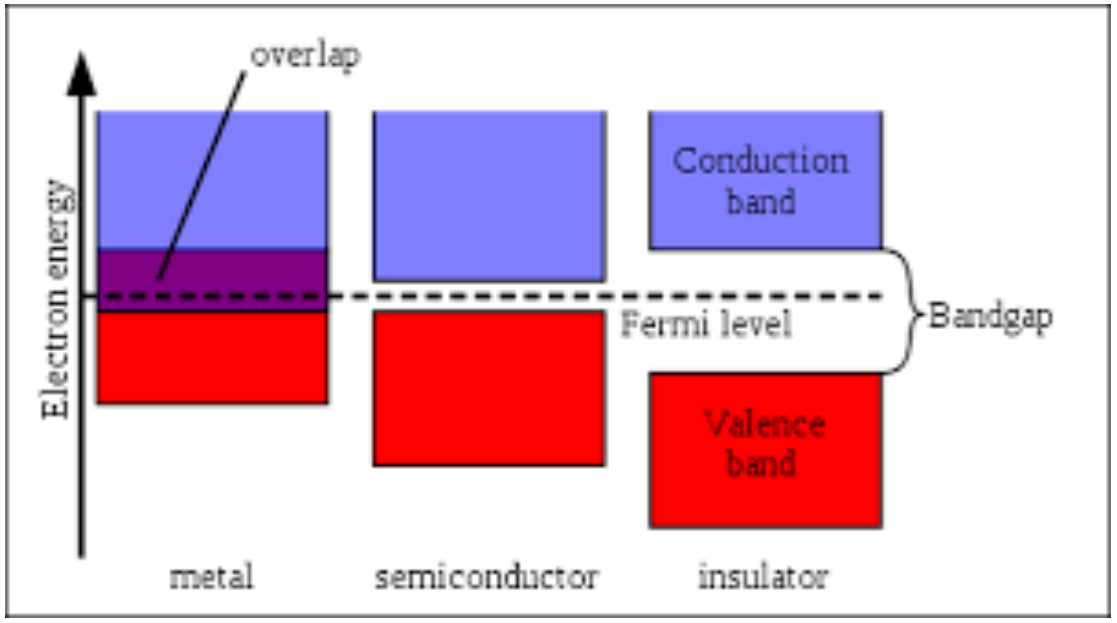
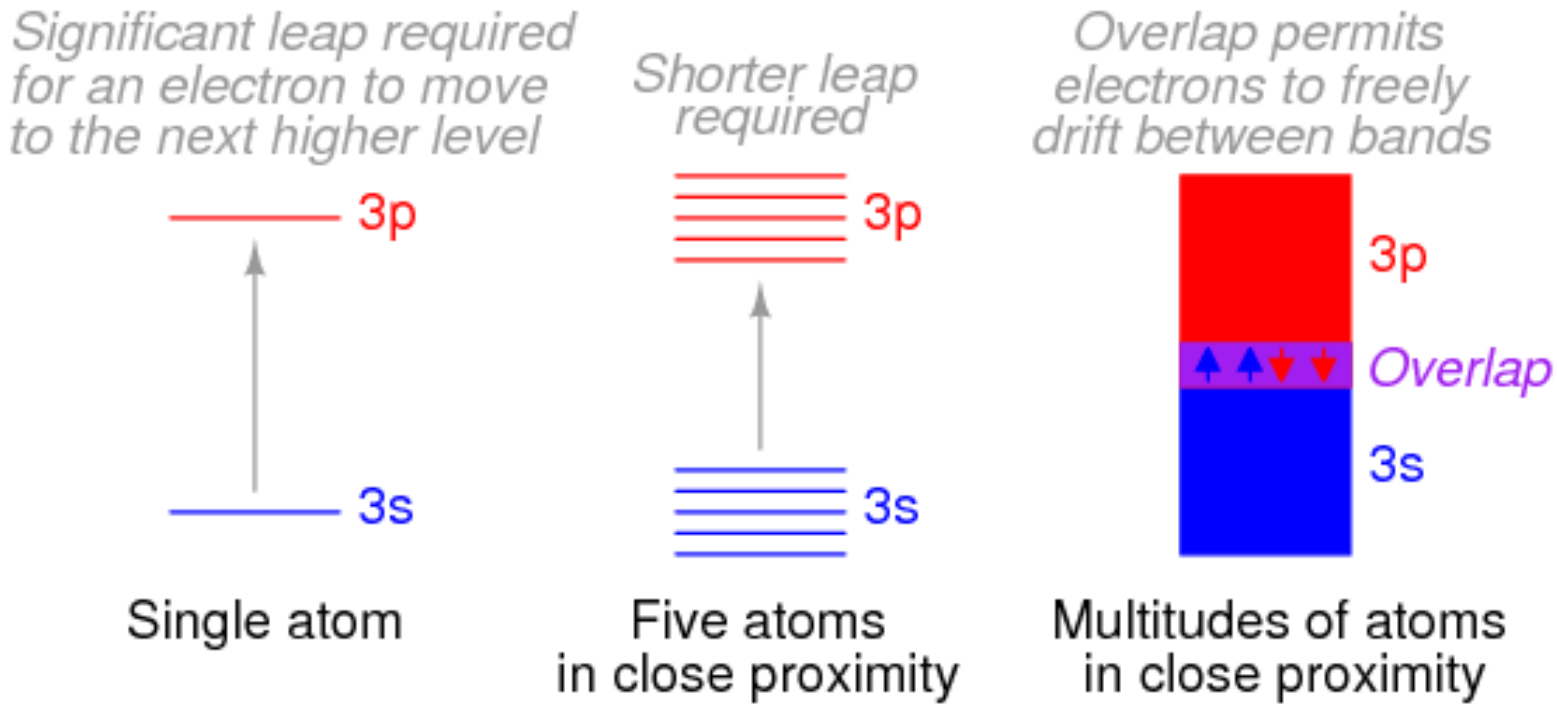
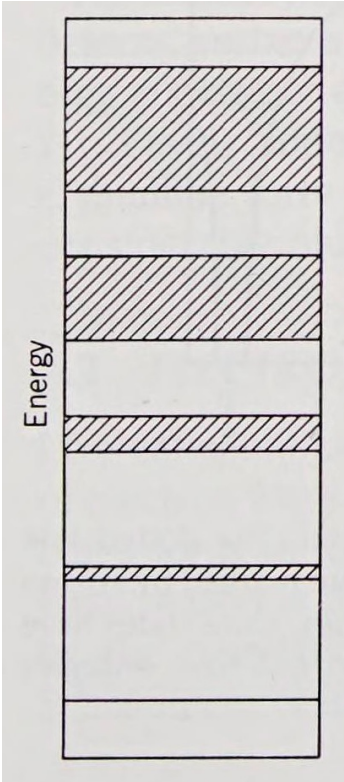
8. Estados electrónicos



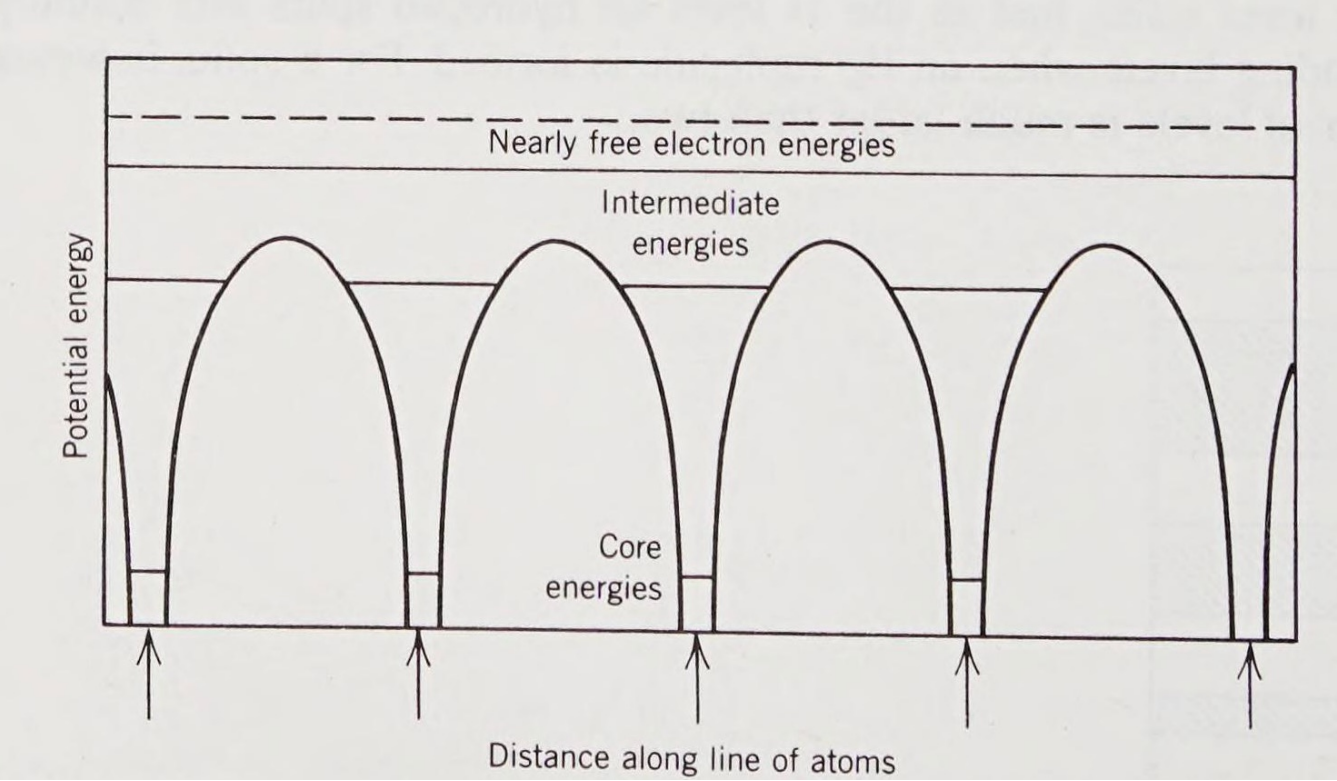
Overlap of atomic states



Energy bands



Electronic energy along a line of atoms

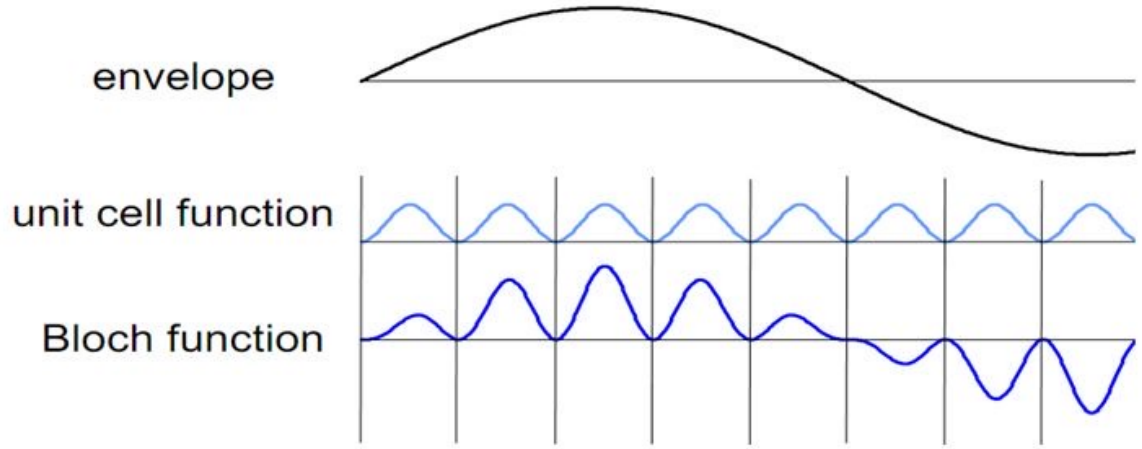


Bloch's theorem

we can rewrite the Bloch theorem equation $\psi(x+a) = \exp(ika)\psi(x)$ alternative form

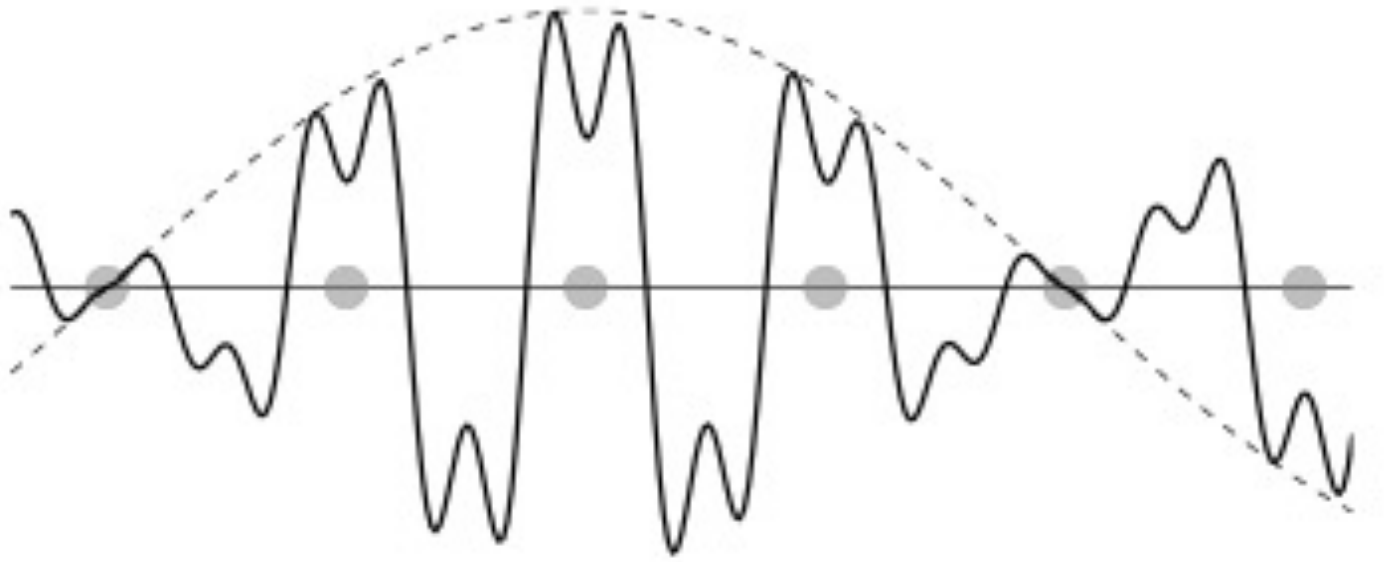
$$\psi(x) = u(x)\exp(ikx)$$

where u(x) is periodic with the lattice periodicity.

