

Handout 2

The quantum mechanics of particles in a periodic potential: Bloch's theorem

2.1 Introduction and health warning

We are going to set up the formalism for dealing with a periodic potential; this is known as *Bloch's theorem*. The next two-three lectures are going to appear to be *hard work* from a conceptual point of view. However, although the algebra *looks* complicated, the underlying ideas are really quite simple; you should be able to reproduce the various derivations yourself (make good notes!).

I am going to justify the Bloch theorem fairly rigorously. This formalism will then be used to treat two opposite limits, a very weak periodic potential and a potential which is so strong that the electrons can hardly move. You will see that both limits give qualitatively similar answers, *i.e.* reality, which lies somewhere in between, must also be like this!

For this part of the course these notes provide a slightly different (Fourier) approach to the results that I will derive in the lectures. I recommend that you work through and understand both methods, as the Bloch theorem forms the foundation on which the rest of the course is based.

2.2 Introducing the periodic potential

We have been treating the electrons as totally free. We now introduce a periodic potential $V(\mathbf{r})$. The underlying translational periodicity of the lattice is defined by the *primitive lattice translation vectors*

$$\mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (2.1)$$

where n_1, n_2 and n_3 are integers and $\mathbf{a}_1, \mathbf{a}_2$ and \mathbf{a}_3 are three noncoplanar vectors.¹ Now $V(\mathbf{r})$ must be periodic, *i.e.*

$$V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r}). \quad (2.2)$$

The periodic nature of $V(\mathbf{r})$ also implies that the potential may be expressed as a Fourier series

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (2.3)$$

where the \mathbf{G} are a set of vectors and the $V_{\mathbf{G}}$ are Fourier coefficients.²

Equations 2.2 and 2.3 imply that

$$e^{i\mathbf{G}\cdot\mathbf{T}} = 1, \quad i.e. \quad \mathbf{G}\cdot\mathbf{T} = 2p\pi, \quad (2.4)$$

¹See *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) pages 4-7.

²Notice that the units of \mathbf{G} are the same as those of the wavevector \mathbf{k} of a particle; $|\mathbf{k}| = 2\pi/\lambda$, where λ is the de Broglie wavelength. The \mathbf{G} are vectors in k -space.

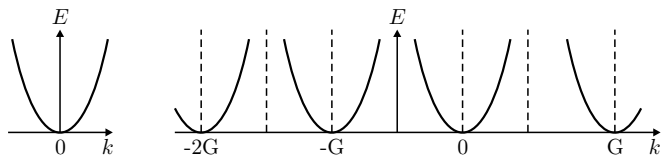


Figure 2.1: The effect of introducing the reciprocal lattice; instead of dealing with just one electron dispersion relationship (left) we have an infinite number of copies (right).

where p is an integer. As $\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, this implies that

$$\mathbf{G} = m_1\mathbf{A}_1 + m_2\mathbf{A}_2 + m_3\mathbf{A}_3, \quad (2.5)$$

where the m_j are integers, and the \mathbf{A}_j are three noncoplanar vectors defined by

$$\mathbf{a}_j \cdot \mathbf{A}_l = 2\pi\delta_{jl}. \quad (2.6)$$

Take a few moments to convince yourself that this is the only way of defining \mathbf{G} which can satisfy Equation 2.4 for all possible \mathbf{T} .

Using very simple reasoning, we have shown that the existence of a lattice in r -space automatically implies the existence of a lattice in k -space. The vectors \mathbf{G} define the *reciprocal lattice*; the \mathbf{A}_j are its primitive translation vectors.

The reciprocal lattice has extraordinary consequences for the electronic motion, even before we “switch on” the lattice potential. Instead of dealing with just one electron dispersion relationship $E(\mathbf{k})$ there must be an infinite number of equivalent dispersion relationships (see Figure 2.1) such that $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$ for all \mathbf{G} (*c.f.* Equation 2.2). However, the k -space periodicity also implies that all information will be contained in the primitive unit cell of the reciprocal lattice, known as *the first Brillouin zone*.³ The first Brillouin zone has a k -space volume

$$V_{k3} = \mathbf{A}_1 \cdot \mathbf{A}_2 \times \mathbf{A}_3. \quad (2.7)$$

2.3 Born–von Karman boundary conditions

We need to derive a suitable set of functions with which we can describe the motion of the electrons through the periodic potential; “motion” implies that we do not want standing waves. The functions should reflect the translational symmetry properties of the lattice; to do this we use *Born–von Karman periodic boundary conditions*.

