Electrons in a Periodic Potential

A. Free Electron Gas (FEG): Model for simple metals

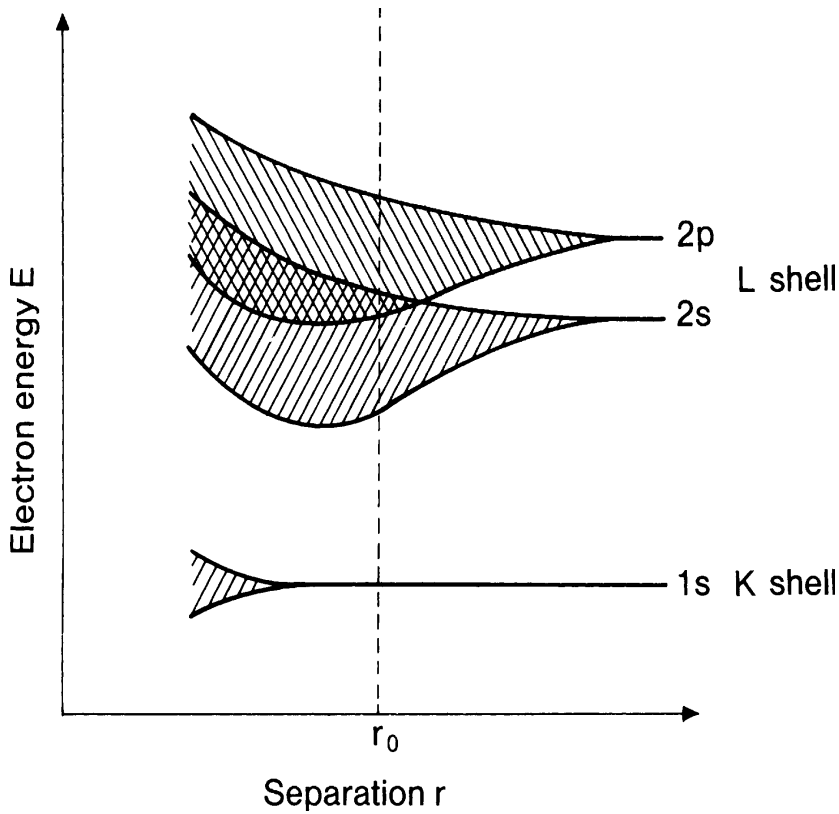
B. Near Free Electron Model

C. Bloch Functions

D. Kronig-Penny Model

E. Energy Bands and Energy Gaps in a Periodic Potential

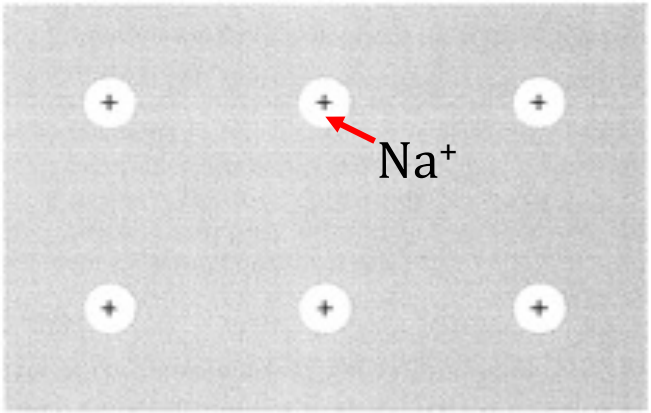
From Bonds to Bands



If a very large number of atoms are involved, as in the case of a real solid, then the energy levels will lie on a quasi- continuous scale and one therefore speaks of energy bands. The broadening of the band depends on the overlap of the wavefunctions concerned. Thus for the deep lying levels the broadening is small, and these ``core levels'' retain their atomic shell-like character even in the solid. For the highest occupied levels, on the other hand, the broadening is so large that the s-, p- and where present, d-levels merge into a single band.

Free Electron Gas (FEG)

Why is condensed matter so transparent to conduction electrons? The answer to the question contains two parts: (a) A conduction electron is not deflected by ion cores arranged on a *periodic* lattice because matter waves can propagate freely in a periodic structure. (b) A conduction electron is scattered only infrequently by other conduction electrons. This property is a consequence of the Pauli exclusion principle.

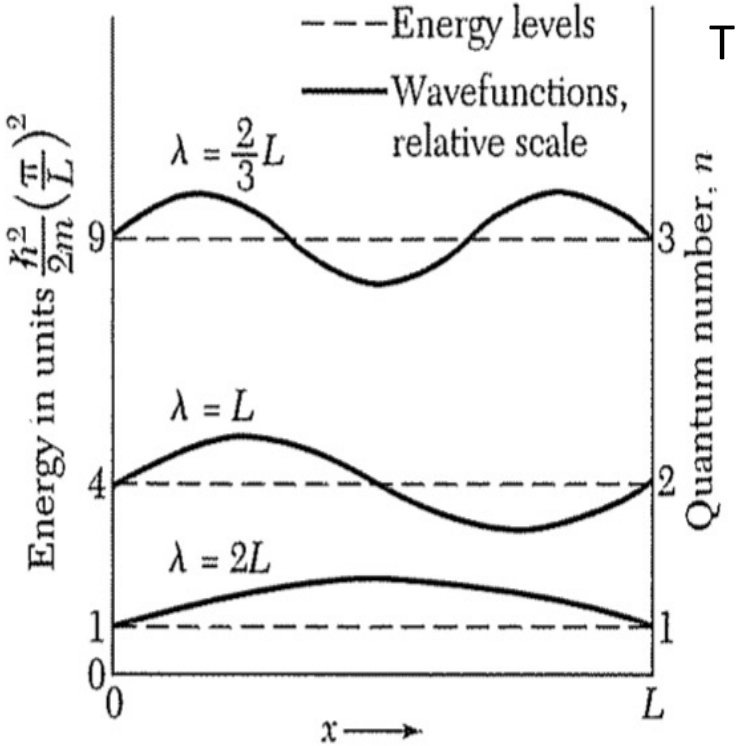


By a **free electron Fermi gas**, we shall mean a gas of free electrons subject to the Pauli principle.

$^{11}\mathrm{Na}$: $1s^2 2s^2 2p^6 3s^1$ Na^+: $1s^2 2s^2 2p^6$

Free Electron Gas in One Dimension

$$\mathcal{H}\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n\psi_n$$



The boundary conditions are $\psi_n(0) = 0;\ \psi_n(L) = 0$

$$\psi_n = A\sin\left(\frac{2\pi}{\lambda_n}x\right) \ ; \qquad \tfrac{1}{2}n\lambda_n = L \ ,$$

$$\frac{d\psi_n}{dx} = A\left(\frac{n\pi}{L}\right)\cos\left(\frac{n\pi}{L}x\right) \ ; \qquad \frac{d^2\psi_n}{dx^2} = -A\left(\frac{n\pi}{L}\right)^2\sin\left(\frac{n\pi}{L}x\right) \ ,$$

whence the energy ϵ_n is given by

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \ .$$

In a linear solid the quantum numbers of a conduction electron orbital are n and m_s, where n is any positive integer and the magnetic quantum number $m_s = \pm 1/2$, according to spin orientation.

Fermi Energy and Fermi-Dirac Distribution

The **Fermi energy** ϵ_F is defined as the energy of the topmost filled level in the ground state of the N electron system. With $n = n_F$ we have in one dimension:

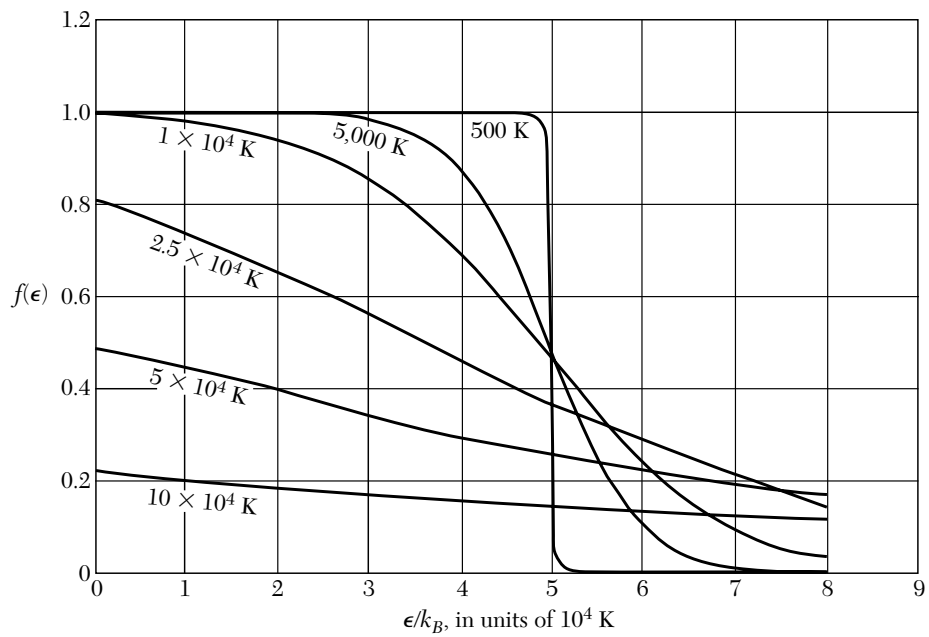
$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F \pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 \quad .$$

Fermi-Dirac distribution gives the probability that an orbital at energy ϵ will be occupied in an ideal electron gas in thermal equilibrium:

$$\boxed{f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} \quad .}$$

At normal and low temperatures

$$\mu \simeq \epsilon_F$$



Free Electron Gas in Three Dimension

The free-particle Schrödinger equation in three dimensions is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_{\mathbf{k}}(\mathrm{r}) = \epsilon_{\mathbf{k}}\,\psi_{\mathbf{k}}(\mathbf{r})$$

If the electrons are confined to a cube of edge *L*, the wavefunction is the standing wave

$$\psi_n(\mathbf{r}) = A\,\sin\left(\pi n_x x/L\right)\sin\left(\pi n_y y/L\right)\sin\left(\pi n_z z/L\right) \ ,$$

where n_x, n_y, n_z are positive integers. The origin is at one corner of the cube.

