Band theory of solids

There are usually two approaches to understand the origin of band theory associated with solids. One is the “nearly free electron model” and the other “tight-binding model”.

1) Nearly free electron model:

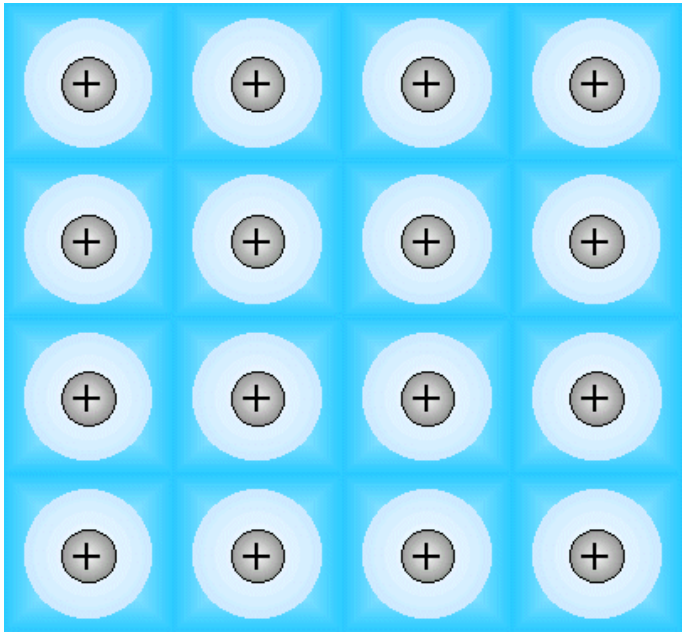
In the nearly free electron approximation, interactions between electrons are completely ignored. This model allows use of Bloch's Theorem which states that electrons in a periodic potential have wavefunctions and energies which are periodic in wavevector up to a constant phase shift between neighboring reciprocal lattice vectors.

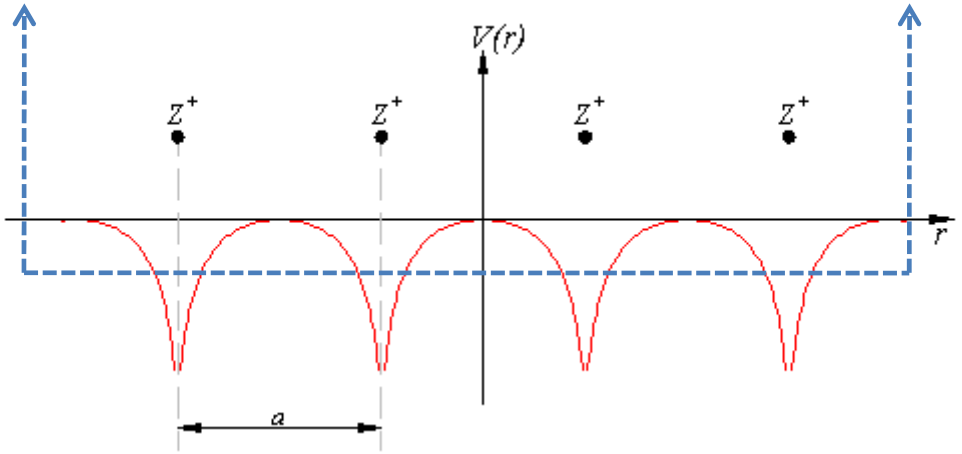
2) Tight-binding model

The opposite extreme to the nearly-free electron model assumes the electrons in the crystal behave much like an assembly of constituent atoms.

Metallic Bonds

Metallic bonding is the electromagnetic interaction between delocalized electrons, called conduction electrons and gathered in an "electron sea", and the metallic nuclei within metals. Metallic bonding accounts for many physical properties of metals, such as strength, malleability, thermal and electrical conductivity, opacity, and luster.





