Section 9: Energy bands

The free electron model gives us a good insight into many properties of metals, such as the heat capacity, thermal conductivity and electrical conductivity. However, this model fails to help us other important properties. For example, it does not predict the difference between metals, semiconductors and insulators. It does not explain the occurrence of positive values of the Hall coefficient. Also the relation between conduction electrons in the metal and the number of valence electrons in free atoms is not always correct. We need a more accurate theory, which would be able to answer these questions.

The problem of electrons in a solid is in general a many-electron problem. The full Hamiltoniam of the solid contains not only the one-electron potentials describing the interactions of the electrons with atomic nuclei, but also pair potentials describing the electron-electron interactions. The many-electron problem is impossible to solve exactly and therefore we need simplified assumptions. The simplest approach we have already considered, it is a free electron model. The next step in building the complexity is to consider an independent electron approximation, assuming that all the interactions are described by an effective potential. One of the most important properties of this potential is that it is periodic on a lattice

$$U(\mathbf{r}) = U(\mathbf{r}+\mathbf{T}), \qquad (1)$$

where **T** is a lattice vector. Qualitatively, a typical crystalline potential might be expected to have a form shown in Fig.1, resembling the individual atomic potentials as the ion is approached closely and flattening off in the region between ions.

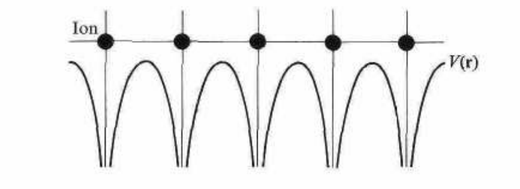


Fig. 1 The crystal potential seen by the electron.

Within the approximation of non-interacting electrons the electronic properties of a solid can be examined by Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \qquad (2)$$

in which $\psi(\mathbf{r})$ is a wave function for one electron. Independent electrons, which obey a one-electron Schrödinger equation (2) with a periodic potential, are known as *Bloch electrons*, in contrast to "free electrons," to which Bloch electrons reduce when the periodic potential is identically zero.

Now we discuss general properties of the solution of the Schrödinger equation (2) taking into account periodicity of the effective potential (1) and discuss main properties of Bloch electrons, which follow from this solution.

We represent the solution as an expansion over plain waves:

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{kr}}. \qquad (3)$$

This expansion in a Fourier series is a natural generalization of the free-electron solution for a zero potential. The summation in (3) is performed over all **k** vectors, which are permitted by the periodic boundary conditions. According to these conditions the wave function (3) should satisfy

$$\psi(x,y,z)=\psi(x+L,y,z)=\psi(x,y+L,z)=\psi(x,y,z+L)\,, \tag{4}$$

so that

$$k_x=\frac{2\pi n_x}{L};\quad k_y=\frac{2\pi n_y}{L};\quad k_z=\frac{2\pi n_z}{L}\,, \tag{5}$$

where n_x, n_y, and n_z are positive or negative integers. Note that in general $\psi(\mathbf{r})$ is *not* periodic in the lattice translation vectors. On the other hand, according to Eq.(1) the potential energy is periodic, i.e. it is invariant under a crystal lattice translation. Therefore, its plane wave expansion will only contain plane waves with the periodicity of the lattice. Therefore, only reciprocal lattice vectors are left in the Fourier expansion for the potential:

$$U(\mathbf{r})=\sum_{\mathbf{G}}U_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}}\,, \tag{6}$$

where the Fourier coefficients $U_{\mathbf{G}}$ are related to $U(\mathbf{r})$ by

$$U_{\mathbf{G}}=\frac{1}{V_c}\int_{cell}e^{-i\mathbf{G}\mathbf{r}}U(\mathbf{r})dr\,, \tag{7}$$

where V_c is the volume of the unit cell. It is easy to see that indeed the potential energy represented by (6) is periodic in the lattice:

$$U(\mathbf{r}+\mathbf{T})=\sum_{\mathbf{G}}U_{\mathbf{G}}e^{i\mathbf{G}(\mathbf{r}+\mathbf{T})}=e^{i\mathbf{G}\mathbf{T}}\sum_{\mathbf{G}}U_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}}=U(\mathbf{r})\,, \tag{8}$$

where the last equation comes from the definition of the reciprocal lattice vectors $e^{i\mathbf{G}\mathbf{T}}=1$. The values of Fourier components $U_{\mathbf{G}}$ for actual crystal potentials tend to decrease rapidly with increasing magnitude of **G**. For example, for a Coulomb potential $U_{\mathbf{G}}$ decreases as $1/G^2$. Note that since the potential energy is real the Fourier components should satisfy $U_{-\mathbf{G}}=U_{\mathbf{G}}^*$.