Applying the periodic boundary condition for x, y, and z,

$$\psi(x+L,y,z) = \psi(x,y,z) \ ,$$

We then have a plane wavefunction:

$$\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = \exp\left(i\mathbf{k}\cdot\mathbf{r}\right) \ ,}$$

provided that the components of the wavevector **k** satisfy

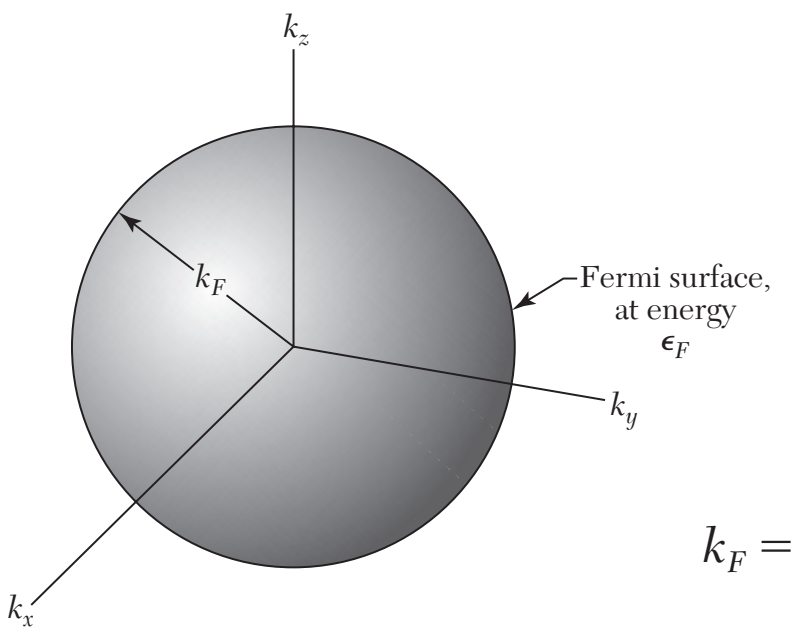
$$k_x = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \quad . \ . \ . \ .$$, and similarly for k_y and k_z.

The energy $\epsilon_{\mathbf{k}}$ of the orbital with wavevector **k**:

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} \left(k_x^2 + k_y^2 + k_z^2\right) \ .$$

In the ground state of a system of *N* free electrons, the occupied orbitals may be represented as points inside a sphere in **k** space. The energy at the surface of the sphere is the Fermi energy; the wavevectors at the Fermi surface have a magnitude k_F such that

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 \ .$$



Then

$$2 \cdot \frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3 = N \ ,$$

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \text{, and } \boxed{\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \ .}$$

Density of States (DOS)

The density of states is

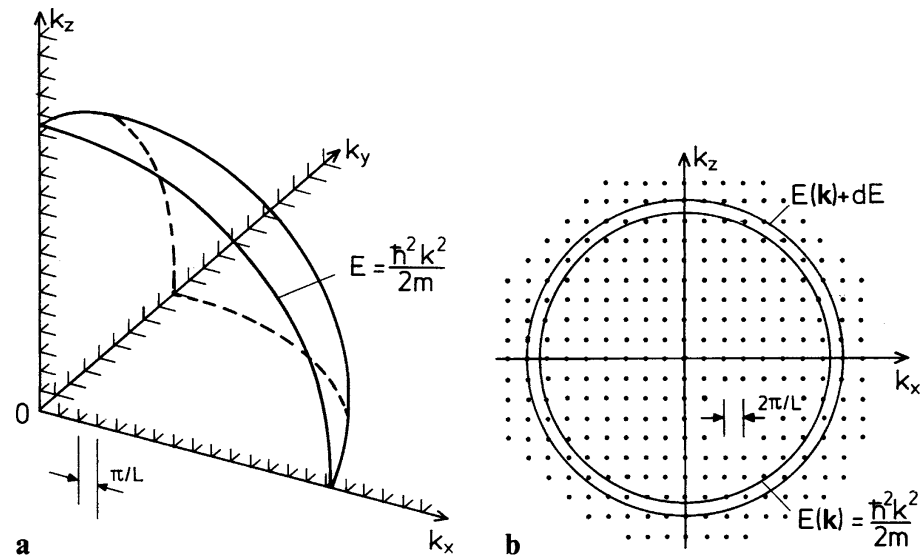
$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \epsilon^{1/2} \quad .$$

since

$$N = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}$$

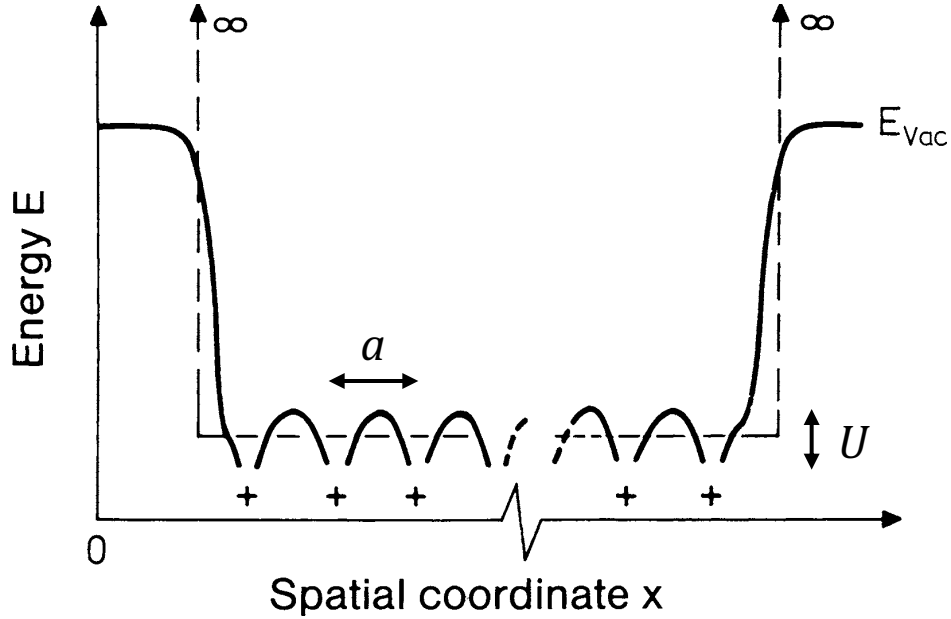
or

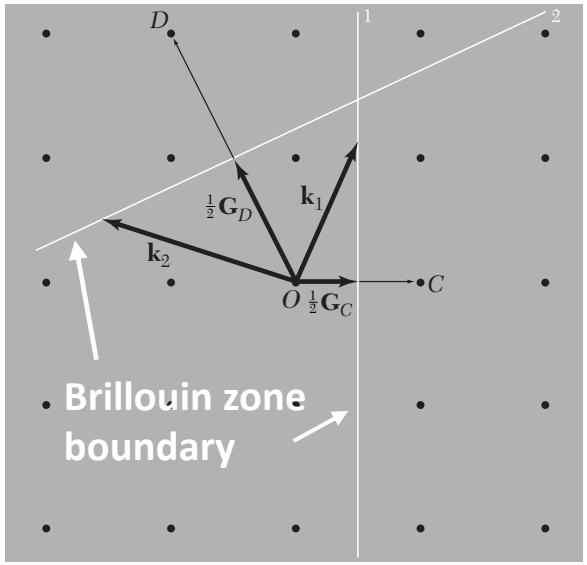
$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon}$$



Near Free Electron Model

Consider a linear solid of lattice *a* and put the magnitude of *U* aside





$$\mathbf{k}\cdot\left(\tfrac{1}{2}\mathbf{G}\right)=\left(\tfrac{1}{2}G\right)^2$$

By the periodicity alone, in 1D the Bragg reflections will occur at

$$k=\pm\tfrac{1}{2}G=\pm n\pi/a \quad ,$$

where $G = 2\pi n/a$ is a reciprocal lattice vector and *n* is an integer.

