Condensed Matter Physics – FK7060 Feb. 1, 2018.

Lecture 6 – Bloch's theorem

Reading

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

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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

  $$\hat{H}\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\psi = \varepsilon\psi$$

  The electrons are no longer free electrons, but are now called *Bloch electrons*.

- **Bloch's theorem**

  Theorem: The eigenstates ψ of the Hamitonian $\hat{H}$ above can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice:

  $$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

  where

  $$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

  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 ψ 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:

  $$\psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}), \qquad i = 1, 2, 3$$

  where $\mathbf{a}_i$ are the primitive vectors and N_i are integers of order $N^{1/3}$ where $N = N_1N_2N_3$ is the total number of primitive cells in the crystal. The quantum number $\mathbf{k}$ can be composed from the reciprocal lattice vectors with (non-integer) coefficients x_i,

  $$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$$

  Since $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ the Bloch theorem then gives $e^{i2\pi x_i N_i} = 1$. Thus, $x_i = m_i/N_i$ and the allowed Bloch wave vectors are given by

  $$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\mathbf{b}_i$$

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

  As for the free electron case, the volume $\Delta\mathbf{k}$ per allowed $\mathbf{k}$ is given by

  $$\Delta\mathbf{k} = \frac{(2\pi)^3}{V}$$

- **Crystal momentum**

  For bloch electrons, $\psi_{n\mathbf{k}}$ is no longer a momentum eigenstate, i.e., $\hat{\mathbf{p}}\psi_{n\mathbf{k}} \neq \hbar\mathbf{k}\psi_{n\mathbf{k}}$. The relation $\mathbf{p} = \hbar\mathbf{k}$ is no longer valid. Some similarities remain, however, and $\hbar\mathbf{k}$ is called the *crystal momentum*.

- **Band index**

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

  $$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\varepsilon_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial\varepsilon_n}{\partial\mathbf{k}}$$

  (Compare with $\varepsilon = \hbar\omega$, $v_g = \partial\omega/\partial k$). 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 $\mathbf{F}$ acting on an electron in the crystal gives rise to a change of $\mathbf{k}$,

  $$\frac{d\mathbf{k}}{dt} = \frac{\mathbf{F}}{\hbar}$$

  To motivate this, study the force $\mathbf{F}$ acting during time δt. The added energy to the electron is given by force times distance, so that

  $$\delta\varepsilon = \mathbf{F} \cdot \mathbf{v}_g\delta t = \mathbf{F} \cdot \left(\frac{1}{\hbar}\frac{\partial\varepsilon}{\partial\mathbf{k}}\right)\delta t$$

  But $\delta\varepsilon$ can also be written as $\delta\varepsilon = (\partial\varepsilon/\partial\mathbf{k})\delta\mathbf{k}$, and thus we see that $\delta\mathbf{k}/\delta t = \mathbf{F}/\hbar$.

- **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, $\mathbf{k}$ needs to be limited to a single primitive cell of the reciprocal lattice, typically the first Brillouin zone. The allowed $\mathbf{k}$ values are still spaced discretely, even though $\varepsilon_n(\mathbf{k})$ are continuous functions of $\mathbf{k}$. Since the volume of the Brillouin zone is $8\pi^3/v_c$ and $\Delta\mathbf{k} = 8\pi^3/V$, 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 $\varepsilon_n(\mathbf{k})$, one may obtain *completely filled* or *partially filled* bands. The Fermi surface is obtained from the condition that

$$\varepsilon_n(\mathbf{k}) = \varepsilon_F$$

- **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,

$$g(\varepsilon) = \sum_n g_n(\varepsilon)$$

  and it can be shown that

$$g_n(\varepsilon) = \frac{1}{4\pi^3} \int_{S_n(\varepsilon)} \frac{dS}{|\nabla_{\mathbf{k}} \varepsilon_n(\mathbf{k})|}$$

  where $S_n(\varepsilon)$ 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, $\nabla_{\mathbf{k}}\varepsilon(\mathbf{k}) = \hbar^2 k/m$ and $\int dS = 4\pi k^2$, so that $g(\varepsilon) = mk/\pi^2\hbar^2 = m(2m\varepsilon)^{1/2}/\pi^2\hbar^3$ as obtained earlier.)

- **van Hove singularities**

  Since $\varepsilon_n(\mathbf{k})$ are periodic and continuous functions, there are values of $\mathbf{k}$ at which $\nabla_{\mathbf{k}}\varepsilon_n(\mathbf{k}) = 0$. The integrand for $g_n(\varepsilon)$ then diverges. Such singularities are still integrable, but give divergences in the slope $dg_n/d\varepsilon$, which are called *van Hove singularities*.