Kronig-Penney Model in Reciprocal Space[2]

As an example of the use of the central equation (31) for a problem that is exactly solvable, we use the Kronig-Penney model of a periodic delta-function potential:

$$U(x) = 2\sum_{G>0} U_G \cos Gx = Aa\sum_s \delta(x - sa) \ , \tag{33}$$

where A is a constant and a the lattice spacing. The sum is over all integers s between 0 and $1/a$. The boundary conditions are periodic over a ring of unit length, which means over $1/a$ atoms. Thus the Fourier coefficients of the potential are

$$\begin{aligned} U_G &= \int_0^1 dx\ U(x) \cos Gx = Aa\sum_s \int_0^1 dx\ \delta(x - sa) \cos Gx \\ &= Aa\sum \cos Gsa = A \ . \end{aligned} \tag{34}$$

We write the central equation with k as the Bloch index. Thus (31) becomes

$$(\lambda_k - \epsilon)C(k) + A\sum_n C(k - 2\pi n/a) = 0 \ , \tag{35}$$

where $\lambda_k \equiv \hbar^2k^2/2m$ and the sum is over all integers n. We want to solve (35)

We define

$$f(k) = \sum_n C(k - 2\pi n/a) \ , \tag{36}$$

so that (35) becomes

$$C(k) = -\frac{(2mA/\hbar^2)f(k)}{k^2 - (2m\epsilon/\hbar^2)} \ . \tag{37}$$

Because the sum (36) is over all coefficients C, we have, for any n,

$$f(k) = f(k - 2\pi n/a) \ . \tag{38}$$

This relation lets us write

$$C(k - 2\pi n/a) = -(2mA/\hbar^2)f(k)[(k - 2\pi n/a)^2 - (2m\epsilon/\hbar^2)]^{-1} \ . \tag{39}$$

We sum both sides over all n to obtain, using (36) and cancelling $f(k)$ from both sides,

$$(\hbar^2/2mA) = -\sum_n \, [(k - 2\pi n/a)^2 - (2m\epsilon/\hbar^2)]^{-1} \ . \tag{40}$$

The sum can be carried out with the help of the standard relation

$$\operatorname{ctn} x = \sum_n \frac{1}{n\pi + x} . \tag{41}$$

After trigonometric manipulations in which we use relations for the difference of two cotangents and the product of two sines, the sum in (40) becomes

$$\frac{a^2 \sin Ka}{2\,\cancel{4}Ka(\cos ka - \cos Ka)} , \tag{42}$$

where we write $K^2 = 2m\epsilon/\hbar^2$ as in (13).

The final result for (40) is

$$\underline{(mAa^2/2\hbar^2)(Ka)^{-1} \sin Ka + \cos Ka = \cos ka} , \tag{43}$$

which agrees with the Kronig-Penney result (21b) with P writte $= 2$ $mAa^2/2\hbar^2$.

Empty Lattice Approximation

Actual band structures are usually exhibited as plots of energy versus wavevector in the first Brillouin zone. When wavevectors happen to be given outside the first zone, they are carried back into the first zone by subtracting a suitable reciprocal lattice vector.

When band energies are approximated fairly well by free electron energies $\epsilon_{\mathbf{k}} = \hbar^2\mathbf{k}^2/2m$, it is advisable to start a calculation by carrying the free electron energies back into the first zone.

