



Keble College - Hilary 2012  
Section VI: Condensed matter physics  
Tutorial 4 - Electrons in periodic potentials and semiconductors

Please leave your work in the Clarendon laboratory's 'J' pigeon hole by 5pm on Monday of 7th week.  
Suggested reading: Hook & Hall 4, 5; Kittel 7,8; Ashcroft/Mermin 8-12,28.

Before embarking on a study of electrons in periodic potentials it is worthwhile summarising:

First, we should be comfortable with the fact that the single electron eigenstates for non-interacting electrons in periodic systems are going to be parameterised by some  $\mathbf{k}$  where we call  $\hbar\mathbf{k}$  the crystal momentum. Therefore their eigenstates can be written as some function  $\epsilon_n(\mathbf{k})$ , where the band number  $n$  labels different eigenstates with the same  $\mathbf{k}$ . This is true for solutions to any periodic system, follows from Bloch's theorem and we will see it again below.

Second, intricately connected to this and implicit in Bloch's theorem,  $\mathbf{k}$ -values are only defined up to additions of vectors  $\mathbf{K}$  satisfying  $e^{i\mathbf{K}\cdot\mathbf{R}}$  for all translations  $\mathbf{R}$  leaving the potential unchanged. So we see that  $\mathbf{k}$ -space has the symmetry of the lattice that is reciprocal to the direct lattice of the crystal. As a result, it is equivalent to think of each  $\mathbf{k}$  having several energies  $\epsilon_n(\mathbf{k})$  associated with it and restricting  $\mathbf{k}$  to a single Brillouin zone (reduced zone interpretation) or to think of some  $\epsilon(\mathbf{k})$  being defined over all reciprocal space and having values  $\epsilon_n(\mathbf{k})$  in the  $n$ -th Brillouin zone (extended zone interpretation).

Third, we should remember that eigenstates of independent electron systems are states in which electrons occupy single electron eigenstates in accordance with the Pauli exclusion principle. In general, the filling of each eigenstate will be given by the Fermi distribution function, but at temperatures much lower than the Fermi temperature (the regime of interest) the many-electron system will be very close to its ground state where the  $N$  single electron eigenstates with lowest  $\epsilon_n(\mathbf{k})$  are occupied.

The first part of this tutorial will involve calculating these single electron eigenenergies  $\epsilon_n(\mathbf{k})$ . In general it is a difficult task, but we will do it approximately in two opposite limits. The first limit is when the Coulomb potential due to each nucleus is very strong and the overlap between orbitals around different nuclei is small — the tight binding model. The second limit is when electrons feel a very weak potential and so we can calculate the single electron eigenstates by perturbing the eigenstates when the potential is zero — the nearly free electron model. The eigenvalue spectrum of the eigenenergies  $\epsilon_n(\mathbf{k})$  is qualitatively similar in these two diverse limits, giving us confidence in the general qualitative conclusions drawn.

The second part is then to study the motion of electrons when an electric field is applied. We will find that a filled Brillouin zone (or filled band in the reduced zone interpretation) containing all  $\mathbf{k}$  does not conduct electricity, while nearly filled or sparsely filled bands behave like positive or negative charge carriers respectively, with an effective mass.

The third part is about visualising how the volume of  $\mathbf{k}$ -space occupied in the ground state (the volume enclosed by the Fermi surface) looks in the extended zone scheme. Of course, as the potential goes to zero this will look more and more like a sphere, as we found for zero potential in tutorial 1. However, a non-zero potential will cause some changes to  $\epsilon(\mathbf{k})$  and it will not fill so evenly, including the important possibility that gaps between bands will give rise to the case where some Brillouin zones are completely filled and other completely empty. For large (small) gaps this gives rise to insulators (semiconductors).

The fourth part of this tutorial will then discuss the properties of semiconductors and how their behaviour depends on temperature, and how they respond to the presence of doping.

# 1 Finding the single-electron eigenvalues

Here we calculate the eigenvalue spectrum in the tight-binding limit. Refer back to tutorial 3 on chemical bonding, Qu. 2. There we took a two-nucleus system, and constructed approximate eigenstates from combining the lowest-lying states of the isolated nuclei.

1. Considering a one-dimensional monatomic chain with a single atomic orbital per nucleus and making the same assumptions as in Qu. 2 of tutorial 3, along with BvK boundary conditions, the single electron Hamiltonian can be written as

$$\mathcal{H}_{\text{se}} = \sum_{j=1}^N (u|j\rangle\langle j| - t|j+1\rangle\langle j| - t|j-1\rangle\langle j|). \quad (1)$$

Here,  $N$  is the number of atoms in the system,  $|j\rangle$  is the orbital around the  $j$ -th atom,  $u$  is the energy of the atomic orbital and  $t$  is a hopping integral, with the simplifying assumption  $\langle i|j\rangle = \delta_{i,j}$ . State the assumptions used to justify the tight-binding form of the Hamiltonian.

