SCPY 371: Solid State Physics **1^{st} Semester 2021**

Lecture 7: Electronic band structure

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So far, we have ignored the interaction between an electron and nucleus. However, in order to explain physics in most materials in particular metals, semimetals, semiconductors, and insulator we need to also include the influence of nuclei, which as we have learned in the beginning of this class form a periodic lattice. This periodicity turns out to be an important feature that results in bands of energy or **band structure** in which our electrons can reside and **band gaps** at which energy there can be no electron. Furthermore, the free electron model fails to explain the positive value of the Hall coefficient and other transport properties such as the effective mass of electron. To summarize, the properties that cannot be explained by the free electron model are the following:

1. The free electron model fails to capture the wide range of resistivity of over 32 decades from $\rho \approx 10^{-10}\ \Omega \cdot \text{cm}$ in metals to $\rho \approx 10^{22}\ \Omega \cdot \text{cm}$ in insulators.
2. We know that in metal $\frac{d\rho}{dT} > 0$ since τ increases with decreasing temperature. However, in semiconductor and semimetals $\frac{d\rho}{dT} < 0$
3. The Hall coefficient R_H can be positive, which means the charge carrier can be a positive charge.

7.1 Bloch Theorem

In the free electron model, the electron-energy dispersion relation (this is different from the phonon dispersion relation) can be calculated from the free electron Hamiltonian:

$$\mathscr{H}\psi(\vec{x}) = \frac{\hbar^2}{2m}\nabla^2\psi(\vec{x}) = E\psi(\vec{x}),$$

where

$$\psi(\vec{x}) = Ae^{i\vec{k}\cdot\vec{x}} + Be^{-i\vec{k}\cdot\vec{x}}.$$

The eigen-energy of this Hamiltonian is $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$, which is a parabolic function and extends to infinity.

Origin of energy gap So why is there band gap in the electron energy when the interaction between electrons and nuclei is included? To answer this question qualitatively, we will approximate the electron wave function with the oscillatory function sine and cosine. Let nuclei reside at $x = 0, \pm a, \pm 2a, \pm 3a, \ldots$ Since electrons are attracted by nuclei, they will spend more time around the nuclei and hence it is more likely to find electrons there. Therefore, the wave function for this electron is $\psi_+(x) \propto \cos(\pi x/a)$ and its probability density is $n_+ = |\psi|^2 \propto \cos^2(\pi x/a)$. The next allowed wave function is $\psi_-(x) \propto \sin(\pi x/a)$ and its probability density is $n_- = |\psi|^2 \propto \sin^2(\pi x/a)$. The energy difference between these two wave functions indicates the energy gap.

Bloch theorem Now, the question is how the eigen-energy changes if we add the interaction between electrons and nuclei. Here we add the periodic potential of the lattice due to the nuclei to obtain a new Hamiltonian:

$$\mathscr{H}\psi(\vec{x}) = \left[\frac{\hbar^2}{2m}\nabla^2 + u(\vec{x})\right]\psi(\vec{x}) = E\psi(\vec{x}),$$

where $u(\vec{x})$ is the periodic potential due to the periodic arrangement of nuclei. Since the wave function must have the same symmetry as the underlying Hamiltonian, our wave function must have a special form that also satisfies this periodic potential. F. Bloch has shown that the wave function must be of a form:

$$\psi(\vec{x}) = u_k(\vec{x})e^{i\vec{k}\cdot\vec{x}},$$

where $u_k(\vec{x})$ is a periodic function such that $u_k(\vec{x}) = u_k(\vec{x}+\vec{R})$ where $\vec{R}$ is the lattice translation vector. In words, the Bloch theorem can be stated as:

> "The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave $e^{i\vec{k}\cdot\vec{x}}$ times a function $u_k(\vec{x})$ with the periodicity of the lattice"-Kittel