$V(r) = C$

Free Fermi electron gas

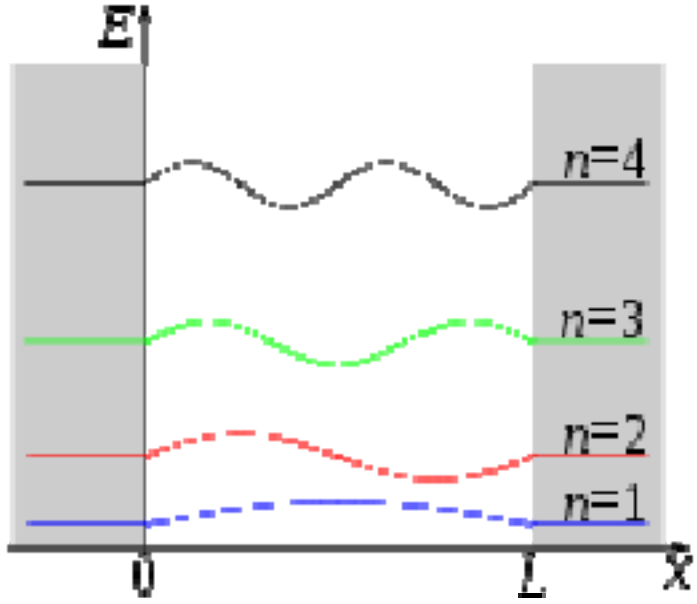
Free electron gas in 1D

$\phi(x) = Ae^{ikx}$

The wavefunction must be continuous at the interfaces, meaning that $\phi(0) = \phi(L) = 0$.

$$k_n = \frac{n\pi}{L}, \quad \text{where} \quad n \in \mathbb{Z}^+$$

$$E = \frac{k^2\hbar^2}{2m} = \hbar^2 n^2/(2m)(\pi/L)^2$$



Free electron gas in 3D

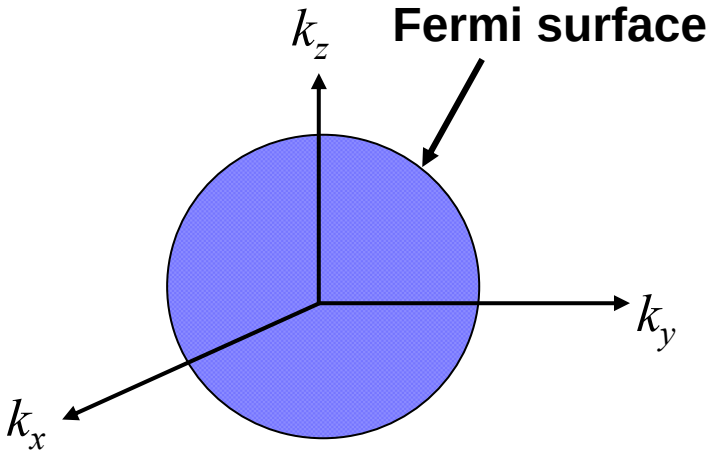
$$\phi(\mathbf{r}) = Ae^{i\mathbf{k}\bullet\mathbf{r}}$$

The wavefunction must be periodic with period L, meaning that

$\phi(x,y,z) = \phi(x+L,y,z) = \phi(x,y+L,z) = \phi(x,y,z+L)$.

$k_x = \pm 2n\pi/L$, $n = 0, 1, 2\ldots$; same for k_y and k_z.