This Hamiltonian is exactly of the form of the dynamical matrix which we diagonalised in Qu. 4 of tutorial 3, using arguments relating to Bloch's theorem. Here, we just quote the diagonalising transformation, though it can be derived in exactly the same way. Define  $|k\rangle$  states by

$$|j\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-ikja} |k\rangle \quad (2)$$

with  $a$  as the lattice parameter and  $k$  as usual takes values  $2\pi p/Na$  for  $p \in \mathbb{Z}$  in the first Brillouin zone. By substituting Eq. 2 into Eq. 1, show that the  $\mathcal{H}_{\text{se}}$  diagonalises to

$$\mathcal{H}_{\text{se}} = \sum_k \epsilon(k) |k\rangle\langle k|,$$

where  $\epsilon(k) = (u - 2t \cos(ka))$ . Sketch the dispersion relation  $\epsilon(k)$  in the repeated zone scheme. What happens to the bandwidth as the hopping term  $t$  gets larger or smaller?

*In this question we found the the single electron eigenstates of a single band. To find the higher bands we would need to consider more than one atomic orbitals, labelled by  $n$ . The result would be several tight-binding bands, one for each orbital, and whether these bands overlapped in energy (as we will see later, this is crucial as to whether a solid is insulating or not) is determined by the overlaps  $t_n$  and energies  $u_n$  of the atomic orbitals.*

*Next we look at the opposite limit, where the potential in which the electrons move is weak. There are many approaches to using perturbation theory to derive the nearly free single electron eigenvalues, as there were many approaches to introducing lattices and reciprocal lattices. Just like in that case, my advice is to read a few of them, build up a intuitive picture and not get bogged down to much in the mathematical intricacies of each. Here we will take one approach.*

2. We will now calculate  $\epsilon_n(\mathbf{k})$  in the nearly-free electron limit. Again, for simplicity we will stick to a one-dimensional system.
  - (a) *Nearly free electrons* — Why might  $V(x)$  effectively be very small for valence electrons moving in some solids, rather than this being just a convenient analytical limit?
  - (b) *Decomposing the potential* — Argue that a periodic potential  $V(x)$  can be written as

$$V(x) = \sum_K v_K \exp(iKx),$$

where  $K$  are reciprocal lattice vectors. What are the values of  $K$  for a period  $a$ ? Assuming  $V(x)$  is real and symmetric, i.e.  $V(x) = V(-x)$ , show that  $v_K = v_{-K} = v_K^*$ . Argue that the contribution corresponding to  $K = 0$  can be ignored, thus the potential becomes

$$V(x) = \sum_{K>0} V_K(x), \quad (3)$$

with  $V_K(x) = v_K[\exp(iKx) + \exp(-iKx)]$ .

- (c) *Perturbation theory* — The single electron Hamiltonian in the position basis may be written as

$$\mathcal{H}_{\text{se}} = \mathcal{H}_{\text{se}}^{(0)} + V(x).$$

The zeroth order Hamiltonian is that for free electrons  $\mathcal{H}_{\text{se}}^{(0)} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$  with momentum eigenfunctions  $\Psi_k^{(0)}(x)$  and eigenvalues  $\epsilon^{(0)}(k) = \frac{\hbar^2 k^2}{2m}$ , where due to BvK boundary conditions  $k$  as usual takes only values  $2\pi p/Na$  for  $p \in \mathbb{Z}$ .

For simplicity let us treat the perturbation due to each term  $V_K(x)$  in the sum of Eq. 3 one at a time.

- i. Show that

$$\int dx \left( \Psi_k^{(0)}(x) \right)^* V_K(x) \Psi_{k'}^{(0)}(x) = v_K \delta_{k-k', \pm K},$$

i.e. the term  $V_K(x)$  connects zeroth order eigenfunctions with  $k - k' = \pm K$ .

- ii. Argue that the dominant contribution to the eigenvalues arises from connections where  $|k| \approx |k'| \approx |K|/2$ . [Hint: Think about the second order term in perturbation theory: is it large if the unperturbed states have very different energies?]
- iii. The first result shows that the zeroth order eigenfunctions are connected such that we can consider the effect of pairs of eigenfunctions  $k - k' = \pm K$  separately. The second result tells us that the eigenvalues  $\epsilon(k)$  away from values  $k \approx \pm K/2$  will be unchanged to leading order, and that the dominant effects will be seen when  $k \approx \pm K/2$ . Show that the effective single electron Hamiltonian in the space spanned by  $\Psi_k^{(0)}(x)$  and  $\Psi_{k \pm K}^{(0)}(x)$  is given by

$$H = \begin{pmatrix} \frac{\hbar^2 k^2}{2m} & v_K \\ v_K & \frac{\hbar^2 (k \pm K)^2}{2m} \end{pmatrix}.$$

Find the eigenvalues of the effective Hamiltonian, expanding to quadratic order in  $\delta = k \pm K/2$ . Show that the eigenfunctions at the Bragg planes are represented by stationary waves, and explain physically which has the higher energy.