Due to the periodicity of the lattice, that is, $u(\vec{x}) = u(\vec{x}+\vec{R})$ where $\vec{R}$ is the lattice translation vector, the wave function (in one dimension) must have the same periodicity, that is,

$$\psi(x+a) \propto \psi(x)$$

or

$$\psi(x+a) = C\psi(x),$$

where a is a one dimensional lattice constant and C is a constant, which is a complex number. Now if we apply the boundary condition such that after N atoms the wave function comes back to itself, that is,

$$\psi(x) = \psi(x+Na) = C^N\psi(x),$$

which implies that C must be one of the N roots of one, that is,

$$C = e^{i2\pi n/N},$$

where $n = 0,1,2,3,...,N-1$. Therefore, we can rewrite $\psi(x)$ as

$$\psi(x) = e^{i2\pi nx/Na}u_k(x) \equiv e^{ikx}u_k(x),$$

where $k = 2\pi n/Na$.

We will now apply Bloch Theorem to one of the simplest problems that illustrate the energy gap and band structure of electrons, that is, the one dimensional lattice of the $\delta-$ function potential.

One dimensional lattice of the $\delta-$ function potential We will consider the $\delta-$ function potential as shown in Fig 7.1, which is of the following form

$$U(x) = \frac{\hbar^2}{m}\lambda\sum_{n=-\infty}^{\infty}\delta(x-na),$$

where a is the separation distance between the nearest $\delta-$function. The one-dimensional Hamiltonian is $\mathscr{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$ and hence the Schrödinger equation become:

$$\mathscr{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{\hbar^2}{m}\lambda\sum_{n=-\infty}^{\infty}\delta(x-na)\psi(x) = E\psi(x).$$

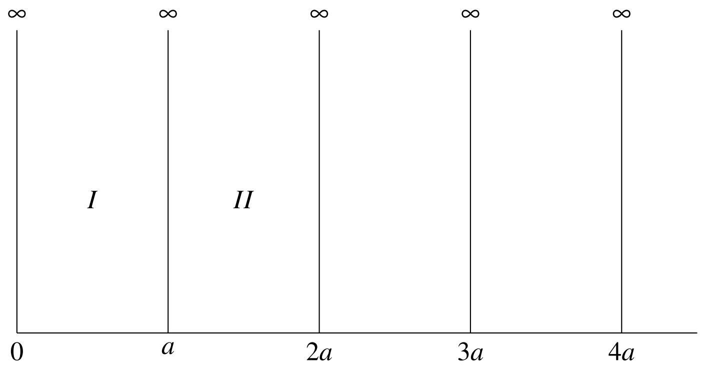

Figure 7.1: One-dimensional lattice of the δ-function potential.

Our goal is to calculate the eigen-energy E of electrons. We will start by writing down the eigen-wavefucntion of an electron in Regions I and II shown in the figure. In Region I (ignoring the end points at $x = 0$ and $x = a$), we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x).$$

The solution to this Schrödinger equation is

$$\psi_I(x) = Ae^{iKx} + Be^{-iKx}, \tag{7.1}$$

where $K = \sqrt{\frac{2mE}{\hbar^2}}$. Next we will apply the Bloch Theorem to obtain the wavefunction in Region II. Applying the Bloch Theorem to $\psi(x)$, we obtain

$$\psi(x+a) = e^{ik(x+a)}u_k(x+a) = e^{ika}\left(e^{ikx}u_k(x)\right) = e^{ika}\psi(x),$$

where k is the wave vector of an electron. Note that k is different from K, which is used to calculate electron's energy. At the end, we would like to find the dispersion relation between k and E(K), or equivalently between k and K. From the above equation, we can write down the wavefunction for Region II by letting $x + a \to x$, that is, $x \to x - a$:

$$\psi_{II}(x) = e^{ika}\psi_I(x-a) = e^{ika}\left(Ae^{iK(x-a)} + Be^{-iK(x-a)}\right). \tag{7.2}$$

Now we will include the boundary condition at $x = a$. The first equation comes from the fact that the wavefunction must be continuous at the boundary, that is,

$$\begin{aligned} \psi_I(a) &= \psi_{II}(a) \\ Ae^{iKa} + Be^{-iKa} &= Ae^{ika} + Be^{ika} \\ \Rightarrow \quad A\left(e^{iKa} - e^{ika}\right) &+ B\left(e^{-iKa} - e^{ika}\right) = 0. \end{aligned} \tag{7.3}$$