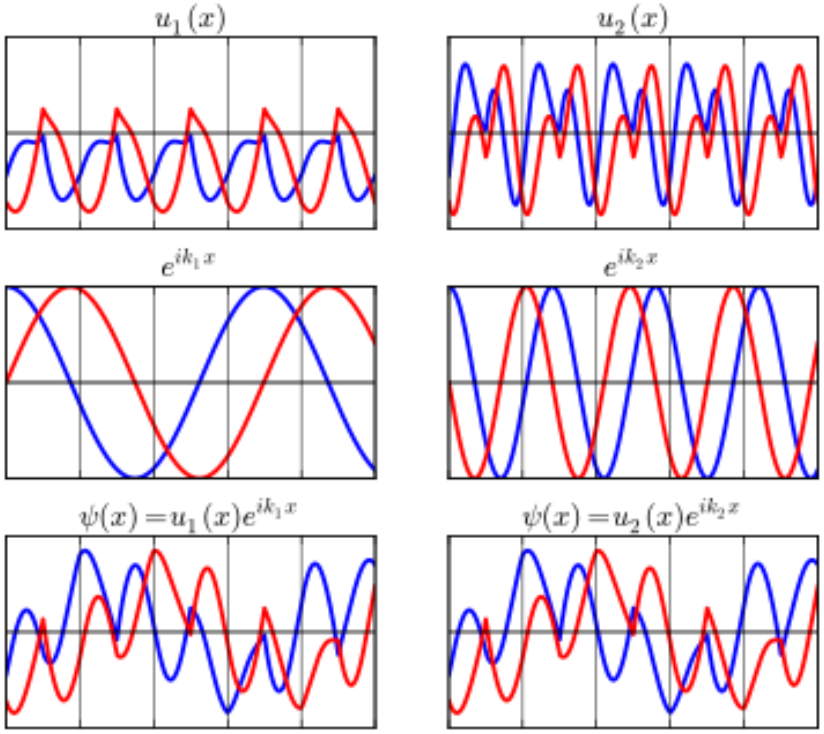


Concept of the Bloch functions. We can think of the exp(ikx) as being an example of an "envelope" function that multiplies the unit cell function u(x)

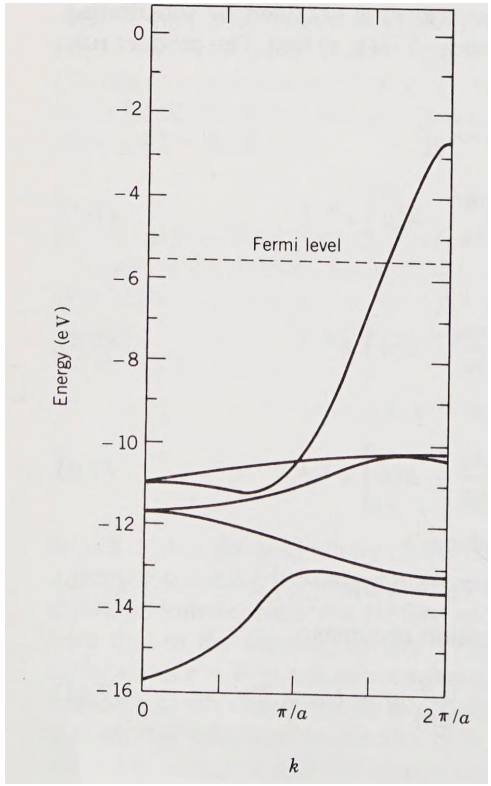
Bloch function (real part)



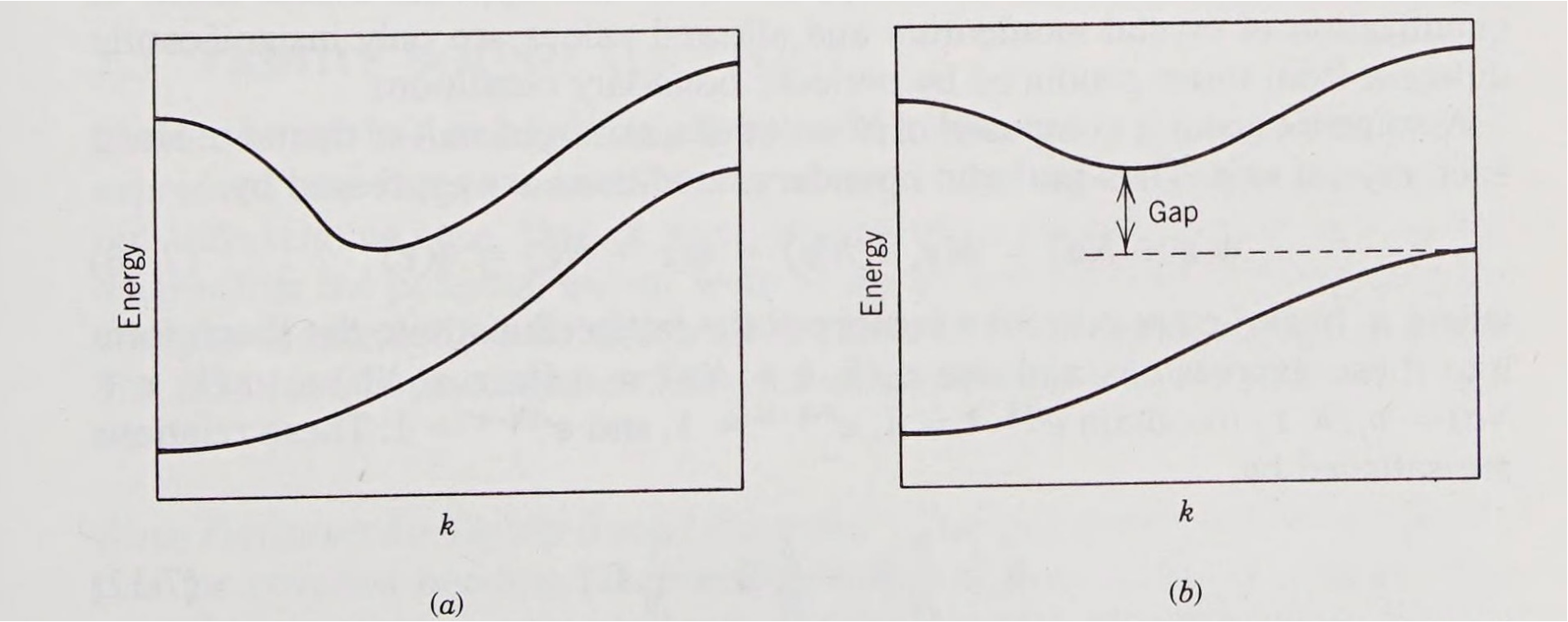
Bloch function (bue real, red imaginary) written in two different ways with (k_1-k_2) a reciprocal lattice vector



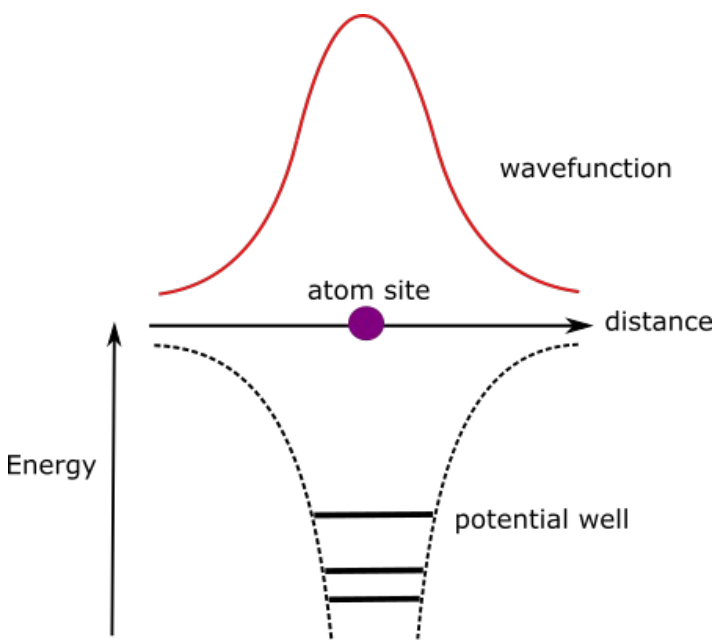
Bands of copper in the 100 direction

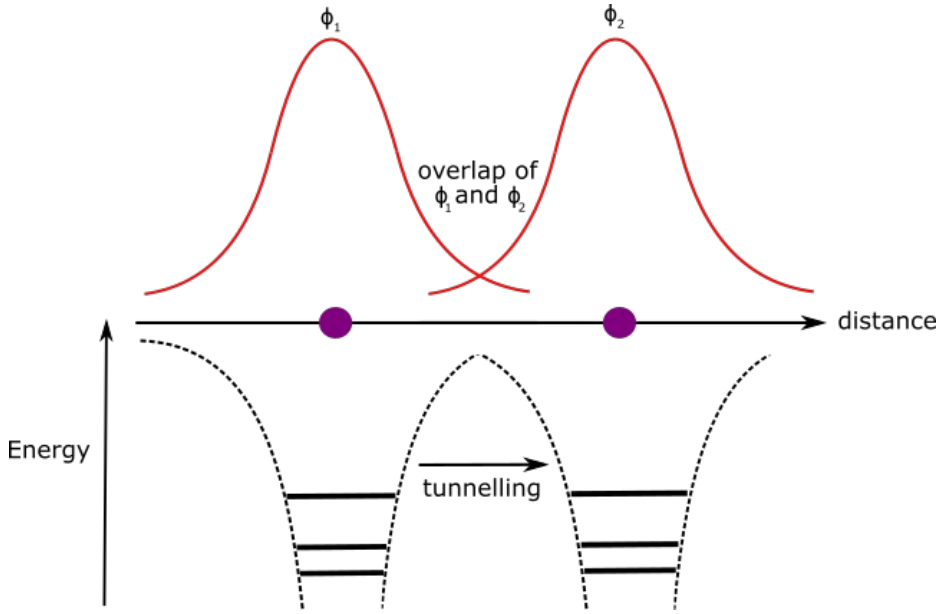


Band overlap

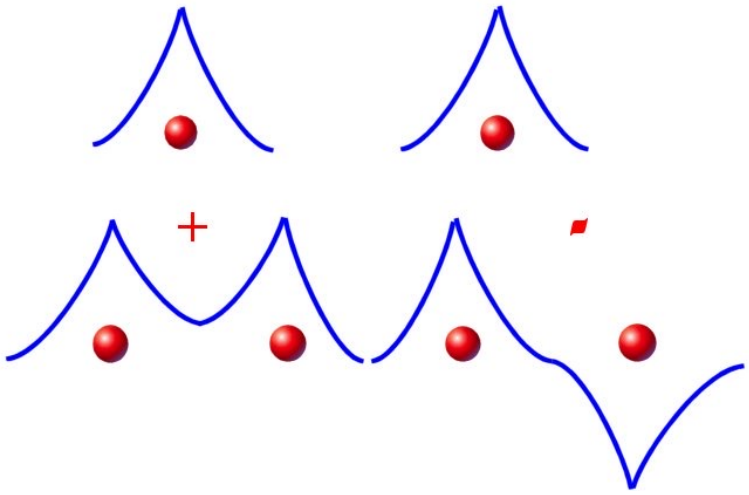


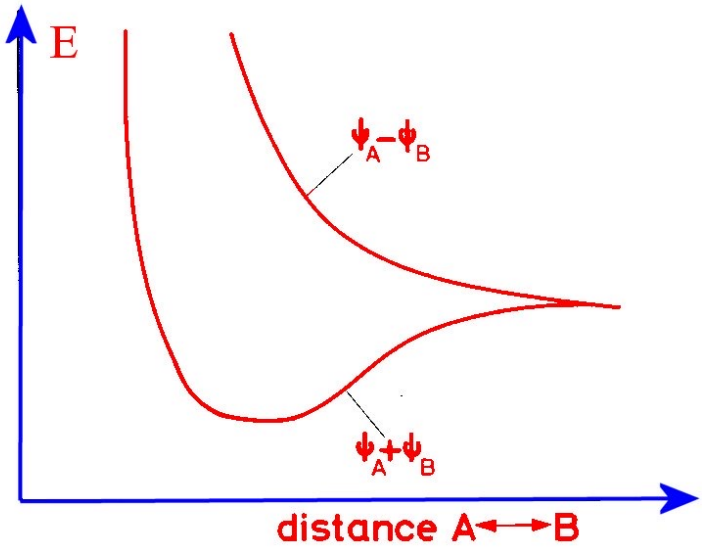
Recap: Covalent Bonding



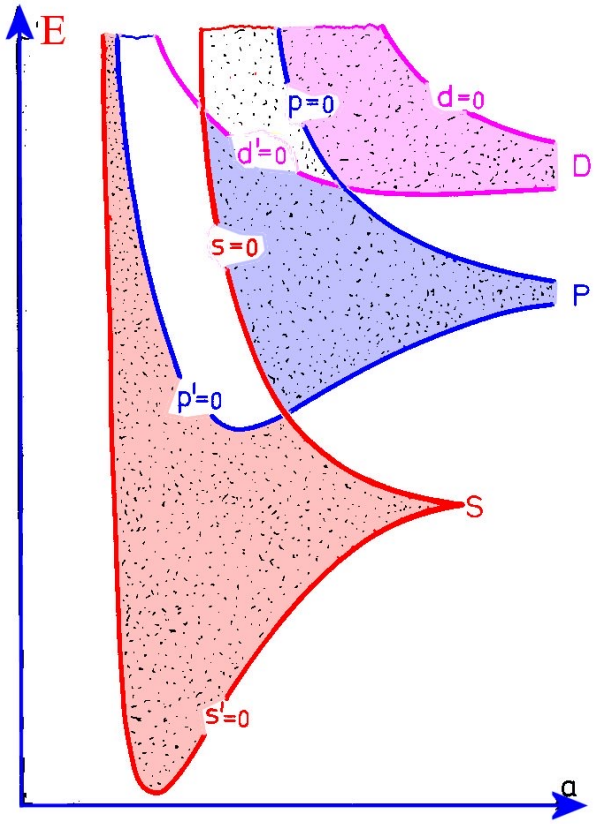


Bonding and anti-bonding states & energies

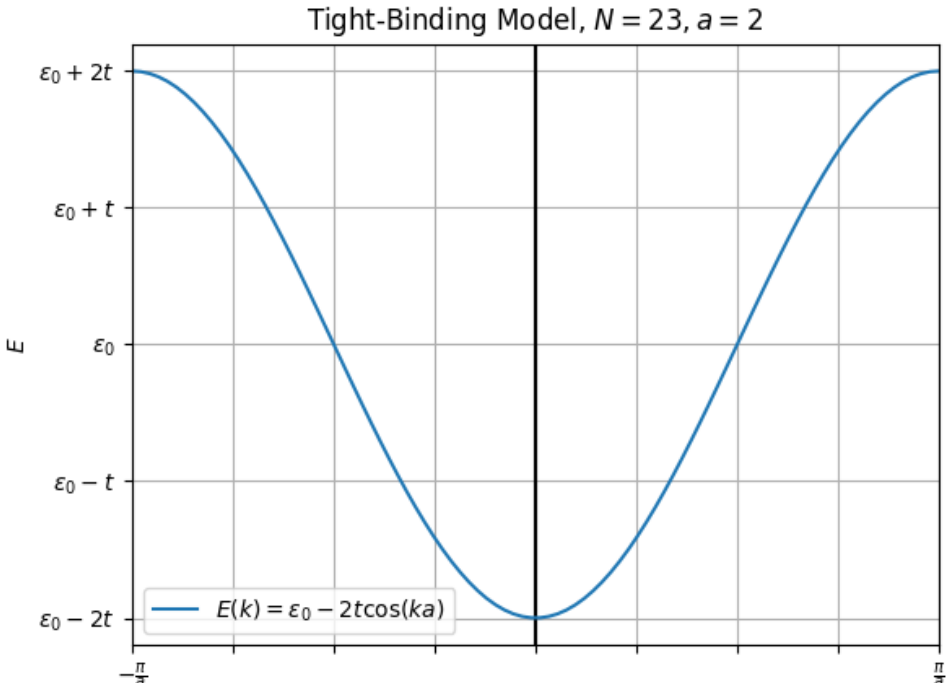


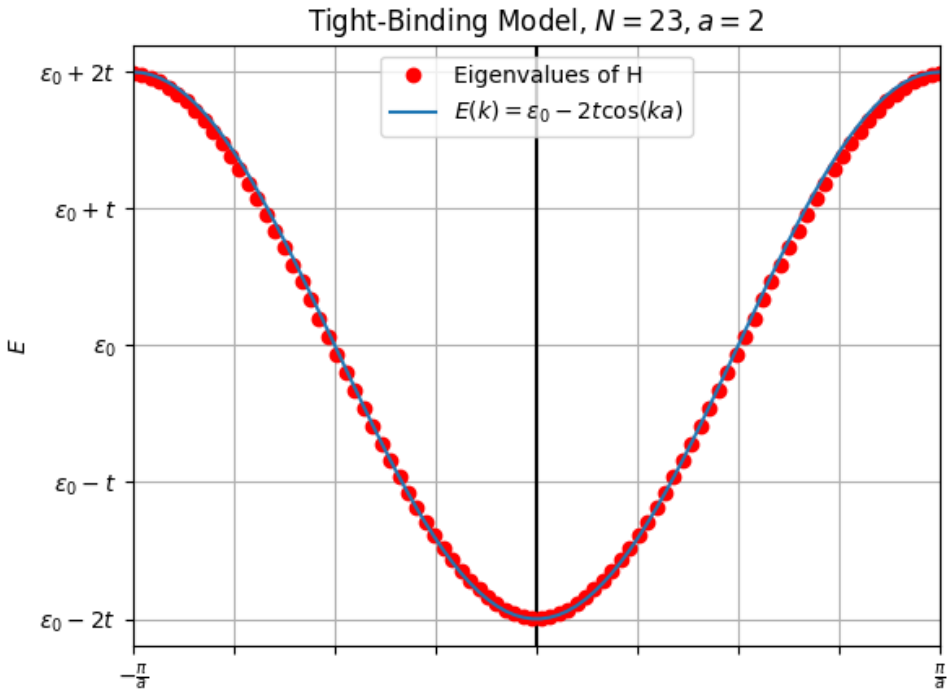


Many atoms: bands



Tight binding model in 1d





Simon, S. H. (2013). *The Oxford solid state basics*. Oxford, UK: Oxford Univ. Press.