We look for a $\mathbf{G}$ such that a $\mathbf{k}'$ in the first zone satisfies

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

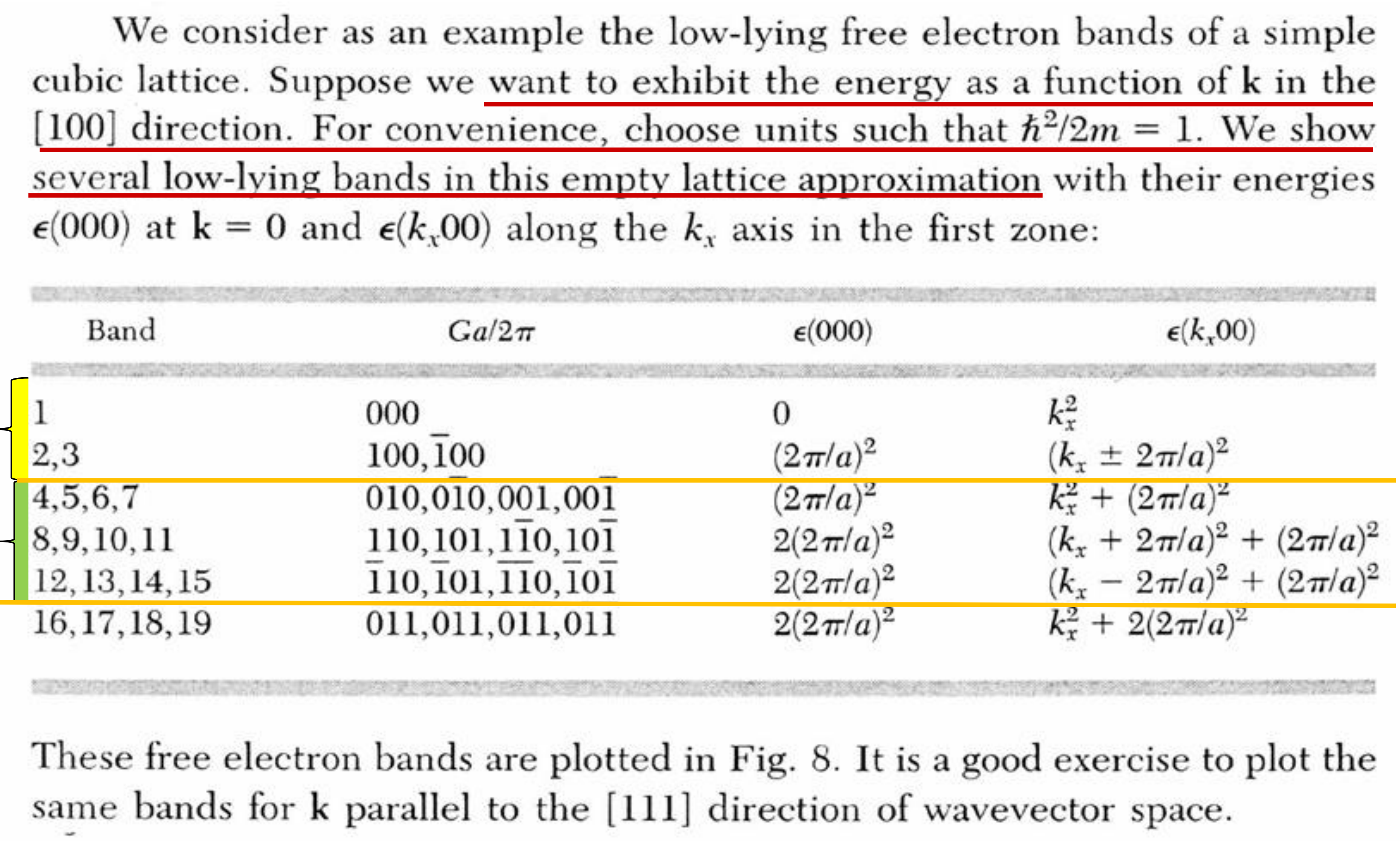
where $\mathbf{k}$ is unrestricted and is the true free electron wavevector in the empty lattice.

If we drop the prime on $\mathbf{k}'$ as unnecessary baggage, the free electron energy can always be written as

$$\begin{aligned}\epsilon(k_x,k_y,k_z) &= (\hbar^2/2m)(\mathbf{k} + \mathbf{G})^2 \\ &= (\hbar^2/2m)\left[(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2\right] \ ,\end{aligned}$$

with $\mathbf{k}$ in the first zone and $\mathbf{G}$ allowed to run over the appropriate reciprocal lattice points.

