

## QCMP-2020/21 — Quantum Condensed Matter Physics

## Problem sheet 2: Band structure

## 1. Optical absorption of simple metals

Sketch the typical energy-wavevector dependence, or dispersion relation, of electrons in a one-dimensional periodic potential within nearly free electron theory. In your sketch, include the unperturbed dispersion, the effects of the periodic potential, the Brillouin zone, the relevant reciprocal lattice wavevector, and the folded-back band structure. How can this approach explain the formation of energy gaps in solids?

In the first Brillouin zone of a body centred cubic (BCC) crystal, the shortest distance from the zone centre to the zone boundary is  $\sqrt{2}\pi/a$ , where  $a$  is the width of the conventional cubic unit cell. Demonstrate that the free electron Fermi surface of a monovalent metal with the BCC structure is contained entirely within the first Brillouin zone.

The absorption of photons in metals excites an electron from a filled state at wavevector  $\mathbf{k}$  to an empty state at the same wavevector, but in a higher band. In the electronic dispersion diagram drawn up above, indicate the absorption process which requires the minimum, or threshold energy  $E_0$ . For a BCC monovalent material, show that this energy is  $E_0 \approx 0.64E_F$ .

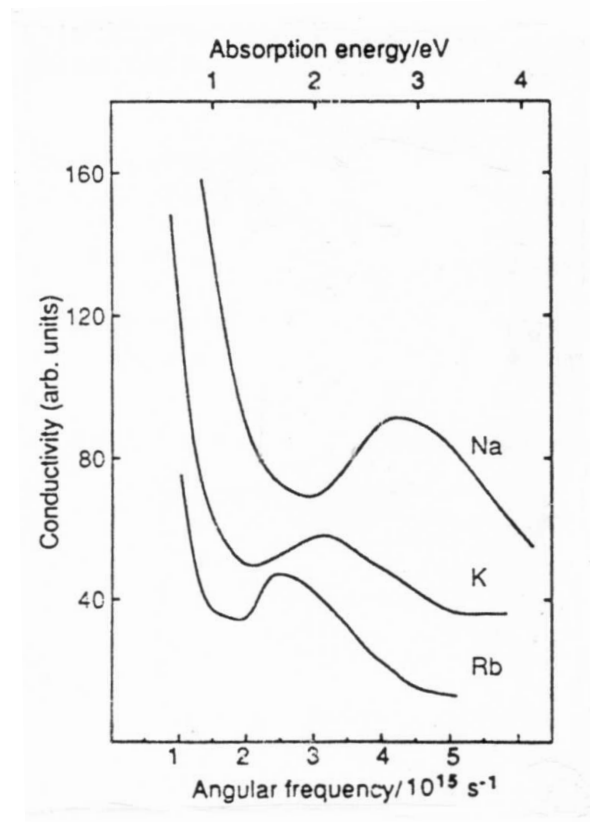


Figure 1: AC-conductivity for three alkaline metals

Alkali metals have a BCC structure. The experimental data on Fig. 1 show the frequency dependence of the conductivity in the alkali metals Na, K, and Rb, which have lattice constants  $a$ , respectively, of 0.423 nm, 0.523 nm, and 0.559 nm. The broad peaks at higher frequencies in each curve have been interpreted as arising from interband optical absorption. Is this qualitatively consistent with nearly free electron behaviour?

## 2. The diatomic chain

The lattice potential  $U(x)$  of a chain of atoms has Fourier components

$$U_g = \frac{1}{L} \int_{-L/2}^{L/2} e^{-igx} U(x) dx, \quad (1)$$

where  $L \rightarrow \infty$  is the length of the chain. Using the NFE approximation valid for momenta near the zone boundary  $k \rightarrow \pi/a$ , show that the energy eigenvalues are given by

$$E^\pm(\mathbf{k}) = \frac{1}{2} \frac{\hbar^2}{2m} (k^2 + (k - 2\pi/a)^2) \pm \frac{1}{2} \sqrt{\left[ \frac{\hbar^2}{2m} (k^2 - (k - 2\pi/a)^2) \right]^2 + 4 |U_{2\pi/a}|^2}. \quad (2)$$

Show that this leads to:

- (a) an energy gap on the zone boundary of magnitude  $2|U_{2\pi/a}|$ , and
- (b) wavefunctions for  $\mathbf{k} \rightarrow \pi/a$  given by  $c_k^\pm / c_{k-2\pi/a}^\pm = \pm U_{2\pi/a} / |U_{2\pi/a}|$ .

Hence show that the probability density for the electronic states at  $k = \pi/a$  take the form

$$\begin{aligned} |\psi^{(1)}(x)|^2 &\propto \cos^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right) \\ |\psi^{(2)}(x)|^2 &\propto \sin^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right), \end{aligned} \quad (3)$$

where  $\phi$  is the phase of the complex Fourier component  $U_{2\pi/a}$ ,  $\psi^{(1)}$  refers to the higher energy ('anti-bonding') state, and  $\psi^{(2)}$  denotes the lower energy ('bonding') state.

