Module P11.4 Quantum physics of solids

Exit module

S570 V1.1

1 Opening items

1.1 Module introduction

In this module, we shall give an overview of the properties of solids and how quantum mechanics helps us to understand these properties.

In the solid state, a material at a given temperature and pressure has a well-defined shape (as opposed, for example, to a liquid, which takes on the shape of its containing vessel). The forces of interaction between the atoms in the solid must therefore be strong and the *bonds* between them stable under the prevailing physical conditions. In Subsection 2.1, we look at the way in which quantum physics may be used to understand how these bonds are formed. In Subsection 2.2, we consider *crystalline solids*, in which the bonds allow the formation of regular arrays of atoms within the solid. We shall then consider some of the properties of solids that may be better understood using quantum mechanics. Of these, we shall concentrate on thermal properties and electrical properties. In Subsection 2.3, we give an introductory treatment of *energy bands* and the *band theory* of solids, which is used in Section 3 to explain *electrical conductivity* and why some solid elements are *conductors* of electricity, whereas others are *semiconductors* or *insulators*. We shall see how these properties depend on the temperature of the solid through the *temperature coefficient of resistivity*. The electrical properties depend predominantly on the electrons in the atoms of the solid.

The thermal properties, such as *specific heat capacity* and *thermal expansivity* are discussed in Section 4. They depend largely on the arrangement of the atoms in the *crystalline lattice*. We shall see how the values of these measured parameters give an indication of the behaviour of the forces that hold the lattice together. A quantum model of the heat capacity is necessary. Here we briefly discuss the *Debye model* and the *Einstein model*. The *thermal conductivity* of conductors is high, as is their electrical conductivity. We shall examine the reasons for this.

Study comment Having read the introduction you may feel that you are already familiar with the material covered by this module and that you do not need to study it. If so, try the *Fast track questions* given in Subsection 1.2. If not, proceed directly to *Ready to study?* in Subsection 1.3.

1.2 Fast track questions

Study comment Can you answer the following *Fast track questions*?. If you answer the questions successfully you need only glance through the module before looking at the *Module summary* (Subsection 5.1) and the *Achievements* listed in Subsection 5.2. If you are sure that you can meet each of these achievements, try the *Exit test* in Subsection 5.3. If you have difficulty with only one or two of the questions you should follow the guidance given in the answers and read the relevant parts of the module. However, *if you have difficulty with more than two of the Exit questions you are strongly advised to study the whole module*.

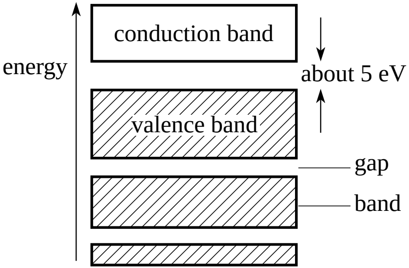


Figure 1 The energy band diagram for a solid element (see Question F1).
(The white box represents empty energy levels; the hatched boxes represent occupied energy levels.)

Question F1

Figure 1 shows the energy band diagram of a solid element. Say whether the solid is a conductor, an insulator or a semiconductor of electricity. Explain your answer in terms of the Pauli exclusion principle.

Question F2

Define the temperature coefficient of resistivity. Explain in terms of the band theory of solids why the coefficient is positive for conductors but negative for semiconductors.

Question F3

What does the thermal expansivity of a solid tell us about the shape of the graph of energy of interaction against separation for two neighbouring atoms in a crystal?

Study comment

Having seen the *Fast track questions* you may feel that it would be wiser to follow the normal route through the module and to proceed directly to *Ready to study?* in Subsection 1.3.

Alternatively, you may still be sufficiently comfortable with the material covered by the module to proceed directly to the *Closing items*.

1.3 Ready to study?

Study comment In order to study this module, you will need to be familiar with the following physics terms: *atom*, *electron*, *proton*, *molecule*, *Coulomb force*, *potential* and *total energy*, *Planck's constant* *h*, *quantum*, the *time-independent Schrödinger equation*, *wavefunction*, *probability density*, *energy level*, *quantum harmonic oscillator*, *quantum numbers*, *spectroscopic (s, p, d, f) notation*, *spin* (of an electron), *Pauli exclusion principle*, (atomic) *shells*, *degeneracy* (of atomic energy levels), *resistivity*, *conductivity* (*thermal* and *electrical*), *specific heat capacity*. You should also be familiar with *differentiation* and *integration*. If you are uncertain about any of these terms, then you can review them now by referring to the *Glossary*, which will also indicate where in *FLAP* they are discussed. The following *Ready to study questions* will allow you to establish whether you need to review some of the topics before embarking on this module.

Question R1

A particular stationary state of a one-dimensional quantum harmonic oscillator is described by the normalized spatial wavefunction (i.e. energy eigenfunction) ☞

$$\psi(x) = \left(2\sqrt{\alpha}/\sqrt{\pi}\right)^{1/2} x\exp\left(-\tfrac{1}{2}\alpha x^2\right)$$

where α is a constant. Write down an expression for the probability that the oscillator will be found between x and $x + \Delta x$.

Question R2

The electrons in an atom are in the states denoted by $1s^2 2s^2 2p$. How many electrons does the atom have? What can you say about their spins? Why is $1s^3$ not a possible arrangement?

Question R3

Figure 2 shows the energy of interaction between two atoms as a function of their separation. Does the equilibrium separation of the atoms correspond to point w, point x or point y?

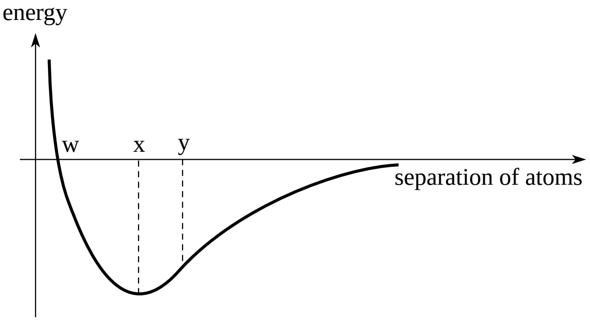


Figure 2 The energy of interaction between two atoms.

2 General considerations of the solid state

2.1 The formation of bonds between atoms

A solid is made up of interacting atoms (or ions or molecules) in the form of a stable configuration ☞. The nuclei of the atoms are electrically positive; their electrons are electrically negative. The force that holds the electrons to the atomic nuclei is electrical. The nuclei are dense concentrations of positive charge, confined within a region of space of radius of the order 10^{-15} to $10^{-14}\,\text{m}$. The electrons are more widely dispersed, typically within 10^{-10} to $10^{-9}\,\text{m}$ of the nucleus, and so there are much less dense concentrations of negative charge. A lone atom is electrically neutral; the positive protons in the nucleus have a total positive charge equal but opposite to the total negative charge of the electrons.

Consider two atoms being brought closer and closer together. At a large distance apart, where the nuclei are well separated and the electron clouds ☞ around them do not overlap, the atoms will exert no appreciable force on each other. Each atom appears neutral to the other. At the other extreme, when the nuclei are much closer than the atomic radius, there will be a strong force of repulsion between the nuclei. Between these two extremes, there may be a force of attraction between the two atoms — with the electrons shielding the nuclei from each other to some extent.