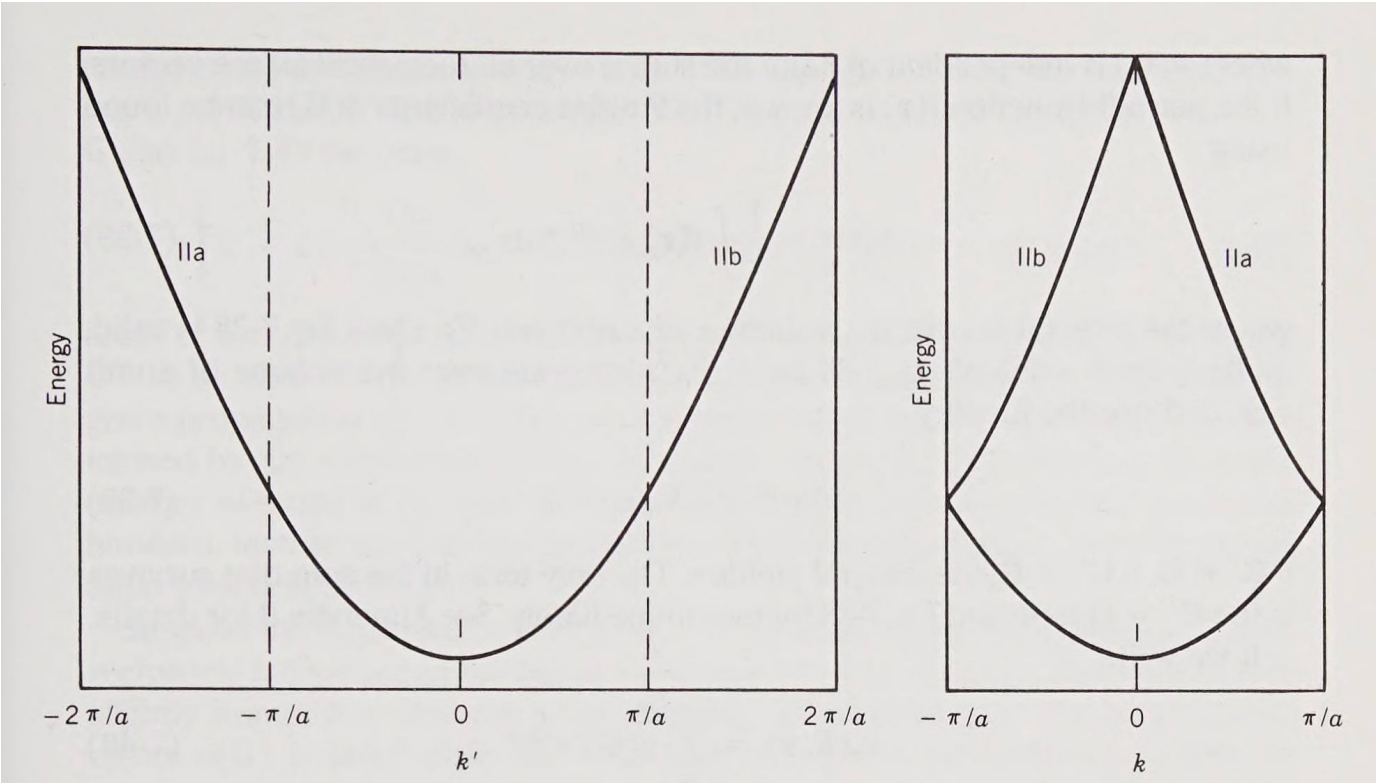
EXAMPLE 7-2 (a) Find an expression for the energies of a tight binding band for a crystal with a simple cubic lattice and a basis of one atom. Assume the atomic orbital $\chi(\mathbf{r})$ is real and spherically symmetric and take $A(\mathbf{R})$ to be zero except for nearest neighbors. (b) Find expressions for the minimum and maximum energies in the band.

SOLUTION (a) Take the unit cell to be a cube with edge a and place a Cartesian coordinate system with axes parallel to cube edges. Each atom has nearest neighbors at $\pm a\hat{\mathbf{x}}$, $\pm a\hat{\mathbf{y}}$, and $\pm a\hat{\mathbf{z}}$. Since χ is spherically symmetric, the integral for $A(\mathbf{R})$ has the same value for all nearest neighbor pairs. If $A = \int \chi^*(\mathbf{r})[U_a(\mathbf{r} - \mathbf{R}) - U(\mathbf{r})]\chi(\mathbf{r} - \mathbf{R})\, d\tau$ for nearest neighbors, then

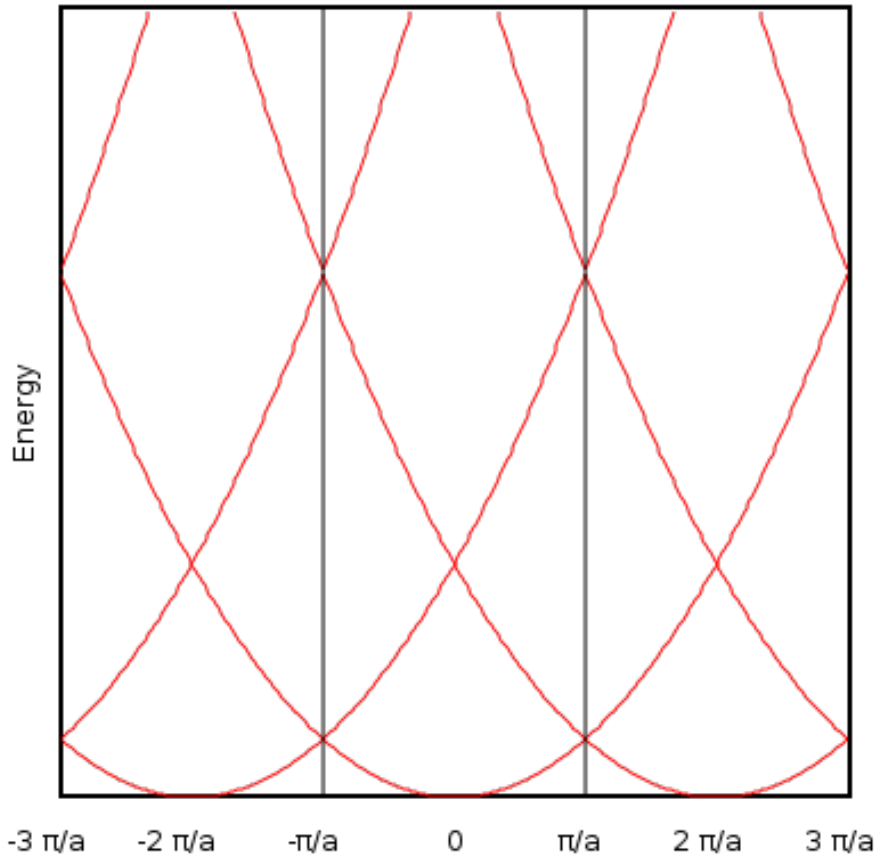
$$\begin{aligned} \mathrm{E}(\mathbf{k}) &= E_a - \alpha \\ &\quad - A[e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} + e^{ik_z a} + e^{-ik_z a}] \\ &= E_a - \alpha - 2A[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)] \,. \end{aligned}$$

(b) Since the Brillouin zone is a cube with edge $2\pi/a$, k_x, k_y, and k_z each range from $-\pi/a$ to $+\pi/a$. If A is positive the minimum energy occurs for $\mathbf{k} = 0$ and is $E_a - \alpha - 6A$. The maximum energy occurs for $k_x = k_y = k_z = \pi/a$ and is $E_a - \alpha + 6A$. The band width is $12A$. ■

Free electron bands in 1d



Free electron bands in 1d



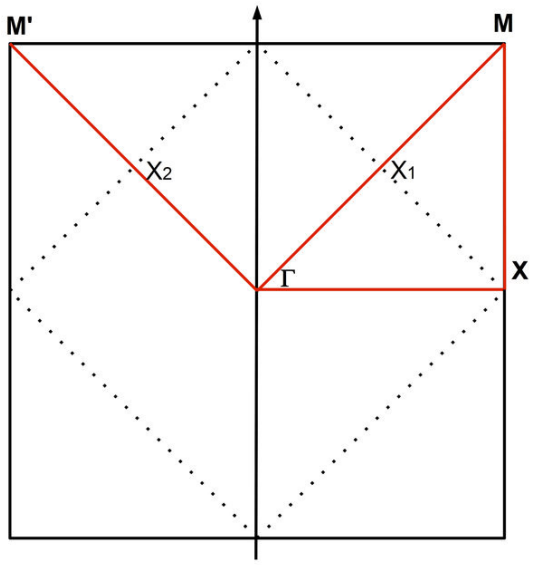
EXAMPLE 7-3 A certain simple cubic crystal has cube edge $a = 5.7$ Å. Calculate the four lowest free electron energies if the wave vector $\mathbf{k}$ in the reduced zone scheme has magnitude $\pi/2a$ and is normal to a cube face.

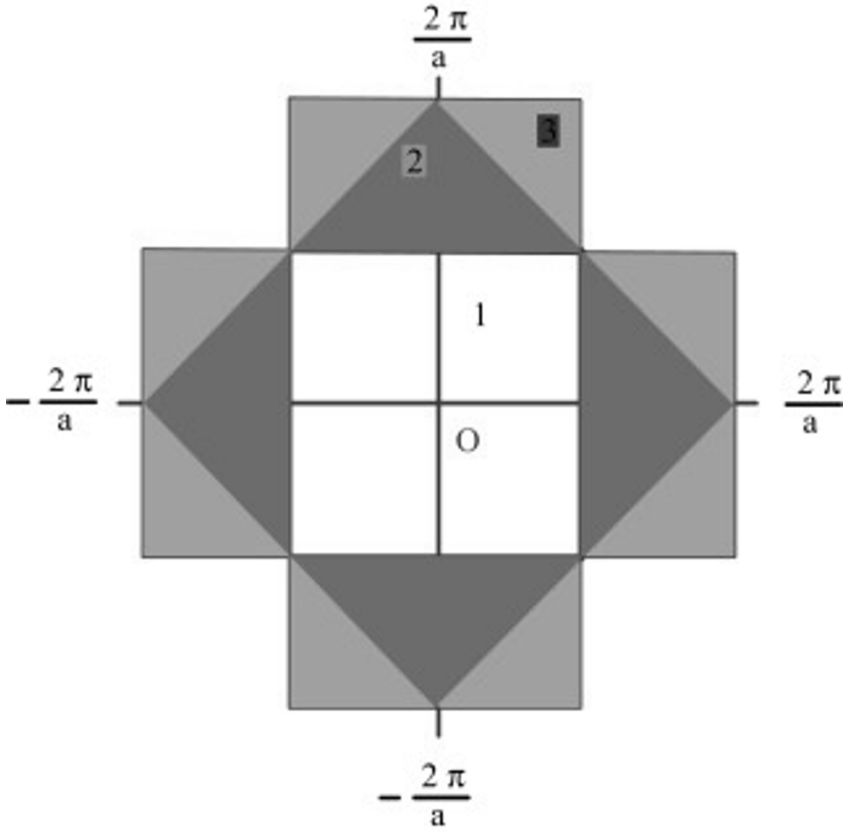
SOLUTION Orient a Cartesian coordinate system with its axes parallel to cube edges and take $\mathbf{k} = (\pi/2a)\hat{\mathbf{x}}$. Reciprocal lattice vectors have the form $\mathbf{G} = h(2\pi/a)\hat{\mathbf{x}} + k(2\pi/a)\hat{\mathbf{y}} + \ell(2\pi/a)\hat{\mathbf{z}}$ so, for $U_0 = 0$, the energy levels are given by

$$E(\mathbf{k}) = \frac{\hbar^2}{2m}\left[\left(\frac{\pi}{2a} + \frac{2\pi h}{a}\right)^2 + \left(\frac{2\pi k}{a}\right)^2 + \left(\frac{2\pi \ell}{a}\right)^2\right]$$
$$= \frac{2\hbar^2\pi^2}{ma^2}\left[\left(\frac{1}{4} + h\right)^2 + k^2 + \ell^2\right].$$

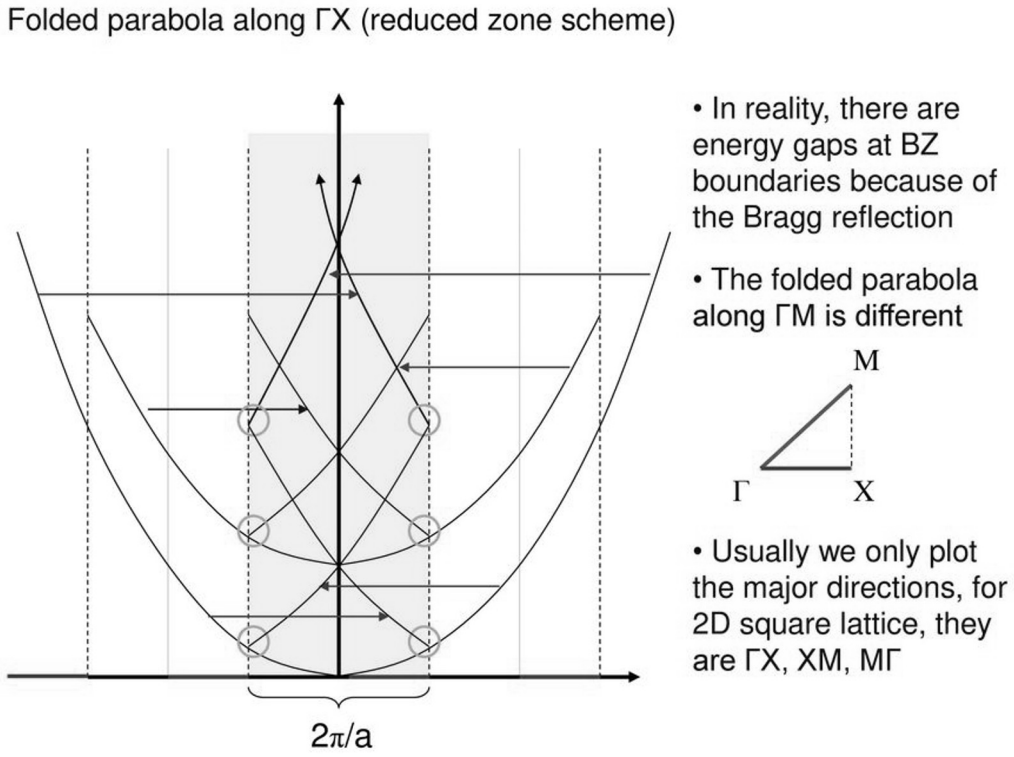
Select integer values for h, k, and ℓ to obtain the lowest four values. For (000), $E = 4.59 \times 10^{-20}$ J (0.287 eV); for $(\bar{1}00)$, $E = 4.14 \times 10^{-19}$ J (2.59 eV); for (010), $E = 7.81 \times 10^{-19}$ J (4.88 eV); and for (100), $E = 1.15 \times 10^{-18}$ J (7.18 eV). ■