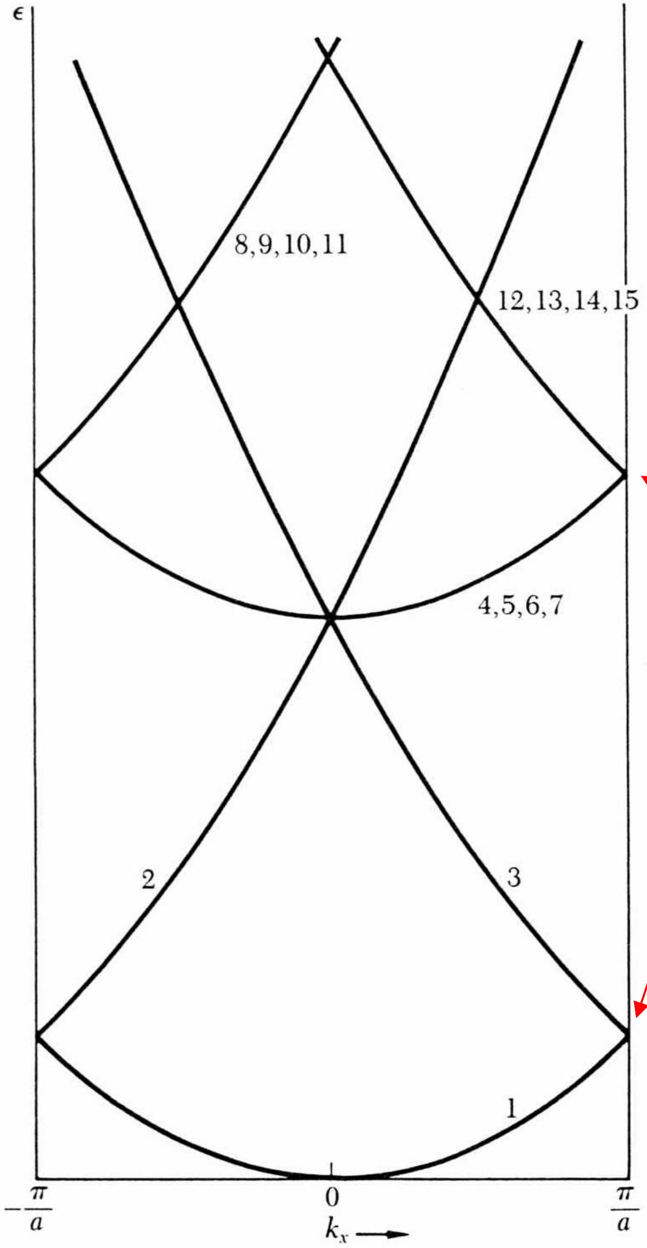
Free electron bands for a simple cubic lattice in [100]



We consider as an example the low-lying free electron bands of a simple cubic lattice. Suppose we want to exhibit the energy as a function of **k** in the [100] direction. For convenience, choose units such that $\hbar^2/2m = 1$. We show several low-lying bands in this empty lattice approximation with their energies $\epsilon(000)$ at $\mathbf{k} = 0$ and $\epsilon(k_x00)$ along the k_x axis in the first zone:

Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x00)$
1	000	0	k_x^2
2,3	$100, \bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	$010, 0\bar{1}0, 001, 00\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	$110, 101, 1\bar{1}0, 10\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10, \bar{1}01, \bar{1}\bar{1}0, \bar{1}0\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
16,17,18,19	011,011,011,011	$2(2\pi/a)^2$	$k_x^2 + 2(2\pi/a)^2$

These free electron bands are plotted in Fig. 8. It is a good exercise to plot the same bands for **k** parallel to the [111] direction of wavevector space.



Reduced zone scheme

Figure 8 Low-lying free electron energy bands of the empty sc lattice, as transformed to the first Brillouin zone and plotted vs. (k_x00). The free electron energy is $\hbar^2(\mathbf{k}+\mathbf{G})^2/2m$, where the $\mathbf{G}$'s are given in the second column of the table. The bold curves are in the first Brillouin zone, with $-\pi/a \leq k_x \leq \pi/a$. Energy bands drawn in this way are said to be in the reduced zone scheme.

Approximate Solution Near a Zone Boundary

We suppose that the Fourier components U_G of the potential energy are small in comparison with the kinetic energy of a free electron at the zone boundary. We first consider a wavevector exactly at the zone boundary at $\frac{1}{2}G$, that is, at π/a. Here

$$k^2 = (\tfrac{1}{2}G)^2 \; ; \qquad (k - G)^2 = (\tfrac{1}{2}G - G)^2 = (\tfrac{1}{2}G)^2 \; ,$$

so that at the zone boundary the kinetic energy of the two component waves $k = \pm\frac{1}{2}G$ are equal.