We choose a plane wave

$$\phi(\mathbf{r}) = e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (2.8)$$

subject to boundary conditions which include the symmetry of the crystal

$$\phi(\mathbf{r} + N_j\mathbf{a}_j) = \phi(\mathbf{r}), \quad (2.9)$$

where $j = 1, 2, 3$ and $N = N_1N_2N_3$ is the number of primitive unit cells in the crystal; N_j is the number of unit cells in the j th direction.

The boundary condition (Equation 2.9) implies that

$$e^{iN_j\mathbf{k} \cdot \mathbf{a}_j} = 1 \quad (2.10)$$

for $j = 1, 2, 3$. Comparing this with Equation 2.4 (and the discussion that follows it) suggests that the allowed wavevectors are

$$\mathbf{k} = \sum_{j=1}^3 \frac{m_j}{N_j} \mathbf{A}_j. \quad (2.11)$$

³The first Brillouin zone is the *Wigner-Seitz primitive cell* of the reciprocal lattice. See *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Section 10.6 or *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) Chapter 2.

Each time that all of the m_j change by one we generate a new state; therefore the volume of k -space occupied by one state is

$$\frac{\mathbf{A}_1}{N_1} \cdot \frac{\mathbf{A}_2}{N_2} \times \frac{\mathbf{A}_3}{N_3} = \frac{1}{N} \mathbf{A}_1 \cdot \mathbf{A}_2 \times \mathbf{A}_3. \quad (2.12)$$

Comparing this with Equation 2.7 shows that *the Brillouin zone always contains the same number of k -states as the number of primitive unit cells in the crystal*. This fact will be of immense importance later on (remember it!); it will be a key factor in determining whether a material is an insulator, semiconductor or metal.

2.4 The Schrödinger equation in a periodic potential.

The Schrödinger equation for a particle⁴ of mass m in the periodic potential $V(\mathbf{r})$ may be written

$$H\psi = \left\{ -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right\} \psi = E\psi. \quad (2.13)$$

As before (see Equation 2.3), we write the potential as a Fourier series

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (2.14)$$

where the \mathbf{G} are the reciprocal lattice vectors. We are at liberty to set the origin of potential energy wherever we like; as a convenience for later derivations we set the uniform background potential to be zero, *i.e.*

$$V_0 \equiv 0. \quad (2.15)$$

We can write the wavefunction ψ as a sum of plane waves obeying the Born–von Karman boundary conditions,⁵

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.16)$$

This ensures that ψ also obeys the Born–von Karman boundary conditions.

We now substitute the wavefunction (Equation 2.16) and the potential (Equation 2.14) into the Schrödinger equation (Equation 2.13) to give

$$\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} C_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} + \left\{ \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \right\} \left\{ \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \right\} = E \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.17)$$

The potential energy term can be rewritten

$$V(\mathbf{r})\psi = \sum_{\mathbf{G}, \mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}} e^{i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}}, \quad (2.18)$$

where the sum on the right-hand side is over all \mathbf{G} and \mathbf{k} . As the sum is over all possible values of \mathbf{G} and \mathbf{k} , it can be rewritten as⁶

$$V(\mathbf{r})\psi = \sum_{\mathbf{G}, \mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k} - \mathbf{G}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.19)$$

Therefore the Schrödinger equation (Equation 2.17) becomes

$$\sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \left\{ \left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k} - \mathbf{G}} \right\} = 0. \quad (2.20)$$

⁴Note that I have written “a particle”; in the proof of Bloch’s theorem that follows, I do not assume any specific form for the energy of the particles in the potential. The derivation will be equally true for photons with $\omega = ck$, electrons with $E = \hbar^2 k^2 / 2m_e$ etc., etc.. Thus, the conclusions will be seen to be true for *any* particle in *any* periodic potential.

⁵That is, the \mathbf{k} in Equation 2.16 are given by Equation 2.11.

⁶Notice that the \mathbf{G} also obey the Born–von Karman boundary conditions; this may be easily seen if values of m_j that are integer multiples of N_j are substituted in Equation 2.11. As the sum in Equation 2.16 is over all \mathbf{k} that obey the Born–von Karman boundary conditions, it automatically encompasses all $\mathbf{k} - \mathbf{G}$.

As the Born-von Karman plane waves are an orthogonal set of functions, the coefficient of each term in the sum must vanish (one can prove this by multiplying by a plane wave and integrating), *i.e.*

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0. \quad (2.21)$$

(Note that we get the Sommerfeld result if we set $V_{\mathbf{G}} = 0$.)