The presence of the electrons between the nuclei will ‘mediate’ a force of attraction between the nuclei (see Figure 3). The electrons will of course repel each other, but their lower density will make this less effective, and the balance of the force between the atoms as a whole will be one of attraction. It is not obvious from classical physics that the energy is lower when the two nuclei have electrons distributed over a region (bond) between them but quantum mechanics provides this result convincingly.

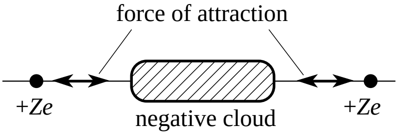


Figure 3 A negative electron cloud provides shielding ‘glue’ between the positive nuclei.

How does quantum mechanics affect the situation? We shall start by looking at the simplest case, in which two hydrogen atoms — each consisting of one proton and one electron — come together. Each atom has an electron cloud described by a spatial wavefunction $\psi(x)$. When far apart, these do not overlap — Figure 4a. Suppose that the nuclei are brought closer together so that the spatial wavefunctions of the individual electrons do overlap — Figure 4b. The situation is now changed. The electron from each atom has a finite probability of being in the ‘space’ of the other atom. Also, since electrons are identical particles, we may not assign them uniquely to one atom or the other — we must treat the two atom system as an entity and solve the Schrödinger equation for the two atom system.

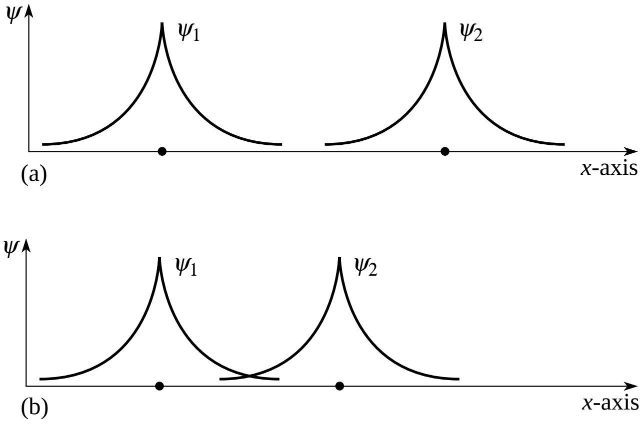


Figure 4 (a) The spatial wavefunctions of well-separated hydrogen atoms. (b) When the nuclei are closer together, the spatial wavefunctions start to overlap significantly.

The spatial wavefunction of the new two-nucleus *molecule* may be constructed from the spatial wavefunctions of the individual electrons—either constructively as shown in Figure 5a or destructively as shown in Figure 5b. ☞

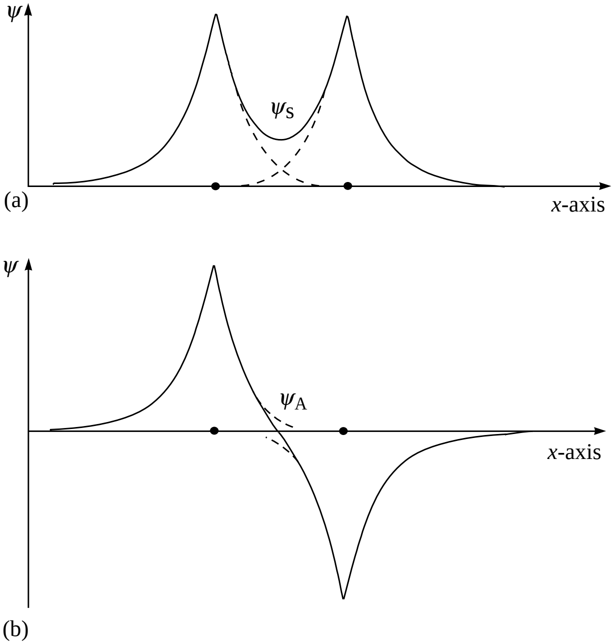


Figure 5 (a) A possible combined spatial wavefunction (shown by the solid line) of the hydrogen molecule. The wavefunctions have interfered constructively to give a spatial wavefunction ψ_s that is symmetric. (b) In the case where the interference is destructive an antisymmetric spatial wavefunction ψ_a is formed.

From these possible spatial wavefunctions, we may calculate the probability densities: these are shown in Figures 6a and 6b.

What do these tell us? Figure 6a indicates an enhanced probability of finding negative charge between the two protons, whereas Figure 6b indicates a reduced probability (even zero at the half-way point).

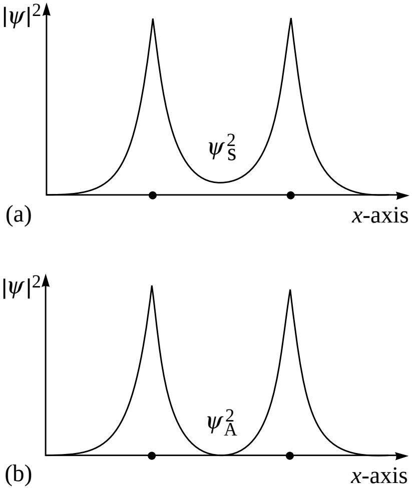


Figure 6 (a) The probability density function for the symmetric spatial wavefunction $\psi_{\rm s}$. (b) The probability density function for the antisymmetric spatial wavefunction $\psi_{\rm a}$.

In Figure 6a we see that the electrons spend more time within the region of negative potential energy, between the positive nuclei; this reduces the energy of the symmetric (*bonding*) state as compared to that of the antisymmetric (*non-bonding*) state and makes the bonding state energetically favoured. Also, in terms of the Heisenberg uncertainty principle, the electrons are rather more confined around the positive ion locations in the antisymmetric state and this also tends to increase the energy.

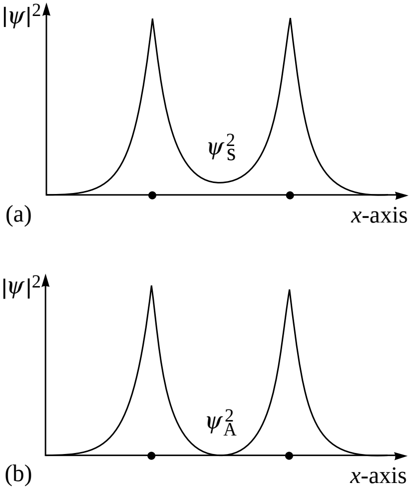


Figure 6 (a) The probability density function for the symmetric spatial wavefunction ψ_s. (b) The probability density function for the antisymmetric spatial wavefunction ψ_a.

So the two atoms are bound together. What is the stable configuration? It is the one with the lowest energy. We can calculate the energy as a function of the separation of the protons. The separation that gives the lowest energy will be the equilibrium state. This, as shown in Figure 7, corresponds to a proton separation of 0.074 nm and an equilibrium energy of the molecule of –32 eV.

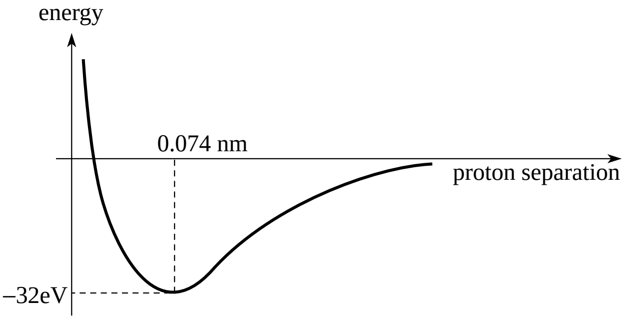


Figure 7 The energy of the symmetric state of the molecule depends on the separation of the protons. The equilibrium state corresponds to the minimum value of this energy. The anti-symmetric state has higher energy at all separations.