$$E_k = \frac{k^2\hbar^2}{2m} = \hbar^2/(2m)(k_x^2 + k_y^2 + k_z^2)$$



Fermi sphere is defined by

$$E_F = \frac{k_F^2\hbar^2}{2m}$$

$$k_F = (3\pi^2 N/V)^{1/3}$$

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

Density of states

$$D(E) = dN/dE = V/(2\pi^2)\bullet(2m/\hbar^2)^{3/2}\bullet E^{1/2}$$

Heat capacity of electron gas

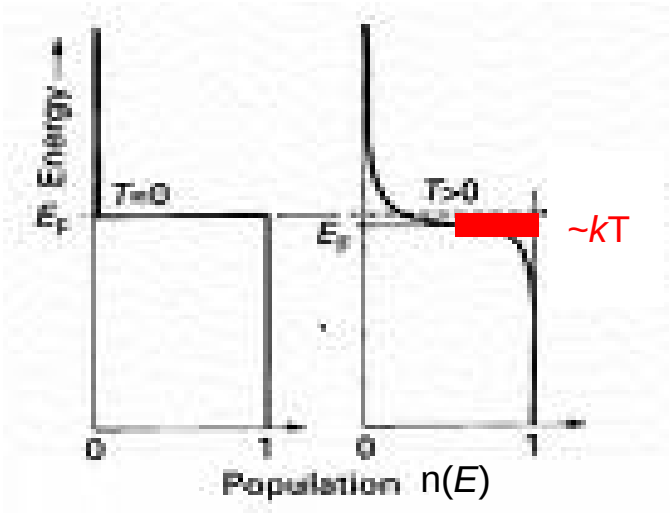
$C_{el} = \partial U/\partial T$

$U = \int D(E)\langle n(E)\rangle E\, dE$

$N = \int_0^{E_F} D(E)\, dE$

Fermi–Dirac (F–D) distribution

$$n(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$



$D(E) = dN/dE = V/(2\pi^2)\cdot(2m/\hbar^2)^{3/2}\cdot E^{1/2}$

$C_{el} = \frac{1}{2}\pi^2 Nk(T/T_F)$ $\quad T_F = E_F/k$

Heat capacity of a metal

$C_{tot} = C_{el} + C_{ph} = AT + BT^3$

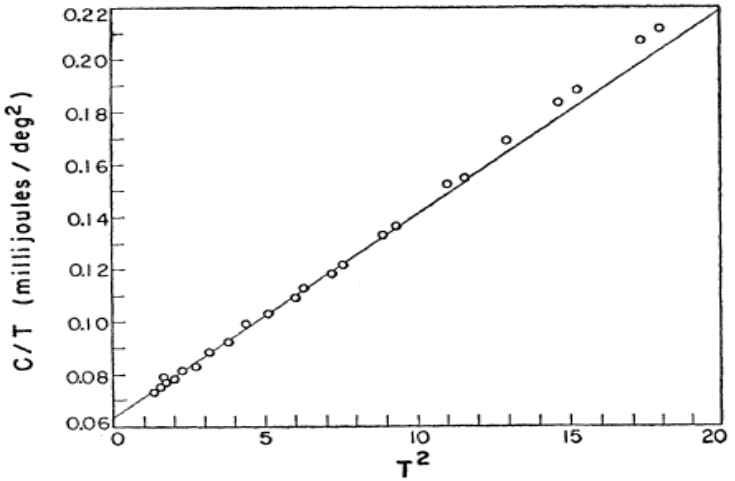
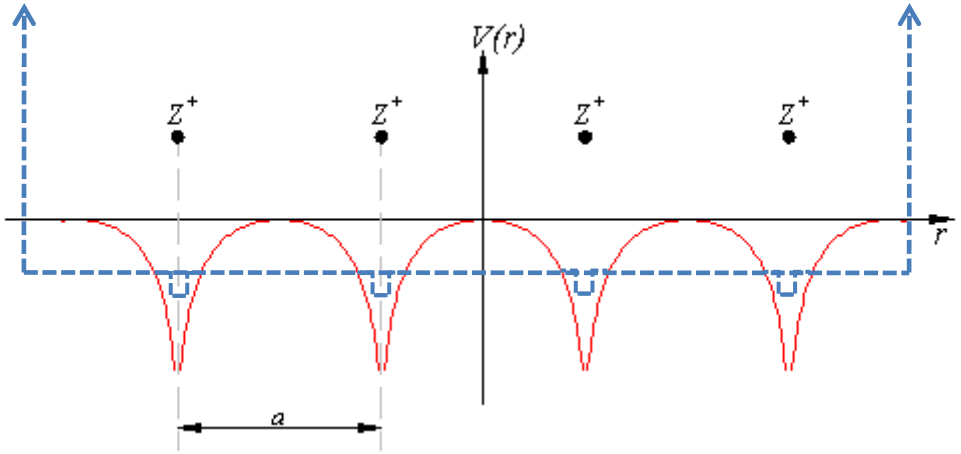


FIG. 3. Heat capacity of the addenda.

N.E. Phillips, Phys. Rev. 114, 676 (1959).