- iv. From Bloch's theorem we know that states labelled by  $k$  and  $k + K$  are identical. Therefore, plot the nearly free eigenvalues in the reduced, extended and repeated zone schemes.

*While the mathematics of what we have done in the previous two questions may take some time to feel comfortable, the physics should be clear. For systems with a periodic potential the single electron eigenstates are arranged in bands. Sometimes in the tight-binding model and always in the one-dimensional free electron model there is a gap between the bands, i.e., energies at which there are no single electron eigenstates. As we will see, this has serious implications for the conductivity of solids.*

## 2 Semiclassical model of electron dynamics

*One of the key properties of a solid is its conductivity. Now we know what the eigenvalues of the single electron states are we next would like to know how they behave when an electric field is applied.*

3. (a) *Equations of motion* — Consider an electron in a one dimensional energy band  $\epsilon(k)$ , where  $k$  is the wavevector. An electric field  $E$  is applied. Justify that, in the semiclassical model, the equations describing the motion of the electron are

$$v(k) = \frac{1}{\hbar} \frac{d\epsilon(k)}{dk}, \quad \hbar \frac{dk}{dt} = -eE.$$

- (b) *Filled bands are inert* — Show that a filled (or empty) band has no net change in velocity when an electric field is applied. It therefore doesn't contribute to the conductivity.
- (c) *Holes* — Show that, in an electric field, we can either consider the motion of electrons or equivalently the absence of electrons, called holes. Relate the charge and mass of a hole to those of an electron. Explain why the concept of a hole is useful.
- (d) *Effective mass* — Consider the electron states near a band edge at  $k = k_0$ , where quite generally to leading order in the distance from the band edge  $\epsilon(k) \approx \epsilon(k_0) + \frac{1}{2} \frac{\partial^2 \epsilon(k_0)}{\partial k^2} (k - k_0)^2$ . Explain what is meant by the effective mass, find an expression for it, and explain why the concept is useful. In your answer to the latter part, argue that bands with electrons occupying the lowest energy states will act like a small number of negative charges moving with an effective mass. How can a negative effective mass be reconciled with the fact that the mass of a free electron is positive?
- (e) *Justification* — Under what conditions is it justified to use the semiclassical model to describe electron dynamics?

*For a density  $n$  of electrons near a band edge, the semi-classical equations predict motion according to Newton's laws, but with an effective mass. Drude's arguments can then be used to show  $\sigma = e^2 \tau n / m^*$  where the scattering time  $\tau$  is small, which is the same as for the Drude-Sommerfeld prediction but with an adjusted mass. However, rather than scattering occurring through collisions with the atoms (the main effect of which is already taken into account through the potential) as Drude thought, the scatterers must be defects in the crystal, vibrations of the atoms, or other electrons. Interestingly, unlike in the free electron picture, we find now that we have introduced a periodic potential that there would be no conduction without scattering (unlike the infinite conduction predicted by the expression above). This occurs because, without scattering, an electric field would move an electron away from the band edge and eventually accelerate it back in the other direction. The result is that the electron merely oscillates. We will discuss this in the class.*

## 3 Fermi distribution vs Brillouin zones

*We have seen that full bands do not contribute to the conductivity, and partly occupied bands (either by electrons or holes) act like negative or positive charges with some effective mass. So conductivity is all about the occupation of bands at the temperatures of interest. The latter is determined by the Fermi distribution, so the conduction of a solid rests on the combination of the Fermi distribution and the shapes of the Brillouin zones (I personally think this is a really nice result). We investigate this now.*

4. (a) *Types of conductor* — Describe what is meant by an insulator, semiconductor and metal, referring to the occupation of single electron eigenstates in different bands at zero and room temperature.
  - (b) *States per band* — How many electron states are in a band, per primitive cells in the solid?
  - (c) *Insulators and semiconductors* — Therefore argue that only solids with an even number of electrons per primitive cell may be insulators or semiconductors.
  - (d) *Metals* — Explain why the converse is not true; how can solids with an even number of electrons per primitive cell be metals?
5. *Examples*— Consider a 2-dimensional crystal with a simple cubic structure and a monoatomic basis. Using the free electron model, draw pictures in  $\mathbf{k}$ -space showing the first Brillouin zone and the Fermi surface when the atoms are
    - (a) monovalent, and
    - (b) divalent.