The second set of equations can be obtained by considering the derivative of the wavefunction at the boundary. Since there is the $\delta-$function at $x = a$, its derivative must be discontinuous. The discontinuity equation can be derived from the Shrödinger equation:

$$\begin{aligned}\int_{a-\varepsilon}^{a+\varepsilon} dx\,\frac{d^2\psi}{dx^2}-2\lambda\int_{a-\varepsilon}^{a+\varepsilon} dx\;\psi(x)\delta(x-a) &= -\frac{2mE}{\hbar^2}\int_{a-\varepsilon}^{a+\varepsilon} dx\;\psi(x)\\ \left.\frac{d\psi}{dx}\right|_{a-\varepsilon}^{a+\varepsilon}-2\lambda\,\psi(a) &= -\frac{2mE}{\hbar^2}\psi(a)\cdot 2\varepsilon\\ \left.\frac{d\psi_{II}}{dx}\right|_{a^+}-\left.\frac{d\psi_I}{dx}\right|_{a^-}-2\lambda\,\psi_{I,II}(a) &= 0, \end{aligned}\tag{7.4}$$

where ε is small and in the last step we let ε go to zero and hence the term on the right hand side vanishes. If we apple the discontinuity of $\frac{d\psi}{dx}$ to ψ_I and ψ_{II}, we obtain

$$\left[-iKAe^{iKa}+iKBe^{-iKa}\right]+\left[iKAe^{ika}-iKBe^{ika}\right]=2\lambda\left(Ae^{iKa}+Be^{-iKa}\right)$$

$$\Rightarrow\quad A\left(2\lambda e^{iKa}+iKe^{iKa}-iKe^{ika}\right)+B\left(2\lambda e^{-iKa}-iKe^{-iKa}+iKe^{ika}\right)=0. \tag{7.5}$$

We can solve Eqs. 7.3 and 7.5 by writing them in a matrix from and letting its determinant equal to zero.

$$\begin{vmatrix} e^{iKa}-e^{ika} & e^{-iKa}-e^{ika}\\ 2\lambda e^{iKa}+iKe^{iKa}-iKe^{ika} & 2\lambda e^{-iKa}-iKe^{-iKa}+iKe^{ika}\end{vmatrix}=0.$$

We can solve this equation and obtain the following equation that shows the relation between k and K:

$$\cos(ka)=\cos(Ka)+\frac{\lambda}{K}\sin(Ka),$$

where we can calculate the eigen-energy from K using $E=\frac{\hbar^2K^2}{2m}$. We can see that the left hand side only depends on k while the right hand side depends only on K. Since $|\cos(ka)|\leqslant 1$, we can only have a solution for K and E if and only if the absolute value of the right hand side is also less than or equal to one. This is the condition that gives rise to the energy gap. Note that if $\lambda\to 0$, $\cos(ka)\to\cos(Ka)$ and we obtain the free-electron dispersion relation as we expect.

What we get from this calculation is that even in the simplest potential of the $\delta-$function, there is an energy gap in the dispersion relation of electrons. In fact, this result is carried to the potential of the real system. What gives rise to the energy gap is the periodic arrangement of atoms or the periodic potential and the existence of the gap is independent of the detail description of the potential.

7.2 Central Equation

Alternatively, the Bloch Theorem can be rewritten in another form. From our discussion at the beginning of this chapter, we know that we can write the periodic potential $U(x)$ in terms of the Fourier components., that is,

$$U(x)=\sum_G U_G e^{iGx},$$

where G's are the reciprocal lattice vectors and U_G's are the Fourier coefficients. Therefore, we will rewrite the Hamiltonian as

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\sum_G U_G e^{iGx}\right)\psi(x)=E\psi(x).$$