If $C(\frac{1}{2}G)$ is an important coefficient in the orbital (29) at the zone boundary, then $C(-\frac{1}{2}G)$ is also an important coefficient. This result also follows from the discussion of (5). We retain only those equations in the central equation that contain both coefficients $C(\frac{1}{2}G)$ and $C(-\frac{1}{2}G)$, and neglect all other coefficients.

One equation of (31) becomes, with $k = \frac{1}{2}G$ and $\lambda \equiv \hbar^2(\frac{1}{2}G)^2/2m$,

$$(\lambda - \epsilon)C(\tfrac{1}{2}G) + UC(-\tfrac{1}{2}G) = 0 \; . \tag{44}$$

Another equation of (31) becomes

$$(\lambda - \epsilon)C(-\tfrac{1}{2}G) + UC(\tfrac{1}{2}G) = 0 \; . \tag{45}$$

These two equations have nontrivial solutions for the two coefficients if the energy ϵ satisfies

$$\begin{vmatrix} \lambda - \epsilon & U \\ U & \lambda - \epsilon \end{vmatrix} = 0 \; , \tag{46}$$

whence,

$$(\lambda - \epsilon)^2 = U^2 \ ; \qquad \epsilon = \lambda \pm U = \frac{\hbar^2}{2m}(\tfrac{1}{2}G)^2 \pm U \ . \tag{47}$$

The energy has two roots, one lower than the free electron kinetic energy by U, and one higher by U. Thus the potential energy $2U \cos Gx$ has created an energy gap $2U$ at the zone boundary.

The ratio of the C's may be found from either (44) or (45):

$$\frac{C(-\tfrac{1}{2}G)}{C(\tfrac{1}{2}G)} = \frac{\epsilon - \lambda}{U} = \pm 1 \ , \tag{48}$$

where the last step uses (47). Thus the Fourier expansion of $\psi(x)$ at the zone boundary has the two solutions

$$\psi(x) = \exp(iGx/2) \pm \exp(-iGx/2) \ .$$

These orbitals are identical to (5).

One solution gives the wavefunction at the bottom of the energy gap; the other gives the wavefunction at the top of the gap. Which solution has the lower energy depends on the sign of U.

We now solve for orbitals with wavevector k near the zone boundary $\frac{1}{2}G$. We use the same two-component approximation, now with a wavefunction of the form

for general k near ½ G

$$\psi(x) = C(k)\, e^{ikx} + C(k-G)\, e^{i(k-G)x} \quad . \tag{49}$$

As directed by the central equation (31), we solve the pair of equations

$$(\lambda_k - \epsilon)C(k) + UC(k-G) = 0 \ ;$$
$$(\lambda_{k-G} - \epsilon)C(k-G) + UC(k) = 0 \ ,$$

with λ_k defined as $\hbar^2k^2/2m$. These equations have a solution if the energy ϵ satisfies

$$\begin{vmatrix} \lambda_k - \epsilon & U \\ U & \lambda_{k-G} - \epsilon \end{vmatrix} = 0 \ ,$$

whence $\epsilon^2 - \epsilon(\lambda_{k-G} + \lambda_k) + \lambda_{k-G}\lambda_k - U^2 = 0$.

The energy has two roots:

$$\epsilon = \tfrac{1}{2}(\lambda_{k-G} + \lambda_k) \pm [\tfrac{1}{4}(\lambda_{k-G} - \lambda_k)^2 + U^2]^{1/2} \ , \tag{50}$$

and each root describes an energy band, plotted in Fig. 9.

It is convenient to expand the energy in terms of a quantity $\tilde{K}$ (the mark over the $\tilde{K}$ is called a tilde), which measures the difference $\tilde{K} \equiv k - \frac{1}{2}G$ in wavevector between k and the zone boundary:

$$\begin{aligned} \epsilon_{\tilde{K}} &= (\hbar^2/2m)(\tfrac{1}{4}G^2 + \tilde{K}^2) \pm [4\lambda(\hbar^2\tilde{K}^2/2m) + U^2]^{1/2} \\ &\simeq (\hbar^2/2m)(\tfrac{1}{4}G^2 + \tilde{K}^2) \pm U[1 + 2(\lambda/U^2)(\hbar^2\tilde{K}^2/2m)] \ , \end{aligned} \tag{51}$$

in the region $\hbar^2 G\tilde{K}/2m \ll |U|$. Here $\lambda = (\hbar^2/2m)(\frac{1}{2}G)^2$ as before.