We have illustrated the way in which the binding together of two atoms can be accounted for by quantum theory. The case we have considered is, of course, a special one. The two hydrogen atoms, each with a single 1s electron, **bond** to form the H_2 molecule. We cannot add a third atom to form an H_3 molecule because there is no 3 electron state of sufficiently low energy to favour bonding. ☞ The H–H bond is said to be **saturated**. As shown in Figure 5a, it is a bond characterized by an increased electron density between the nuclei. Such a bond, whether saturated or not, is called a **covalent bond**.

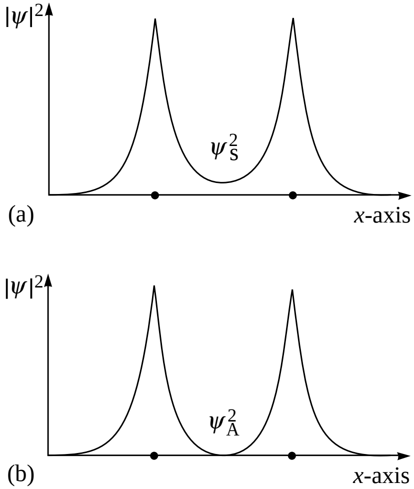


Figure 5 (a) A possible combined spatial wavefunction (shown by the solid line) of the hydrogen molecule. The wavefunctions have interfered constructively to give a spatial wavefunction $\psi_{\rm s}$ that is symmetric. (b) In the case where the interference is destructive an antisymmetric spatial wavefunction $\psi_{\rm a}$ is formed.

Other types of bond are possible for more complicated atoms. We shall give one simple example.

Consider the interaction of two atoms of lithium in their ground state. Lithium has three electrons — two 1s electrons (with opposite spins to satisfy the Pauli principle) plus one 2s electron in the $n = 2$ shell. The electron configuration is denoted $1s^22s$. If these two atoms are brought together, there will again be the possibility of a covalent bond involving, in this case, the 2s electrons. However, unlike the hydrogen case, there are not just two states involved. This is because for $n = 2$, there are both 2s and 2p levels *all at about the same energy*. For the 2p states, there are a further six electron states available ($m_s = \pm 1/2$ for $m_l = -1, 0$ or $+1$). Therefore, following the formation of the Li_2 molecule, the bond is not saturated and it will still be possible to form Li_3, Li_4, and so on.

Lithium at room temperature is a solid; it is also an *electrical conductor*. Why should that be so? To answer this question we must take a more detailed look at the atomic interaction. Since a lithium atom can bond with more than one other lithium atom, the stable arrangement of lithium atoms that has the lowest energy is a **crystalline structure** in which the atoms form a regular three-dimensional array. This is characterized by a **lattice** made up of a typical **unit cell** which repeats itself in all directions. The unit cell for lithium, and the way in which several cells stack together, are illustrated in Figure 8. The cell has a lithium atom at each of the eight corners of a cube plus one at the centre of the cube. Each lithium atom therefore has eight nearest neighbours and it forms a bond with each of them. So with one (the 2s) electron per atom contributing to the bond, each bond involves one quarter of an electron, *on average*, rather than the two in the ordinary covalent bond such as that which holds together the hydrogen molecule.

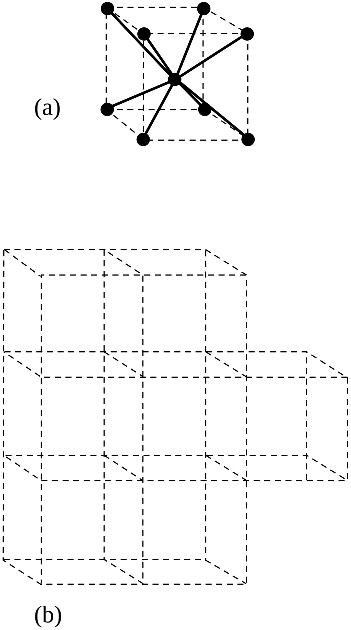


Figure 8 The body-centred cubic structure of lithium. (a) Each cell has an atom at each corner of an imaginary cube and one at its centre. There are eight nearest neighbour bonds shown by bold lines. (b) The cells occur repetitively throughout space.

This bond is therefore by no means saturated. Indeed, in the case of the lithium lattice, it does not even involve the localization of a particular electron with a particular atom. The electrons are effectively free to move through the lattice — an effect that contributes to the electrical conductivity of the solid. This type of bond is known as a **metallic bond**.

We shall not go on to consider any further types of bond. The two we have mentioned — the covalent and the metallic — will be adequate as illustrations.

2.2 The lattice structure of solids

We have considered an example — lithium — which has a body-centred structure held together by metallic bonds. There are other possible lattice structures; the other cubic ones are shown in Figure 9. Which one a particular element will adopt depends on the detail of its atomic structure.

So far, we have considered the properties of the electrons in the atoms. But what of the nuclei? We have looked at the situation as if the nuclei remained fixed. Over a short time span, this would be a good approximation, since the nucleus is so much heavier than an electron. However, over the time span of a macroscopic measurement, this would not be the case. For example, the nuclei in the lattice will be subject to thermal agitation. We may construct a simple model in which these vibrations are harmonic in nature. We can suppose that a lattice behaves as if the bonds act like springs offering resistance to any changes from their natural length.

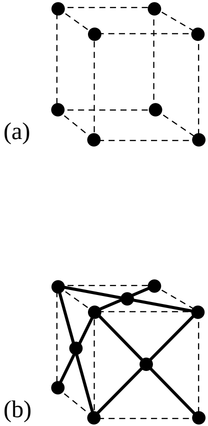


Figure 9 (a) The simple cubic lattice. (b) The face-centred cubic lattice. For clarity only visible faces are shown. It should be noted that these lattices are actually arrangements of *points* in space, not of atoms. There may be one, two or many atoms associated wth each lattice — it doesn’t matter as long as the arrangement is the same at every lattice point in a particular structure.

The potential that a nucleus would experience due to a neighbour would, near the equilibrium position, have the shape shown in Figure 7.

In this model, the nuclei would behave as coupled harmonic oscillators. If energy were added to the system, by heating for instance, then the energy of these oscillators would be changed. Quantum theory can be used to predict what these changes might be. We shall look at this in more detail in Section 4.

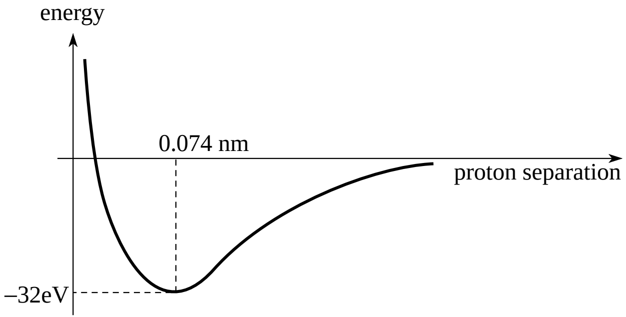


Figure 7 The energy of the symmetric state of the molecule depends on the separation of the protons. The equilibrium state corresponds to the minimum value of this energy. The anti-symmetric state has higher energy at all separations.