Nearly free electron gas



$V(r+a) = V(r) \sim 0$

The Bragg reflection condition in 1D:

$$(k + G)^2 = k^2$$

$$k = \pm G/2 = \pm n\pi/a$$

Bloch functions

A **Bloch wave** or **Bloch state**, named after Felix Bloch, is the wavefunction of a particle (usually, an electron) placed in a periodic potential. It consists of the product of a plane wave envelope function and a periodic function (*periodic Bloch function*) $u_{n\mathbf{k}}(r)$ which has the same periodicity as the potential:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}).$$

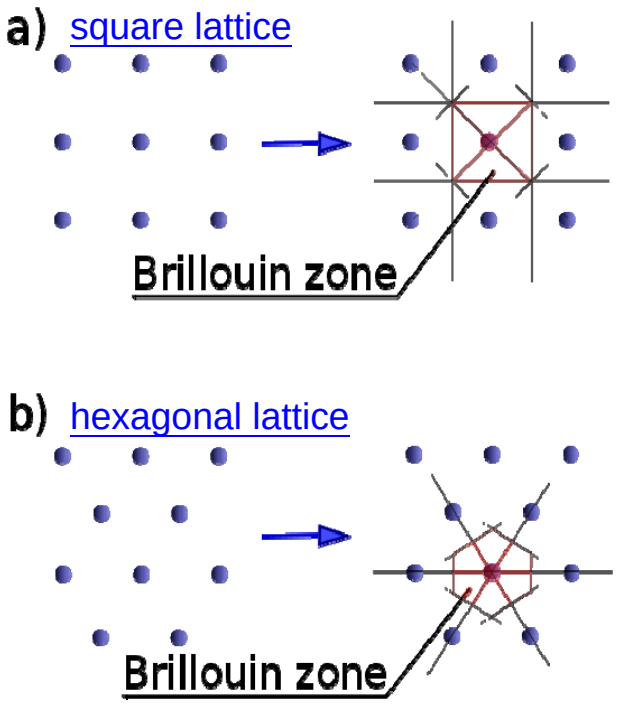
$$u_{nk}(\mathbf{r}+\mathbf{T}) = u_{nk}(\mathbf{r})$$

The corresponding energy eigenvalue is

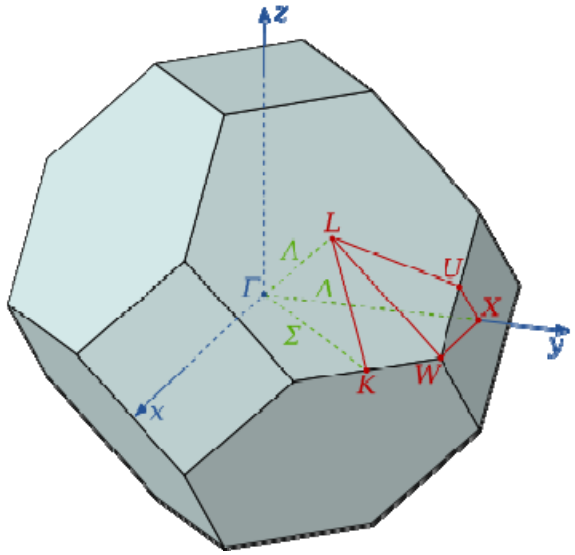
$$\in_n(\mathbf{k}) = \in_n(\mathbf{k} + \mathbf{G}).$$

Brillouin zone

The first **Brillouin zone** is a uniquely defined **primitive cell** in **reciprocal space**.



First Brillouin zone of FCC lattice showing symmetry labels for high symmetry lines and points