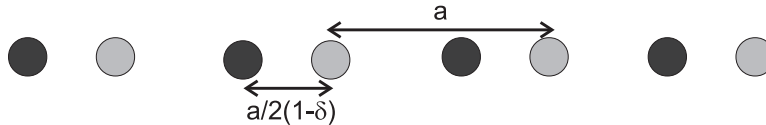


Figure 2: Diatomic chain of atoms. Note that if the potentials on the two atoms are identical, and  $\delta = 0$ , the chain converts to a monatomic chain of period  $a/2$

Consider a one-dimensional diatomic lattice with lattice constant  $a$  (Fig. 2), in which two atoms labelled A (light grey circles) and B (dark grey circles) take positions  $R_n^{(A)} = na + (a/4)(1 - \delta)$  and  $R_n^{(B)} = na - (a/4)(1 - \delta)$ .

Show that  $U_{2\pi/a}$  can be written

$$U_{2\pi/a} = \sin\left(\frac{\pi\delta}{2}\right)(U_{2\pi/a}^A + U_{2\pi/a}^B) - i \cos\left(\frac{\pi\delta}{2}\right)(U_{2\pi/a}^A - U_{2\pi/a}^B), \quad (4)$$

where

$$U_{2\pi/a}^{A,B} = \frac{1}{L} \int_{-L/2}^{L/2} dx e^{-i2\pi x/a} \sum_n U^{A,B}(x - na), \quad (5)$$

and  $U^{A,B}(x)$  is the potential due to a single atom of type A, B centred at  $x = 0$ .

The system contains an average of one electron per atom, or equivalently two electrons per unit cell. Discuss the values of the energy gaps and plot the charge densities corresponding to the highest filled electron state and the lowest empty electron state in the three cases;

- (a) identical atoms,  $U_A = U_B$ , and  $\delta = 0$ ;
- (b) different atoms  $U_A \neq U_B$ , and  $\delta = 0$ ;
- (c) identical atoms,  $U_A = U_B$ , and  $\delta \neq 0$ .

Explain how this provides a simple model of either an *ionic* or *covalent* solid.

### 3. Nearly free electron approximation for a square lattice

The potential in a 2-dimensional square crystal of side  $a$  is given by

$$V(x, y) = -2V_0 \left[ \cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right] . \quad (6)$$

Use the nearly-free electron approximation to calculate the electron energies at the wave-vectors

$$\mathbf{k}_0 = \frac{2\pi}{a}(0, 0) , \mathbf{k}_1 = \frac{2\pi}{a}\left(\frac{1}{2}, 0\right) , \mathbf{k}_2 = \frac{2\pi}{a}\left(\frac{1}{2}, \frac{1}{2}\right) . \quad (7)$$

(a) Write down the form of the wavefunction within the nearly-free-electron approximation, using 1 plane wave at  $\mathbf{k}_0$ , 2 plane waves at  $\mathbf{k}_1$ , and 4 plane waves at  $\mathbf{k}_2$ .

(b) In each case, substitute these wavefunctions into the Schrödinger equation, and write the resulting equations in matrix form.

(c) Solve the three eigenvalue problems for the energy levels at  $\mathbf{k}_0$ ,  $\mathbf{k}_1$ , and  $\mathbf{k}_2$ .

### 4. Tight binding for BCC and FCC lattices

Show that the tightbinding bandstructure based on a single orbital per site for a body centred cubic lattice (include only the hopping to the eight nearest neighbours) is

$$E(\mathbf{k}) = \epsilon_0 + 8t \cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{1}{2}k_y a\right) \cos\left(\frac{1}{2}k_z a\right) , \quad (8)$$

and for the face centred cubic lattice (twelve nearest neighbours)

$$E(\mathbf{k}) = \epsilon_0 + 4t \left[ \cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{1}{2}k_y a\right) + \cos\left(\frac{1}{2}k_y a\right) \cos\left(\frac{1}{2}k_z a\right) + \cos\left(\frac{1}{2}k_z a\right) \cos\left(\frac{1}{2}k_x a\right) \right] . \quad (9)$$

### 5. 2D tight binding band

This question is to encourage you to visualise bands in two dimensions (and higher!). Using a simple numerical package to plot representative cases will help.

Consider a two-dimensional band structure on a rectangular lattice

$$E(k) = 2 * t_1 \cos(ak_x) + 2 * t_2 \cos(bk_y) \quad (10)$$

(a) What is the reciprocal lattice? Draw the first Brillouin zone boundary.

(b) What is the real space lattice?

(c) Suppose that  $t_1 < 0$ ,  $t_2 < 0$ ,  $|t_1| > |t_2|$ , and  $a < b$ . (Do you expect there to be a relation?) Plot some contours of constant energy. At which momenta do you find the band minima, maxima, and saddle points? What are the effective masses of electrons at these points (keep track of signs)?

(d) For what range of energies are the energy contours open or closed? Does this bear any relationship to the energies of the saddle points?

(e) \* Make a numerical estimation of the density of states as a function of energy (plot a histogram, say). Can you give an analytic form for the energy- dependence of the density of states near the singular points?