Since $\psi(x)$ is itself a periodic function, we can write our wavefunction in the form of the Fourier series, that is,

$$\psi(x)=\sum_k C_k e^{ikx}. \tag{7.6}$$

We then substitute the wavefunction back into the Hamiltonian and obtain

$$\begin{aligned}
\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\sum_G U_G e^{iGx}\right)\sum_k C_k e^{ikx} &= E\sum_k C_k e^{ikx} \\
\frac{\hbar^2}{2m}\sum_k k^2 C_k e^{ikx}+\sum_G\sum_k U_G C_k e^{i(G+k)x} &= E\sum_k C_k e^{ikx} \\
\sum_k\left(\frac{\hbar^2 k^2}{2m}C_k+\sum_G U_G C_{k-G}-EC_K\right)e^{ikx} &= 0. \qquad (7.7)
\end{aligned}$$

In the last step, we change $k \to k-G$ for the second term on the left hand side and hence obtain

$$\sum_G\sum_k U_G C_k e^{i(G+k)x}=\sum_G\sum_{k-G} U_G C_{k-G}e^{i(G+k-G)x}=\sum_G\sum_k U_G C_{k-G}e^{ikx},$$

since $\sum_{k-G}=\sum_k$; the variable k is just shifted but the sum runs over all values of k for both cases. We will let $\lambda_k=\frac{\hbar^2k^2}{2m}$. Eq. 7.7 can only be true if and only if its coefficient is equal to zero, that is,

$$(\lambda_k-E)\,C_k+\sum_G U_G C_{k-G}=0.$$

This equation is called the **central equation**. Using this equation to solve for all C_k, our wavefunction can be given by

$$\psi(x)=\sum_G C_{k-G}e^{i(k-G)x}.$$

Can you convince yourself that the sum over G is equivalent to the sum over all k as written in Eq. 7.6? This equation can be rearranged such that it is equivalent to the Bloch wave function:

$$\psi(x)=\left(\sum_G C_{k-G}e^{-iGx}\right)e^{ikx}=e^{ikx}u_k(x),$$

where $u_k(x)$ is defined as

$$u_k(x)\equiv\sum_G C_{k-G}e^{-iGx}.$$

This version of $\psi(x)$ is considered as the restatement of the Bloch Theorem. In fact, we can show that $u_k(x)$ satisfies the condition of the Bloch Theorem that $u_k(x)=u_k(x+a)$ where a is the lattice translation distance.

$$u_k(x+a)=\sum_G C_{k-G}e^{-iG(x+a)}=e^{-iGa}\sum_G C_{k-G}e^{-iGx}=e^{iGa}u_k(x)=u_k(x),$$

since $e^{iGa}=1$.

Applications of the Central Equation Now we will use the central equation to solve simple problems. At first, you might think that solving the central equation is complicated since we have to solve all equations involving C_k simultaneously. However, in a real problem, only a few terms are important and we can ignore most of the C_k's.

Energy gap near the zone boundary In the first problem, we will try to approximate a solution to the central equation near a zone boundary. In this case, the most important C_k are at $k=\pm\frac{1}{2}G$. Therefore, we obtain two equations for both k points.

$$\begin{aligned}
(\lambda-E)C_{\frac{1}{2}G}+UC_{-\frac{1}{2}G} &= 0 \\
(\lambda-E)C_{-\frac{1}{2}G}+UC_{\frac{1}{2}G} &= 0.
\end{aligned}$$

We can again solve this set of equations using a matrix, that is,

$$\begin{vmatrix} \lambda - E & U \\ U & \lambda - E \end{vmatrix} = 0.$$

Therefore,

$$E_{\pm} = \lambda \pm U = \frac{\hbar^2}{2m}\left(\frac{1}{2}G\right)^2 \pm U.$$

We can see one solution is larger than the other solution and the difference is the gap energy. In this case the gap energy is equal to $2U$.