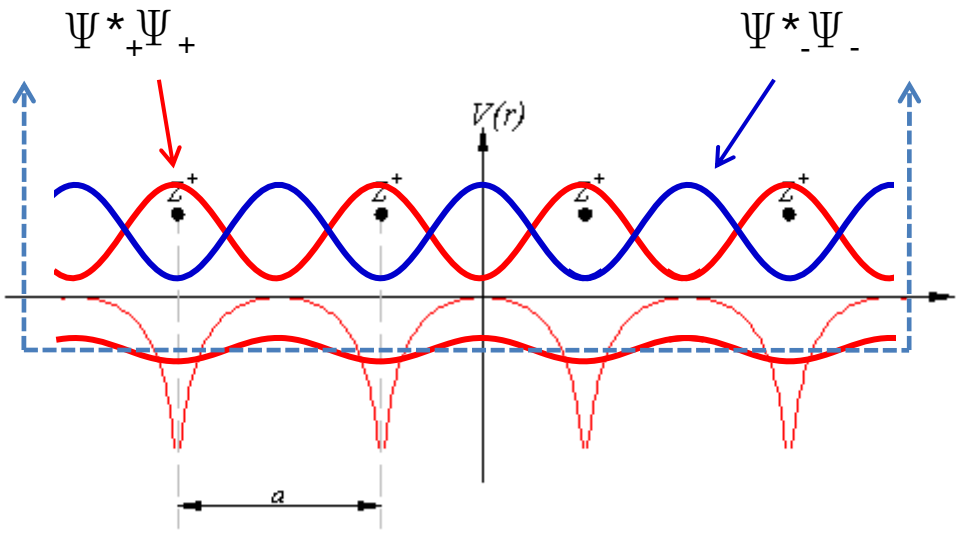


K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face

At k = $\pm \pi/a$

$$\Psi_+(x) = e^{ikx} + e^{-ikx} = 2\cos(\pi x/a)$$

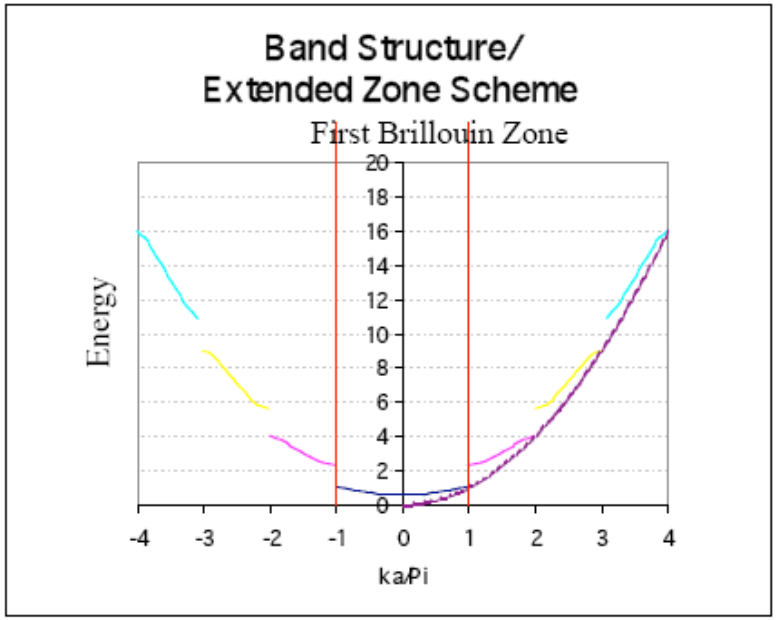
$$\Psi_-(x) = e^{ikx} - e^{-ikx} = 2i\sin(\pi x/a)$$



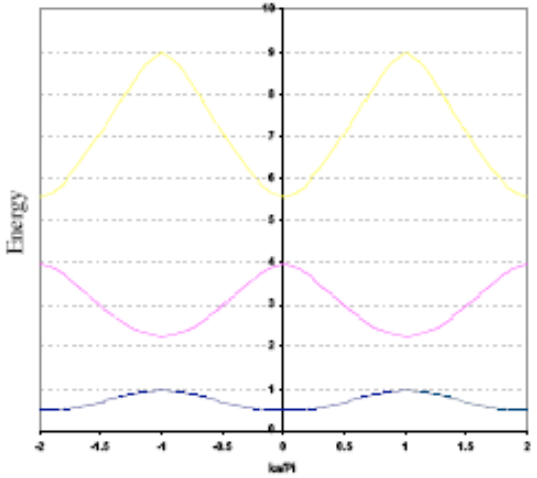
$$U(x) = 2U\cos(2\pi x/a)$$

$$E_g = \int_0^1 dx\, U(x)\,[\Psi^*_+\Psi_+ - \Psi^*_-\Psi_-] = U$$

Expression of band structure in different schemes



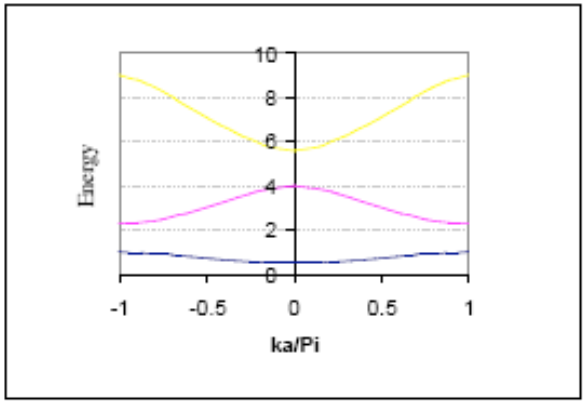
Periodic Zone Scheme



$\psi_n(\mathbf{k}) = \psi_n(\mathbf{k} + \mathbf{G})$

$\epsilon_n(\mathbf{k}) = \epsilon_n(\mathbf{k} + \mathbf{G})$

Reduced Zone Scheme



•Bands folded into First Brillouin Zone

Kronig-Penney model

i) $0 < x < a - b$:

