FoP3B Part I Lecture 3: Bloch waves

Consider the electron mean free path λ in a crystal, i.e. the average distance an electron travels before being scattered by an atomic nucleus. $\lambda = v_F \tau$, where v_F is the speed of Fermi surface electrons and τ is the average collision time. From the first lecture $v_F \sim 1\%$ speed of light and τ for a metal such as copper is $\sim 10^{-15}$s. This gives $\lambda \sim 10$ Å, which is several times larger than the average spacing between the atoms ($\sim$1-2 Å). How can this be? In this lecture we will develop **Bloch wave theory**, which explains the apparent anomaly. Unlike nearly-free electron theory, Bloch wave theory is valid for electron-nuclear interactions of any strength.

Bloch wave theory

An electron in a solid must satisfy Schrödinger's Equation $\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$. Here $V(\mathbf{r})$ is the total potential energy, i.e. it includes electron-electron and electron-nuclear interactions. For a crystal $V(\mathbf{r})$ is periodic and can therefore be written as a Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}\, e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\ldots (1)$$

Assume the wavefunction has the form ($\mathbf{k}$ is the wavevector and $C_{\mathbf{G}}$ are constants that are functions of $\mathbf{k}$):

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}}(\mathbf{k})\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\ldots (2)$$

Substituting in the Schrödinger's Equation gives:

$$\sum_{\mathbf{G}} \left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 - E\right) C_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G},\mathbf{G}'} C_{\mathbf{G}} V_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} e^{i\mathbf{G}'\cdot\mathbf{r}} = 0$$

$$\ldots (3)$$

We can simplify the expression by making the substitution $\mathbf{G} \rightarrow \mathbf{G} - \mathbf{G}'$ in the <u>second summation</u>:

$$\sum_{\mathbf{G}} \left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 - E\right) C_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G},\mathbf{G}'} C_{\mathbf{G}-\mathbf{G}} V_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = 0$$

$$\text{or } \sum_{\mathbf{G}} \left\{\left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 - E\right) C_{\mathbf{G}} + \sum_{\mathbf{G}'} C_{\mathbf{G}-\mathbf{G}'} V_{\mathbf{G}'}\right\} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = 0$$

$$\ldots (4)$$

The above must be valid at all points $\mathbf{r}$ in the crystal, so that the term within the curly brackets must be zero. This gives the so-called **characteristic equation** for Bloch waves:

$$\left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 - E\right) C_{\mathbf{G}} + \sum_{\mathbf{G}'} C_{\mathbf{G}-\mathbf{G}'} V_{\mathbf{G}'} = 0$$

$$\ldots (5)$$

We can write down a characteristic equation for each **G**, so that Equation 5 represents a set of simultaneous linear equations linking the C_G coefficients.

Our analysis has shown that the proposed wavefunction (Equation 2) is a valid solution for a periodic crystal. Let us first examine the implications of this solution. We can express the *Bloch wavefunction* as:

$$\psi_k(\mathbf{r}) = \sum_G C_G(\mathbf{k})\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \left(\sum_G C_G(\mathbf{k})e^{i\mathbf{G}\cdot\mathbf{r}}\right) e^{i\mathbf{k}\cdot\mathbf{r}} = u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

Note that $u(\mathbf{r}) = \sum_G C_G(\mathbf{k})e^{i\mathbf{G}\cdot\mathbf{r}}$ is a periodic function, since for any lattice translation vector **T** it follows that $u(\mathbf{r}+\mathbf{T}) = u(\mathbf{r})$, after making use of the fact that $\mathbf{G}\cdot\mathbf{T} = 2\pi n$ (n = integer). This leads us to **Bloch's theorem** which states that the electron wavefunction in a crystal is simply a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ multiplied by a periodic function. Note that a plane wave was also the solution for a free electron solid, where electron-nuclear interactions were ignored. This implies that Bloch electrons can travel freely through the crystal despite the presence of nuclei! Hence the mean free path λ can be larger than the atomic spacing[1].

Bloch waves and Band structure

Let us explore Equation 5 in more detail. There are an infinite number of reciprocal vectors **G**, since by definition any periodic object is infinitely repeating, but in reality the potential $V(\mathbf{r})$ will only depend on a finite number of reciprocal vectors, with the Fourier coefficients V_G for higher order reciprocal vectors being zero. Assume that we need only N reciprocal vectors $\mathbf{G}_1$, $\mathbf{G}_2$, …, $\mathbf{G}_N$ to represent $V(\mathbf{r})$. Equation 5 can then be written in matrix form:

$$\begin{pmatrix} \left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}_1|^2 - E\right) & \cdots & V_{\mathbf{G}_1-\mathbf{G}_N} \\ \vdots & \ddots & \vdots \\ V_{\mathbf{G}_N-\mathbf{G}_1} & \cdots & \left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}_N|^2 - E\right) \end{pmatrix} \begin{Bmatrix} C_{\mathbf{G}_1} \\ \vdots \\ C_{\mathbf{G}_N} \end{Bmatrix} = \begin{Bmatrix} 0 \\ \vdots \\ 0 \end{Bmatrix}$$

$$\cdots (6)$$

For non-trivial solutions of the C_G coefficients the determinant of the square matrix must be zero:

$$\begin{vmatrix} \left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}_1|^2 - E\right) & \cdots & V_{\mathbf{G}_1-\mathbf{G}_N} \\ \vdots & \ddots & \vdots \\ V_{\mathbf{G}_N-\mathbf{G}_1} & \cdots & \left(\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}_N|^2 - E\right) \end{vmatrix} = 0$$

$$\cdots (7)$$

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[1] Strictly speaking λ should be infinite, but finite values are obtained in practice because thermal vibration of the atoms lead to small deviations from exact periodicity.