Formation of Standing Waves

The wavefunctions at $k = \pm\pi/a$ are not the traveling waves $\exp(i\pi x/a)$ or $\exp(-i\pi x/a)$ of free electrons. At these special values of k the wavefunctions are made up of equal parts of waves traveling to the right and to the left.

Two standing waves are formed from two traveling waves:

$$\psi(+) = \exp(i\pi x/a) + \exp(-i\pi x/a) = 2\cos(\pi x/a) \ ;$$

$$\psi(-) = \exp(i\pi x/a) - \exp(-i\pi x/a) = 2i\sin(\pi x/a) \ .$$

Both standing waves are composed of equal parts of right- and left-directed traveling waves.

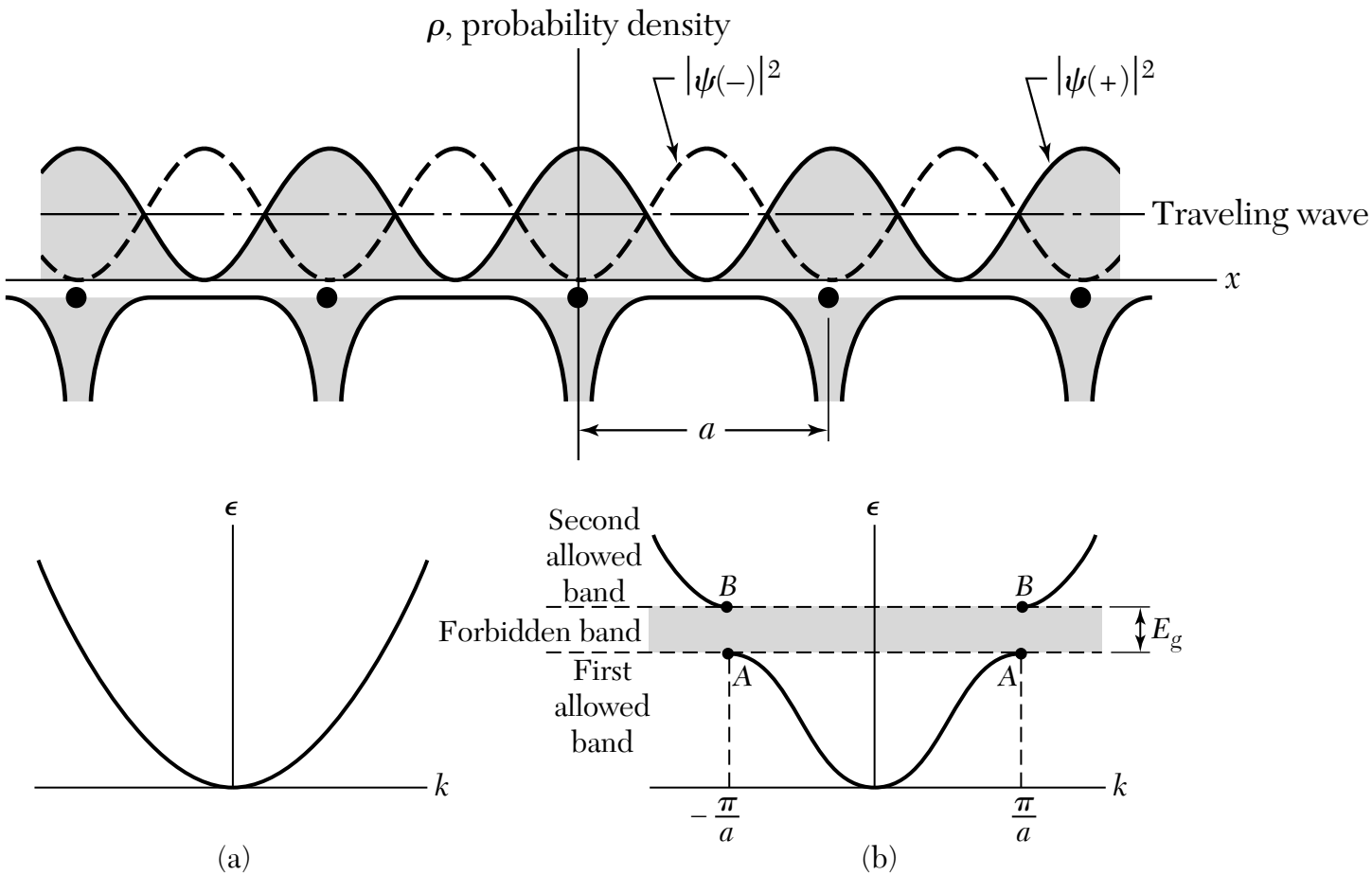
Two corresponding electron density are

$$\rho(+) = |\psi(+)|^2 \propto \cos^2 \pi x/a$$

$$\rho(-) = |\psi(-)|^2 \propto \sin^2 \pi x/a$$

Origin of Energy Gap

The two standing waves $\psi(+)$ and $\psi(-)$ pile up electrons at different regions, and therefore the two waves have different values of the potential energy in the field of the ions of the lattice. This is the origin of the energy gap.



Magnitude of Energy Gap

Let's assume the potential energy of an electron in the crystal at point x is $U(x) = U \cos 2\pi x/a$

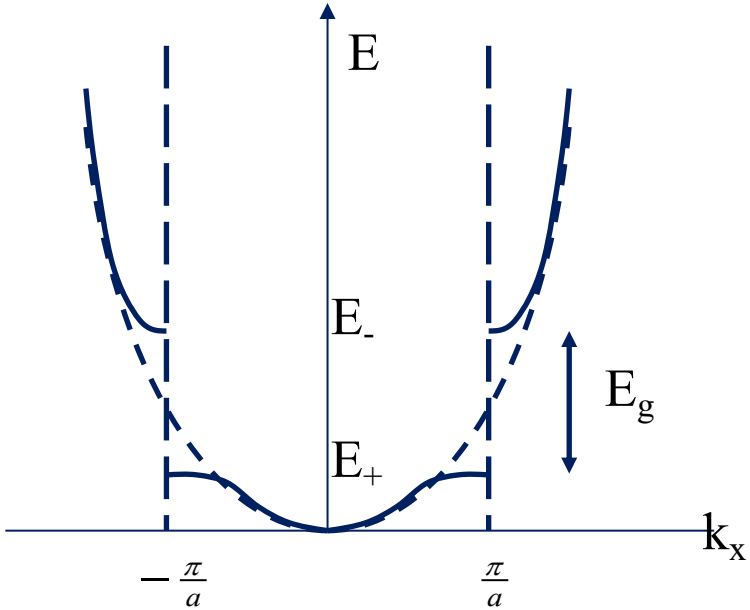
The first-order energy difference between the two standing wave states is

$$E_g = \int_0^1 dx\, U(x)\, [|\psi(+)|^2 - |\psi(-)|^2]$$

$$= 2\int dx\, U \cos(2\pi x/a)(\cos^2 \pi x/a - \sin^2 \pi x/a) = U$$ ≡ "energy gap"

In between the two energies there are no allowed energies; i.e., an energy gap exists. We can sketch these 1-D results schematically:

The periodic potential U(x) splits the free-electron E(k) into "energy bands" separated by gaps at each BZ boundary.



Bloch Theorem and Bloch Wavefunctions

In the independent-electron approximation, the time-independent Schrodinger equation for an electron in a periodic potential is:

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

where the potential energy is invariant under a lattice translation vector ***T***:

$$U(\vec{r}+\vec{T}) = U(\vec{r}) \qquad \text{and} \qquad \vec{T} = u\vec{a} + v\vec{b} + w\vec{c}$$

Bloch showed that the solutions to the SE are the product of a plane wave and a function with the periodicity of the lattice:

$$\boxed{\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}}$$

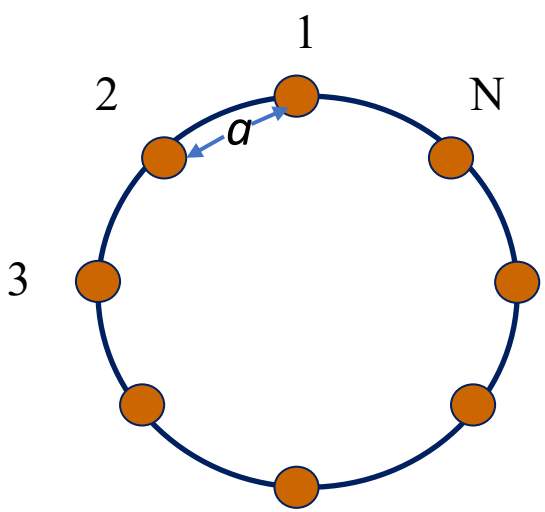
where $u_{\vec{k}}(\vec{r}+\vec{T}) = u_{\vec{k}}(\vec{r})$

Bloch Theorem in 1D

$$\psi_{\vec{k}}(\vec{r}+\vec{T}) = u_{\vec{k}}(\vec{r}+\vec{T})e^{i\vec{k}\cdot\vec{r}}e^{i\vec{k}\cdot\vec{T}} \quad = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}e^{i\vec{k}\cdot\vec{T}} \quad = \psi_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{T}}$$