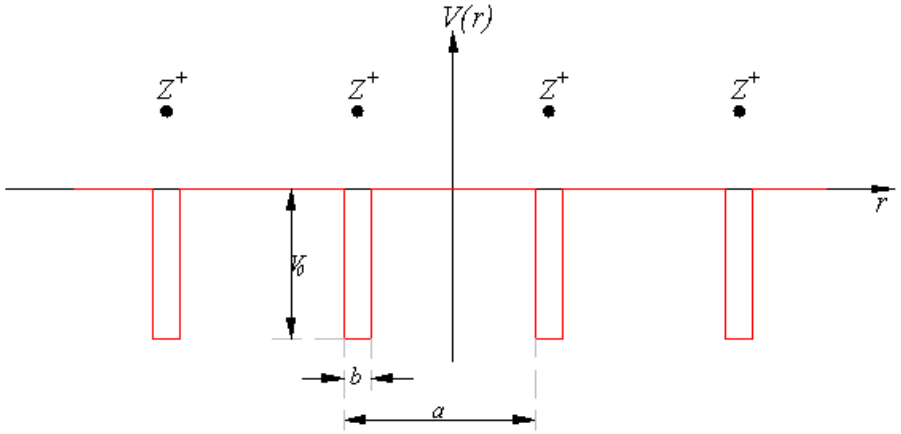
$$\frac{-\hbar^2}{2m}\psi_{xx} = E\psi$$

$$\Rightarrow \psi = Ae^{i\alpha x} + A'e^{-i\alpha x} \qquad \left(\alpha^2 = \frac{2mE}{\hbar^2}\right)$$

ii) $-b < x < 0$:

$$\frac{-\hbar^2}{2m}\psi_{xx} = (E + V_0)\psi$$

$$\Rightarrow \psi = Be^{i\beta x} + B'e^{-i\beta x} \qquad \left(\beta^2 = \frac{2m(E+V_0)}{\hbar^2}\right).$$



Probability function must be continuous and smooth:

$$\psi(0^-) = \psi(0^+) \qquad \psi'(0^-) = \psi'(0^+).$$

and that *u*(*x*) and *u'*(*x*) are periodic:

$$u(-b) = u(a-b) \qquad u'(-b) = u'(a-b).$$

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ \alpha & -\alpha & -\beta & \beta \\ e^{i(\alpha-k)(a-b)} & e^{-i(\alpha+k)(a-b)} & -e^{-i(\beta-k)b} & -e^{i(\beta+k)b} \\ (\alpha-k)e^{i(\alpha-k)(a-b)} & -(\alpha+k)e^{-i(\alpha+k)(a-b)} & -(\beta-k)e^{-i(\beta-k)b} & (\beta+k)e^{i(\beta+k)b} \end{pmatrix} \begin{pmatrix} A \\ A' \\ B \\ B' \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