2.3 The band theory of solids

Let us now consider what happens to electron energy levels when atoms are brought together to form a crystal.

❖ What happens to the lowest energy levels of a pair of hydrogen atoms as they are brought together?

In the same way, the electron energy levels of the atoms in a crystal, which would have been the same for each atom when the atoms were well separated, will spread out, and since there are so many of them — several for each atom when there are of the order of 10^{23} atoms — they will be so close together that they will appear to form a continuous **energy band**. The closer the atoms are to one another, the more marked this effect becomes.

For example, in Figure 10, we show the electronic energy levels of sodium as a function of the internuclear distance in a lattice, a typical **band theory** calculation. Sodium has eleven electrons, so the 1s, 2s and 2p levels are full. The remaining electron is in the 3s state. The 3p, 3d, 4s etc. levels are empty. As may be seen, at a separation of 1.5 nm, the empty levels are already broadened into bands. The 3d and 4s bands are so broad that they overlap. At about 1 nm, the 3s level starts to broaden. A single electron always goes into the lowest energy level available, to give the most stable configuration.

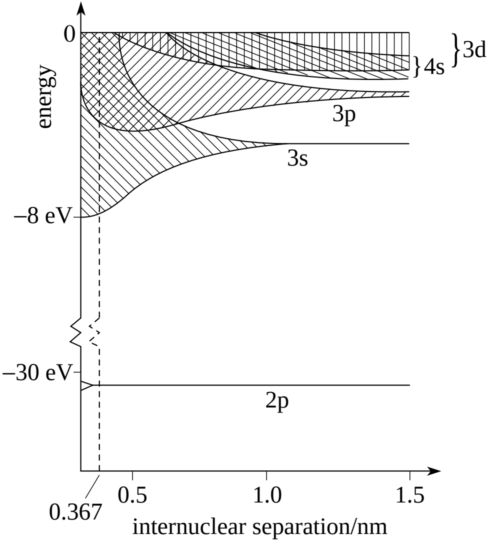


Figure 10 The energy levels of sodium atoms as a function of the internuclear distance.

By the time the internuclear separation is 0.367 nm, the observed value for solid sodium, the bands are all overlapping, giving a continuous range of energies for the outer electrons ranging from about –8 eV upwards. The last of the inner levels, the 2p level, is still not split.

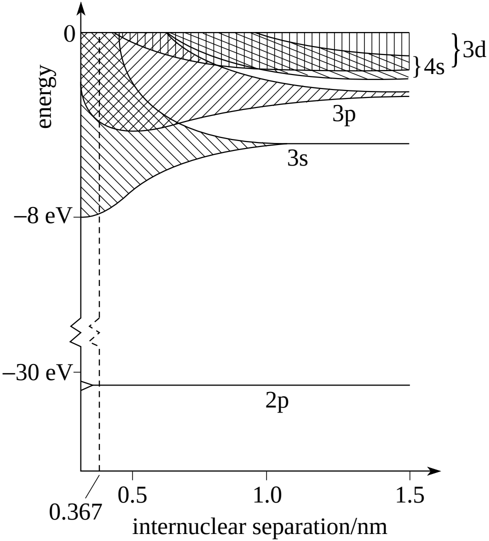


Figure 10 The energy levels of sodium atoms as a function of the internuclear distance.

The electronic configuration of an isolated sodium atom and of sodium atoms in the solid state are compared in Figure 11. In the isolated sodium atom there is a single electron in the 3s outer subshell; this subshell is capable of holding two such electrons and so is half-filled. When sodium atoms are brought together to form solid sodium these 3s levels become the 3s *band*, which is then half-filled, as shown hatched in in Figure 11. The effect of the proximity of the nuclei on the electron energy levels is the basis of the band theory of solids.

You should not think of a 3s band electron as belonging to any particular sodium atom; as each atom is bound to all its neighbours, a 3s electron can wander over the whole crystal, and can be thought of as being 'free' to a first approximation. Furthermore, all electrons are identical, and it is not possible to label one as having come from a particular source. We will not pursue this any further here.

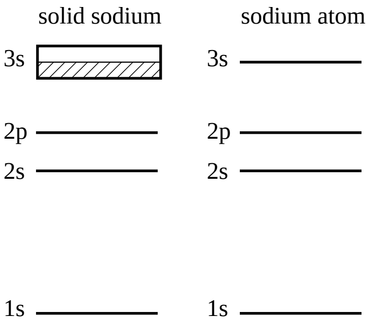


Figure 11 The energy levels of the sodium atom and the corresponding situation in solid sodium. (The diagrams are not drawn to scale.)

We have simplified the picture so far, to illustrate the ideas involved, by considering only the effect of nearest-neighbour atoms on each other.

In practice, the electrons of one atom will experience the presence of several atoms in its neighbourhood. This is illustrated in Figure 12, in which the 4s spatial wavefunction of an electron in an isolated nickel atom is plotted. It will be seen that the electron's spatial wavefunction extends so that there is a significant probability of interaction with three nearest neighbour atoms which would be at distances r_1, r_2, r_3 in a nickel crystal. This does not affect the formation of bands of energy levels, but does add to the complexity of deriving them from the appropriate Schrödinger equation.

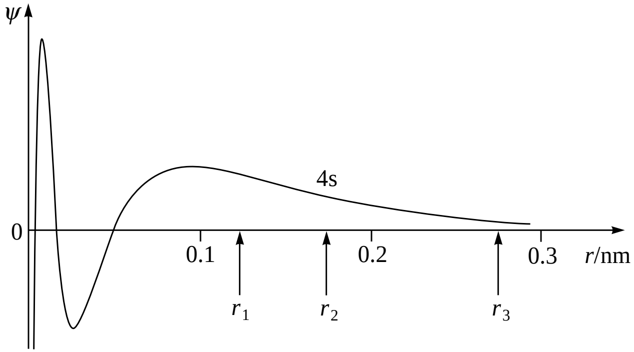


Figure 12 The 4s wavefunction for an isolated nickel atom compared with the distance r_1 between any given atom and its nearest neighbour in solid nickel. r_2 and r_3 are the distances to the second and third nearest neighbours, respectively.

3 Electrical properties of solids

In this section we look initially at classical accounts of electrical conductivity. We shall then see how quantum mechanics, in the form of band theory, helps us to understand why some solids are conductors and others are not. We shall take as an example the case of a metal. The classical picture of the conduction of electricity in a metal has electrons as carriers of charge. These move in the lattice made up of the positive ions that are left when the carrier electrons are removed. When a potential difference is applied across the solid, the negative electrons are attracted in one direction, the positive ions in the opposite direction. The positive ions are however heavy and bound in the lattice whereas the carrier electrons are light and relatively free. Consequently, only negative charges move; this is the origin of the *current* that flows. The flow of charge is associated with a change in the average velocity of the electrons.