Now suppose that we would like know not only the gap energy but also the function form of the dispersion relation near the zone boundary, that is, how the energy varies with k near the zone boundary. In this case, our set of equations becomes

$$\begin{aligned} (\lambda_k - E)C_k + UC_{k-G} &= 0 \\ (\lambda_{k-G} - E)C_{k-G} + UC_k &= 0. \end{aligned}$$

And the determinant form is

$$\begin{vmatrix} \lambda_k - E & U \\ U & \lambda_{k-G} - E \end{vmatrix} = 0.$$

Therefore, the solutions are

$$E_{\pm k} = \frac{1}{2}(\lambda_{k-G} + \lambda_k) \pm \left[\frac{1}{4}(\lambda_{k-G} - \lambda_k)^2 + U^2\right]^{1/2}.$$

Since we would like to focus only on the region near the zone boundary, we will change the variable to center around the zone boundary, that is, we will let $\tilde{k} = k - \frac{1}{2}G$. Therefore, in terms of $\tilde{k}$, we can rewrite the solutions as

$$E_{\pm\tilde{k}} = \frac{\hbar^2}{2m}\left(\frac{1}{4}G^2 + \tilde{k}^2\right) \pm \left[4\lambda\left(\frac{\hbar^2\tilde{k}^2}{2m}\right) + U^2\right]^{1/2}.$$

Since near the zone boundary $|U| \gg \sqrt{\lambda\left(\frac{\hbar^2\tilde{k}^2}{2m}\right)}$, we can approximate that

$$\begin{aligned} E_{\pm\tilde{k}} &= \frac{\hbar^2}{2m}\left(\frac{1}{4}G^2 + \tilde{k}^2\right) \pm U\left[1 + \frac{4\lambda}{U^2}\left(\frac{\hbar^2\tilde{k}^2}{2m}\right)\right]^{1/2} \\ &\approx \frac{\hbar^2}{2m}\left(\frac{1}{4}G^2 + \tilde{k}^2\right) \pm U\left[1 + \frac{2\lambda}{U^2}\left(\frac{\hbar^2\tilde{k}^2}{2m}\right)\right]. \end{aligned} \tag{7.8}$$

But we can rewrite this equation in terms of the energy at the zone boundary $E_{\pm}$ that we obtain above.

$$E_{\pm\tilde{k}} = E_{\pm} + \frac{\hbar^2\tilde{k}^2}{2m}\left[1 \pm \frac{2\lambda}{U}\right].$$

We can immediately see that this is an equation of two parabolic curves with opposite curvature and shifted along the energy axis.

Periodic $\delta-$function potential We will revisit the periodic $\delta-$function potential and apply the central equation. We can rewrite to the Fourier series of $U(x)$ as

$$U(x) = \sum_G U_G e^{iGx},$$

where we can calculate U_G for $U(x) = \frac{\hbar^2}{m}\lambda \sum_n \delta(x-na)$ by:

$$\begin{aligned} U_G &= \int_0^1 dx\, U(x) e^{-iGx} \\ &= \frac{\hbar^2}{m}\lambda \sum_n \int_0^1 dx\, \delta(x-na) e^{-iGx} \\ &= \frac{\hbar^2}{m}\lambda \sum_n e^{-iGna} = \frac{\hbar^2}{m}\lambda \cdot \frac{1}{a}, \end{aligned} \tag{7.9}$$

where the sum runs over all integers of the fixed size of crystal. We assume that the size is equal to 1 and hence n can be from 0 to $1/a$ where a is very large. Therefore, we get a factor of $1/a$ from the sum. We can then apply the central equation:

$$(\lambda_k - E) C_k + \frac{1}{a}\frac{\hbar^2}{m}\lambda \sum_n C_{k-\frac{2\pi n}{a}} = 0$$

Let $f(k) = \sum_n C_{k-\frac{2\pi n}{a}}$.