Writing the two zone boundary roots of (47) as $\epsilon(\pm)$, we may write (51) as

$$\boxed{\epsilon_{\tilde{K}}(\pm) = \epsilon(\pm) + \frac{\hbar^2\tilde{K}^2}{2m}\left(1 \pm \frac{2\lambda}{U}\right) .} \tag{52}$$

These are the roots for the energy when the wavevector is very close to the zone boundary at $\frac{1}{2}G$.

ϵ_K is symmetric about the 1/2 G zone boundary

Note the quadratic dependence of the energy on the wavevector $\tilde{K}$. For U negative, the solution $\epsilon(-)$ corresponds to the upper of the two bands, and $\epsilon(+)$ to the lower of the two bands. The two C’s are plotted in Fig. 10.

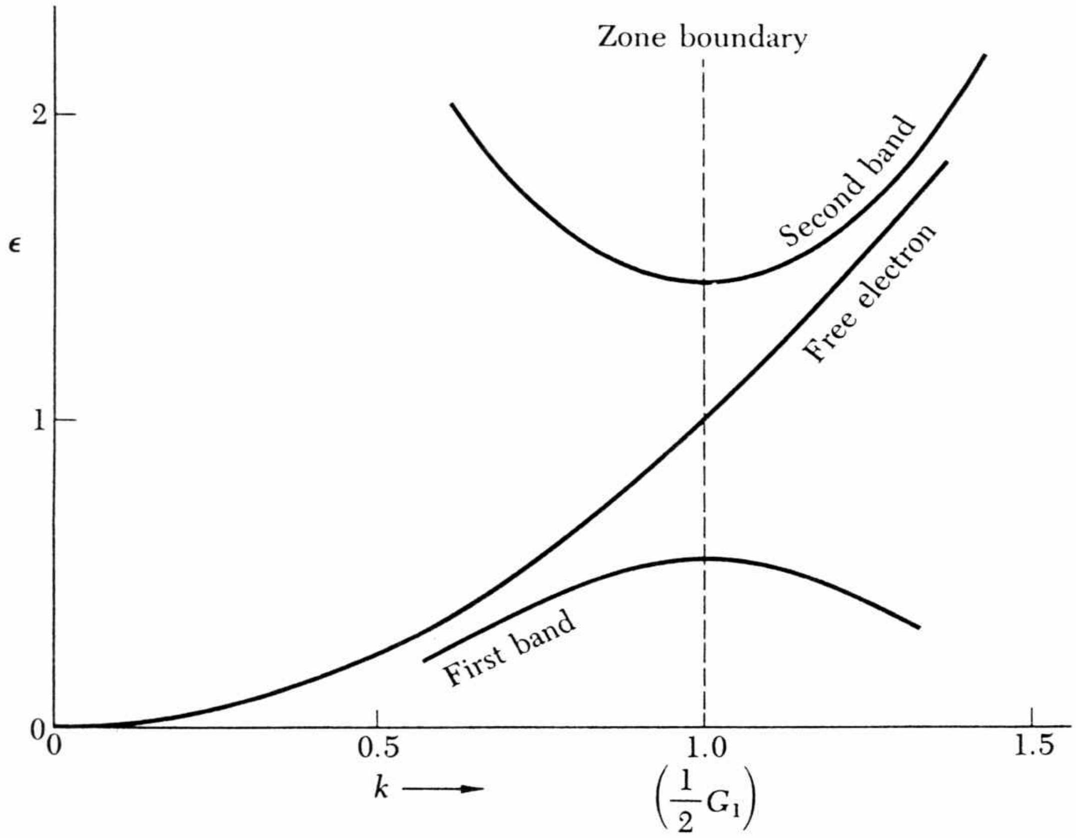


Figure 9 Solutions of (50) in the periodic zone scheme, in the region near a boundary of the first Brillouin zone. The units are such that $U = -0.45$; $G = 2$, and $\hbar^2/m = 1$. The free electron curve is drawn for comparison. The energy gap at the zone boundary is 0.90. The value of U has deliberately been chosen large for this illustration, too large for the two-term approximation to be accurate.