The flow of electrons is not, however, unimpeded — the electrons will, in the classical picture, collide with the positive ions in the lattice. The electrons will not therefore accelerate indefinitely under the influence of the potential difference. There will be many collisions of different kinds, but there will be an average velocity of progression of the electrons — this is usually called the *drift velocity*. Thus a steady current is caused. The quantum-mechanical picture includes the wave nature of matter, but it is still the interaction between the electrons and the lattice that is the source of electrical resistance. There is an astonishing feature of the wave nature of matter. If the crystal lattice were *perfectly* regular, the Schrödinger equation would have a travelling wave solution for the conduction electrons. It is the lattice vibrations that spoil this perfect regularity. *This lack of regularity* is the origin of electrical resistance.

3.1 Localized and non-localized electrons

The brief outline above shows that the model of conductivity in metals depends on the existence of ‘free’ electrons — or, put another way, electrons that can be given the kinetic energy to move to another part of the solid. In the last section, we looked at the mechanisms whereby atoms are bound together to form a solid. We saw how, in the two instances we looked at, the electronic structure of the atom led to a particular sort of bond.

In the covalent bond, the electrons — in picturesque language — are shared between atoms. These electrons cannot easily be detached from the participating atoms without breaking the bonds and disrupting the lattice. They are localized and cannot contribute to a current. Where the bonds are strong, therefore, such a solid would not be expected to conduct electricity.

With the metallic bond, on the other hand, the highest energy electron is attached only very weakly to any particular atom. These electrons are non-localized. They may be regarded as being shared by all the ions in the lattice. In the absence of a potential difference, however, they move randomly, and there is no a net movement of charge in any direction. However, in the presence of a potential difference, they would be available to contribute to a current. Of course, the lower energy electrons will be localized to the parent atom — for example, the 2p electrons of the metal sodium considered in Section 2.3. The electrons contributing to the current — the **conduction electrons** — will be relatively small in number compared with the other electrons in the inner shells.

3.2 Electron energy bands and band gaps

We have seen in Section 2 that a characteristic of the energy levels in a solid is that they occur in bands.

> *Energy bands*
>
> The energy levels in a solid form bands of very closely spaced levels. The bands may be separated by relatively large gaps.

Because electrons are governed by the *Pauli exclusion principle*, they cannot all have the lowest energy. They progressively fill the bands, occupying the lowest energy levels available. We will call the highest of the bands that is filled, or substantially filled, the **valence band**. Higher, but unoccupied, bands are called **conduction bands**. It is this band structure that determines whether a solid is a conductor, an *insulator* or a *semiconductor*. ☞

For electrical conduction it is necessary for some electrons to be able to gain energy easily from an applied *electric field*. This cannot happen for the vast majority of electrons, since they are embedded in bands of levels which are completely filled. It is only electrons near the top of the filled levels which may be able to move into unoccupied levels and may therefore contribute to electrical conduction. The electrical properties of a material are thus determined by the band structure near the top of the filled levels.

We can extend this a little by considering the probability $f(E)$ of an electron energy level being filled. Figure 13 shows this probability which depends on temperature. In Figure 13a the situation at 0 K is shown and the highest occupied level is E_F, the Fermi level. The probability of a level being filled is unity up to this level and zero above it. As the temperature is raised (Figure 13b) some electrons near the top of the distribution move into unoccupied levels above E_F, allowing vacancies below E_F. It is only these electrons with energy close to E_F, which contribute to electron conduction.

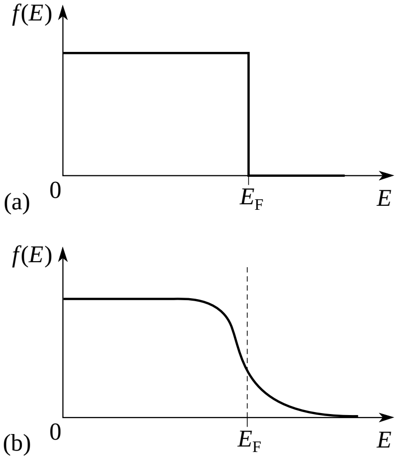


Figure 13 The probability of an electron energy level being filled. (a) The situation at 0 K, (b) at a higher temperature. This distribution is known as the Fermi function.

The characteristics of a conductor

Figure 14a shows the band structure in a **conductor**. The electrons in a conductor do not fill the valence band but the Fermi level lies within the valence band. In consequence, for the higher energy electrons, there are unfilled energy levels close to the Fermi level that are available to them and to which they can move without violating the Pauli exclusion principle. As a result, when the metal is subjected to a potential difference, the electrons can acquire the kinetic energy associated with a current flow and thus increase their energy. A solid with this band structure will therefore be a conductor.

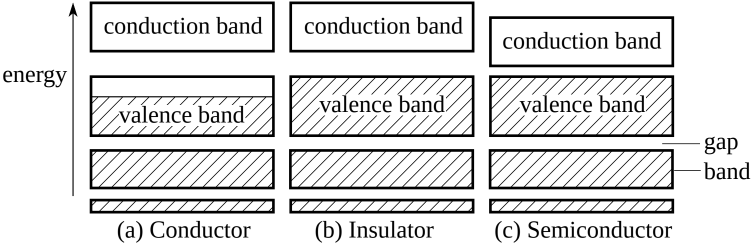


Figure 14 (a) In a metallic conductor, the valence band is only partially filled. (b) In an insulator, the valence band is completely filled. The gap between the valence band and the conduction band is relatively large. (c) In a semiconductor, the valence band resembles that of the insulator but the gap between the valence band and the conduction band is relatively small. (The white boxes represent empty energy levels; the hatched boxes represent occupied energy levels.)

The characteristics of an insulator

If, on the other hand, we look at Figure 14b, we see that, in this case, the valence band is full. Electrons at the top of the valence band do not have adjacent energy levels. There is a gap (in which there are no allowed energy levels) between the valence band and the next available energy levels in the conduction band. The electrons in a solid with this band occupancy, if subjected to a potential difference, will not be able to increase their energy — there will be no higher energy levels available. The solid can only be an **insulator**. A typical band gap for an insulator is of the order of 5 eV.

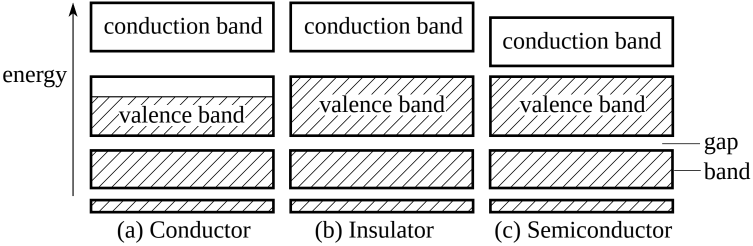
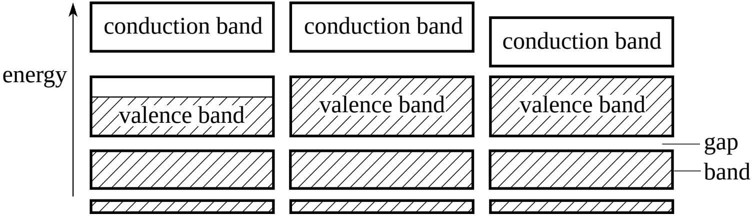


Figure 14 (a) In a metallic conductor, the valence band is only partially filled. (b) In an insulator, the valence band is completely filled. The gap between the valence band and the conduction band is relatively large. (c) In a semiconductor, the valence band resembles that of the insulator but the gap between the valence band and the conduction band is relatively small. (The white boxes represent empty energy levels; the hatched boxes represent occupied energy levels.)