We now substitute (3) and (6) in Eq.(2) and obtain:

$$\frac{\hbar^2}{2m}\sum_{\mathbf{k}}k^2c_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}+\sum_{\mathbf{k}}\sum_{\mathbf{G}}U_{\mathbf{G}}c_{\mathbf{k}}e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}=E\sum_{\mathbf{k}}c_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}\,. \tag{9}$$

Changing the summation index in the second sum on the left from **k** to **k**+**G** this equation can be rewritten in a form:

$$\sum_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}\left\{\left(\frac{\hbar^2}{2m}k^2-E\right)c_{\mathbf{k}}+\sum_{\mathbf{G}}U_{\mathbf{G}}c_{\mathbf{k}-\mathbf{G}}\right\}=0\,. \tag{10}$$

Since this equation must be satisfied for any **r** the Fourier coefficients in each separate term of (10) must vanish and therefore

$$\left(\frac{\hbar^2}{2m}k^2-E\right)c_{\mathbf{k}}+\sum_{\mathbf{G}}U_{\mathbf{G}}c_{\mathbf{k}-\mathbf{G}}=0\,. \tag{11}$$

This is a set of linear equations for the coefficients $c_{\mathbf{k}}$. These equations are nothing but restatement of the original Schrödinger equation in the momentum space, simplified by the fact that the potential is periodic. This set of equations does not look very pleasant because, in principle, an infinite number of coefficients should be determined. However, a careful examination of Eq.(11) leads to important consequences.

First, we see that for a fixed value of **k** the set of equations (11) couples only those coefficients, whose wave vectors differ from **k** by a reciprocal lattice vector. In the one-dimensional case these are k, k±2π/a, k±4π/a, and so on. We can therefore assume that the **k** vector belongs to the first Brillouin zone. The original problem is decoupled to *N* independent problems (*N* is the total number of atoms in a lattice): for each allowed value of **k** in the first Brillouin zone. Each such problem has solutions that are superposition of plane waves containing only the wave vector **k** and wave vectors differing from **k** by the reciprocal lattice vector.

Putting this information back into the expansion (3) of the wave function $\psi(\mathbf{r})$, we see that the wave function will be of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}}, \tag{12}$$

where the summation is performed over the reciprocal lattice vectors and we introduced index **k** for the wave function. We can rearrange this so that

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}}, \tag{13}$$

or

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \tag{14}$$

where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T})$ is a periodic function which is defined by

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}}. \tag{15}$$

Equation (14) is known as Bloch theorem, which plays an important role in electronic band structure theory. Now we discuss a number of important conclusions which follow from the Bloch theorem.

1. Bloch's theorem introduces a wave vector **k**, which plays the same fundamental role in the general problem of motion in a periodic potential that the free electron wave vector **k** plays in the free-electron theory. Note, however, that although the free electron wave vector is simply $\mathbf{p}/\hbar$, where **p** is the momentum of the electron, in the Bloch case **k** is not proportional to the electronic momentum. This is clear on general grounds, since the Hamiltonian does not have complete translational invariance in the presence of a non-constant potential, and therefore its eigenstates will not be simultaneous eigenstates of the momentum operator. This conclusion is confirmed by the fact that the momentum operator, $\mathbf{p} = -i\hbar\nabla$, when acting on $\psi_{\mathbf{k}}(\mathbf{r})$ gives

$$-i\hbar\nabla\psi_{\mathbf{k}}(\mathbf{r}) = -i\hbar\nabla\left[e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})\right] = \hbar\mathbf{k}\psi_{\mathbf{k}}(\mathbf{r}) - i\hbar e^{i\mathbf{k}\mathbf{r}}\nabla u_{\mathbf{k}}(\mathbf{r}), \tag{16}$$

which is not, in general, just a constant times $\psi_{\mathbf{k}}(\mathbf{r})$; i.e., $\psi_{\mathbf{k}}(\mathbf{r})$ is not a momentum eigenstate.