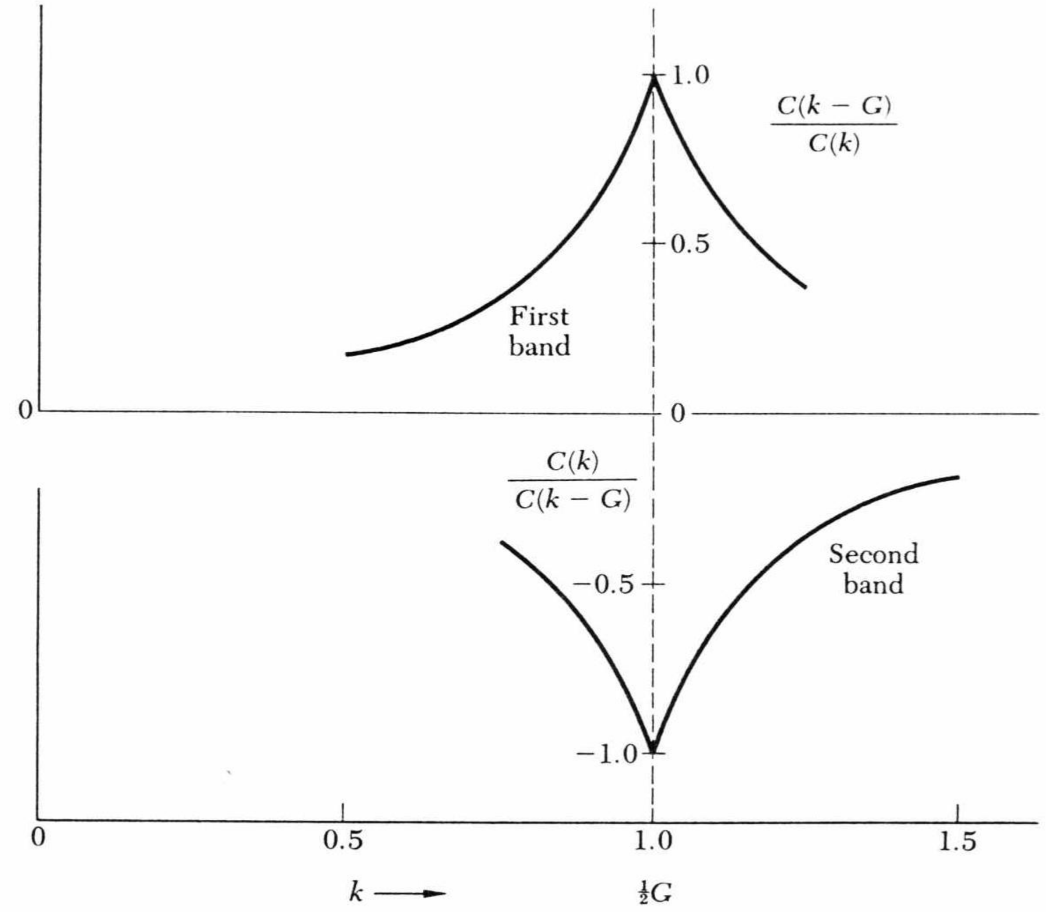


Figure 10 Ratio of the coefficients in $\psi(x) = C(k)\exp(ikx) + C(k-G)\exp[i(k-G)x]$ as calculated near the boundary of the first Brillouin zone. One component dominates as we move away from the boundary.

NUMBER OF ORBITALS IN A BAND

Consider a linear crystal constructed of an even number N of primitive cells of lattice constant a. In order to count states we apply periodic boundary conditions to the wavefunctions over the length of the crystal. The allowed values of the electron wavevector k in the first Brillouin zone are given by (2):

L = N a

$$k = 0 \; ; \quad \pm\frac{2\pi}{L} \; ; \quad \pm\frac{4\pi}{L} \; ; \quad \ldots \; ; \quad \frac{N\pi}{L} \qquad \pm(N/2)\cdot 2\pi/L \qquad (53)$$

We cut the series off at $N\pi/L = \pi/a$, for this is the zone boundary. The point $-N\pi/L = -\pi/a$ is not to be counted as an independent point because it is connected by a reciprocal lattice vector with π/a. The total number of points is exactly N, the number of primitive cells. *“ # of K is 2N, counting spins x 2 ”*

Each primitive cell contributes exactly one independent value of k to each energy band. This result carries over into three dimensions. With account taken of the two independent orientations of the electron spin, **there are $2N$ independent orbitals in each energy band.** If there is a single atom of valence one in each primitive cell, the band can be half filled with electrons. If each atom contributes two valence electrons to the band, the band can be exactly filled. If there are two atoms of valence one in each primitive cell, the band can also be exactly filled.