The characteristics of a semi-conductor



(a) Conductor (b) Insulator (c) Semiconductor

Figure 14 (a) In a metallic conductor, the valence band is only partially filled. (b) In an insulator, the valence band is completely filled. The gap between the valence band and the conduction band is relatively large.
(c) In a semiconductor, the valence band resembles that of the insulator but the gap between the valence band and the conduction band is relatively small.
(The white boxes represent empty energy levels; the hatched boxes represent occupied energy levels.)

Figure 14c shows an intermediate band structure. In this case, the valence band is full — as with the insulator — but now the band gap is much smaller than it was for the insulator. (In silicon, for example, the gap is 1.1 eV.) There will now be a small, but significant, probability that an electron in the valence band will be able to jump to a higher level in the conduction band by thermal agitation. So, in this case, *some* electrons will be available in the conduction band to take part in a conduction current. ☞ The name **semiconductor** has been adopted for materials with this band structure. Compared with the metal, however, the number of electrons that can be excited by thermal means will be *very* small, so that the conductivity will also be correspondingly very much lower than is typical for a metal.

Table 1 gives comparative figures for two examples, copper and silicon. The Table illustrates the very large difference between the ability to conduct of the two types of material.

Table 1 The contrasting electrical properties of a conductor and a semiconductor.

	density of charge carriers, n/m^{-3}	resistivity, $\rho/\Omega\,\mathrm{m}$	conductivity = $\rho^{-1}/(\Omega\,\mathrm{m})^{-1}$
copper (conductor)	9×10^{28}	2×10^{-8}	0.5×10^{8}
silicon (semiconductor)	1×10^{16}	3×10^{3}	0.3×10^{-3}

The conductivity of the material as described above is a property of the material in its pure form and it is called **intrinsic conduction** of the semiconductor.

In practice, the properties of semiconductors are usually controlled by introducing minute quantities of impurity atoms. These will have either one more or one less outer electron than the atoms of the bulk material, and therefore will provide either extra free electrons or leave some levels unfilled creating so-called **holes**, which can enhance the conductivity of the material. This is known as **impurity conduction**. Where the impurity added is an electron donor the conduction process takes place effectively with negative charge carriers and the material is said to be an **n-type semiconductor**. If the impurity added is an electron acceptor the conduction effectively involves the absence of electrons — i.e. the presence of positive holes — and the material is said to be a **p-type semiconductor**.

Question T1

Some of the energy levels for the atoms of an element are shown in Figure 15 as a function of the internuclear distance of the atoms. What would you expect the electrical category of the element to be if the equilibrium separation in the solid state were (a) s_1, (b) s_2 and (c) s_3? ❏

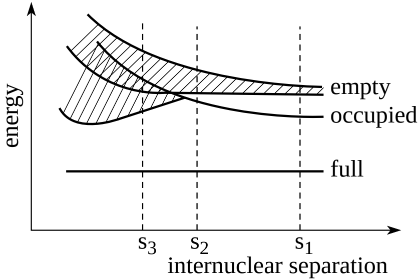


Figure 15 Some of the energy levels of the atoms of an element as a function of the internuclear separation of the atoms. The labels full, occupied and empty refer to the outer electron states in the *isolated* atoms.

Question T2

The band structure of a solid is shown in Figure 16.

Explain what happens when a potential difference is applied across a specimen of the solid. Explain your answer with reference to the Pauli exclusion principle. ❏

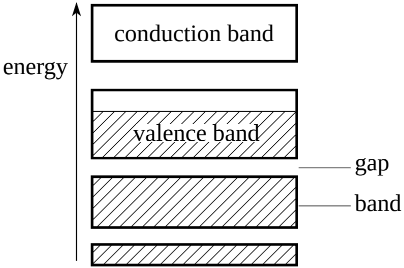


Figure 16 The band diagram for a solid element. The hatched portion corresponds to levels containing electrons.

4 Thermal properties of solids

So far, we have concentrated largely on the properties of the electrons in a solid. We shall now turn to the properties that depend predominantly on the state of the atoms of the solid in the lattice. Let us look first at the effect of temperature on the lattice. In Section 2, we considered the energy of the interaction between atoms in the lattice.

Figure 7 shows the energy function for the protons in the hydrogen molecule. This is the typical *shape* of the energy graph of the interaction of neighbouring atoms in a lattice. The separation of the atoms where the potential energy function has its minimum value corresponds to stable equilibrium. However, this ignores *thermal* energy. Even at room temperature, the atoms will have some thermal energy, so that they will oscillate about the position of equilibrium.

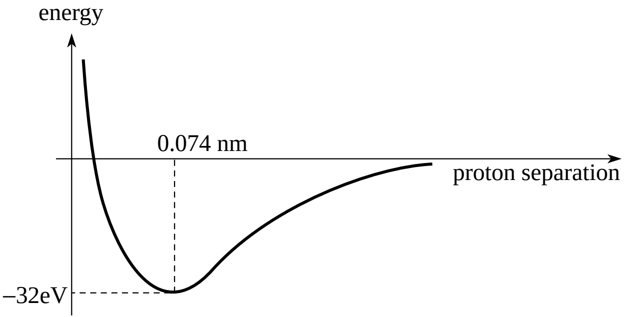


Figure 7 The energy of the symmetric state of the molecule depends on the separation of the protons. The equilibrium state corresponds to the minimum value of this energy. The anti-symmetric state has higher energy at all separations.

The extent of the oscillation is shown by the range x^+ to x^- in Figure 17. (The extent of the oscillation is greatly exaggerated, for clarity, in the Figure.) If the temperature is now raised, the thermal energy will increase and as is clear from Figure 17, the amplitude of the oscillation will increase. This is the basic background for a discussion of the effect of temperature on a solid. We shall look at the following: the dependence of electrical conductivity on temperature for conductors and for semiconductors, the *specific heat capacity*, the *thermal expansivity* and the *thermal conductivity* of solids.

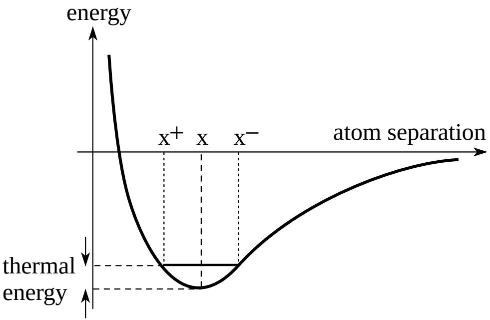


Figure 17 The energy function for the interaction of neighbouring atoms in a crystal lattice. The extent of the oscillation due to thermal energy is shown by x^+ and x^-.