Nevertheless, in many ways $\hbar\mathbf{k}$ is a natural extension of **p** to the case of a periodic potential. It is known as the *crystal momentum* or *quasimomentum* of the electron, to emphasize this similarity, but one should not be misled by the name into thinking that $\hbar\mathbf{k}$ is a momentum.

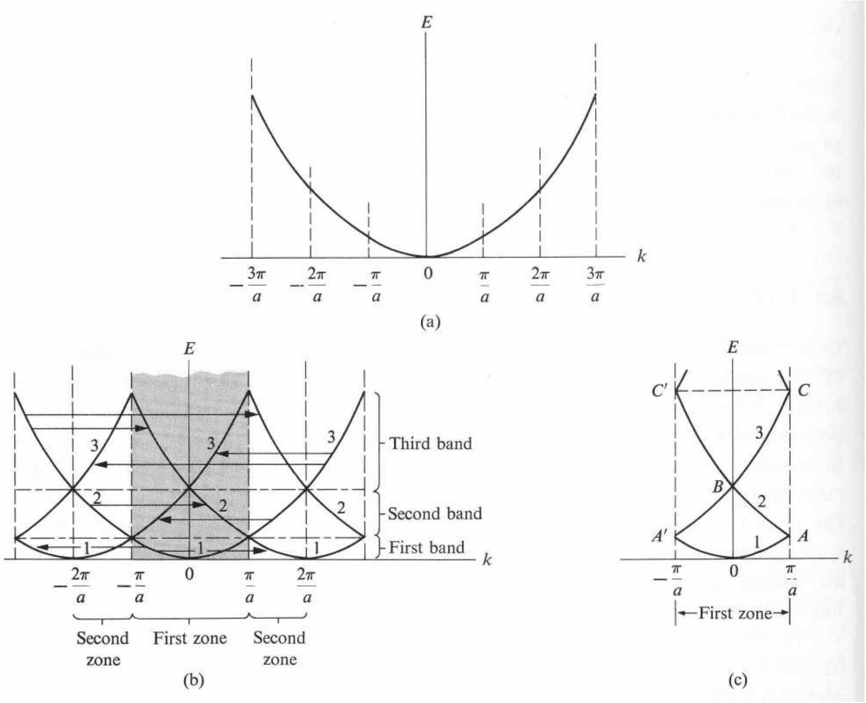
2. The wave vector **k** appearing in Bloch's theorem can always be confined to the first Brillouin zone (or to any other convenient primitive cell of the reciprocal lattice). This is because any **k**' not in the first Brillouin zone can be written as

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}, \tag{17}$$

where **G** is a reciprocal lattice vector and **k** does lie in the first zone. Since $e^{i\mathbf{G}\mathbf{T}} = 1$ for any reciprocal lattice vector, if the Bloch form (14) holds for **k**', it will also hold for **k**. An example is given below for a nearly free electron model.

The energy E of free electrons which is plotted versus k in Fig.2a exhibits a curve in the familiar parabolic shape. Figure 2b shows the result of translations. Segments of the parabola of Fig.2a are cut at the edges of the various zones, and are translated by multiples of $G = 2\pi/a$ in order to ensure that the energy is the same at any two equivalent points. Fig.2c displays the shape of the energy spectrum when we confine our consideration to the first Brillouin zone only.

The type of representation used in Fig.2c is referred to as the *reduced-zone scheme.* Because it specifies all the needed information, it is the one we shall find most convenient. The representation of Fig.1a, known as the *extended-zone scheme,* is convenient when we wish to emphasize the close connection between a crystalline and a free electron. Fig.2b employs the *periodic-zone* scheme, and is sometimes useful in topological considerations involving the **k**-space. All these representations are strictly equivalent; the use of any particular one is dictated by convenience, and not by any intrinsic advantages it has over the others.



(a)

(b)

(c)

Fig.2 Free electron bands within *reduced-* (a), *extended-* (b) and *periodic-zone* (c) scheme.