Metals and Insulators

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.

A crystal can be an insulator only if the number of valence electrons in a primitive cell of the crystal is an even integer. (An exception must be made for electrons in tightly bound inner shells which cannot be treated by band theory.) If a crystal has an even number of valence electrons per primitive cell, it is necessary to consider whether or not 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. 11).

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.

Insulator Metal or semi-metal Metal

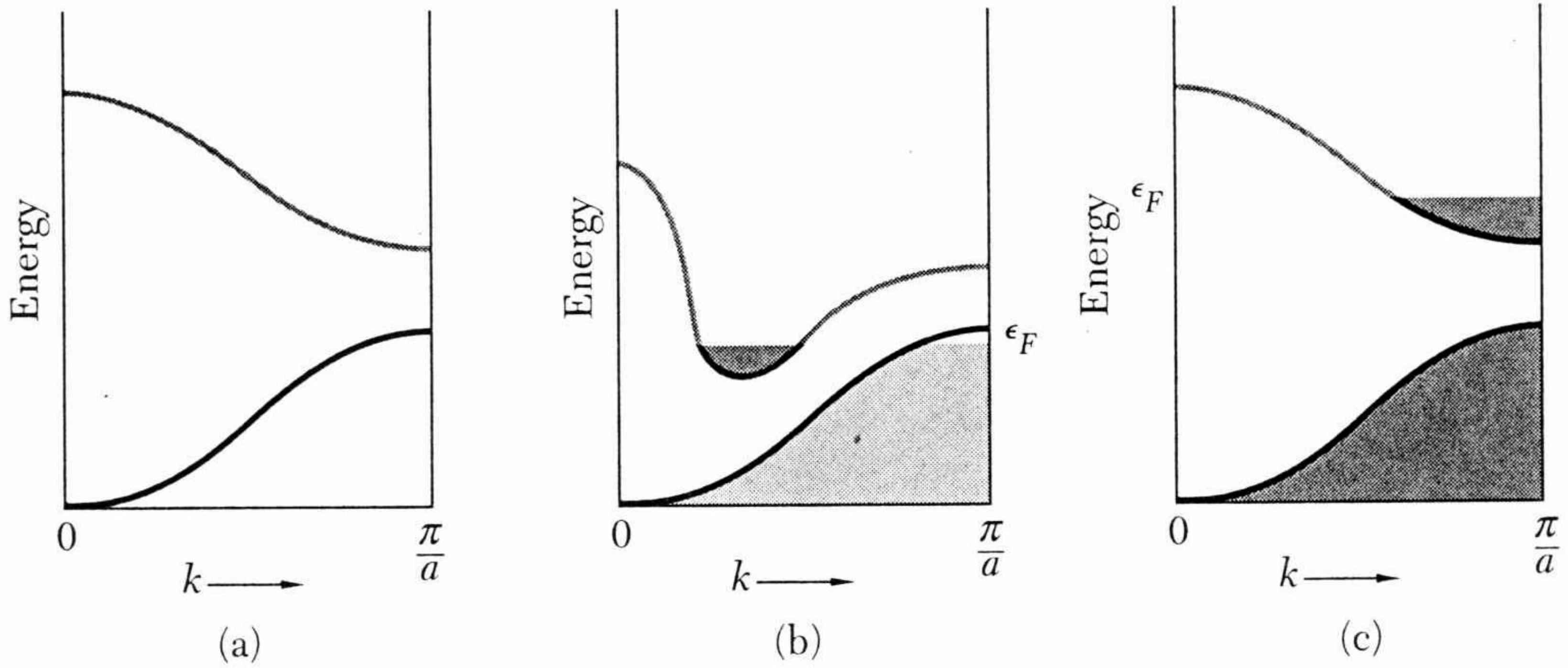


Figure 11 Occupied states and band structures giving (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration. In (b) the overlap need not occur along the same directions in the Brillouin zone. If the overlap is small, with relatively few states involved, we speak of a semimetal.