$$(\lambda_k - E) C_k + \frac{1}{a}\frac{\hbar^2}{m}\lambda f(k) = 0$$

Now we will change the variable $k \to k - \frac{2\pi n}{a}$ and sum this equation over n and obain

$$\begin{aligned} \sum_n \left[\left(\lambda_{k-2\pi n/a} - E\right) C_{k-2\pi n/a} + \frac{1}{a}\frac{\hbar^2}{m}\lambda f(k-2\pi n/a) \right] &= 0 \\ \sum_n C_{k-2\pi n/a} + \sum_n \left[\frac{1}{\lambda_{k-2\pi n/a} - E} \cdot \frac{\hbar^2}{ma}\lambda f(k) \right] &= 0 \\ f(k) + \sum_n \frac{2\lambda/a}{(k-2\pi n/a)^2 - 2mE/\hbar^2} f(k) &= 0 \\ \Rightarrow \quad \frac{a}{2\lambda} = -\sum_n \frac{1}{(k-2\pi n/a)^2 - K^2}, \end{aligned}$$

where $K^2 = 2mE/\hbar^2$. Now let focus on the term in the right hand side.

$$\begin{aligned} -\sum_n \frac{1}{(k-2\pi n/a)^2 - K^2} &= -\sum_n \frac{1}{[(k-2\pi n/a) - K]\,[(k-2\pi n/a) + K]} \\ &= -\frac{1}{2K}\sum_n \left[\frac{1}{(k-2\pi n/a) - K} - \frac{1}{(k-2\pi n/a) + K} \right] \\ &= \frac{1}{2K}\frac{a}{2}\sum_n \left[\frac{1}{\pi n - \frac{a}{2}(k-K)} - \frac{1}{\pi n - \frac{a}{2}(k+K)} \right]. \end{aligned}$$

Here we will apply the relation $\cot(x) = \sum_n \frac{1}{n\pi + x}$. We obtain

$$-\sum_n \frac{1}{(k-2\pi n/a)^2 - K^2} = \frac{a}{4K}\left[-\cot\left(\frac{a(k-K)}{2}\right) + \cot\left(\frac{a(k+K)}{2}\right) \right].$$

We will use the following trigonometry relation (I will let you prove this relation yourself):

$$\cot a - \cot b = \frac{2\sin(b-a)}{\cos(a-b) - \cos(a+b)}$$

At the end , we will get

$$\begin{aligned} \frac{a}{2\lambda} &= \frac{a}{4K}\frac{2\sin(Ka)}{\cos(ka)-\cos(Ka)} \\ \Rightarrow \quad \cos(ka) &= \cos(Ka)+\frac{\lambda}{K}\sin(Ka), \end{aligned} \tag{7.10}$$

which is in agreement with the derivation we have done using the Bloch Theorem in the previous section.

Now let come back to physics. So far, we know that with the interaction between nuclei and electrons, electron energy becomes bands and there is an energy at which electrons cannot reside. This region of energy is called the energy gap. So how can we put electrons into all these electronic bands? First, we have to count a number of electrons in a unit cell. Second, we know that for each unit cell there is a corresponding $k-$point. Therefore, at a particular $k-$point we need to put at most the number of electron in one unit cell. Now, we have to figure out how many electrons can we put at one $k-$point. Since electrons are Femions, they cannot occupy the same energy state. However, since they have spins, one energy state can afford two electrons. Therefore, at any $k-$point on the electron band, we can put two electrons.

Knowing this and the band structure are enough for us to describe electronic properties of a material. We can now roughly tell whether the material is a metal, semiconductor or insulator. A metal is a material with the top band is not filled and hence electrons on that band can move freely. The insulator is a material with all bands filled, hence prohibiting an electron to move; electrons are all bounded to the nuclei. A semiconductor is a material which the top filled band and the next band are close enough that the thermal energy k_BT can excite electrons to become free. This also explains why for the semiconductor $\frac{d\rho}{dt}$ is negative. When temperature increases, there are more electrons that can move freely, and hence the resistivity decreases. Similarly for the insulator, $\frac{d\rho}{dt} < 0$ but we will have to go to very high temperature since for the insulator the energy gap is much larger than in the semiconductor.

References

[1] Kittel, C.: Introduction to Solid State Physics 7th Edition (Chapter 3), John Wiley & Sons, Inc. (1996).

[2] Ashcroft, N. W. and Mermin, N. D.: Solid State Physics (Chapter 20), Thomson Learning, Inc. (1976).