3. An important consequence of the Bloch theorem is the appearance of the energy bands.

All solutions to the Schrodinger equation (2) have the Bloch form $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}u_{\mathbf{k}}(\mathbf{r})$ where **k** is fixed and $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the Bravais lattice. Substituting this into the Schrodinger equation, we find that $u_{\mathbf{k}}(\mathbf{r})$ is determined by the eigenvalue problem

$$H(\mathbf{k})u_{\mathbf{k}}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\left(i\mathbf{k}+\nabla\right)^2 + U(\mathbf{r})\right]u_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})u_{\mathbf{k}}(\mathbf{r}), \tag{18}$$

with boundary condition

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T}), \tag{19}$$

Because of the periodic boundary condition we can regard (18) as an eigenvalue problem restricted to a single primitive cell of the crystal. Because the eigenvalue problem is set in a fixed finite volume, we expect on general grounds to find an infinite family of solutions with *discretely* spaced eigenvalues, which we label with the band index *n*. The Bloch function can therefore be denoted by $\psi_{n\mathbf{k}}(\mathbf{r})$ which indicates that each value of the band index *n* and the vector **k** specifies an electron state, or orbital with energy $E_n(\mathbf{k})$.

Note that in terms of the eigenvalue problem specified by (18) and (19), the wave vector **k** appears only as a parameter in the Hamiltonian $H(\mathbf{k})$. We therefore expect each of the energy levels, for given **k**, to vary continuously as **k** varies. In this way we arrive at a description of the levels of an electron in a periodic potential in terms of a family of continuous functions $E_n(\mathbf{k})$. For each *n*, the set of electronic levels specified by $E_n(\mathbf{k})$ is called an *energy band*. The information contained in these functions for different *n* and **k** is referred to as the *band structure* of the solid.

4. Number of states in a band.

The *number of orbitals in a band within the first Brillouin zone is equal to the number of unit cells N in the crystal.* This is much the same as the statement made in connection with the number of lattice vibrational modes, and is proved in a like manner, by appealing to the boundary conditions.

Consider first the one-dimensional case. The allowed values of *k* form a uniform mesh whose unit spacing is $2\pi/L$. The number of states inside the first zone, whose length is $2\pi/a$, is therefore equal to $(2\pi/a)/(2\pi/L) = L/a = N$, where *N* is the number of unit cells, in agreement with the assertion made earlier.

A similar argument may be used to establish the validity of the statement in two- and three-dimensional lattices.

It has been shown that each band has *N* states inside the first zone. Since each such state can accommodate at most two electrons, of opposite spins, in accordance with the Pauli exclusion principle, it follows that the maximum number of electrons that may occupy a single band is *2N*. This result is significant, as it will be used in a later section to establish the criterion for predicting whether a solid is going to behave as a metal or an insulator.

5. Now we show that an electron in a level specified by band index *n* and wave vector **k** has a nonvanishing mean velocity, given by

$$\mathbf{v}_n(\mathbf{k}) = \frac{dE_n(\mathbf{k})}{\hbar d\mathbf{k}} . \tag{20}$$

To show this we calculate the expectation value of the derivative of the Hamiltonian $H(\mathbf{k})$ in Eq.(18) with respect to **k**:

$$\langle u_n | \frac{dH(\mathbf{k})}{d\mathbf{k}} | u_n \rangle = \langle u_n | -i\frac{\hbar^2}{m}(i\mathbf{k}+\nabla) | u_n \rangle = \langle \psi_n | \hbar(-\frac{i\hbar}{m}\nabla) | \psi_n \rangle . \tag{21}$$

Since $\mathbf{v} = (-i\hbar/m)\nabla$ is the velocity operator, this establishes (20).

This is a remarkable fact. It asserts that there are stationary levels for an electron in a periodic potential in which, in spite of the interaction of the electron with the fixed lattice of ions, it moves forever without any degradation of its mean velocity. This is in striking contrast to the idea of Drude that collisions were simply encounters between the electron and a static ion.

Weak potential

When the potential is zero the solutions of the Schrödinger equation (11) are plane waves:

$$E^0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}, \tag{22}$$

$$\psi^0_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_c}} e^{i\mathbf{kr}}, \tag{23}$$

where the wave function is normalized to the volume of unit cell V_c. In the reduced-zone representation shown in Fig.3, for each **k** there is an infinite number of solutions which correspond to different **G** (and can be labeled by index *n*), as we have already discussed. Each band in Fig.3 corresponds to a different value of **G** in the extended scheme.