Or just: $\psi_{\vec{k}}(\vec{r}+\vec{T}) = \psi_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{T}}$

Consider a 1D case, N identical lattice points around a circular ring, each separated by a distance a:



The ring model fulfills the periodic boundary condition:

$$\psi(x+Na) = \psi(x)$$

The symmetry of the ring implies that we can find a solution to the wave equation:

$$\psi(x+a) = C\psi(x)$$

If we apply this translation N times we will return to the initial atom position:

$$\psi(x+Na) = C^N \psi(x) = \psi(x)$$

This requires $C^N = 1$ or $C^N = e^{2\pi n i}$ $n = 0, \pm 1, \pm 2, \ldots$

so $C = e^{2\pi n i / N} = e^{ika}$ <u>Bloch wavevector</u>: $k = \dfrac{2\pi n}{Na}$

Now we can rewrite

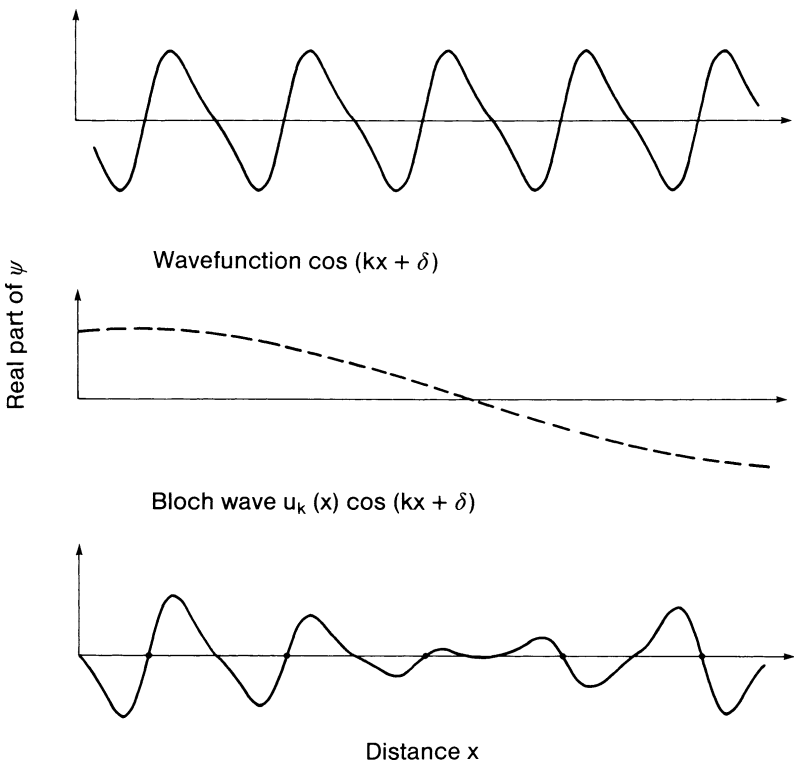
$$\psi(x+a) = C\psi(x) = e^{ika}\psi(x)$$

It can be generalized to 3D: $\psi_{\vec{k}}(\vec{r}+\vec{T}) = \psi_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{T}}$

$$\boxed{\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}}$$

Bloch Wavefunctions

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$$



This result gives evidence to support the nearly-free electron approximation, in which the periodic potential is assumed to have a very small effect on the plane-wave character of a free electron wavefunction. It also explains why the free-electron gas model is so successful for the simple metals.

Wave Equation of Electron in 1D Lattice

Let's assume the periodic potential energy of an electron in a 1D lattice of *a* at point *x* is *U*(*x*+*a*) = *U*(*x*), so *U*(*x*) can be expressed by

$$U(x) = \sum_G U_G \, e^{iGx}$$, and the wave equation is

$$\left(\frac{1}{2m}p^2 + U(x)\right)\psi(x) = \left(\frac{1}{2m}p^2 + \sum_G U_G \, e^{iGx}\right)\psi(x) = \epsilon\psi(x)$$

The wavefunction $\psi(x)$ may be expressed as a Fourier series summed over all values of the wavevector permitted by the boundary conditions, so that

$$\psi = \sum_k C(k) \, e^{ikx} \quad , \qquad k = 2\pi n/L$$

The kinetic energy term is

$$\frac{1}{2m}p^2\psi(x) = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \frac{\hbar^2}{2m}\sum_k k^2 C(k) \, e^{ikx} \quad ;$$

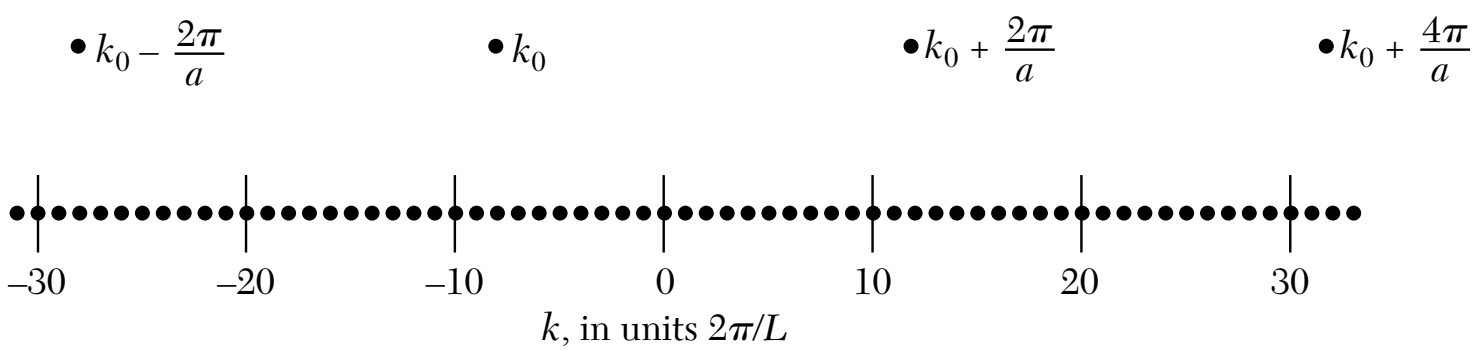
and the potential energy term is $$\left(\sum_G U_G e^{iGx}\right)\psi(x) = \sum_G \sum_k U_G e^{iGx} C(k) \, e^{ikx} \quad .$$

The wave equation is obtained as the sum:

$$\sum_k \frac{\hbar^2}{2m} k^2 C(k)\, e^{ikx} + \sum_G \sum_k U_G C(k)\, e^{i(k+G)x} = \epsilon \sum_k C(k)\, e^{ikx} \quad .$$

The central equation:

$$\boxed{(\lambda_k - \epsilon) C(k) + \sum_G U_G C(k-G) = 0 \quad .} \qquad \lambda_k = \hbar^2 k^2 / 2m \quad .$$



Restatement of Bloch Theorem

The given wavefunction: $\psi_k(x) = \sum_G C(k-G)\, e^{i(k-G)x}$,

which may be rearranged as

$$\psi_k(x) = \left(\sum_G C(k-G)\, e^{-iGx}\right) e^{ikx} = e^{ikx} u_k(x) \ , \quad \text{with} \quad u_k(x) \equiv \sum_G C(k-G)\, e^{-iGx} \, .$$

Since $u_k(x) = u_k(x+T)$, so $\psi_k(x+T) = \psi_k(x)\, e^{ikT}$

The quantity **k** enters in the conservation laws that govern collision processes in crystals. (The conservation laws are really selection rules for transitions.) Thus $\hbar$**k** is called the **crystal momentum** of an electron. If an electron **k** absorbs in a collision a phonon of wavevector **q**, the selection rule is **k** + **q** = **k'** + **G**. In this process the electron is scattered from a state **k** to a state **k'**, with **G** a reciprocal lattice vector. Any arbitrariness in labeling the Bloch functions can be absorbed in the **G** without changing the physics of the process.