Brillouin zones in 2d





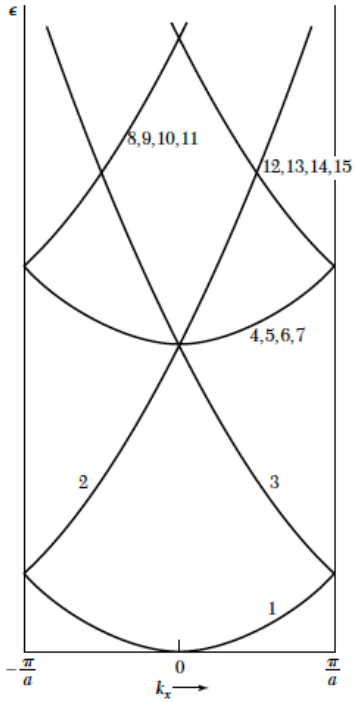
Free electron bands of the square lattice (2d)



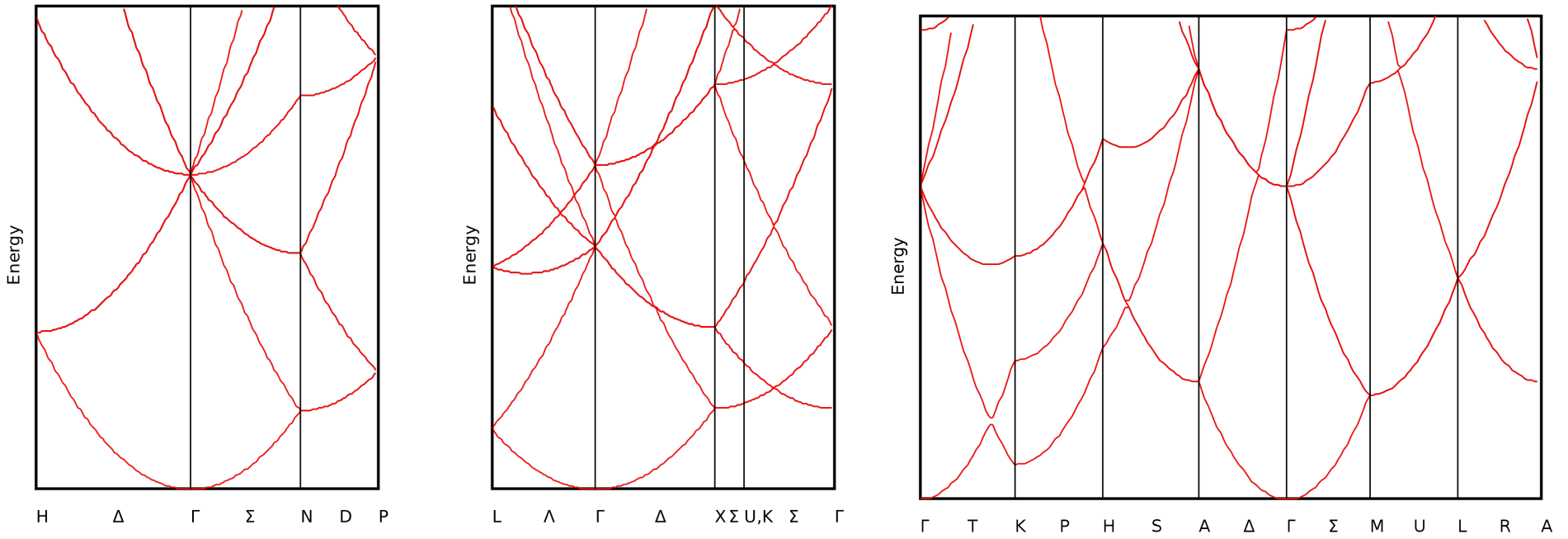
Free electron bands of sc lattice in the [100] direction

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

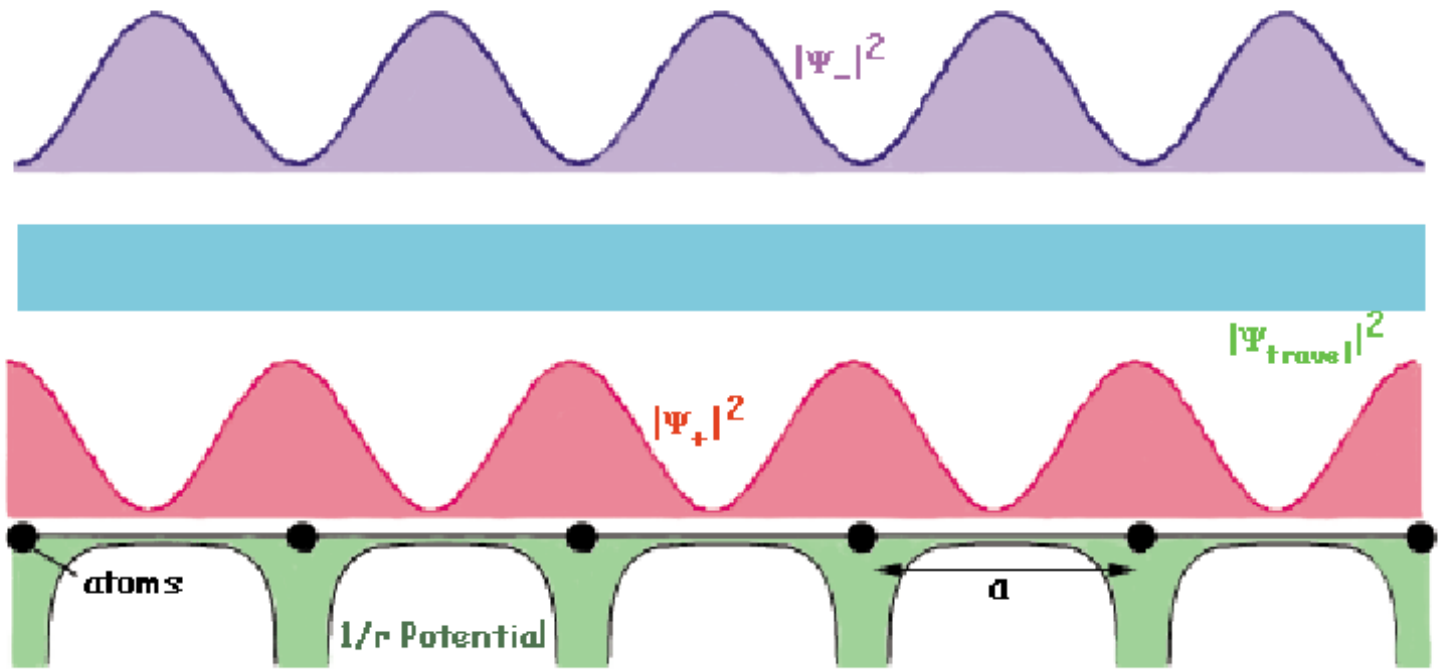
Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x 00)$
1	000	0	k_x^2
2,3	$100,\bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	$010,0\bar{1}0,001,00\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	$110,101,1\bar{1}0,10\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10,\bar{1}01,\bar{1}\bar{1}0,\bar{1}0\bar{1}$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



Free electron bands for bcc, fcc and hexagonal closed packed (empty lattice)



Bragg reflection of free electrons



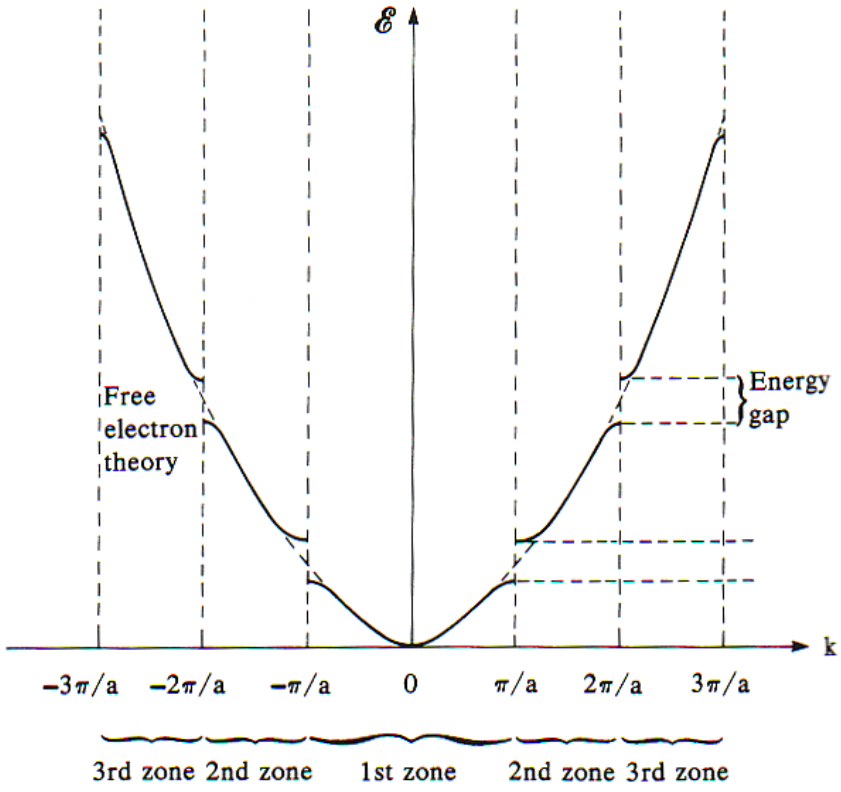
$$e^{ikx} - e^{-ikx}$$

$$\sim \sin(kx)$$

$$e^{ikx} + e^{-ikx}$$

$$\sim \cos(kx)$$

Band gaps of nearly free electrons in 1d



Nearly free electron bands in 1d

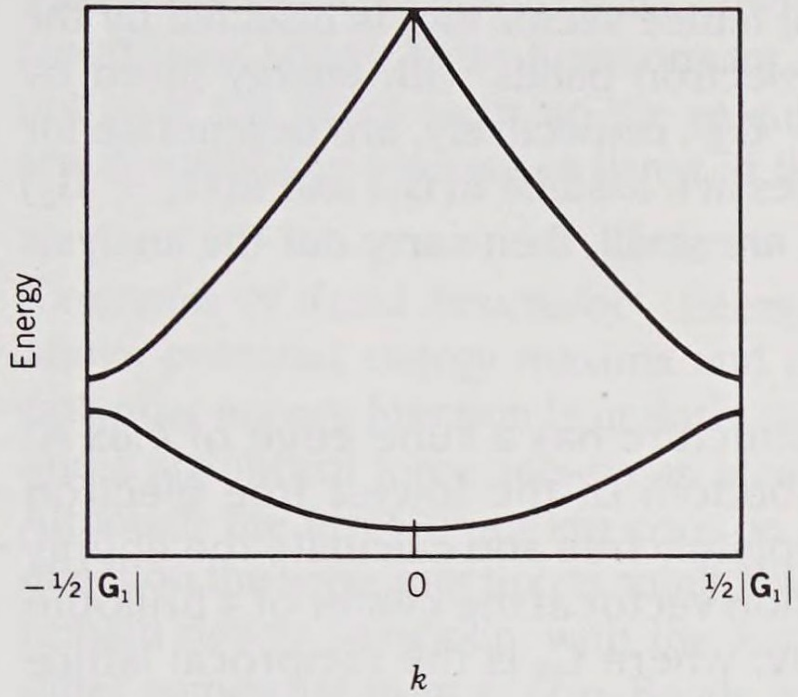
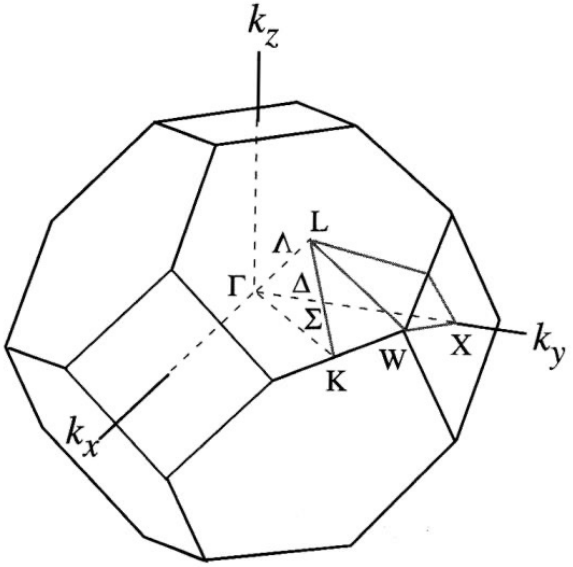


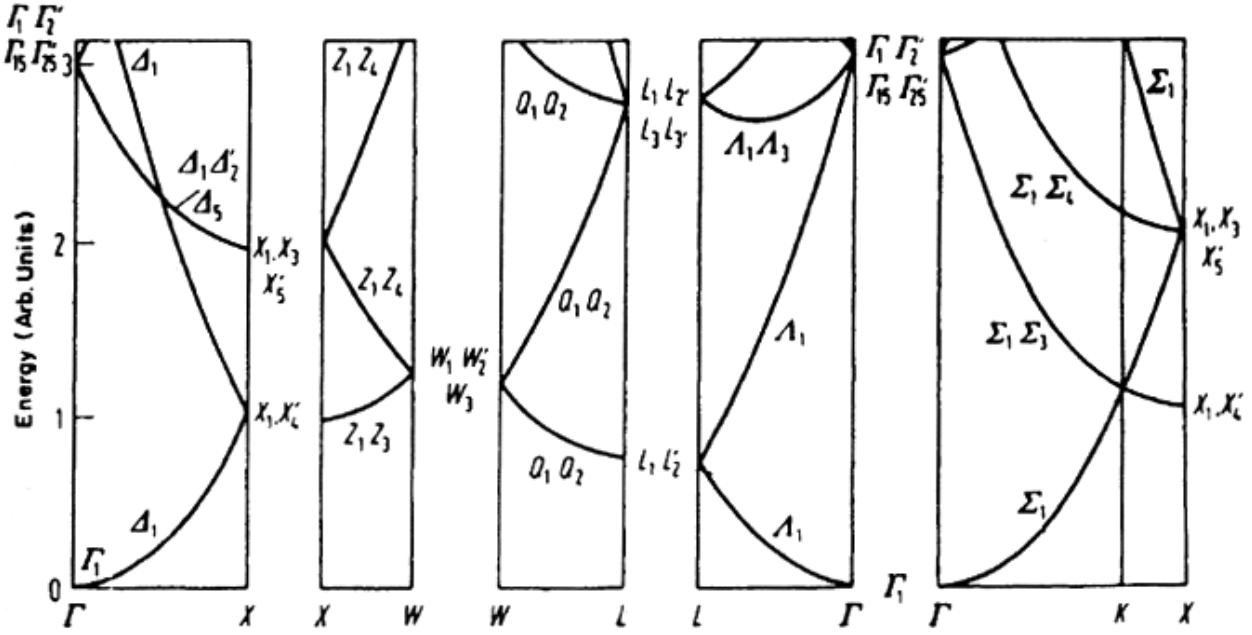
FIGURE 7-7 Energy as a function of propagation vector magnitude for nearly free electrons. The propagation vector is taken to be parallel to reciprocal lattice vector $\mathbf{G}_1$, which is bisected by a Brillouin zone boundary. The curves are similar to those of Fig. 7-6*b* but gaps occur at $\mathbf{k} = \pm\frac{1}{2}\mathbf{G}_1$. The gap width depends on the Fourier component $U(\mathbf{G}_1)$ of the potential energy function.

EXAMPLE 7-4 A certain simple cubic structure has a cube edge of 4.85 Å. Take the zero of energy to be at the bottom of the lowest free electron band. (a) Assume the electrons are completely free and calculate the energy of the lowest energy state with propagation vector at the center of a Brillouin zone face. (b) Suppose $U(\mathbf{G}_1) = 0.24$ eV, where $\mathbf{G}_1$ is the reciprocal lattice vector perpendicular to the Brillouin zone face of part a. Calculate the energy of the two lowest nearly free electron states with the propagation vector used in part a.