With reference to band structure, explain briefly why

- (c) sodium (bcc crystal with trivial basis) is a metal,
- (d) calcium (fcc crystal with trivial basis) is a metal, and
- (e) diamond (fcc lattice with 2 atom basis) is an insulator whereas silicon and germanium, which have similar structures, are semiconductors.

## 4 Semiconductors and doping

6. (a) Sketch the single electron energies for a semiconductor doped with both donors and acceptors, assuming a direct band gap. Label the lowest energy in the conduction band, the highest energy in the valence band, the donor energy and acceptor energy by  $\epsilon_c$ ,  $\epsilon_v$ ,  $\epsilon_d$ , and  $\epsilon_a$ , respectively.
- (b) Write down the expressions for the densities of free electrons ( $n$ ) and holes ( $p$ ) in a semiconductor in terms of the density of states in the conduction and valence bands and the Fermi-Dirac distribution function.
- (c) Explain why the chemical potential  $\mu$  at  $T = 0$  (Fermi energy), lies in the band gap.
- (d) Assuming the free electron form of the density of states, that the chemical potential stays in the gap and that the temperature is low  $k_B T \ll \epsilon_c - \mu, \mu - \epsilon_v$ , derive an expression for the hole and electron densities as a function of temperature and Fermi energy in a semiconductor with electron and hole effective masses  $m_e^*$  and  $m_h^*$ .

$$\left[ \int_0^\infty dx x^{1/2} e^{-x} = \frac{\sqrt{\pi}}{2}. \right]$$

- (e) Show that the results give a product  $np = n_i^2$  which is independent of the chemical potential. Denote  $\epsilon_g = \epsilon_c - \epsilon_v$ . [Note: this is the law of mass action.]
- (f) For an intrinsic semiconductor, calculate the dependence of  $\mu$  and  $n$  on  $T$  and comment on the validity of the assumption  $k_B T \ll \epsilon_c - \mu, \mu - \epsilon_v$ .
- (g) For an extrinsic semiconductor with densities  $n_d$  and  $n_a$  of donors and acceptors, explain why  $n - p = n_d - n_a$ . What does this assume?
- (h) Assuming additionally that  $n \gg p$  and  $n_d \gg n_a$ , show that  $n \approx n_d$  and  $p \approx n_i^2/n_d$ .
- (i) A material with gap  $\epsilon_g = 1 \text{ eV}$  and  $m_e^* = m_h^* = 0.1 m_e$  is doped with  $n_d = 1 \times 10^{23} \text{ m}^{-3}$  shallow donor impurities. Calculate the density of holes present at room temperature.

- (j) Describe the behaviour of the dependence of  $n$  on  $T$  as  $n_d$  is adjusted such the semiconductor goes from the intrinsic regime to the regime with large n-type doping and conduction dominated by electrons.
  - (k) Finally, summarise the principle of doping a semiconductor with impurities to produce an excess of electrons or holes. Give an example of a suitable material with which to dope silicon to produce an excess of electrons.
7. (a) Explain what the terms *direct gap* and *indirect gap* mean when used to describe semiconductors.
- (b) Recall from the previous question that the number of electrons per unit volume in the conduction band of an intrinsic semiconductor at a temperature  $T$  is given by

$$n = AT^{3/2} \exp\left(\frac{-\epsilon_g}{2k_B T}\right),$$

where  $\epsilon_g$  is the energy gap and  $A$  has only a small dependence on  $T$  which need not be evaluated. The Hall coefficient  $R_H$  for a sample of undoped silicon is measured to be  $625 \text{ m}^3 \text{ C}^{-1}$  at 300 K and  $0.016 \text{ m}^3 \text{ C}^{-1}$  at 500 K. Assuming only one type of carrier contributes to  $R_H$  deduce a value for  $\epsilon_g$  from these data.

- (c) The optical absorption of silicon as a function of photon energy exhibits large increases at 1.2 eV and 3.3 eV. Comment on your value for  $\epsilon_g$  in relation to these optical data.
8. Explain how to find the following properties of a semiconductor experimentally:
- (a) the sign of the majority charge carrier;
  - (b) the concentration of charge carriers;
  - (c) the band gap;
  - (d) the effective mass;
  - (e) the mobility of the majority carrier; and
  - (f) the displacement of the conduction band minimum and valence band maximum.

## 5 Look at the progress we have made!

9. Think back to tutorial 1 where we looked at the free electron model. It worked quite well in some cases but completely failed to explain others. Explain, in as much detail as you would like, why in some cases the free electron model gave the right results, and how, in this tutorial, we have predicted many features of solids unexplained by that model.