If we expand Equation 7 we obtain a *N*-order polynomial in the energy (E) [2]. This means that for a given wavevector **k** there are *N* number of energies for the electron. This important result has a straightforward physical interpretation. In the free electron theory the electron energy has the form $E \propto k^2$ and increases monotonically about the **k** = 0 point. However, because a crystal is periodic, and there is nothing to distinguish **G** from **k** = 0, we must create copies of the dispersion curve at each reciprocal point **G** (Figure 1). Extrapolating these extra dispersion curves into the first Brillouin zone (i.e. the region between –**G**/2 and **G**/2) we obtain the additional electron energy values predicted by Equation 7.
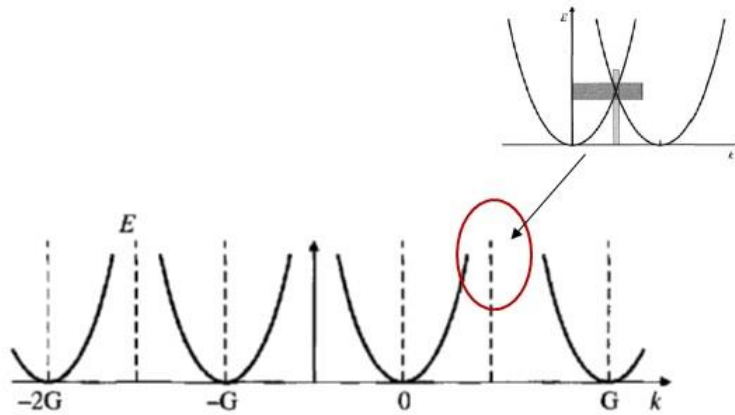

The energies do not always correspond to the free electron case; we have already seen from the nearly-free electron model that whenever electrons have similar energy (e.g. at the Brillouin zone boundary where two of the dispersion curves cross; Figure 1) there will be strong mixing between the electron states leading to non-degenerate energy levels.

Figure 1

There is a more useful way to think about the situation depicted in Figure 1. Consider the dispersion curve centred about **k** = 0 (Figure 2a). Overall the curve has the free electron form $E \propto k^2$ except at the Brillouin zone boundaries, where strong mixing of states give rise to band gaps. This is called the **extended zone scheme**, since all **k**-vectors are represented. However, for a crystal the periodicity means that the electron wavefunction is uniquely defined for **k**-vectors within the first Brillouin zone, i.e. if **k′** is a wavevector within the first Brillouin zone then $\psi_{\mathbf{k'}}(\mathbf{r}) = \psi_{\mathbf{k'+G}}(\mathbf{r})$ (note that the vector **k′** + **G** lies outside the first Brillouin zone). Therefore, the dispersion curve in the extended zone scheme can be folded back into the first Brillouin zone as shown in Figure 2b. This is known as the **reduced zone scheme** and is equivalent to Figure 1. The reduced zone scheme also predicts multiple electron energies for a given **k**. The different branches of the electron energy represent the **band structure** of the solid. The number of available electronic states in a given band is equal to twice the number of primitive unit cells in the material (see previous lecture). Electrons will occupy the band with the lowest energy first, before moving onto the next band higher up in energy.
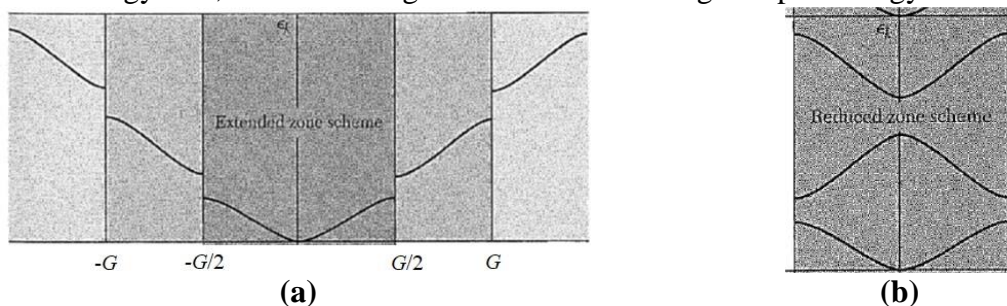

Figure 2: (a) Extended and (b) reduced zone schemes for the dispersion curve.

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[2] If you have difficulty seeing how this comes about consider the simpler case where *N* =2. The matrix elements are then as given in Equation 6 and the determinant in Equation 7 leads to a quadratic expression in *E*.