## 6. \* Graphite

A single sheet of graphite has two carbon atoms in the unit cell at positions  $\mathbf{d}_1 = 0$  and  $\mathbf{d}_2 = (a/\sqrt{3})(0, 1, 0)$ . The translation vectors for the two-dimensional hexagonal lattice are  $\mathbf{t}_1 = (a/2)(1, \sqrt{3}, 0)$  and  $\mathbf{t}_2 = (a/2)(-1, \sqrt{3}, 0)$ .

The electronic configuration of the carbon atom is  $1s^2 2s^2 2p^2$ , and ignoring the  $1s$  core states, we need to make a band structure from the  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  orbitals. Because  $s$ ,  $p_x$  and  $p_y$  orbitals are even under reflection through the plane, and  $p_z$  odd, the two sets do not mix. The first three states hybridise to form  $\sigma$ -bonds with a large gap between the bonding and anti-bonding orbitals. Within this gap lie the  $\pi$ -orbitals arising from the hybridised  $p_z$ . The three bonding  $\sigma$  orbitals will accommodate 6 electrons per cell, leaving 2 electrons per unit cell in the  $\pi$ -bands. This question considers the electronic  $\pi$ -bands only.

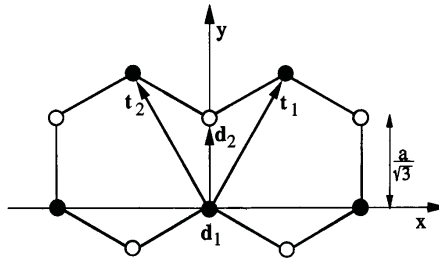


Figure 3: Two dimensional structure of graphite

(a) Construct Bloch states that consist of a linear mixture of the two  $p_z$  orbitals in the unit cell, and show how this gives rise to the secular equation to determine the eigenstate energies

$$\begin{vmatrix} E_p - E & tF(\mathbf{k}) \\ tF^*(\mathbf{k}) & E_p - E \end{vmatrix} = 0, \quad (11)$$

where  $t$  is the two center hopping matrix element between neighbouring  $p_z$  orbitals, and

$$F(\mathbf{k}) = 1 + 2 \cos\left(\frac{k_x a}{2}\right) \exp\left(-i \frac{\sqrt{3} k_y a}{2}\right). \quad (12)$$

(b) Show that the reciprocal lattice is also a hexagonal lattice, at an angle of  $\pi/6$  to the real-space lattice. Show that the first Brillouin zone is a hexagon centred at the point  $\Gamma = (000)$ , whose corners are at the points  $P = (2\pi/a)(2/3, 0, 0)$

(c) Determine a formula for the dispersion curves for the two eigenstates, and plot them in the directions  $\Gamma P$ , and  $\Gamma Q$ . (Here  $Q = (2\pi/a)(1/2, 1/2\sqrt{3}, 0)$  is at the middle of a zone face.

(d) Where will the  $\pi$ -bands lie in energy relative to the  $sp^2$   $\sigma$ - orbitals? Is a single layer of graphite a metal or an insulator?

(e) Carbon nanotubes are formed by curling a graphite sheet into a tube, connecting the atoms with periodic boundary conditions. There are many ways to do this, and the different nanotubes can be indexed by the vector  $m\mathbf{t}_1 + n\mathbf{t}_2$  that identifies which atoms are connected periodically. Assuming the band-structure is unchanged, show that the allowed  $\mathbf{k}$ -states now lie on a set of lines whose direction is parallel to the tube. Discuss the situations under which the resulting tube will be semiconducting or metallic.

## 7. Band structure of d-band metals

In many transition metals a narrow  $d$ -band lies within a broad energy band originating from  $s$ -orbitals. This question discusses the band structure using a simple one-dimensional model constructed from a tight-binding Hamiltonian with one  $s$ -orbital  $\phi_s(r)$  and one  $d$ -orbital  $\phi_d(r)$  per atom; the atoms are arranged in a linear chain of lattice constant  $a$ .

- (a) Write down two Bloch states  $\phi_s(k)$  and  $\phi_d(k)$  formed from the atomic  $s$ - and  $d$ - states respectively. The eigenstates must be linear combinations of these.
- (b) Hence show that the one-particle bandstructure  $E(k)$  can be found from the determinantal equation

$$\begin{vmatrix} E_s - 2t_{ss} \cos(ka) - E(k) & -2t_{sd} \cos(ka) \\ -2t_{sd} \cos(ka) & E_d - 2t_{dd} \cos(ka) - E(k) \end{vmatrix} = 0 \quad .$$

Identify and explain the parameters appearing in the determinantal equation, and discuss the approximations made that lead to this form.

- (c) Discuss why you would expect that  $t_{ss} > |t_{sd}| > t_{dd}$ .
- (d) Plot the dispersion of the two bands when  $|E_d - E_s| \ll 2|t_{ss}|$ , and  $t_{sd}$  and  $t_{dd}$  are neglected.
- (e) How is the dispersion modified from (d) by the inclusion of small values of  $t_{sd}$  and  $t_{dd}$ ?
- (f) Discuss the relevance of this model to the electronic bandstructure of Cu metal.

**Note:** Starred questions are challenge problems; they will do you good, but they go beyond the minimum requirements of the course.