4.1 The effect of temperature on electrical conductivity

As we noted in the introduction to Section 3, the resistance to the conduction of electricity in a conductor results from the interaction of the carrier electrons with the atoms in the lattice. As we now see, at a given temperature, the atoms in the lattice are not stationary, but oscillate about their equilibrium positions. When the temperature of the solid is increased, more energy is transferred to the lattice and the amplitude of the oscillation increases. The larger oscillation will mean that the chance of a collision of a conduction electron with a lattice atom must be increased. Consequently, it would be expected that the value of the resistivity should increase with temperature. This is indeed the case for conductors. The increase in resistivity for small increases in temperature is approximately linear. The resistivity, ρ, at temperature T is related to ρ_0, the resistivity at temperature T_0, by:

$$\rho = \rho_0[1 + \alpha(T - T_0)]$$

The coefficient α is called the **temperature coefficient of resistivity**. For conductors, this has a positive value which agrees with the model we have proposed above. For copper, it has a value of $+\,4 \times 10^{-3}\,\mathrm{K}^{-1}$ in the region of room temperature. For conductors, the effect of an increase in temperature on the number of conduction electrons is very small. So we ignore this entirely.

However, for intrinsic conduction semiconductors, the situation is very different. The existence of this conductivity depends on the thermal agitation, which causes electrons in the valence band to jump in energy into the conduction band. When the temperature is raised, therefore, and the thermal energy available is increased, the number of electrons reaching the conduction band will be greater. So, with the increase in the number of charge carriers, the resistivity of the semiconductor will *decrease*. Opposing this will be the effect of the increased lattice vibrations — as for the metal — but this is a relatively small effect; the coefficient α for a semiconductor is therefore negative. The value for silicon, for instance, is $-70 \times 10^{-3}\,\mathrm{K}^{-1}$ in the region of room temperature (the effect is not linear over a large temperature range). Table 2 highlights the very distinctive properties of conductors relative to semiconductors.

Table 2 The relative sizes and signs of carrier density n, resistivity ρ, and temperature coefficient α for conductors and semiconductors.

	n	ρ	α
conductor	high	low	positive
semiconductor	low	high	negative

4.2 The specific heat capacity of a solid

The **specific heat capacity** of a material is a measure of the heat required to raise its temperature. More precisely, it is the heat required to raise one mole through one kelvin. In SI units, it is therefore measured in $\mathrm{J\,mol^{-1}\,K^{-1}}$ ☞. At the atomic level, the heat is communicated as energy to the atoms in the lattice, and in the case of a conductor, to the 'free' electrons. Except for conductors at very low temperatures, the thermal energy stored within a solid is predominantly in the oscillations in the lattice.

Classical theory predicts that the specific heat capacity of a crystal should be the same at all temperatures. However, experimentally it is found that for all solids, the specific heat tends to zero as the temperature approaches absolute zero, although the classical value is correct at high temperatures. Einstein proposed a quantum mechanical model to explain this behaviour, based on two simple assumptions:

○ The atoms behave as quantum harmonic oscillators. ☞

○ Although the lattice is in fact many oscillators coupled together, there is effectively a single frequency of oscillation f_E, that applies to each oscillator independently.

From the quantum theory of the harmonic oscillator it then follows that each atom has the following energy levels associated with its thermal agitation

$$E_n = \left(n + \tfrac{1}{2}\right) h f_E \quad \text{with } n = 0,\ 1,\ 2,\ 3\ \ldots$$

At very low temperatures, there will not be enough thermal energy to excite any of the oscillators from its lowest state, so the solid can be heated without any energy being contributed to the excitation of the lattice. In other words, the specific heat will be very small at low temperatures. Only when one reaches higher temperatures, when the thermal energy kT is comparable with the separation of the oscillator levels, hf_E, will there be significant excitation of the oscillators, and a significant amount of energy required to increase the temperature of the crystal.

This **Einstein model** was qualitatively correct, but was made quantitatively correct by a modification due to Debye ☞. Debye dropped the second assumption above, and replaced it with a more realistic distribution of frequencies arising from the fact that the oscillators are *not independent but coupled*. This refinement then gives the correct dependence of the specific heat C on temperature near absolute zero: $C \propto T^3$. The **Debye model**, although very important, is a relatively minor step compared with the revolutionary step taken by Einstein in using *quantized* energy levels. The classical model, which has a continuous energy spectrum, leads to a *totally wrong* prediction of the behaviour of solids at low temperatures.

The Debye model is very good for *insulators*. For *conductors* at room temperature, it also fits experimental values well, but falls down near absolute zero.

The reason for this is the neglect of the energy that will be communicated to the conduction electrons. These are essentially free and do not take part in the lattice vibrations. This is not serious at room temperature when the lattice energy is very much larger than the free electron energy. However, at very low temperatures, the lattice energy becomes very much smaller and the electron energy can no longer be neglected.

With its inclusion into the Debye model, a contribution to C proportional to the temperature is added to the lattice contribution. The new prediction, $C = AT^3 + BT$, where A and B are constants, closely fits experimental results for conductors.

What do these results tell us about the atomic lattice?

Both models assume that the lattice oscillations are harmonic. The potential energy function for a simple harmonic oscillator is parabolic: $U_{\rm SHO}(x) = \frac{1}{2}kx^2$. For *small* oscillations near a minimum in the energy curve, a parabola is a good approximation to the curve. [Remember that in Figure 17 the thermal oscillation was greatly exaggerated for visibility on the graph.]

The success of the Debye model shows that only small oscillations need be considered *in practice*.

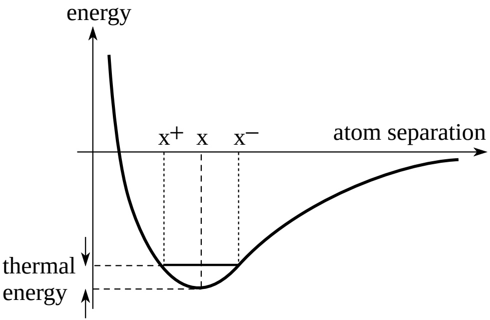


Figure 17 The energy function for the interaction of neighbouring atoms in a crystal lattice. The extent of the oscillation due to thermal energy is shown by x^+ and x^-.

Question T3

The specific heat capacity C for a solid depends on temperature T as shown in Table 3. Plot a graph of C/T against T^2.

Is the solid a conductor or an insulator? ❑

Table 3 Values of the specific heat capacity C as a function of temperature for a solid.

T/K	C/mJ mol^{-1} K^{-1}
5	20.8
10	61.4
15	142
20	281
25	499

4.3 The thermal expansivity of a solid

A property which illustrates another feature of the potential is the **thermal expansivity**. When a solid is heated, it expands in volume. This is wholly a property arising from the effect on the lattice. The increase in volume arises because the atoms in the lattice move further apart as the temperature rises. Let us look again at the energy function to see how this may happen. In Figure 18, we show the oscillation of the lattice at a given temperature (and energy) E_1. At a higher temperature, the lattice oscillation will have a higher energy, E_2, and consequently a larger amplitude. If the shape of the potential around the equilibrium point were parabolic — that is symmetrical about the equilibrium position — then the centre of oscillation X would not change. In this case, the solid should not be expected to expand with increased temperature.

Figure 18 shows, however, a potential that is not symmetrical about the equilibrium point. In this case, with $E_1 < E_2$ and the shape of potential shown, we see that the new centre of oscillation Y is at an increased separation at the higher temperature. The solid will expand when heated. Thus, an external observation gives a clue about the shape of the potential energy of the microscopic interaction.