SOLUTION (a) At the zone face center $k = \pi/a$ and $E = \hbar^2k^2/2m = (1.05 \times 10^{-34})^2(\pi/4.85 \times 10^{-10})^2/(2 \times 9.11 \times 10^{-31}) = 2.54 \times 10^{-19}$ J (1.59 eV). (b) There are now two distinct levels, one $|U(\mathbf{G}_1)|$ below the free electron level, at 1.35 eV, and one $|U(\mathbf{G}_1)|$ above the free electron level, at 1.83 eV. ■

Free electron bands in 3d: Al





Nearly free electron bands in 3d: Al

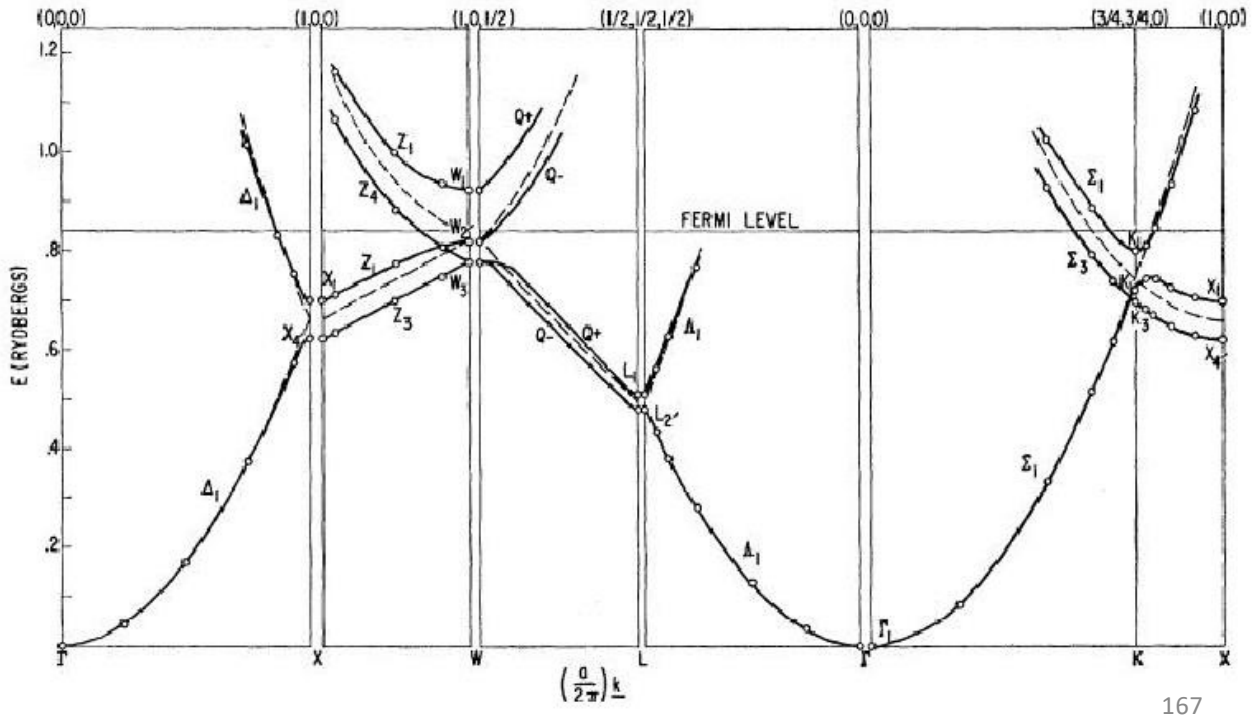
Γ- point: (0,0,0)

X- point: $\frac{2\pi}{a}$ (1,0,0)

L- point: $\frac{\pi}{a}$ (1,1,1)

K- point: $\frac{2\pi}{a}\left(\frac{3}{4},\frac{3}{4},0\right)$

W- point: $\frac{2\pi}{a}\left(1,\frac{1}{2},0\right)$



Bands of potassium in 3 directions

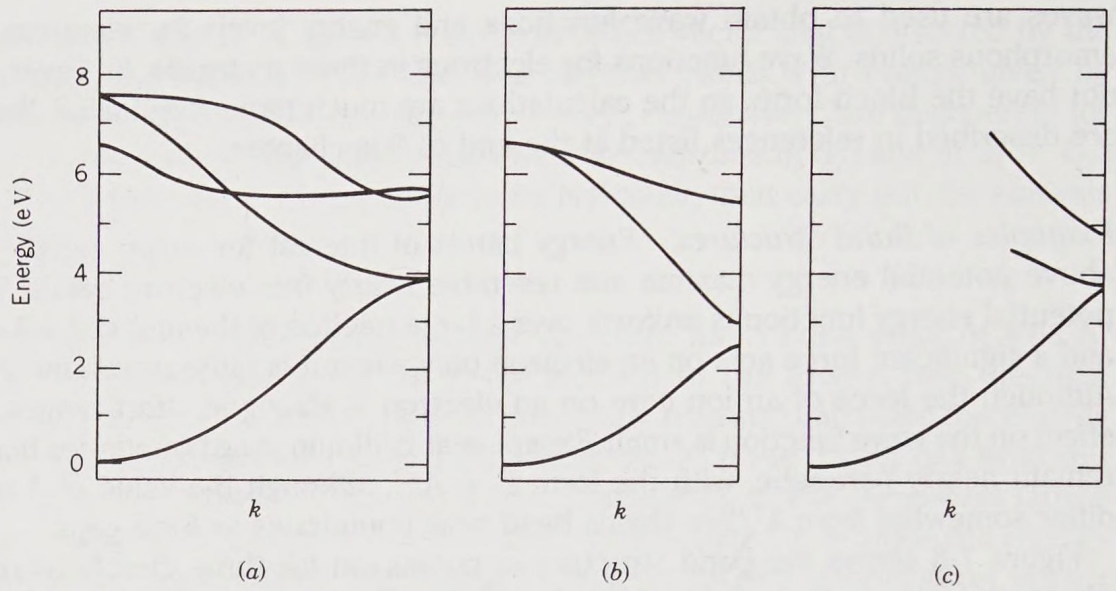


FIGURE 7-8 Electron band structure of potassium for energies near the 4*s* atomic level: (*a*) **k** in the [100] direction; (*b*) **k** in the [110] direction; and (*c*) **k** in the [111] direction. Some curves are incomplete. The bands shown are quite similar in form to those predicted by the nearly free electron model. (From F. S. Ham, *Phys. Rev.* **128**:82, 1962. Used with permission.)

Bands of silicon in 3 directions

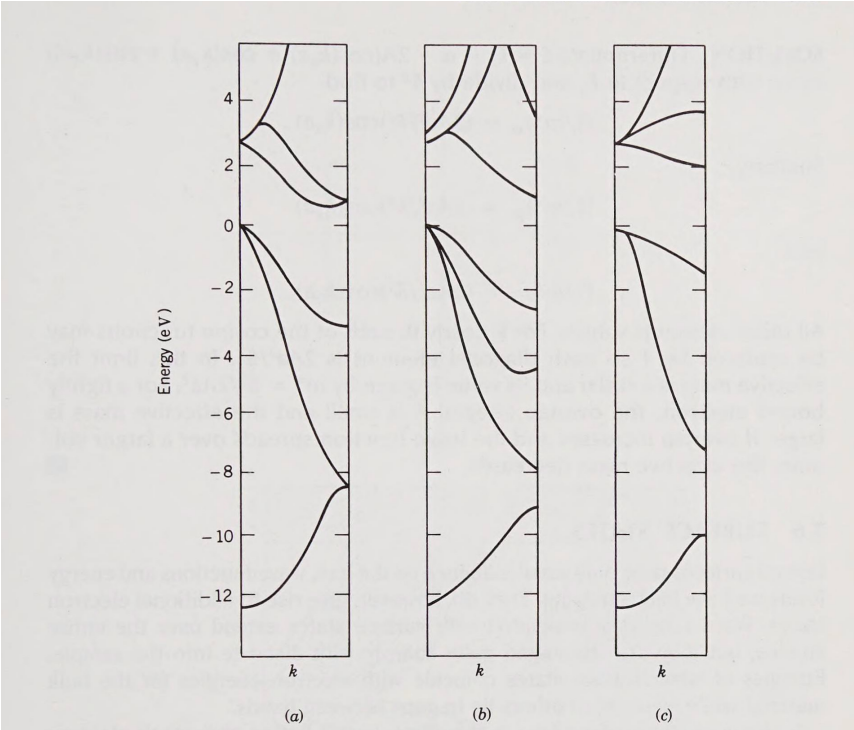


FIGURE 7-9 Electron band structure of crystalline silicon for energies near the 3*s* and 3*p* atomic levels: (*a*) **k** in the [100] direction; (*b*) **k** in the [110] direction; and (*c*) **k** in the [111] direction. Bands below $E = 0$ are valence bands and are associated with bonding. Higher bands are conduction bands and are important for the electrical properties of silicon. A gap exists between the valence and conduction bands. (From A. Zunger and M. L. Cohen, *Phys. Rev.* **B 20:**4082, 1979. Used with permission.)

Effective mass

Effective Mass. Over much of the Brillouin zone electron energies in some bands can be approximated by an expression of the form

$$E_n(\mathbf{k}) = A|\mathbf{k} - \mathbf{k}_0|^2, \tag{7-58}$$

where A is a constant and $\mathbf{k}_0$ is the propagation vector associated with the minimum energy state of the band. For a free electron band $A = \hbar^2/2m$, but for other bands it has a different value. By analogy with free electrons, A is usually replaced by $\hbar^2/2m^*$, where m^* is called the electron effective mass. The effective mass is not usually the same as the mass of a free electron because electrons interact with ion cores of the crystal. The stronger those interactions, the more tightly electrons are bound to atoms and the larger the effective mass. A band with $m^* > m$ is flatter than a free electron band.

The definition of effective mass can be generalized so it is valid for every band, even those that do not have the form given in Eq. 7-58. The generalization takes the form of a tensor called the reciprocal effective mass tensor, defined by

$$\left[\frac{1}{m^*}\right]_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E(\mathbf{k})}{\partial k_i \partial k_j}, \tag{7-59}$$

where i and j represent Cartesian coordinates. A reciprocal effective mass tensor is defined for each electron state.

EXAMPLE 7-5 Derive expressions for elements of the reciprocal effective mass tensor for the tight binding band of Example 7-2. Find limiting values for states near $\mathbf{k} = 0$.

SOLUTION Differentiate $E = E_a - \alpha - 2A[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]$ twice with respect to k_x and divide by $\hbar^2$ to find

$$(1/m^*)_{xx} = (2Aa^2/\hbar^2)\cos(k_x a) .$$

Similarly,

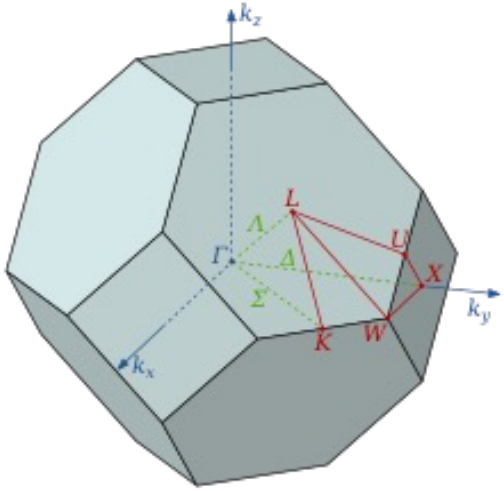
$$(1/m^*)_{yy} = (2Aa^2/\hbar^2)\cos(k_y a)$$

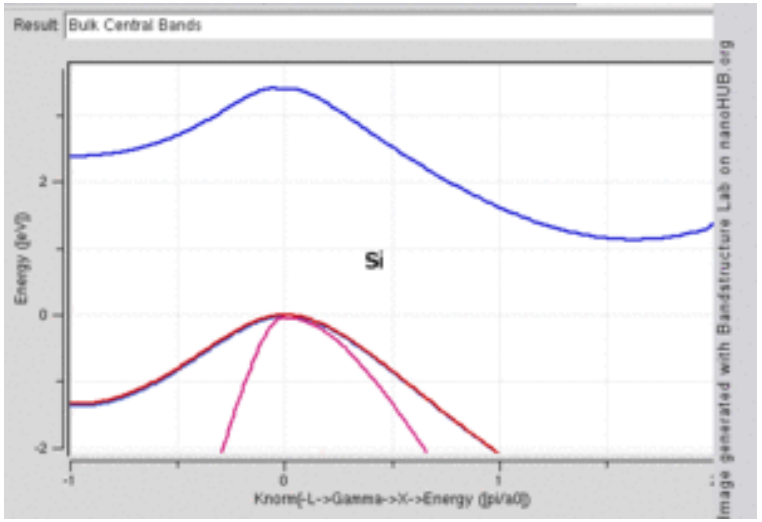
and

$$(1/m^*)_{zz} = (2Aa^2/\hbar^2)\cos(k_z a) .$$

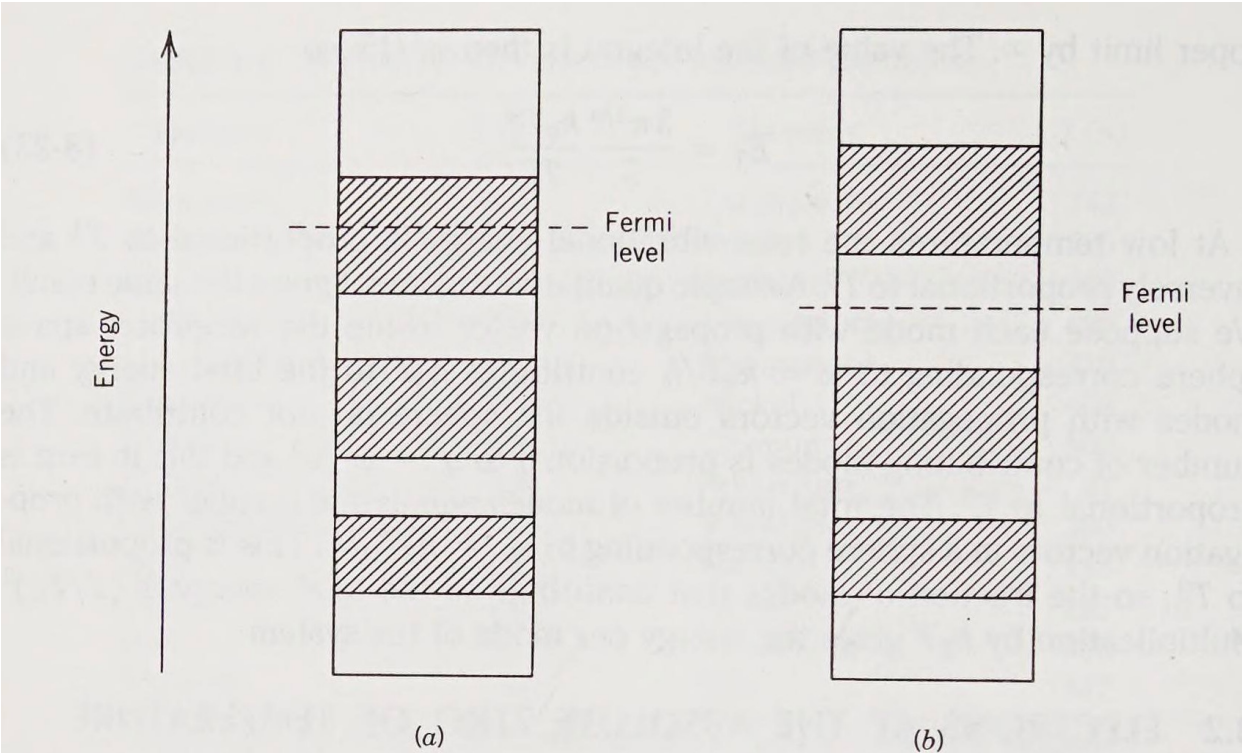
All other elements vanish. For $\mathbf{k}$ nearly 0, each of the cosine functions may be replaced by 1 so each diagonal element is $2Aa^2/\hbar^2$. In this limit the effective mass is a scalar and its value is given by $m^* = \hbar^2/2Aa^2$. For a tightly bound electron, the overlap integral A is small and the effective mass is large. If overlap increases and the wave function spreads over a larger volume, the effective mass decreases. ■