Consequence of Bloch Theorem

From a knowledge of the dispersion relation, we can calculate the propagation speed (group velocity) of a wave pulse :

group velocity in 1D: $v_g = \dfrac{d\omega}{dk}$ and in 3D: $\vec{v}_g(\vec{k}) = \vec{\nabla}_{\vec{k}}\,\omega(\vec{k})$

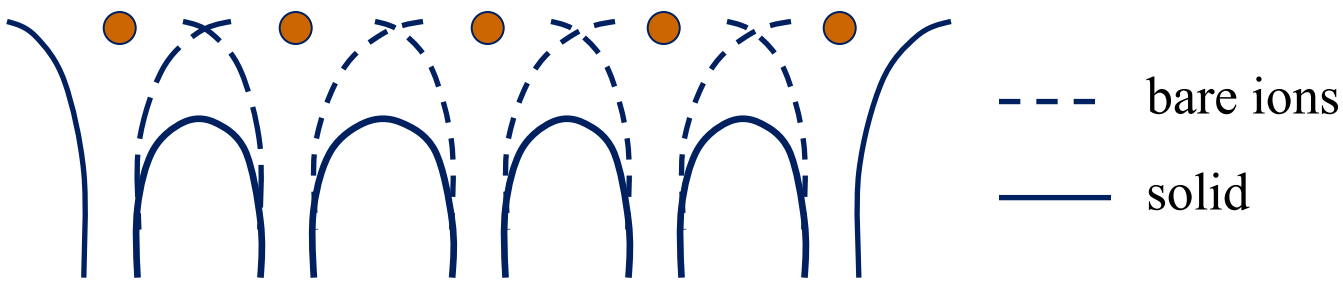
Similarly, it can be shown using Bloch's theorem that the propagation speed of an electron wavepacket <u>in a periodic crystal</u> can be calculated from a knowledge of the energy band along that direction in reciprocal space:

electron velocity in 1D: $v_g = \dfrac{d\omega}{dk} = \dfrac{1}{\hbar}\dfrac{dE}{dk}$ in 3D: $\vec{v}_g(\vec{k}) = \dfrac{1}{\hbar}\vec{\nabla}_{\vec{k}}\,E(\vec{k})$

This means that an electron (with a specified wavevector) moves through a perfect periodic lattice with a constant velocity; i.e., <u>it moves without being scattered or in any way having its velocity affected.</u>

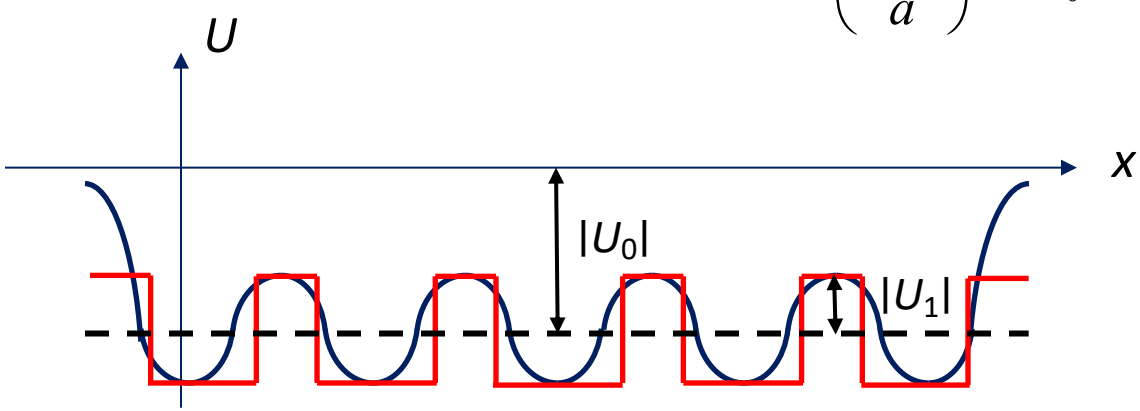
Periodic Potential from Atomic Orbitals

Electrostatic potential energy in a crystalline solid along a line passing through a line of atoms:



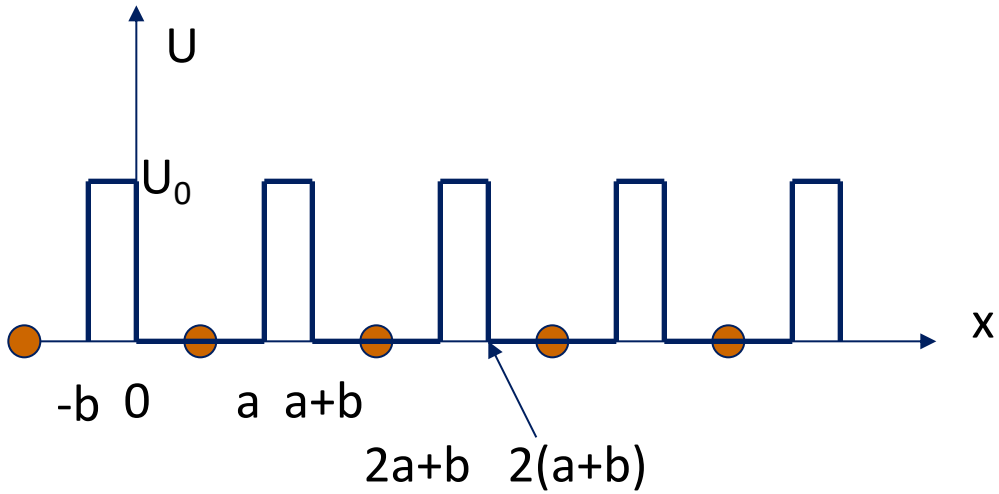
This 1D model can be approximated with a cosine or square potential:

$$U(x) = U_0 + U_1 \cos\left(\frac{2\pi x}{a}\right) \qquad U_0 < U_1 < 0$$



The Krönig-Penney Model

Solve the SE in each region of space: $$\left[-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+U(x)\right]\psi = E\psi$$



$$U(x) = 0, \quad 0 < x < a$$
$$= U_0, \quad -b < x < 0$$

<u>0 < x < a</u> $$\psi_I(x) = Ae^{i\kappa x} + Be^{-i\kappa x} \qquad E = \frac{\hbar^2\kappa^2}{2m}$$

<u>-b < x < 0</u> $$\psi_{II}(x) = Ce^{Qx} + De^{-Qx} \qquad U_0 - E = \frac{\hbar^2 Q^2}{2m}$$

Boundary Conditions and Bloch Theorem

The solutions of the SE require that the wave-function and its *derivative* be continuous across the potential boundaries. Thus, at the two boundaries (which are infinitely repeated):

$$\psi_I(x) = Ae^{i\kappa x} + Be^{-i\kappa x}$$

$$\psi_{II}(x) = Ce^{Qx} + De^{-Qx}$$

<u>x = 0</u> $\quad A + B = C + D \quad (1) \qquad i\kappa(A - B) = Q(C - D) \quad (2)$

<u>x = a</u> $\quad Ae^{i\kappa a} + Be^{-i\kappa a} = \psi_{II}(a)$

Now using Bloch's theorem for a periodic potential with period a+b: $\psi_{II}(a) = \psi_{II}(-b)e^{ik(a+b)}$

Now we can write the boundary conditions at x = a:

$$Ae^{i\kappa a} + Be^{-i\kappa a} = (Ce^{-Qb} + De^{Qb})e^{ik(a+b)} \qquad (3)$$

$$i\kappa(Ae^{i\kappa a} - Be^{-i\kappa a}) = Q(Ce^{-Qb} - De^{Qb})e^{ik(a+b)} \qquad (4)$$

Results of the Krönig-Penney Model

The four simultaneous equations (1-4) can be written compactly in matrix form

$$\begin{bmatrix} 1 & 1 & -1 & -1 \\ i\kappa & -i\kappa & -Q & Q \\ e^{i\kappa a} & e^{-i\kappa a} & -e^{-Qb}e^{ik(a+b)} & -e^{Qb}e^{ik(a+b)} \\ i\kappa e^{i\kappa a} & -i\kappa e^{-i\kappa a} & -Qe^{-Qb}e^{ik(a+b)} & Qe^{Qb}e^{ik(a+b)} \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = 0$$

Since the values of a and b are inputs to the model, and Q depends on U_0 and the energy E, we can solve this system of equations to find the energy E at any specified value of the Bloch wavevector *k*.

Taking the determinant and setting it equal to zero gives:

$$\left(\frac{Q^2-\kappa^2}{2Q\kappa}\right)\sin(\kappa a)\sinh(Qb)+\cos(\kappa a)\cosh(Qb)=\cos[k(a+b)]$$