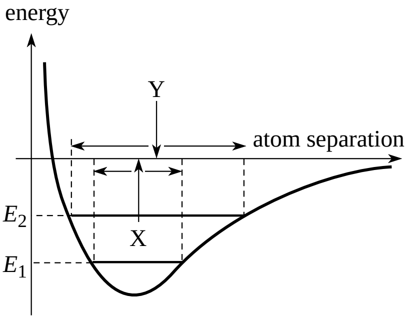


Figure 18 Thermal oscillation at energy E_1 is centred on X. If the shape of the energy curve is not symmetrical about the equilibrium position, the thermal oscillation at energy E_2 is centred on a different point Y.

Remember, however, that the specific heat capacity was explained, in the simplest theories, by the assumption that the thermal vibrations of the lattice were simple harmonic. For this to be the case, the potential must be parabolic — the potential energy function of a simple harmonic oscillator is given by: $U_{\rm SHO}(x) = \frac{1}{2}kx^2$.

Thus a more complete theory of specific heat capacity should also allow for the so-called *anharmonic* effects, however small these might be in practice. We shall not pursue that further here; we only wish to demonstrate the importance, in the development of any theory (in this case of the solid state), of considering more than one measurable quantity. Degree courses may be divided up, for convenience of teaching and learning, into segments labelled electricity, heat, and so forth, but the laws of nature transcend such artificial constraints.

4.4 The thermal conductivity of a solid

If one end of a solid bar is raised to a higher temperature than the other end, heat will flow from the end at the higher temperature to the end at the lower temperature. The property of a material which determines the rate of this process is called its **thermal conductivity**. On the atomic scale, this can be understood as the transmission of energy between the atomic oscillators in the lattice. As one end is heated to raise its temperature, the oscillators at that end will vibrate more vigorously and in doing so will cause their neighbouring atoms to oscillate more vigorously. This effect of atoms on their interacting neighbours will apply all the way down the bar.

The thermal conductivity is measured macroscopically by the **coefficient of thermal conductivity** κ, which we shall now define. Suppose that a bar of length l and constant cross section A has its ends maintained at temperatures T_1 and T_2. The rate of flow of heat H down the bar, assuming no heat escapes laterally is given by:

$$\frac{dQ}{dt} = -\kappa A \frac{T_2 - T_1}{l}$$

The larger the value of κ for a solid, the better the solid conducts heat.

Some values of κ are given in Table 4.

You will note that there is a marked correlation between the ability of a substance to conduct electricity and its ability to conduct heat. This is an indication that the conduction electrons, as well as the lattice vibrations, play a role in the conduction of heat energy. This is noticeable because, although the energy of the atoms vibrating in the lattice is relatively large, only small amounts of this energy are *communicated* to neighbours and so contribute to the conduction of heat. On the other hand, the conduction electrons have relatively small energies, but especially in metals, can transmit energy much more easily since they are mobile.

Table 4 Values of the coefficient of the thermal conductivity κ and electrical conductivity σ for some solids at room temperature.

	$\kappa/\mathrm{W\,m^{-1}\,K^{-1}}$	$\sigma/\Omega^{-1}\,\mathrm{m}^{-1}$
silver	428	0.62×10^8
copper	401	0.59×10^8
aluminium	235	0.36×10^8
silicon	168	0.3×10^{-3}
glass	≈ 1	$\approx 10^{-12}$

5 Closing items

5.1 Module summary

1 The atoms of an element in a solid *crystalline solid* are arranged in a regular array that may be characterized by a *lattice* of points.

2 The atoms are held in the array by interatomic *bonds*.

3 The nature of the bond depends on the electronic structure of the atom.

4 The energy levels of the electrons in an isolated atom always broaden when atoms are in close proximity. In the stable crystalline configuration, the energy levels become continuous *energy bands* with *gaps* containing no energy levels between the bands.

5 A solid is a *conductor* of electricity if its electrons only partly fill an energy band. It is an *insulator* if the electrons completely fill a band and there is a large gap to the next empty band above the filled band.

6 If the electrons of a solid completely fill an energy band, but the gap above this band is narrow enough to allow thermally excited electrons to jump across it, the solid is a *semiconductor*. Such gaps must be larger than about 1 eV.

7 The *temperature coefficient of resistivity* α is positive for a conductor but negative for a semiconductor.

8 The *specific heat capacity* of a solid insulator may be accounted for in terms of the quantum theory of the harmonic oscillations of the atoms in the lattice.

9 The specific heat capacity of a conductor is explained by the same theory *except* at very low temperatures, near absolute zero, where the contribution from the energy of the *conduction electrons* becomes significant.

10 The *thermal expansivity* of a solid provides evidence that the curve of interaction energy against separation for the atoms in the lattice is not quite symmetrical about the minimum.

11 Conduction electrons contribute to the high *thermal conductivity* of electrical conductors. In an insulator, only the interaction of the atoms with their neighbours is available as a means of propagating thermal energy.

5.2 Achievements

Having completed this module, you should be able to:

A1 Define the terms that are emboldened and flagged in the margins of the module.

A2 Give a qualitative description of the broadening of electronic energy levels when atoms are brought close to each other.

A3 Given an energy band diagram of a solid, say whether the solid is an insulator, a conductor or a semiconductor, and justify your choice.

A4 Explain why the density of electrical carriers in a conductor is very much larger than in a semiconductor.

A5 Explain why the temperature coefficient of resistivity of a conductor is positive, while that for a semiconductor is negative.

A6 Relate the thermal expansivity of a solid to the shape of the interaction energy against separation curve for the atoms in the crystal lattice.

A7 Explain why good electrical conductors are also good thermal conductors.

Study comment You may now wish to take the *Exit test* for this module which tests these Achievements. If you prefer to study the module further before taking this test then return to the *Module contents* to review some of the topics.

5.3 Exit test

Study comment Having completed this module, you should be able to answer the following questions each of which tests one or more of the Achievements.

Question E1

(*A2*) Describe the effect on the energy levels of isolated atoms of bringing the atoms closer to each other as in a solid element.

Question E2

(*A3*) Figure 19 shows the energy band diagram for a solid element. Is the element a conductor, an insulator or a semiconductor of electricity? Give the reason for your answer.

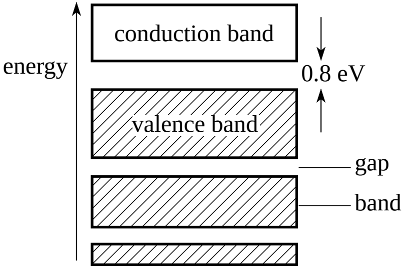


Figure 19 See Question E2.

Question E3

(*A4* and *A5*) The density of electrical carriers in a conductor is very much greater than in a semiconductor. The temperature coefficient of resistivity of a conductor is positive, while that for a semiconductor is negative. How are these two statements connected?

Question E4

(*A6* and *A7*) Sketch the curve for the energy of interaction between neighbouring atoms and their internuclear separation. If the solid is an insulator, what features of the shape of the curve determine: (a) the quantum model that will be used to describe the specific heat capacity of the solid, and (b) the thermal expansivity of the solid?

What other factor enters the model of the specific heat capacity if the solid is an electrical conductor?

Question E5

(*A8*) Why are good electrical conductors generally also good thermal conductors?

Study comment This is the final *Exit test* question. When you have completed the *Exit test* go back to Subsection 1.2 and try the *Fast track questions* if you have not already done so.

If you have completed **both** the *Fast track questions* and the *Exit test*, then you have finished the module and may leave it here.