9. Termodinâmica de electrões

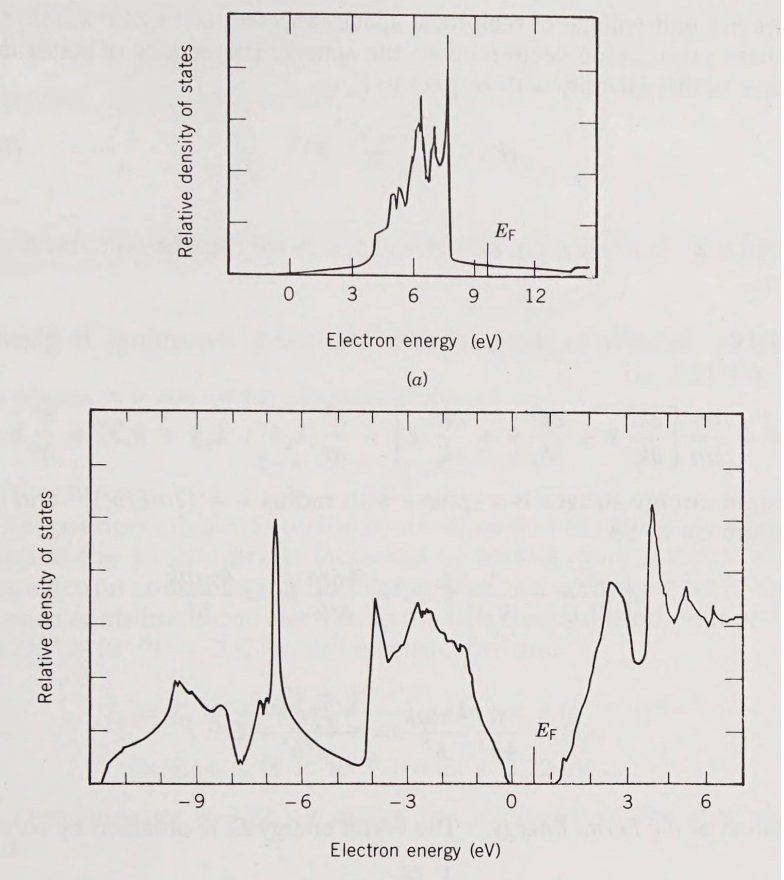




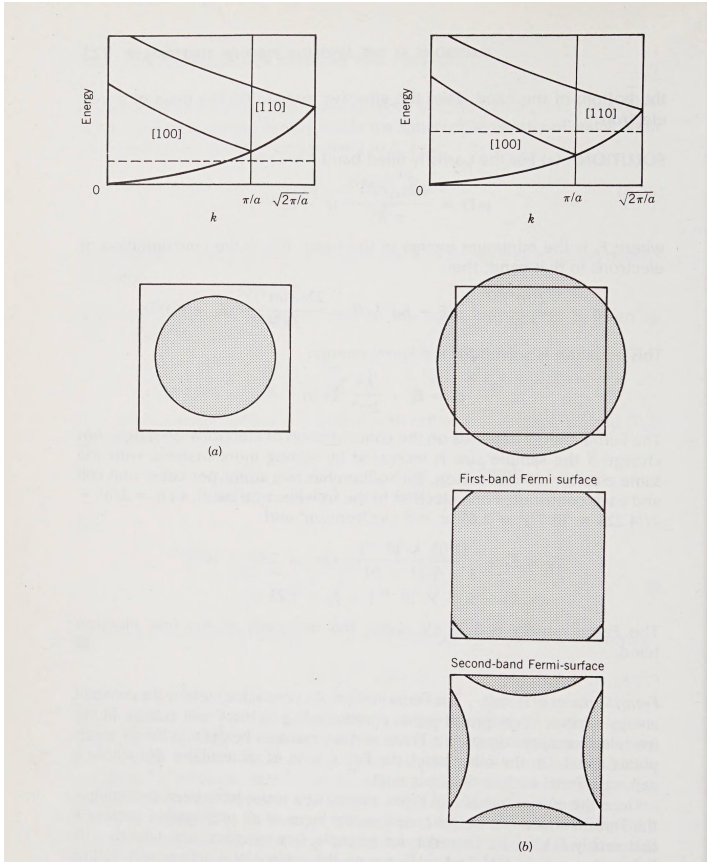
Fermi level



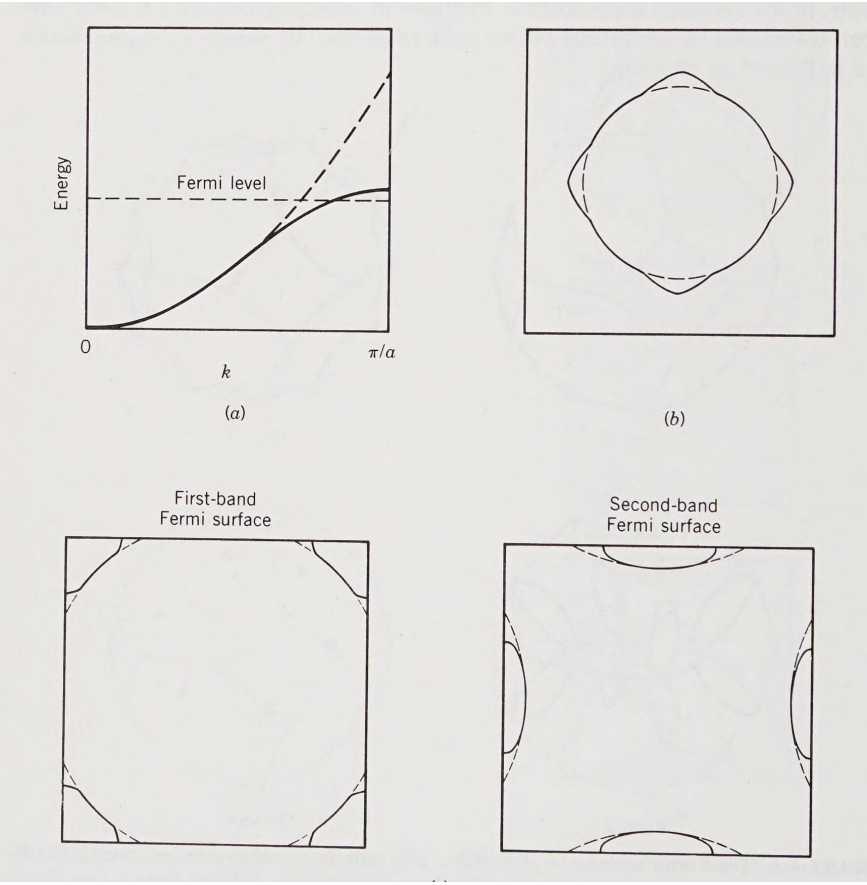
Density of states



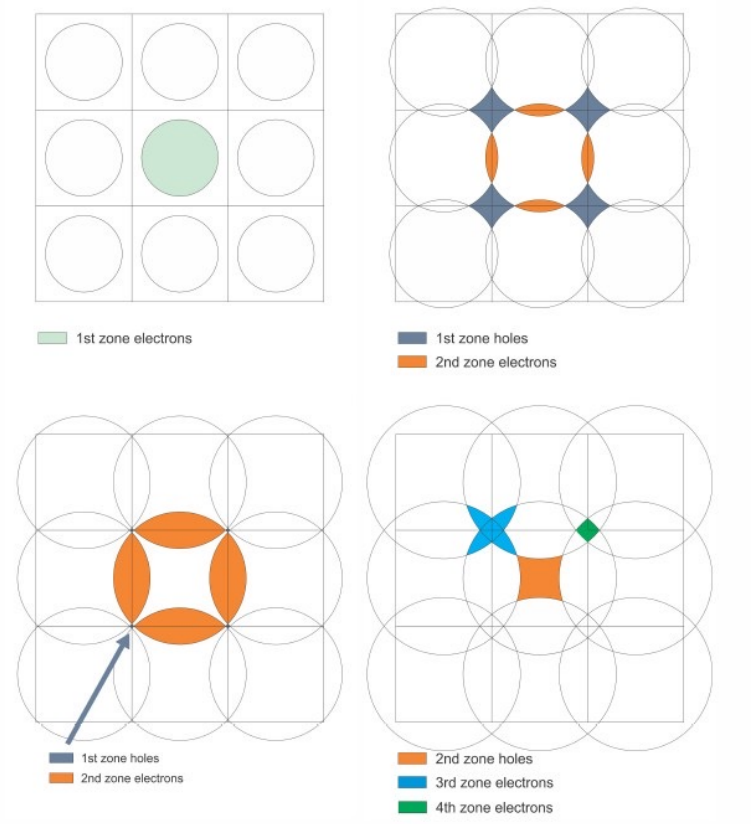
Fermi surface of free electrons in 2d (square)



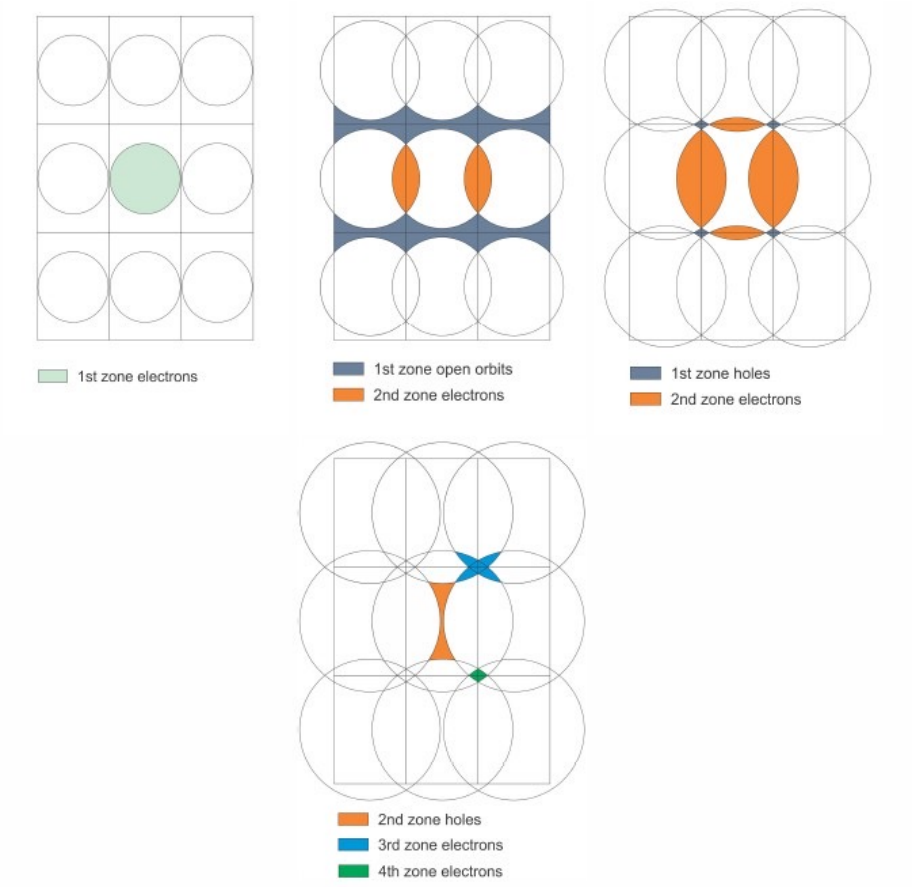
Fermi surface of nearly free electrons in 2d (square)



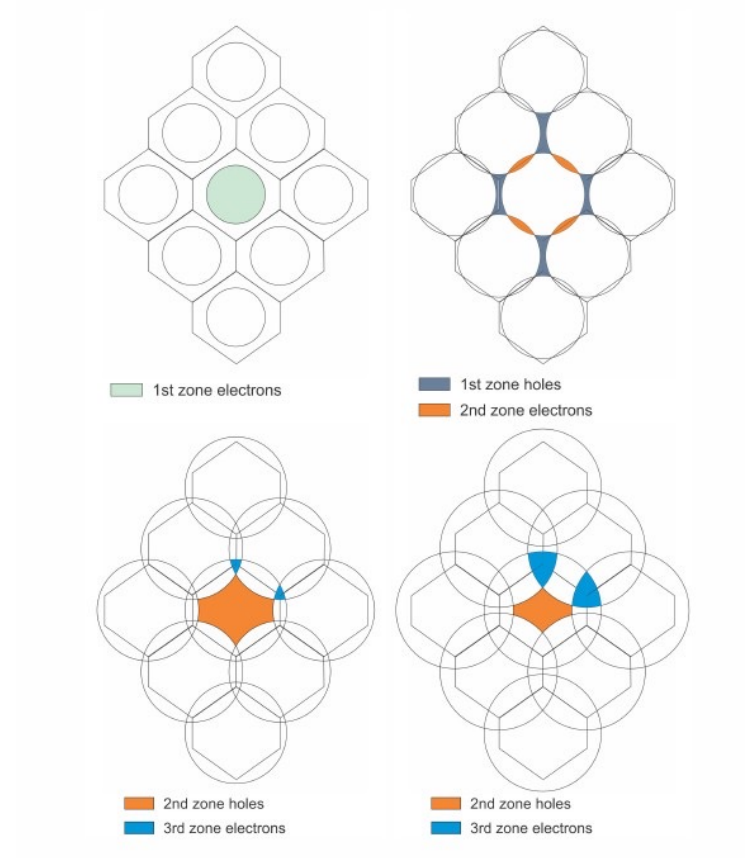
BZ of the square lattice: electrons & holes



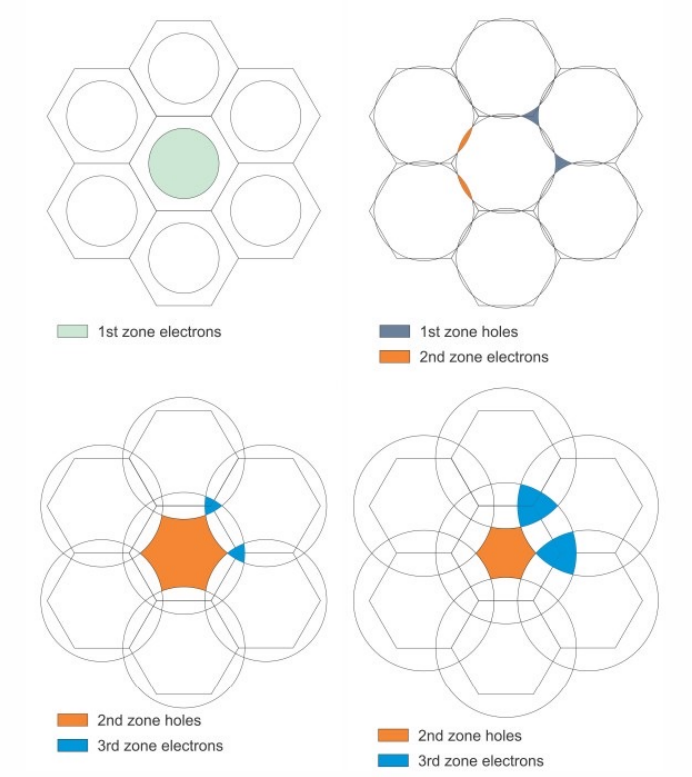
BZ of the rectangular lattice: electrons & holes