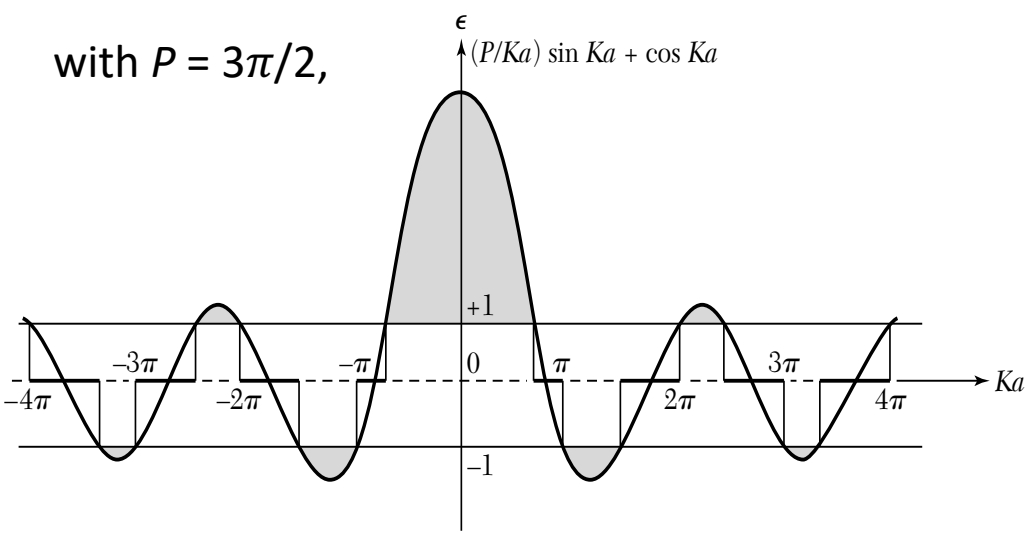
δ-Function Approximation

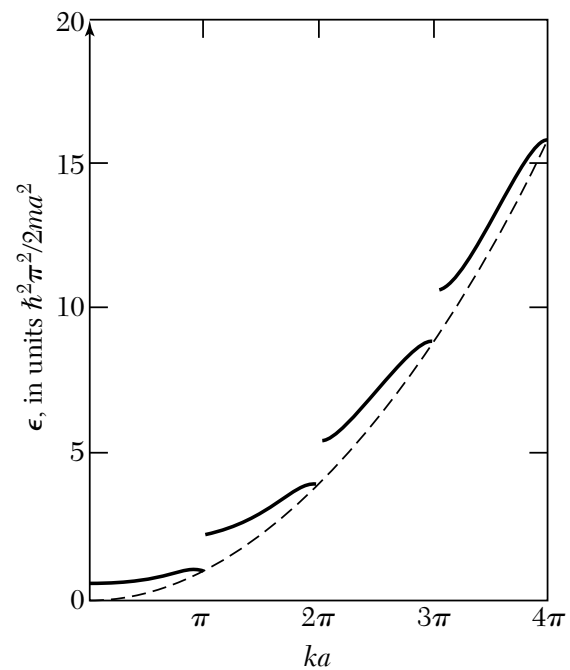
$$\left(\frac{Q^2-\kappa^2}{2Q\kappa}\right)\sin(\kappa a)\sinh(Qb)+\cos(\kappa a)\cosh(Qb)=\cos[k(a+b)]$$

The result is simplified if we represent the potential by the periodic delta function obtained when we pass to the limit $b = 0$ and $U_0 = \infty$ in such a way that $Q^2ba/2 = P$, a finite quantity. In this limit $Q >> \kappa$ and $Qb << 1$. Then the above equation reduces to

$$(P/\kappa a)\sin\kappa a + \cos\kappa a = \cos ka$$

with $P = 3\pi/2$,

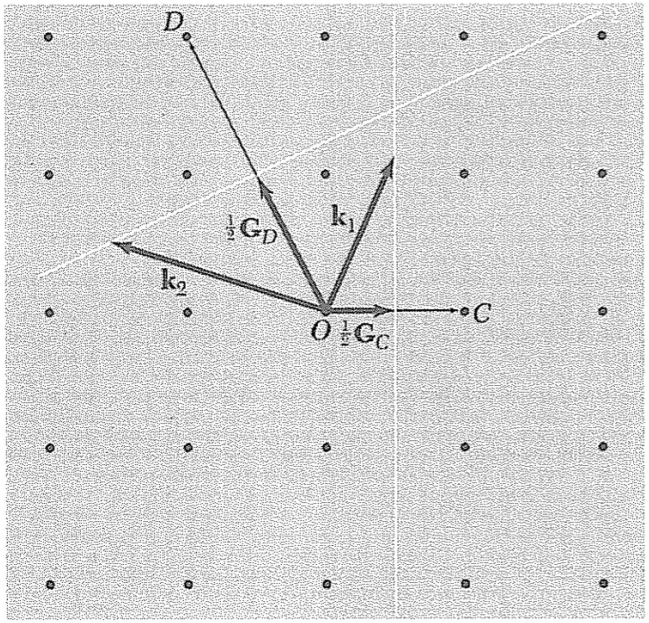


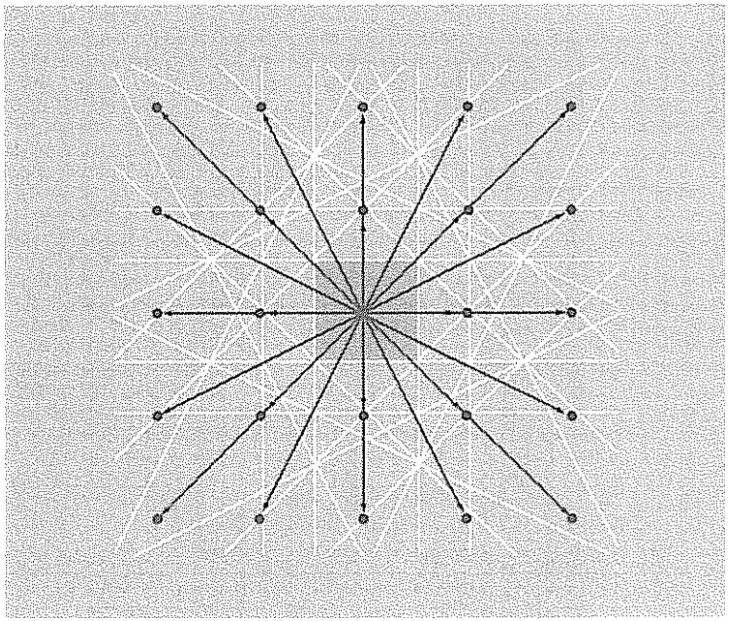


Brillouin Zone

A Brillouin zone is defined as a Wigner-Seitz cell in the reciprocal lattice.

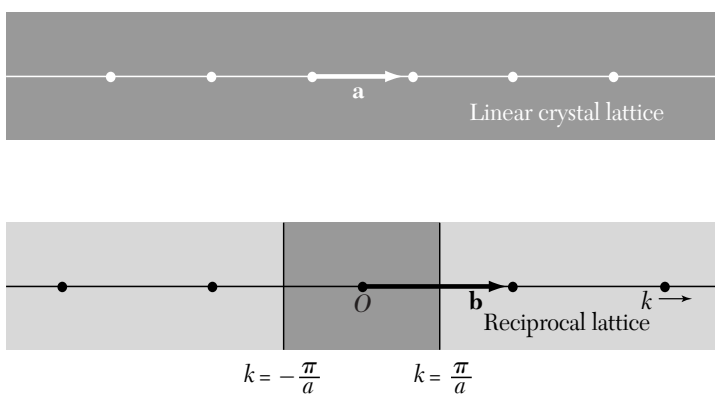
$$\mathbf{k} \cdot \left(\tfrac{1}{2}\mathbf{G}\right) = \left(\tfrac{1}{2}G\right)^2$$