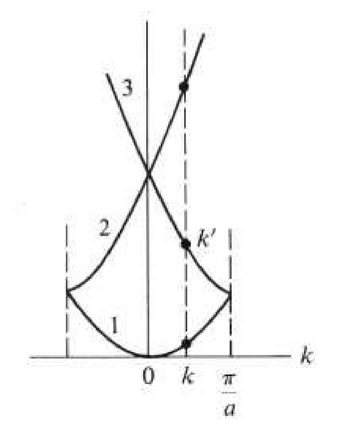


Fig.3 Only those states which have the same k in the First Brillouin zone are coupled by perturbation

Suppose now that a weak potential is switched on. According to the Schrödinger equation (11) only those states, which differ by **G**, are coupled by a perturbation. In the reduced zone scheme those states have same **k** and different *n* (see Fig.3). As you know from quantum mechanics, if the perturbation is small compared to the energy difference between the states, which are coupled by the perturbation, we can use the perturbation theory to calculated wave functions and energy levels. Assuming for simplicity that we are looking for the correction to the energy of the lowest band $E^0(\mathbf{k})$, the condition for using the perturbation theory is

$$\left|E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})\right| \gg U, \tag{24}$$

for any $\mathbf{G} \neq 0$. According to the perturbation theory the energy is given by

$$E(\mathbf{k}) = E^0(\mathbf{k}) + \left\langle \psi^0_{\mathbf{k}} \middle| U \middle| \psi^0_{\mathbf{k}} \right\rangle + \sum_{\mathbf{G}\neq 0} \frac{\left|\left\langle \psi^0_{\mathbf{k}} \middle| U \middle| \psi^0_{\mathbf{k}-\mathbf{G}} \right\rangle\right|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})}, \tag{25}$$

The first term in Eq.(25) is the undisturbed free-electron value for the energy. The second term is the mean value of the potential in the state $\psi^0_{\mathbf{k}}(\mathbf{r})$:

$$\left\langle \psi^0_{\mathbf{k}} \middle| U \middle| \psi^0_{\mathbf{k}} \right\rangle = \frac{1}{V_c} \int_{cell} U(\mathbf{r}) dr = U_0 . \tag{26}$$

This term gives is a constant independent of **k**. Its effect on the spectrum is a rigid shift by a constant value without causing any change in the shape of the energy spectrum. This term can be set equal to zero. The third term can be rewritten as

$$\left\langle \psi_{\mathbf{k}}^{0} \left| U \right| \psi_{\mathbf{k}-\mathbf{G}}^{0} \right\rangle = \frac{1}{V_c}\int_{cell} e^{-i\mathbf{kr}} U(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}} dr = \frac{1}{V_c}\int_{cell} U(\mathbf{r}) e^{-i\mathbf{Gr}} dr = U_{\mathbf{G}} . \tag{27}$$

Finally we obtain for the energy:

$$E(\mathbf{k}) = E^0(\mathbf{k}) + \sum_{\mathbf{G}\neq 0} \frac{\left|U_{\mathbf{G}}\right|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})} . \tag{28}$$

The perturbation theory breaks down, however, in those cases when the potential cannot be considered as a small perturbation. This happens when the magnitude of the potential becomes comparable with the energy separation between the bands, i.e.

$$\left| E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G}) \right| \leq U , \tag{29}$$

In this case we have to include these levels in the Schrödinger equation and solve it explicitly.

There are special **k** points for which the energy levels become degenerate and the relationship (29) holds for any non-zero value of the potential. For these **k** points

$$E^0(\mathbf{k}) = E^0(\mathbf{k}-\mathbf{G}) , \tag{30}$$

and consequently

$$\left|\mathbf{k}\right| = \left|\mathbf{k}-\mathbf{G}\right| . \tag{31}$$

The latter conduction implies that **k** must lie on a Bragg plane bisecting the line joining the origin of **k** space and the reciprocal lattice point **G**, as is shown in Fig.4.