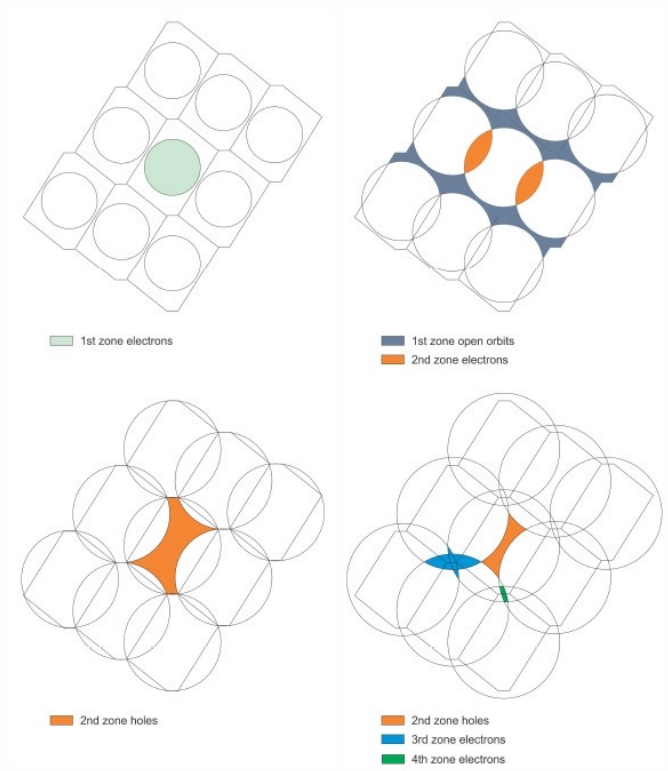
BZ of the face centred rectangular lattice: electrons & holes



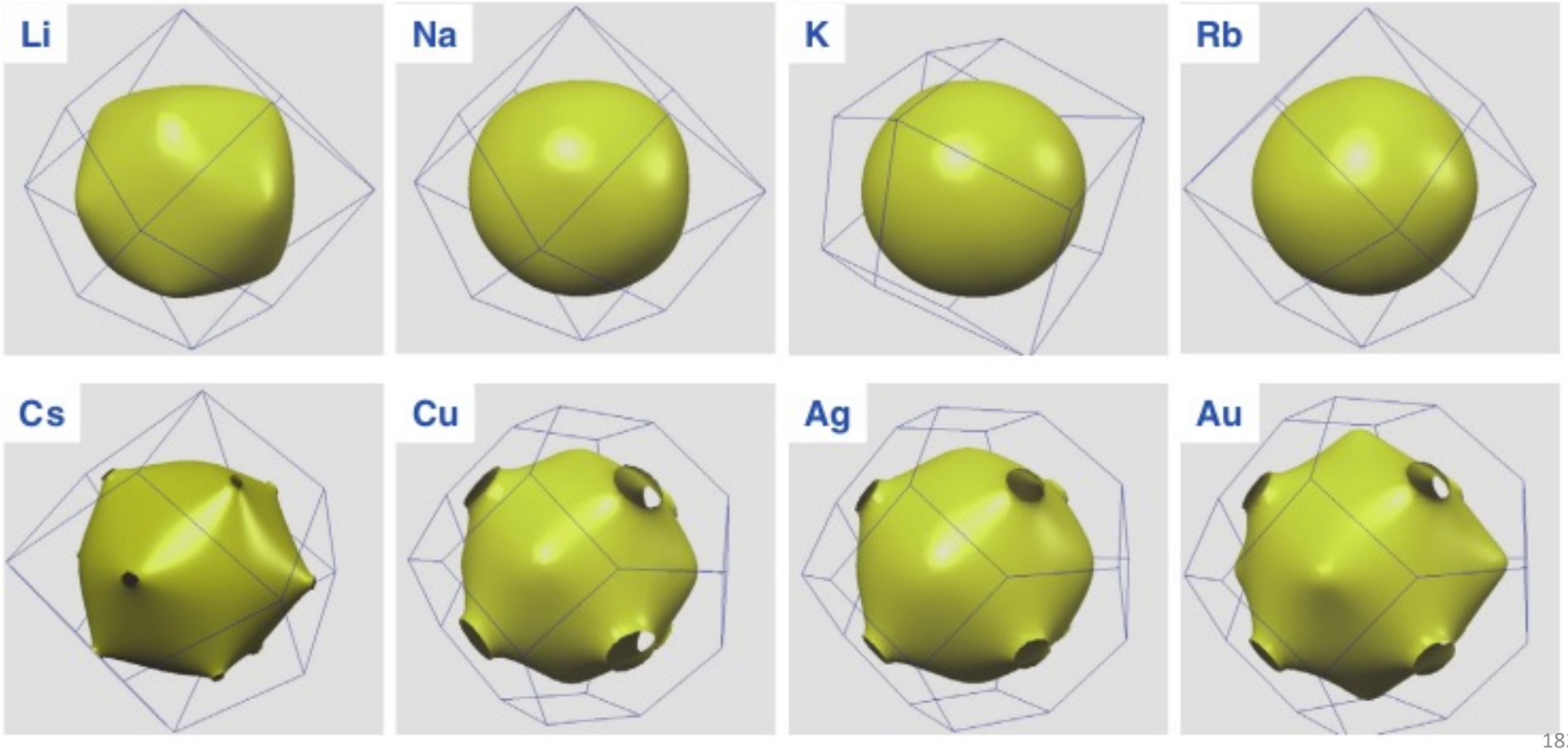
BZ of the hexagonal lattice: electrons & holes



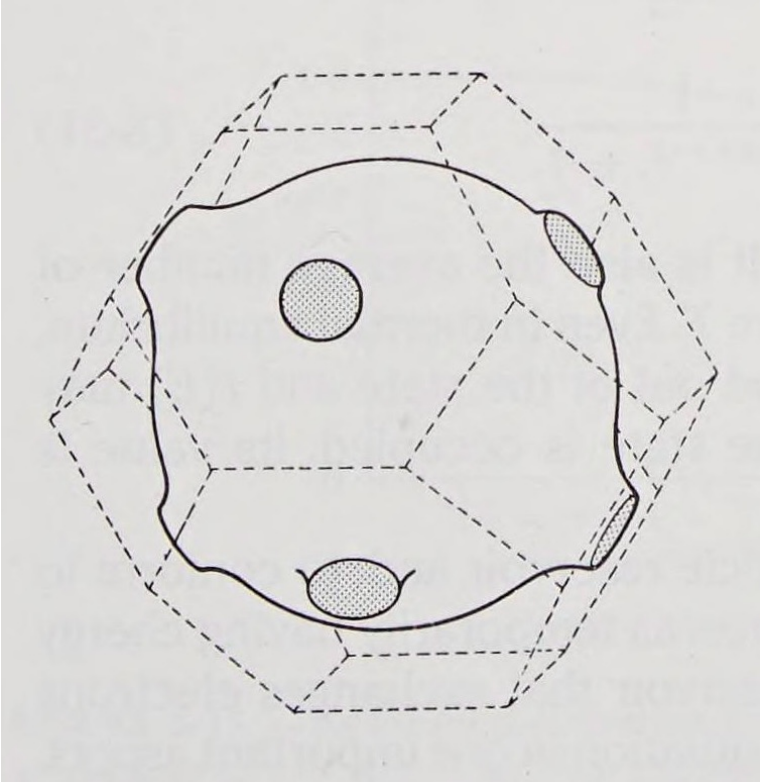
BZ of the oblique lattice: electrons & holes

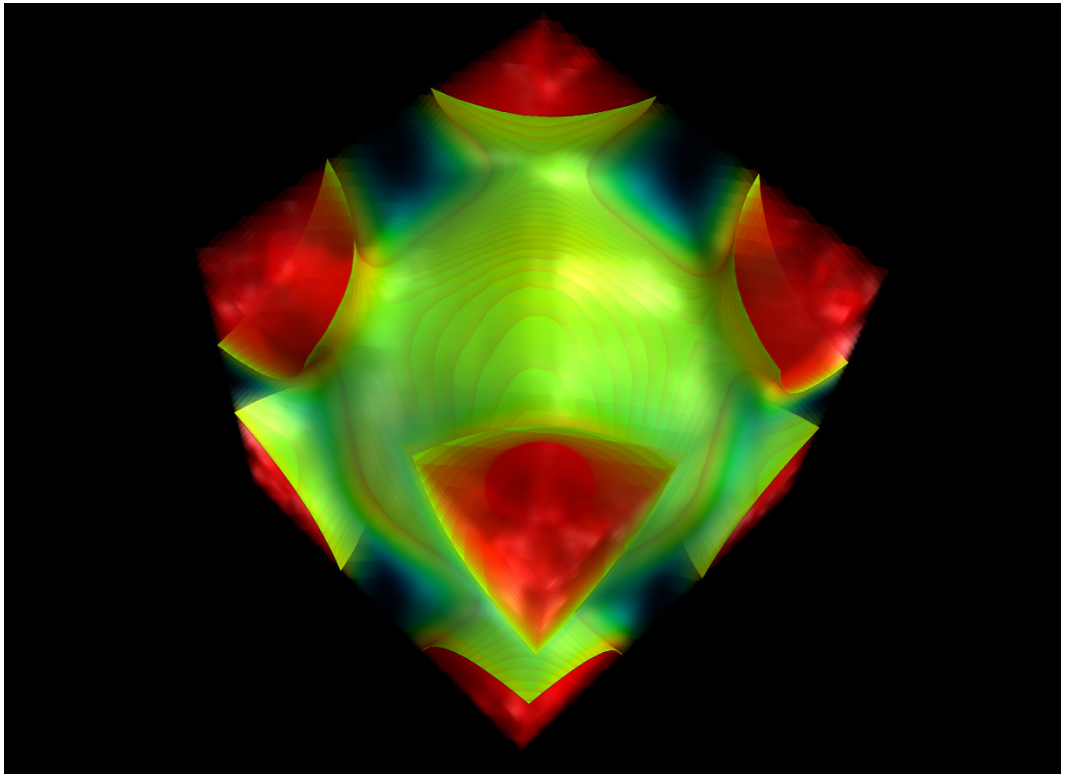


Fermi surface of alkali (bcc) and noble (fcc) metals of valence 1

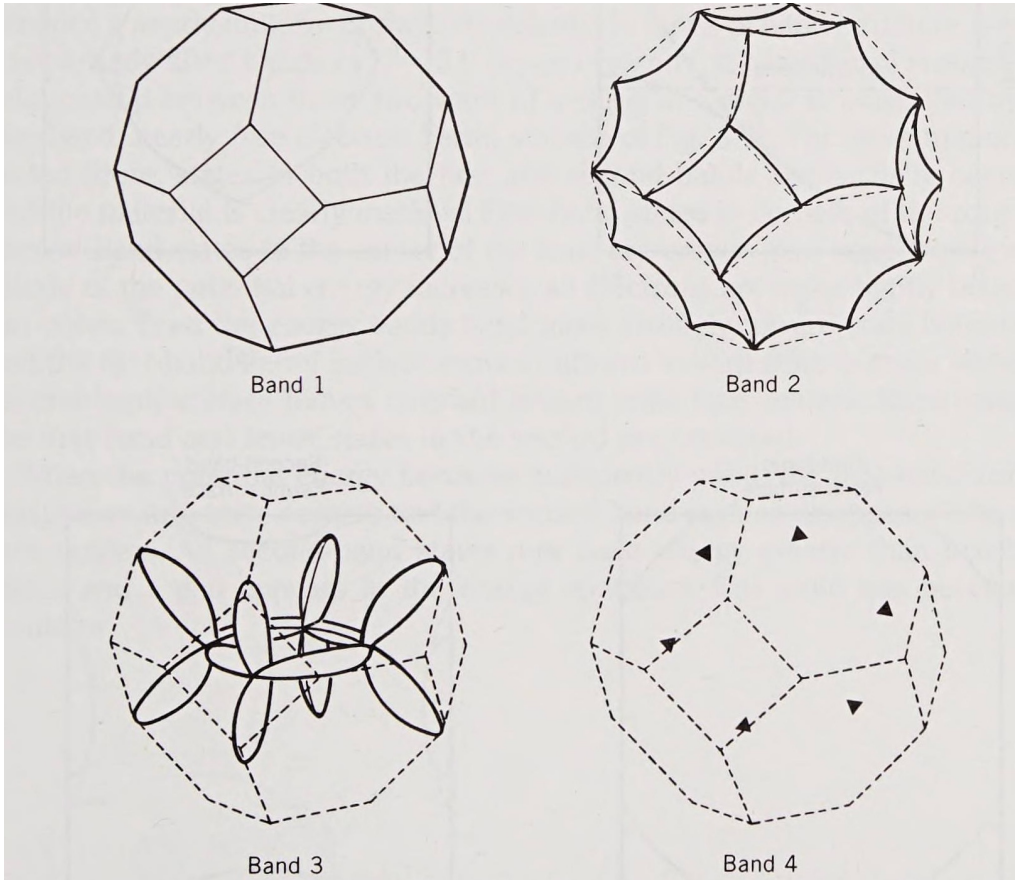


Fermi surface of Cu (fcc valence 1)