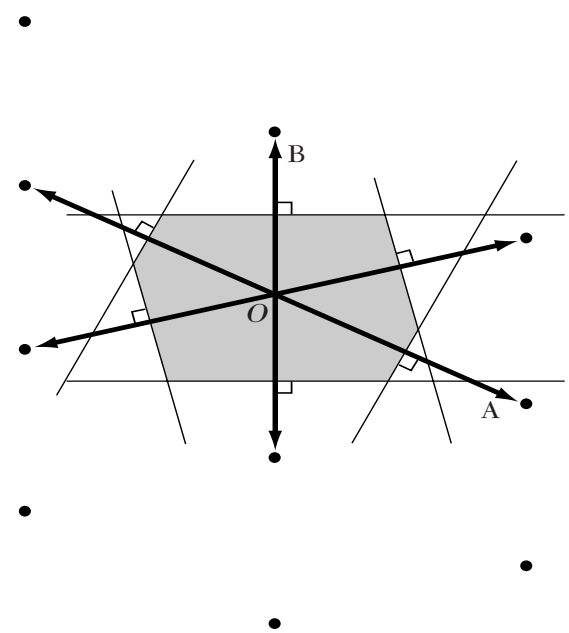




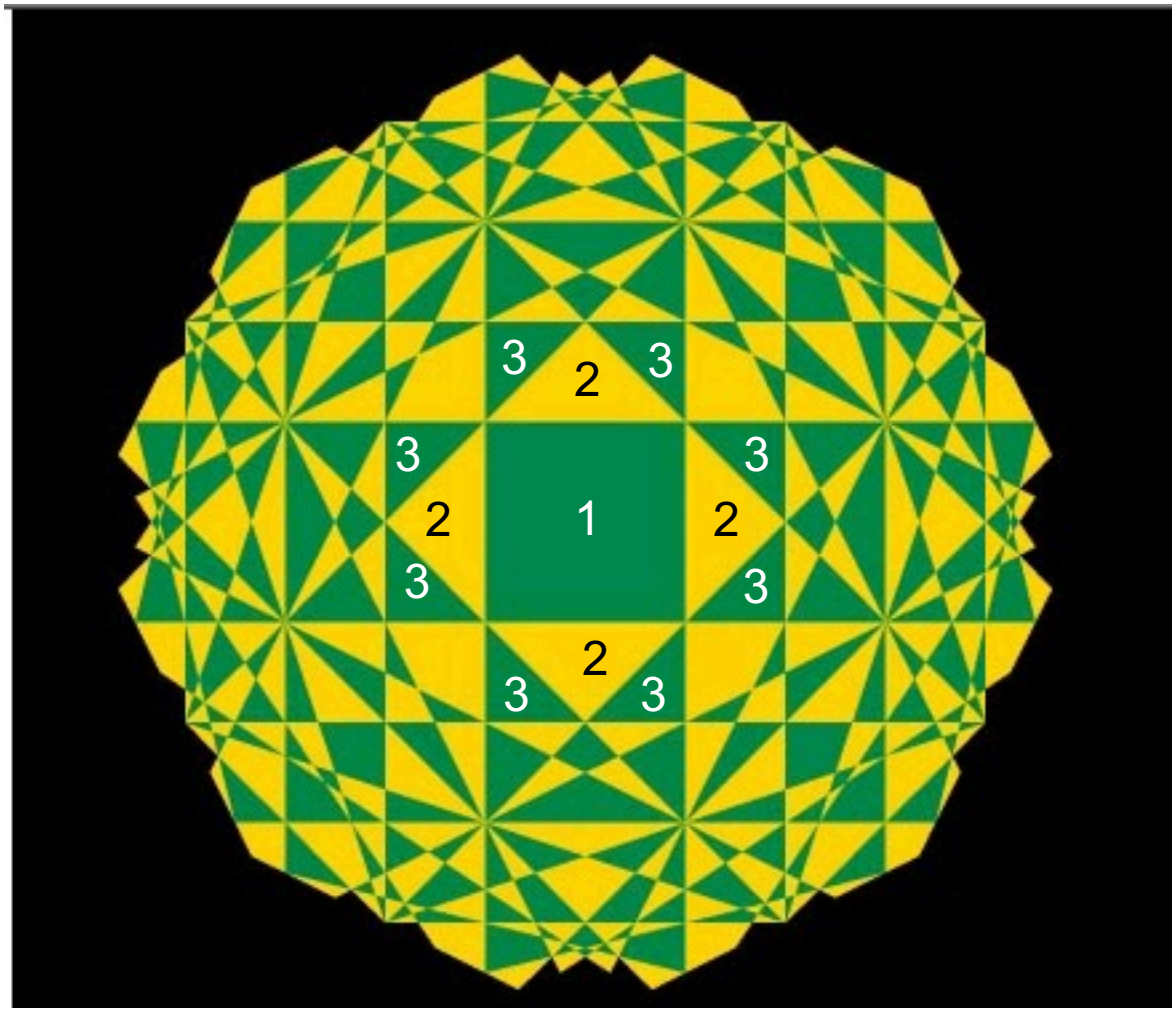
Brillouin Zone in 1D and 2D

The central cell in the reciprocal lattice is of special importance in the theory of solids, and we call it the first Brillouin zone. *The first Brillouin zone is the smallest volume entirely enclosed by planes that are the perpendicular bi-sectors of the reciprocal lattice vectors drawn from the origin.*





All Brillouin Zones: Square Lattice



At the Zone Boundary

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

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

$$\boxed{(\lambda_k - \epsilon)C(k) + \sum_G U_G C(k-G) = 0}$$

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

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

The energy ϵ satisfies

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

whence $\quad (\lambda - \epsilon)^2 = U^2 \;\; ; \qquad \epsilon = \lambda \pm U = \dfrac{\hbar^2}{2m}(\tfrac{1}{2}G)^2 \pm U \;\; .$

$$\frac{C(-\frac{1}{2}G)}{C(\frac{1}{2}G)} = \frac{\epsilon - \lambda}{U} = \pm 1 \;\; , \quad \text{and} \quad \psi(x) = \exp(iGx/2) \pm \exp(-iGx/2) \;\; .$$

Near a Zone Boundary

We use the same two-component approximation, now with a wavefunction of the form

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

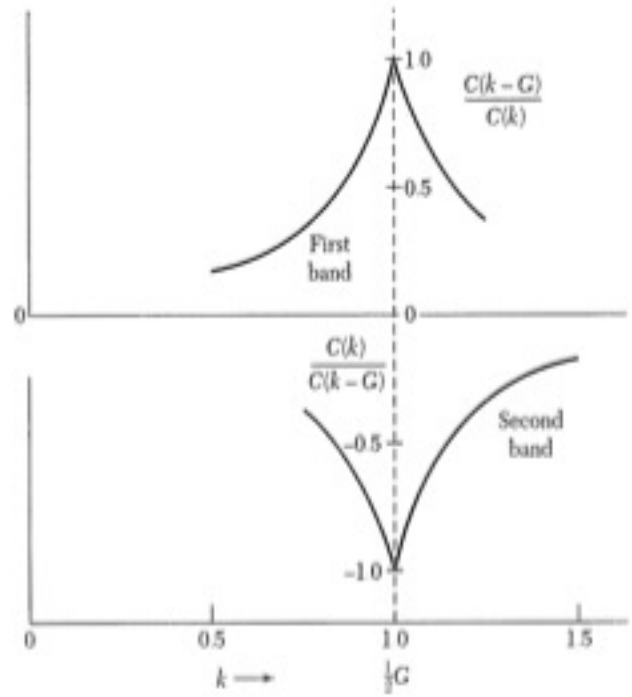
We solve

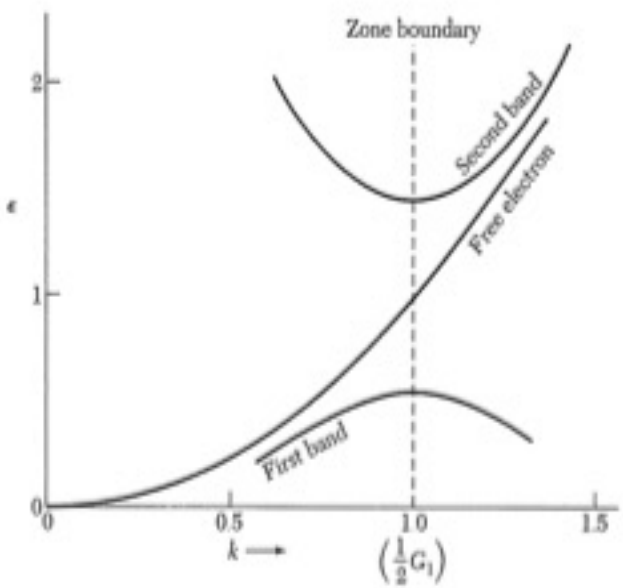
$$(\lambda_k - \epsilon)C(k) + UC(k-G) = 0 \ ;$$

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

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

and each root describes an energy band below.





Let

$$\tilde{K} \equiv k - \tfrac{1}{2}G$$

$$\epsilon_{\tilde{K}} = (\hbar^2/2m)(\tfrac{1}{4}G^2 + \tilde{K}^2) \pm [4\lambda(\hbar^2\tilde{K}^2/2m) + U^2]^{1/2}$$

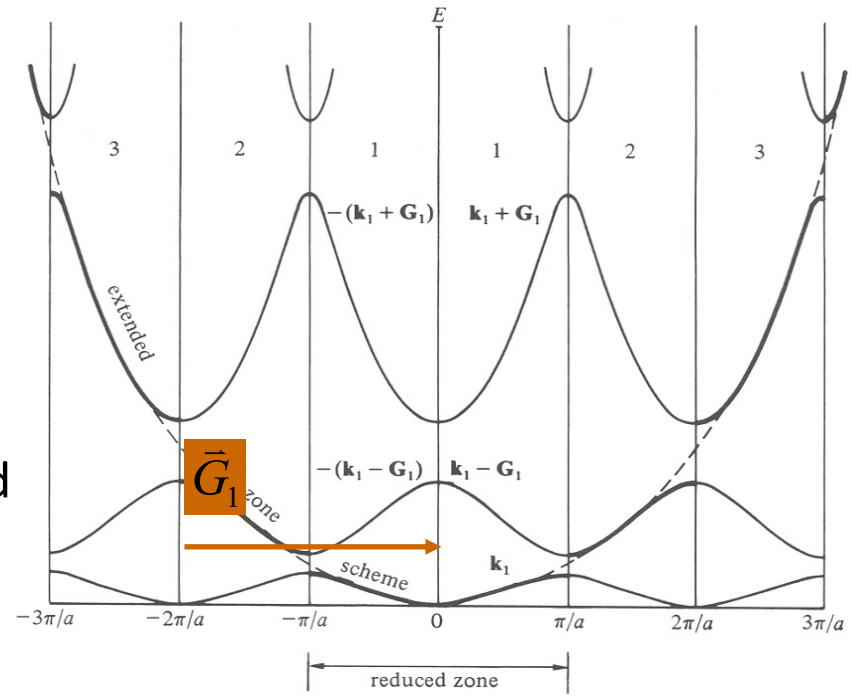
$$\simeq (\hbar^2/2m)(\tfrac{1}{4}G^2 + \tilde{K}^2) \pm U[1 + 2(\lambda/U^2)(\hbar^2\tilde{K}^2/2m)]$$

Different Representations of E(k)

If we apply periodic boundary conditions to the 1-D crystal, the energy bands are invariant under a reciprocal lattice translation vector:

$$E(\vec{k}+\vec{G}) = E(\vec{k}) \qquad \vec{G} = \frac{2\pi n}{a}\hat{i}$$

The bands can be graphically displayed in either the (i) extended zone scheme; (ii) periodic zone scheme; or (iii) reduced zone scheme.