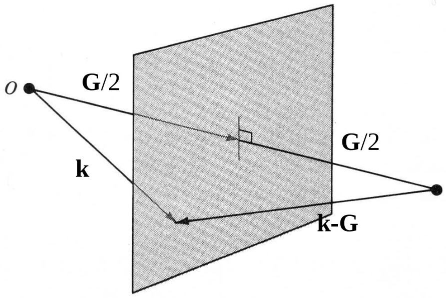


Fig. 4 If |**k**| = |**k** – **G**| , then the point **k** must lie in the Bragg plane determined by **G**.

Therefore, a weak periodic potential has its major effect on those free electron levels whose wave vectors are close to ones at which the Bragg reflection can occur. In order to find the energy levels and the wave functions of near these points we include to the equation (11) only the two levels: one which corresponds to **k** and the other which corresponds to **k**–**G** assuming that **k** lies near the Bragg plane:

$$\begin{aligned} \left(E^0(\mathbf{k}) - E\right) c_{\mathbf{k}} + U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} &= 0, \\ \left(E^0(\mathbf{k}-\mathbf{G}) - E\right) c_{\mathbf{k}-\mathbf{G}} + U_{-\mathbf{G}} c_{\mathbf{k}} &= 0. \end{aligned} \tag{32}$$

These equations have the solution when the determinant is equal to zero, i.e.

$$\begin{vmatrix} E^0(\mathbf{k})-E & U_{\mathbf{G}} \\ U_{\mathbf{G}}^* & E^0(\mathbf{k}-\mathbf{G})-E \end{vmatrix} = 0\,, \tag{33}$$

which leads to the quadratic equation

$$\left(E^0(\mathbf{k})-E\right)\left(E^0(\mathbf{k}-\mathbf{G})-E\right)-\left|U_{\mathbf{G}}\right|^2=0\,. \tag{34}$$

The two roots are

$$E=\frac{1}{2}\left(E^0(\mathbf{k})+E^0(\mathbf{k}-\mathbf{G})\right)\pm\left[\frac{1}{4}\left(E^0(\mathbf{k})-E^0(\mathbf{k}-\mathbf{G})\right)^2+\left|U_{\mathbf{G}}\right|^2\right]^{1/2}. \tag{35}$$

These solutions are plotted in Fig.4 for **k** parallel to **G**.

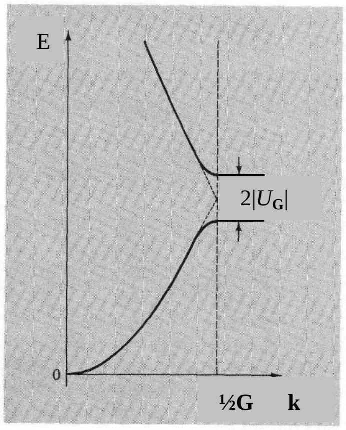


Fig.4 Plot of the energy bands given by Eq.(35) for **k** parallel to **G**. The lower band corresponds to the choice of a minus sign in Eq.(35) and the upper band to a plus sign. When **k** =1/2**G**, the two bands are separated by a band gap of magnitude 2|$U_{\mathbf{G}}$|. When **k** is far removed from the Bragg plane, the levels (to leading order) are indistinguishable from their free electron values (denoted by dotted lines).

This results is particularly simple for point lying on the Bragg plane, since in this case $E^0(\mathbf{k})=E^0(\mathbf{k}-\mathbf{G})$. We find from (35) then that

$$E=E^0(\mathbf{k})\pm\left|U_{\mathbf{G}}\right|. \tag{36}$$

Thus, at all points in the Bragg plane, one level is uniformly raised by $\left|U_{\mathbf{G}}\right|$ and the other is uniformly lowered by the same amount. This means that there are no states in the energy interval between $E_1=E^0(\mathbf{k})-\left|U_{\mathbf{G}}\right|$ and $E_2=E^0(\mathbf{k})+\left|U_{\mathbf{G}}\right|$, which implies the creation of the band gap. The magnitude of the band gap is equal to twice the Fourier component of the crystal potential.

We illustrate this behavior using a one-dimensional lattice shown in Fig.5. We see the splitting of the bands at each Bragg plane in the extended-zone scheme (Fig.5b). This results in the splitting of the bands both at the boundaries and at the centre of the first Brillouin zone (Fig.5a).