It is going to be convenient to deal just with solutions in the first Brillouin zone (we have already seen that this contains all useful information about k -space). So, we write $\mathbf{k} = (\mathbf{q} - \mathbf{G}')$, where \mathbf{q} lies in the first Brillouin zone and \mathbf{G}' is a reciprocal lattice vector. Equation 2.21 can then be rewritten

$$\left(\frac{\hbar^2 (\mathbf{q} - \mathbf{G}')^2}{2m} - E\right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}'-\mathbf{G}} = 0. \quad (2.22)$$

Finally, we change variables so that $\mathbf{G}'' \rightarrow \mathbf{G} + \mathbf{G}'$, leaving the equation of coefficients in the form

$$\left(\frac{\hbar^2 (\mathbf{q} - \mathbf{G}')^2}{2m} - E\right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}'} C_{\mathbf{q}-\mathbf{G}''} = 0. \quad (2.23)$$

This equation of coefficients is very important, in that it specifies the $C_{\mathbf{k}}$ which are used to make up the wavefunction ψ in Equation 2.16.

2.5 Bloch's theorem

Equation 2.23 only involves coefficients $C_{\mathbf{k}}$ in which $\mathbf{k} = \mathbf{q} - \mathbf{G}$, with the \mathbf{G} being general reciprocal lattice vectors. In other words, if we choose a particular value of \mathbf{q} , then the only $C_{\mathbf{k}}$ that feature in Equation 2.23 are of the form $C_{\mathbf{q}-\mathbf{G}}$; these coefficients specify the form that the the wavefunction ψ will take (see Equation 2.16).

Therefore, for each distinct value of \mathbf{q} , there is a wavefunction $\psi_{\mathbf{q}}(\mathbf{r})$ that takes the form

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{i(\mathbf{q}-\mathbf{G})\cdot\mathbf{r}}, \quad (2.24)$$

where we have obtained the equation by substituting $\mathbf{k} = \mathbf{q} - \mathbf{G}$ into Equation 2.16. Equation 2.24 can be rewritten

$$\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot\mathbf{r}} u_{j,\mathbf{q}}, \quad (2.25)$$

i.e. (a plane wave with wavevector within the first Brillouin zone) \times (a function $u_{j,\mathbf{q}}$ with the periodicity of the lattice).⁷

This leads us to *Bloch's theorem*. “The eigenstates ψ of a one-electron Hamiltonian $H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})$, where $V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r})$ for all Bravais lattice translation vectors \mathbf{T} can be chosen to be a plane wave times a function with the periodicity of the Bravais lattice.”

Note that Bloch's theorem

- is true for *any* particle propagating in a lattice (even though Bloch's theorem is traditionally stated in terms of electron states (as above), in the derivation we made no assumptions about what the particle *was*);
- makes no assumptions about the *strength* of the potential.

⁷You can check that $u_{j,\mathbf{q}}$ (*i.e.* the sum in Equation 2.25) has the periodicity of the lattice by making the substitution $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{T}$ (see Equations 2.2, 2.3 and 2.4 if stuck).

2.6 Electronic bandstructure.

Equation 2.25 hints at the idea of *electronic bandstructure*. Each set of $u_{j,\mathbf{q}}$ will result in a set of electron states with a particular character (*e.g.* whose energies lie on a particular dispersion relationship⁸); this is the basis of our idea of an *electronic band*. The number of possible wavefunctions in this band is just going to be given by the number of distinct \mathbf{q} , *i.e.* the number of Born-von Karman wavevectors in the first Brillouin zone. Therefore the number of electron states in each band is just $2\times$ (the number of primitive cells in the crystal), where the factor two has come from spin-degeneracy. This is going to be very important in our ideas about *band filling*, and the classification of materials into metals, semimetals, semiconductors and insulators.

We are now going to consider two tractable limits of Bloch's theorem, a very weak periodic potential and a very strong periodic potential (so strong that the electrons can hardly move from atom to atom). We shall see that both extreme limits give rise to *bands*, with *band gaps* between them. In both extreme cases, the bands are qualitatively very similar; *i.e.* real potentials, which must lie somewhere between the two extremes, must also give rise to qualitatively similar bands and band gaps.

2.7 Reading.

This topic is treated with some expansion in Chapter 2 of *Band theory and electronic properties of solids*, by John Singleton (Oxford University Press, 2001). A simple justification of the Bloch theorem is given in *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) in the first few pages of Chapter 7 and in *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Section 10.4; an even more elementary one is found in *Electricity and Magnetism*, by B.I. Bleaney and B. Bleaney, revised third/fourth editions (Oxford University Press, Oxford) Section 12.3. More rigorous and general proofs are available in *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) pages 133-140.

⁸A *dispersion relationship* is the function $E = E(\mathbf{q})$.