(i) extended zone scheme: plot E(k) from k = 0 through all possible BZs

(ii) periodic zone scheme: redraw E(k) in each zone and superimpose

(iii) reduced zone scheme: all states with |k| > π/a are translated back into 1st BZ

Empty Lattice Approximation

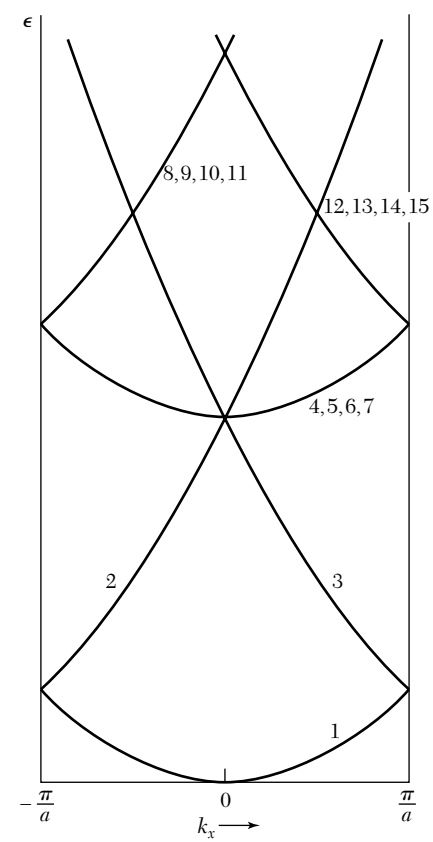
Actual band structures are usually exhibited as plots of energy versus wavevector in the first Brillouin zone. When wavevectors happen to be given outside the first zone, they are carried back into the first zone by subtracting a suitable reciprocal lattice vector. Such a translation can always be found.

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

with **k** in the first zone and **G** allowed to run over the appropriate reciprocal lattice points.

Example: Low-lying free electron bands of a simple cubic lattice plotted along the k_x in the first Brillouin 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	$011,0\bar{1}1,01\bar{1},0\bar{1}\bar{1}$	$2(2\pi/a)^2$	$k_x^2+2(2\pi/a)^2$



Number of Orbitals in a Band

For free electron model: $\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$

where, for periodic boundary conditions over a cube of side *L*,

$$k_x, k_y, k_z = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \ . \ . \ . \ .$$

At the 1BZ boundary $k = \pi/a$, so the total allowed *k*'s are

$$k = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \ \ldots \ ; \ \frac{N\pi}{L} \ .$$

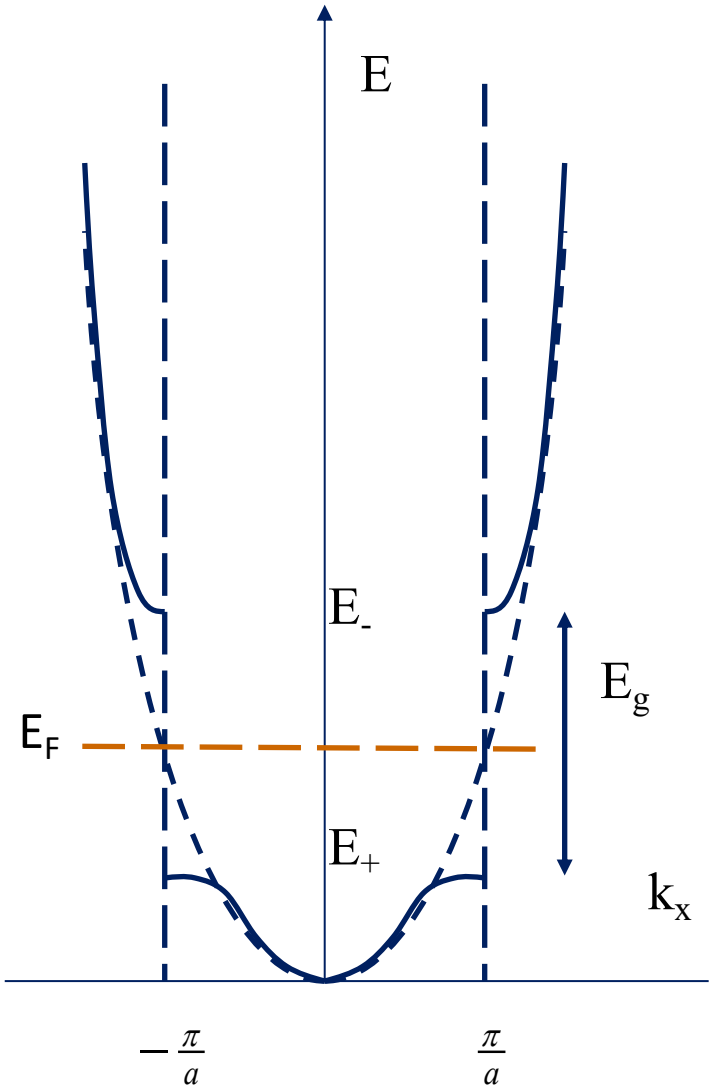
Each primitive cell contributes exactly one independent value of *k* to each energy band. This result carries over into three dimensions. With account taken of the two independent orientations of the electron spin, **there are 2*N* independent orbitals in each energy band**. If there is a single atom 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, Insulators, and Semiconductors

It is easy to show that the number of k values in each BZ is just N, the number of primitive unit cells in the sample. Thus, each band can be occupied by 2N electrons due to their spin degeneracy.

A monovalent element with one atom per primitive cell has only 1 valence electron per primitive cell and thus N electrons in the lowest energy band. This band will only be half-filled.

The Fermi energy is the energy dividing the occupied and unoccupied states, as shown for a monovalent element.

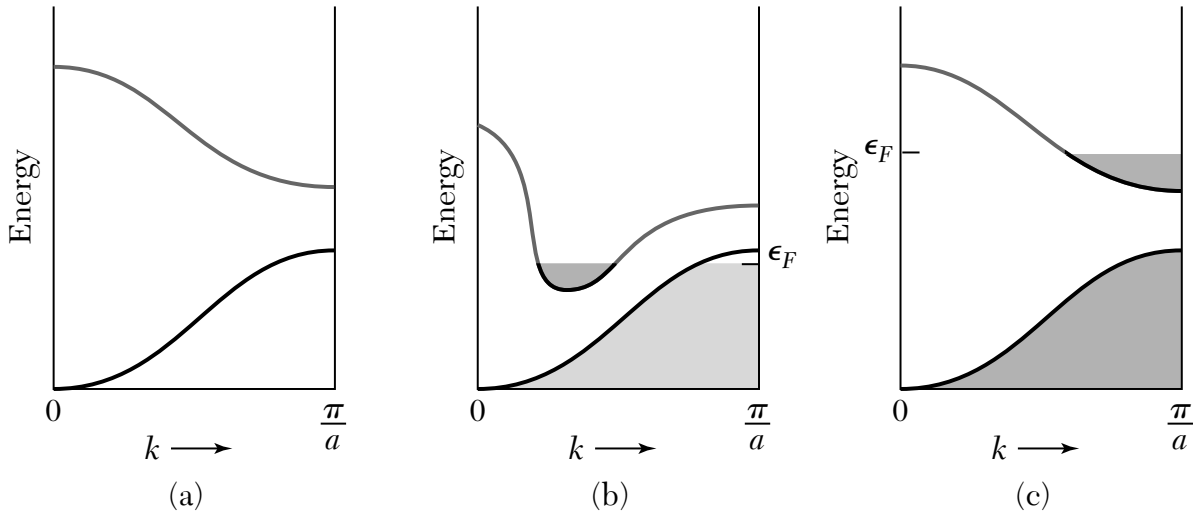


Metals, Insulators, and Semiconductors

For reasons that will be explained more fully later:

- Metals are solids with incompletely filled energy bands

- Semiconductors and $\hbar$ insulators have a completely filled or empty bands and an energy gap separating the highest filled and lowest unfilled band. Semiconductors have a small energy gap (E_g < 2.0 eV).



Problems

1. ***Square lattice, free electron energies*.** (a) Show for a simple square lattice (two dimensions) that the kinetic energy of a free electron at a corner of the first zone is higher than that of an electron at midpoint of a side face of the zone by a factor of 2. (b) What is the corresponding factor for a simple cubic lattice (three dimensions)? (c) What bearing might the result of (b) have on the conductivity of divalent metals?

2. ***Square lattice*.** Consider a square lattice in two dimensions with the crystal potential

$$U(x,y) = -4U\cos(2\pi x/a)\cos(2\pi y/a) \ .$$

Apply the central equation to find approximately the energy gap at the corner point (π/a, π/a) of the Brillouin zone. It will suffice to solve a 2×2 determinantal equation.

3. Suppose we want to exhibit the energy as a function of **k** in the [100] direction for a *bcc* lattice. Show the four lowest-lying bands in the empty lattice approximation with their energies (000) at **k** = 0 and (k_x00) along the k_x axis in the first zone. (For convenience, choose units such that $\hbar^2/2m = 1$)