There are two important points to note. First, since the energy there increases as k^2, the higher the band, the greater its width. Second, the higher the energy, the narrower the gap; this follows from the fact that the gap is proportional to a Fourier component of the crystal potential and that the order of the component increases as the energy rises. Since the Fourier components of the potential decrease rapidly as the order increases, this leads to a decrease in the energy gap. It follows therefore that, as we move up the energy scale, the bands become wider and the gaps narrower; i.e., the electron behaves more and more like a free particle.

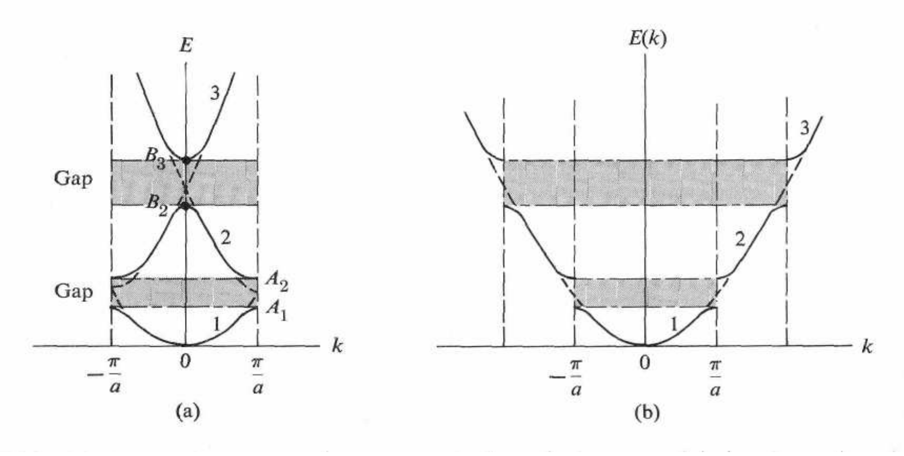


Fig. 5 (a) Dispersion curves in the nearly-free-electron model, in the reduced-zone scheme; (b) The same dispersion curves in the extended-zone scheme.

Now we discuss the origin of the appearance of the band gaps at the Bragg planes. When **k** lies on a Bragg plane we can easily find the form of the wave function corresponding to the two solutions (36). Assuming for simplicity that the potential is real we obtain from Eqs.(32)

$$c_{\mathbf{k}} = \pm c_{\mathbf{k}-\mathbf{G}} \,. \tag{37}$$

For simplicity we consider a one-dimensional lattice, for which the Bragg reflection occurs at **k**=½**G**. We have then

$$\psi_{\pm} = \frac{1}{\sqrt{2V_c}}\left[e^{iGr/2} \pm e^{iGr/2}\right]. \tag{38}$$

We see that at the zone edge, the scattering is so strong that the reflected wave has the same amplitude as the incident wave. The electron is represented there by a *standing* wave, very unlike a free particle.

The distribution of the charge density is proportional to $|\psi|^2$, so that

$$\begin{aligned} |\psi_+|^2 &\propto \cos^2(G\cdot r/2), \\ |\psi_-|^2 &\propto \sin^2(G\cdot r/2) \end{aligned} \,. \tag{39}$$

Since the origin lies at the ion, the ψ_- state distributes the electron so that it is piled predominantly at the nuclei (see Fig.6). Since the potential is most negative there, this distribution has a low energy. The function ψ_- therefore corresponds to the energy at the top of band 1, that is, point A_1 in Fig. 5a.

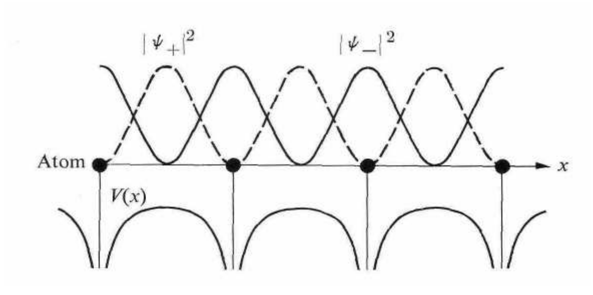


Fig. 6. Spatial distributions of the charge density described by the functions ψ_+ and ψ_-.

By contrast, the function ψ_+ deposits its electron mostly between the ions (as shown in Fig.6), corresponds to the bottom of band 2 in Fig.5a, that is, point A_2. The gap arises, therefore, because of the two different distributions for the same value of **k**, the distributions having different energies.