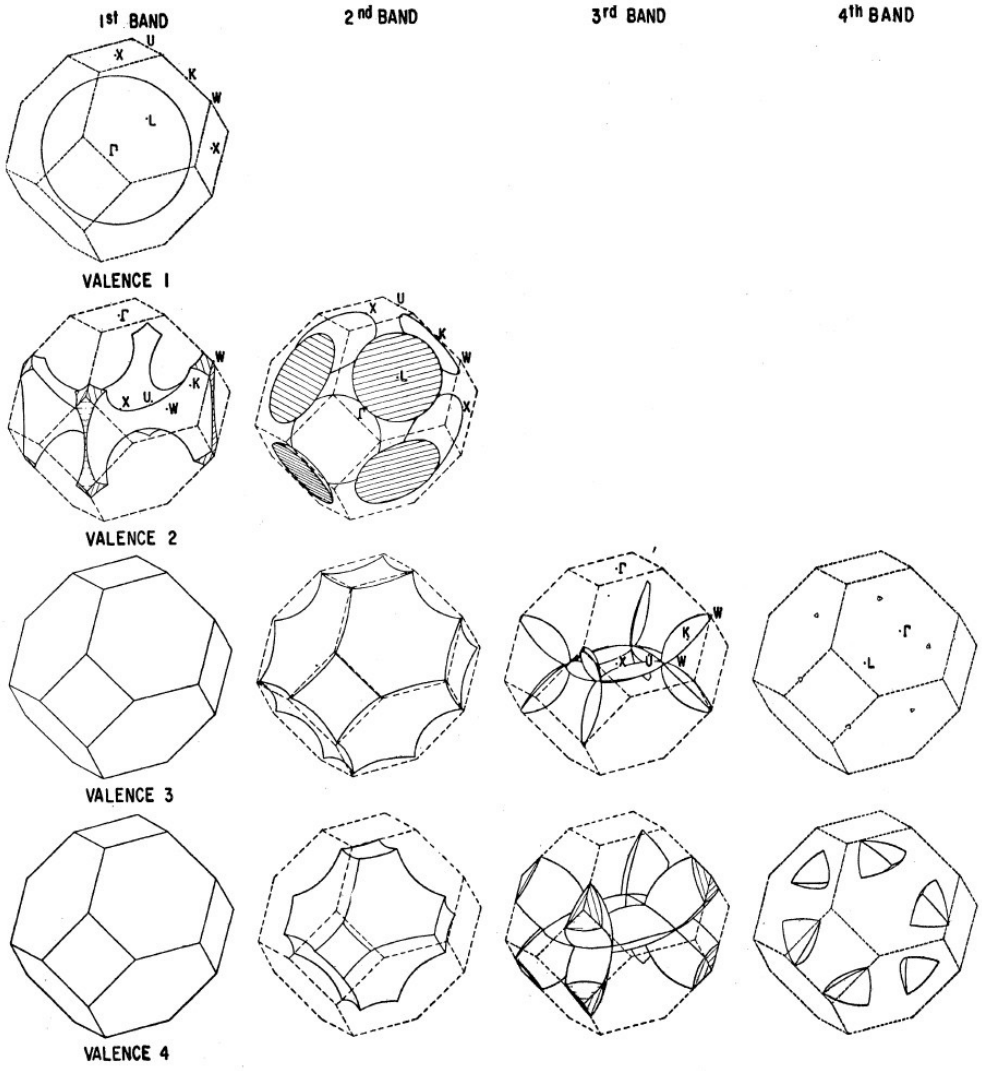




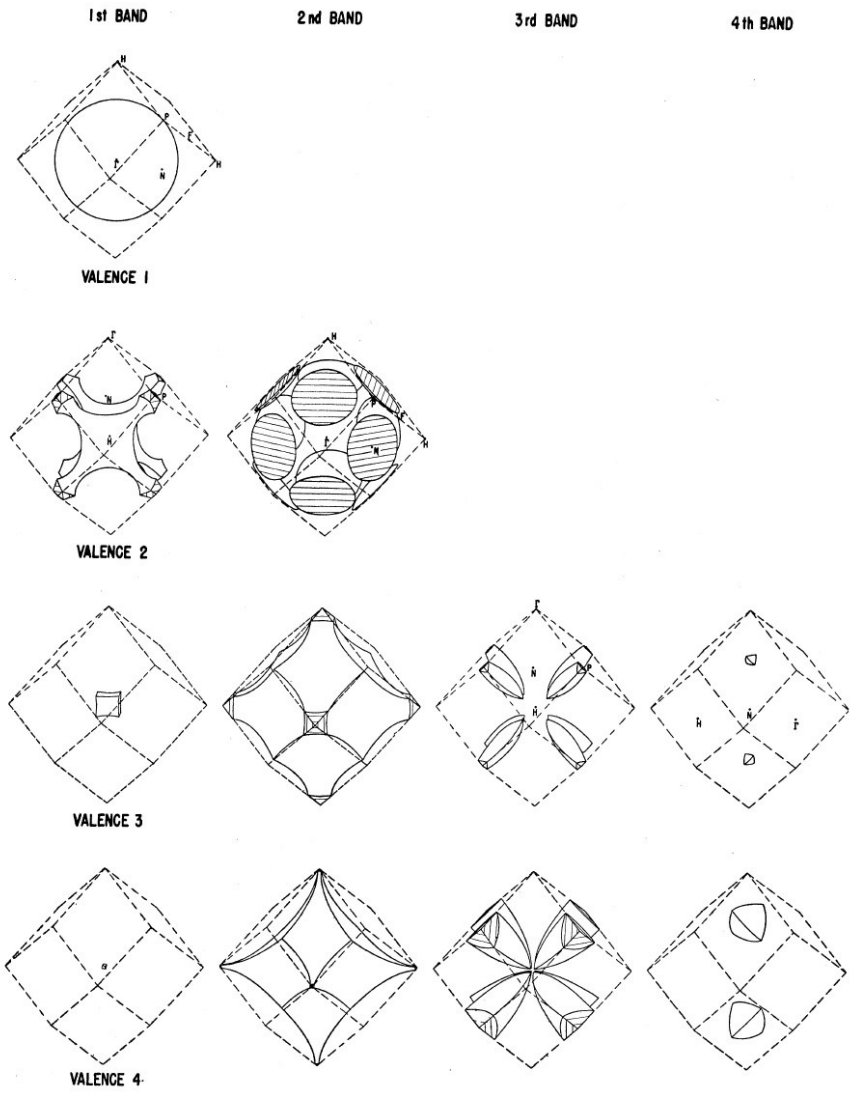
Fermi surface in 3d of Al (fcc valence 3)



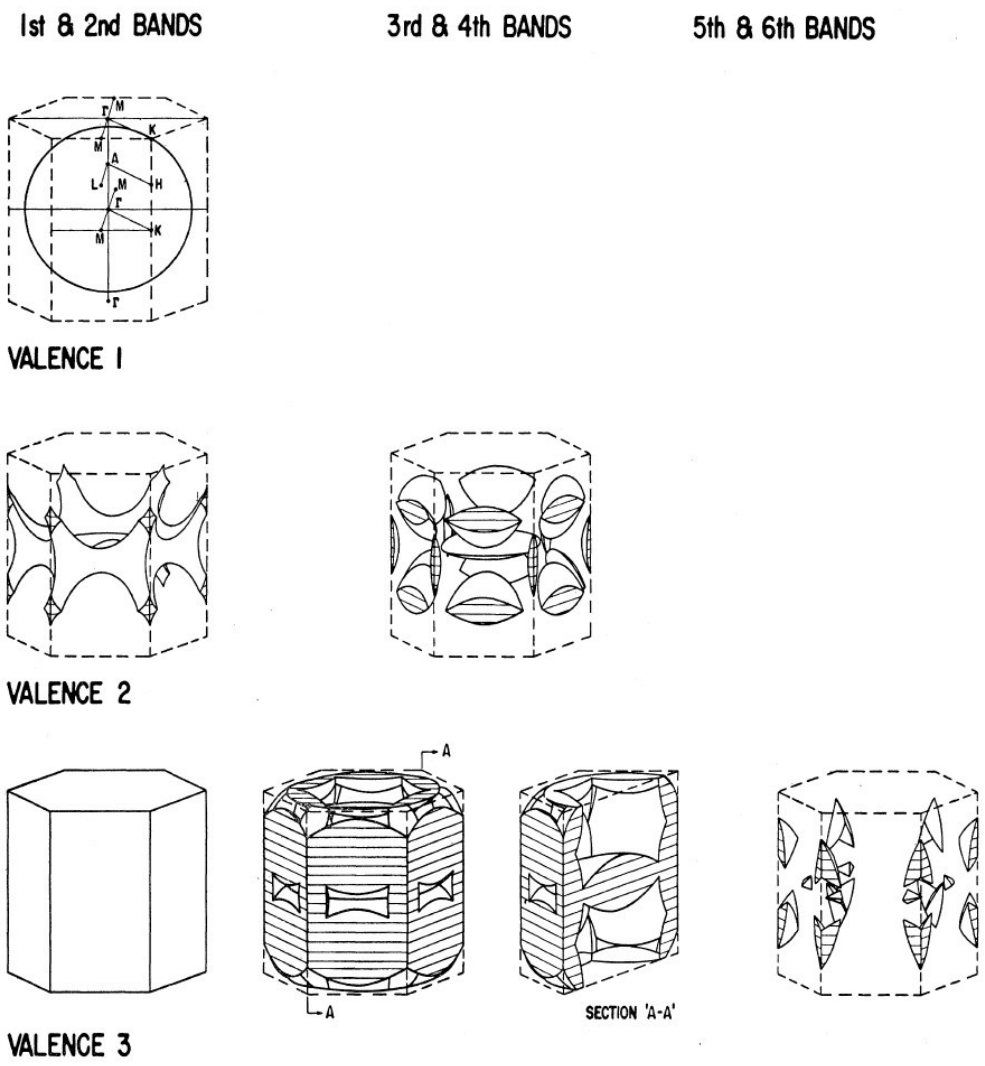
Fcc lattice


1st BAND
2nd BAND
3rd BAND
4th BAND
VALENCE 1
VALENCE 2
VALENCE 3
VALENCE 4

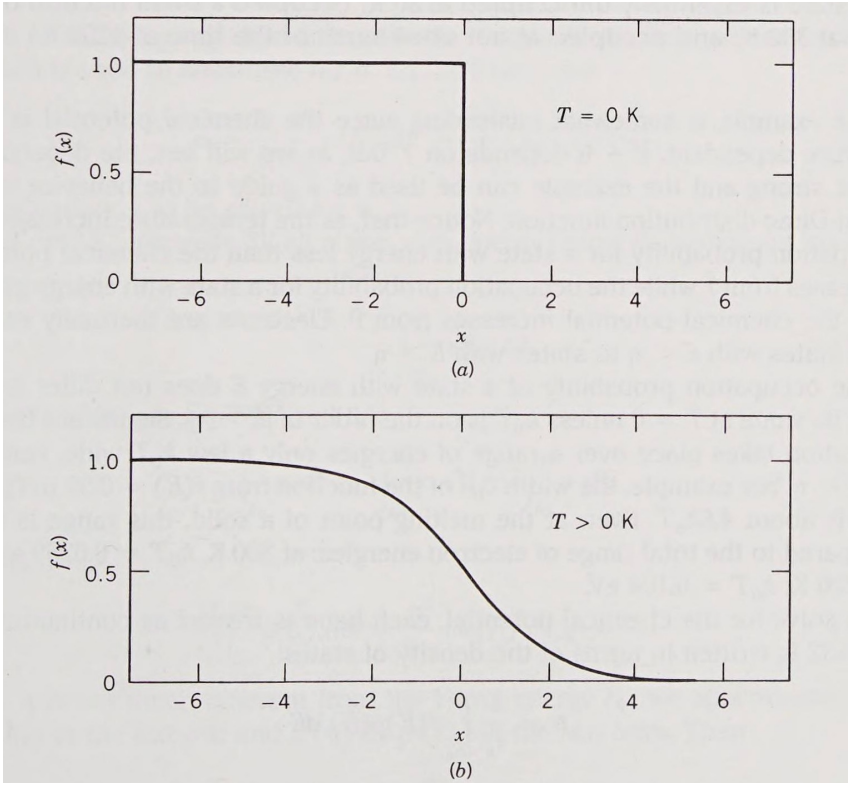
Bcc lattice


1st BAND
2nd BAND
3rd BAND
4th BAND
VALENCE 1
VALENCE 2
VALENCE 3
VALENCE 4

Hexagonal lattice



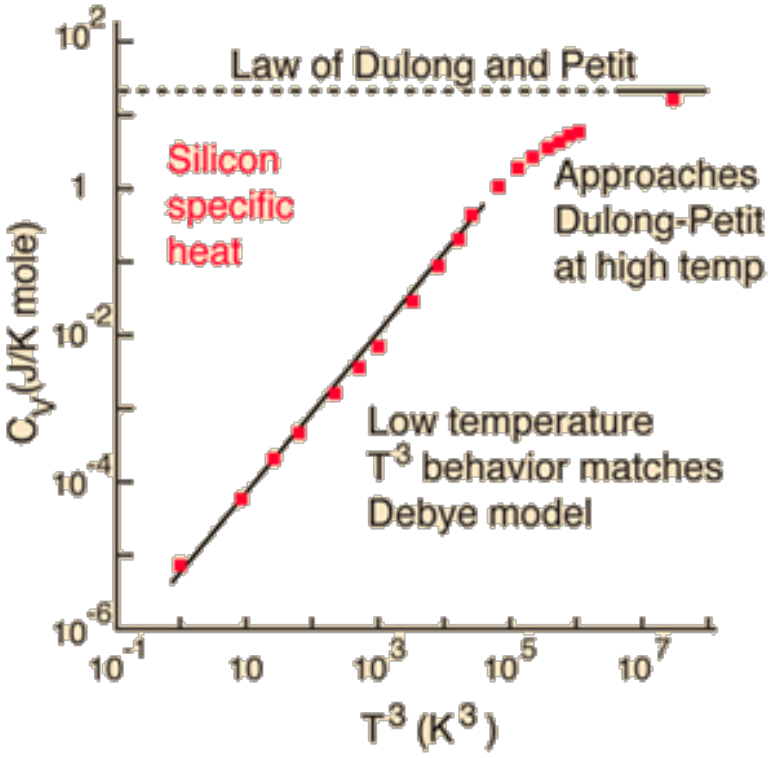
Fermi-Dirac distribution

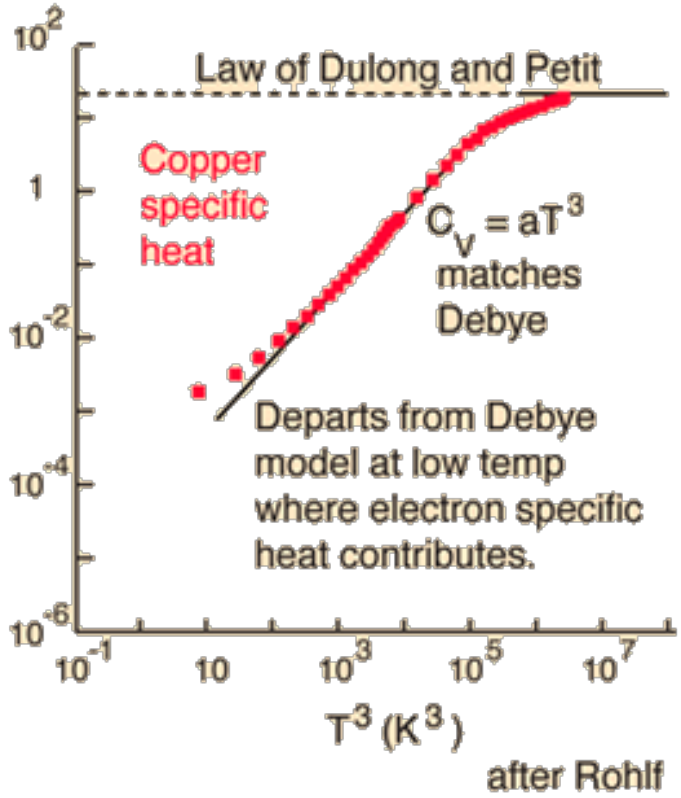


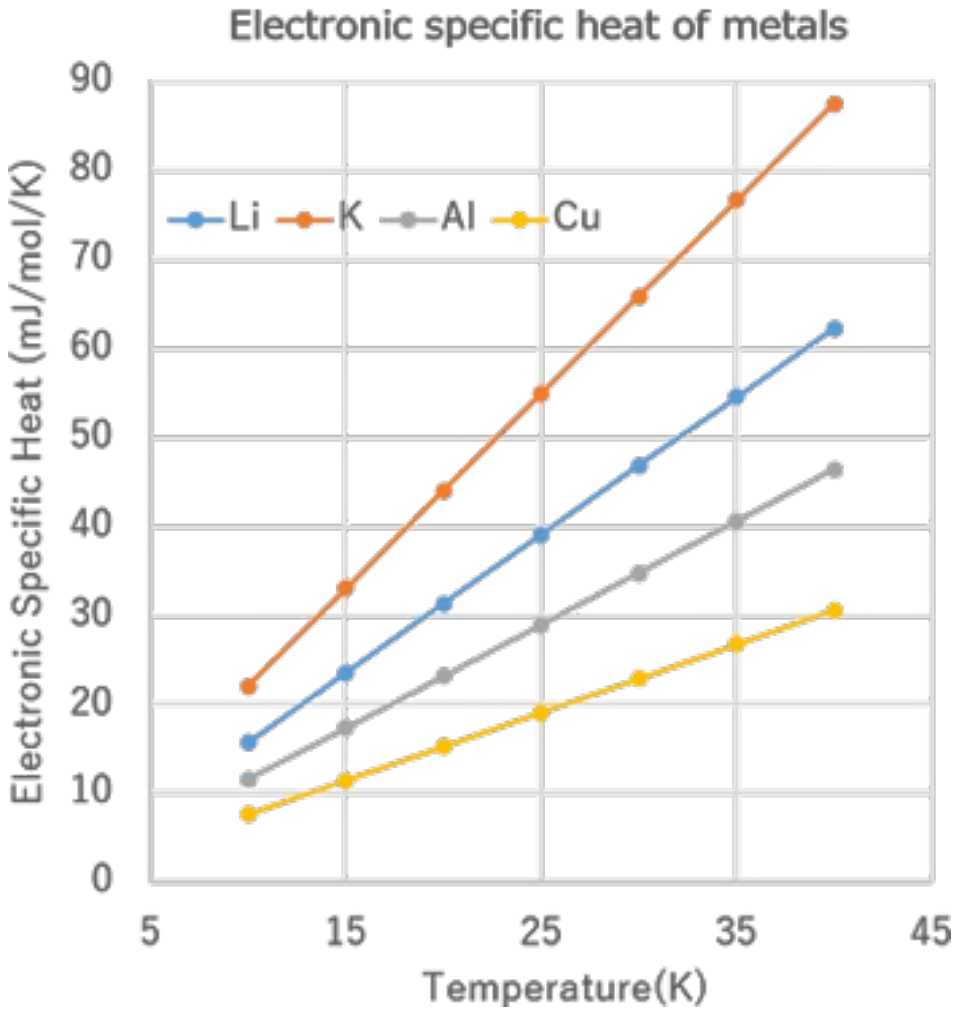
Electronic specific heat

$$C_{electrons} = \frac{\pi^2 N_A k^2 T}{2E_F} mole^{-1}$$

Specific heat of solids






Electronic specific heat of metals
Electronic Specific Heat (mJ/mol/K)
90
80
70
60
50
40
30
20
10
0
Li
K
Al
Cu
5
15
25
35
45
Temperature(K)