varepsilon_n \). As a function of \( k \), these are continuous functions \( \varepsilon_n(k) \), called bands with band index \( n \). The family of continuous functions \( \varepsilon_{nk} = \varepsilon_n(k) \) describes the band structure of the material. Since \( \varepsilon_{nk} \) is periodic, each band has an upper and a lower bound for the corresponding energies.

• Group velocity, external force

The mean (group) velocity of a Bloch electron given by \( n \) and \( k \) is

\[ v_n(k) = \frac{1}{\hbar} \nabla_k \varepsilon_n(k) = \frac{1}{\hbar} \frac{\partial \varepsilon_n}{\partial k} \]

(Compare with \( \varepsilon = \hbar \omega, \ v_c = \partial \omega / \partial k \)). This means that the electron does not collide with the periodic potential but remains in a stationary state if the lattice is ideal.

An external force \( F \) acting on an electron in the crystal gives rise to a change of \( k \),

\[ \frac{\delta k}{\delta t} = \frac{F}{\hbar} \]

To motivate this, study the force \( F \) acting during time \( \delta t \). The added energy to the electron is given by force times distance, so that

\[ \delta \varepsilon = F \cdot v_g \delta t = F \cdot \left( \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} \right) \delta t \]

But \( \delta \varepsilon \) can also be written as \( \delta \varepsilon = (\partial \varepsilon / \partial k) \delta k \), and thus we see that \( \delta k / \delta t = F / \hbar \).
• **Fermi surface**

The ground state of a system of Bloch electrons can be constructed by filling up energy levels just as in the free electron case. To count each level only once, \( k \) needs to be limited to a single primitive cell of the reciprocal lattice, typically the first Brillouin zone. The allowed \( k \) values are still spaced discretely, even though \( \epsilon_n(k) \) are continuous functions of \( k \). Since the volume of the Brillouin zone is \( 8\pi^3/v_c \) and \( \Delta k = 8\pi^3/V, \) the number of levels per band is \( V/v_c = N \), which gives \( 2N \) electron states per band.

Depending on the number of valence electrons \( Z \) per cell \( v_c \) and the band structure \( \epsilon_n(k) \), one may obtain *completely filled* or *partially filled* bands. The Fermi surface is obtained from the condition that \( \epsilon_n(k) = \epsilon_F \).

• **Band gap**

If some bands are completely filled and all others remain empty, the gap between the highest occupied level and the lowest unoccupied level is called the *band gap*. In this case, there is no Fermi surface. This may happen - but does not need to happen - if \( Z \) is even. If \( Z \) is odd, there are always partially filled bands and a Fermi surface is formed. If the material has a Fermi surface, it also has metallic properties.

• **Density of states**

The density of states of the system with a periodic potential can be divided into each band,

\[
g(e) = \sum_n g_n(e)
\]

and it can be shown that

\[
g_n(e) = \frac{1}{4\pi^3} \int_{S_n(e)} \frac{dS}{|\nabla_k \epsilon_n(k)|}
\]

where \( S_n(e) \) is a surface of constant energy. The density of states at the Fermi energy is, thus, obtained by an integral over the Fermi surface. (For free electrons, \( \nabla_k \epsilon(k) = \hbar^2 k/m \) and \( \int dS = 4\pi k^2 \), so that \( g(e) = mk/\pi^2 \hbar^2 = m(2me)^{3/2}/\pi^2 \hbar^3 \) as obtained earlier.)

• **van Hove singularities**

Since \( \epsilon_n(k) \) are periodic and continuous functions, there are values of \( k \) at which \( \nabla_k \epsilon_n(k) = 0 \). The integrand for \( g_n(e) \) then diverges. Such singularities are still integrable, but give divergences in the slope \( dg_n/de \), which are called *van Hove singularities*. 