Metals and Insulators

Solids are divided into two major classes: *metals and insulators*. A metal – or a conductor – is a solid in which an electric current flows under the application of electric field. By contrast, application of an electric field produces no electric current in an insulator. There is a simple criterion for distinguishing between the two classes on the basis of the band structure. If the valence electrons exactly fill one or more bands, leaving others empty, the crystal will be an insulator. An external electric field will not cause current flow in an insulator. Provided that a filled band is separated by an energy gap from the next higher band, there is no continuous way to change the total momentum of the electrons if every accessible state is filled. Nothing changes when the field is applied.

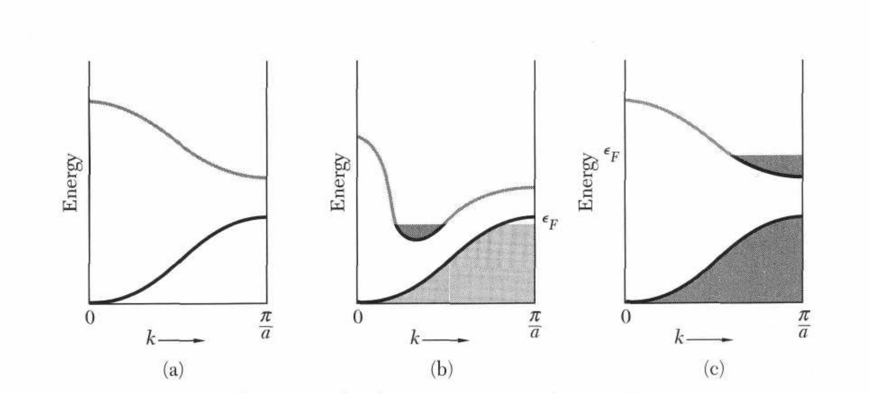


Fig. 7 Occupied states and band structures giving (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration. In (b) the overlap need not occur along the same directions in the Brillouin zone. If the overlap is small, with relatively few states involved, we speak of a semimetal.

On the contrary if the valence band is not completely filled the solid is a metal. In a metal there are empty states available above the Fermi level like in a free electron gas. An application of an external electric field results in the current flow.

It is possible to determine whether a solid is a metal of an insulator by considering the number of valence electrons. A crystal can be an insulator only if the number of valence electrons in a primitive cell of the crystal is an even integer. This is because each band can accommodate only two electrons per primitive cell. For example, diamond has two atoms of valence four, so that there are eight valence electrons per primitive cell. The band gap in diamond is 7eV and this crystal is a good insulator.

However, if a crystal has an even number of valence electrons per primitive cell, it is not necessarily an insulator. It may happen that the bands overlap in energy. If the bands overlap in energy, then instead of one filled band giving an insulator, we can have two partly filled bands giving a metal (Fig.7b). For example, the divalent metals, such as Mg or Zn, have two valence electrons per cell. However, they are metals, although a poor ones – their conductivity is small.

If this overlap is very small, we deal with *semimetals*. The best known example of a semimetal is bismuth (Bi).

If the number of valence electrons per cell is odd the solid is a metal. For example, the alkali metals and the noble metals have one valence electron per primitive cell, so that they have to be metals.

The alkaline earth metals have two valence electrons per primitive cell; they could be insulators, but the bands overlap in energy to give metals, but not very good metals. Diamond, silicon, and germanium each have two atoms of valence four, so that there are eight valence electrons per primitive cell; the bands do not overlap, and the pure crystals are insulators at absolute zero.

There are substances, which fall in an intermediate position between metals and insulators. If the gap between the valence band and the band immediately above it is small, then electrons are readily excitable thermally from the former to the latter band. Both bands become only partially filled and both contribute to the electric condition. Such a substance is known as a *semiconductor*. Examples are Si and Ge, in which the gaps are about 1 and 0.7 eV, respectively. Roughly speaking, a substance behaves as a semiconductor at room temperature whenever the gap is less than 2 eV. The conductivity of a typical semiconductor is very small compared to that of a metal, but it is still many orders of magnitude larger than that of an insulator. It is justifiable, therefore, to classify semiconductors as a new class of substance, although they are, strictly speaking, insulators at very low temperatures.