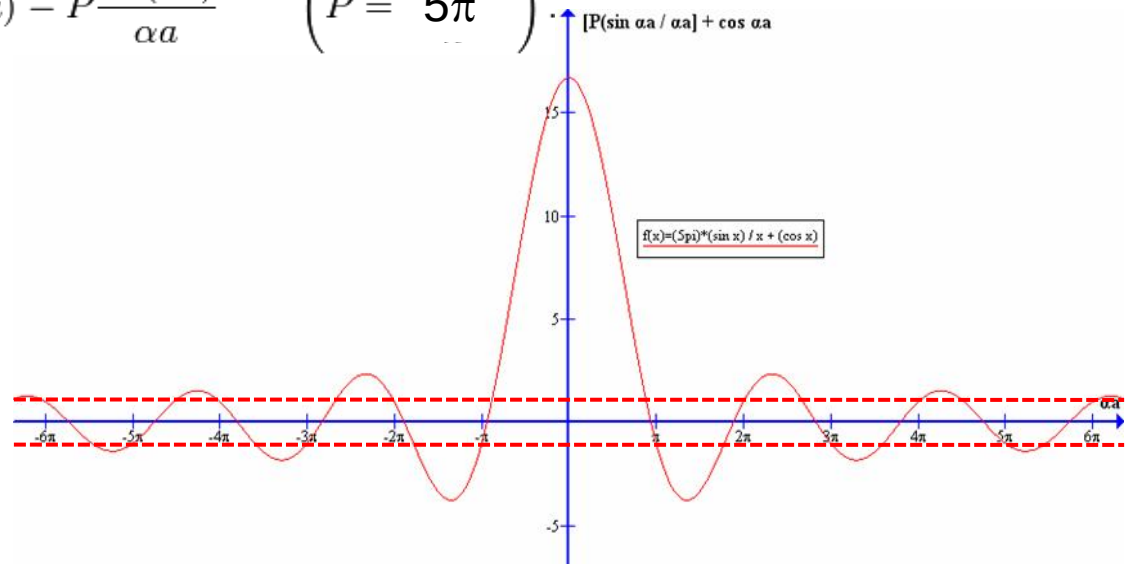
$$\Rightarrow \quad \cos(ka) = \cos(\beta b)\cos[\alpha(a-b)] - \frac{\alpha^2+\beta^2}{2\alpha\beta}\sin(\beta b)\sin[\alpha(a-b)].$$

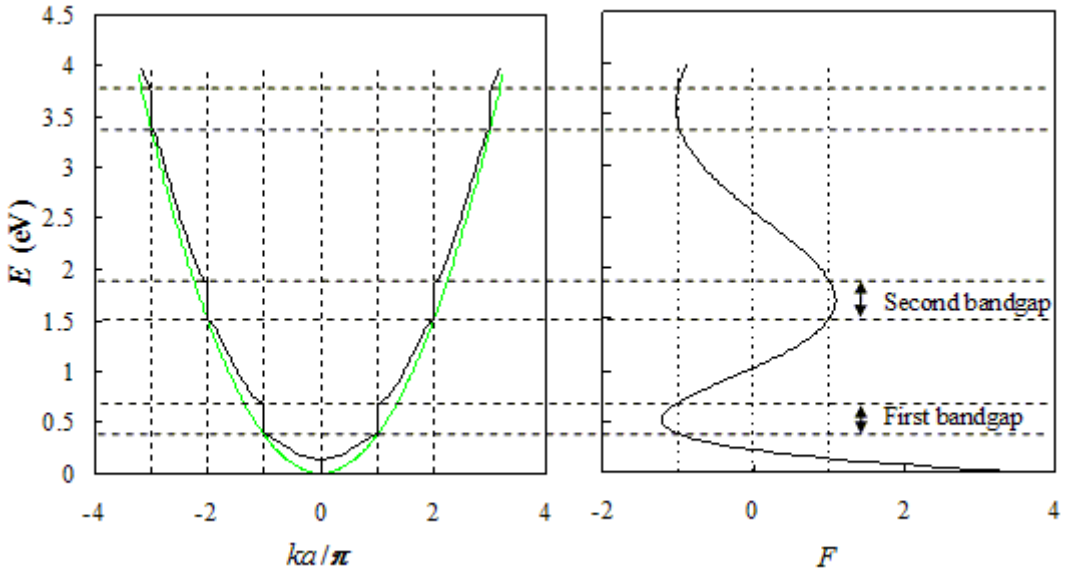
If we approximate:

$$b \to 0 \ ; \ V_0 \to \infty \ ; \ V_0 b = \text{constant}$$
$$\Rightarrow \beta^2 b = \text{constant} \ ; \ \alpha^2 b \to 0$$
$$\Rightarrow \beta b \to 0 \ ; \ \sin(\beta b) \to \beta b \ ; \ \cos(\beta b) \to 1.$$

$$\Rightarrow \quad \cos(ka) = \cos(\alpha a) - P\frac{\sin(\alpha a)}{\alpha a} \qquad \left(P = \frac{mV_0 ba}{h^2}\right).$$

$$\cos(ka) = \cos(\alpha a) - P\frac{\sin(\alpha a)}{\alpha a} \qquad \left(P = \ 5\pi \ \right)$$





Tight binding model

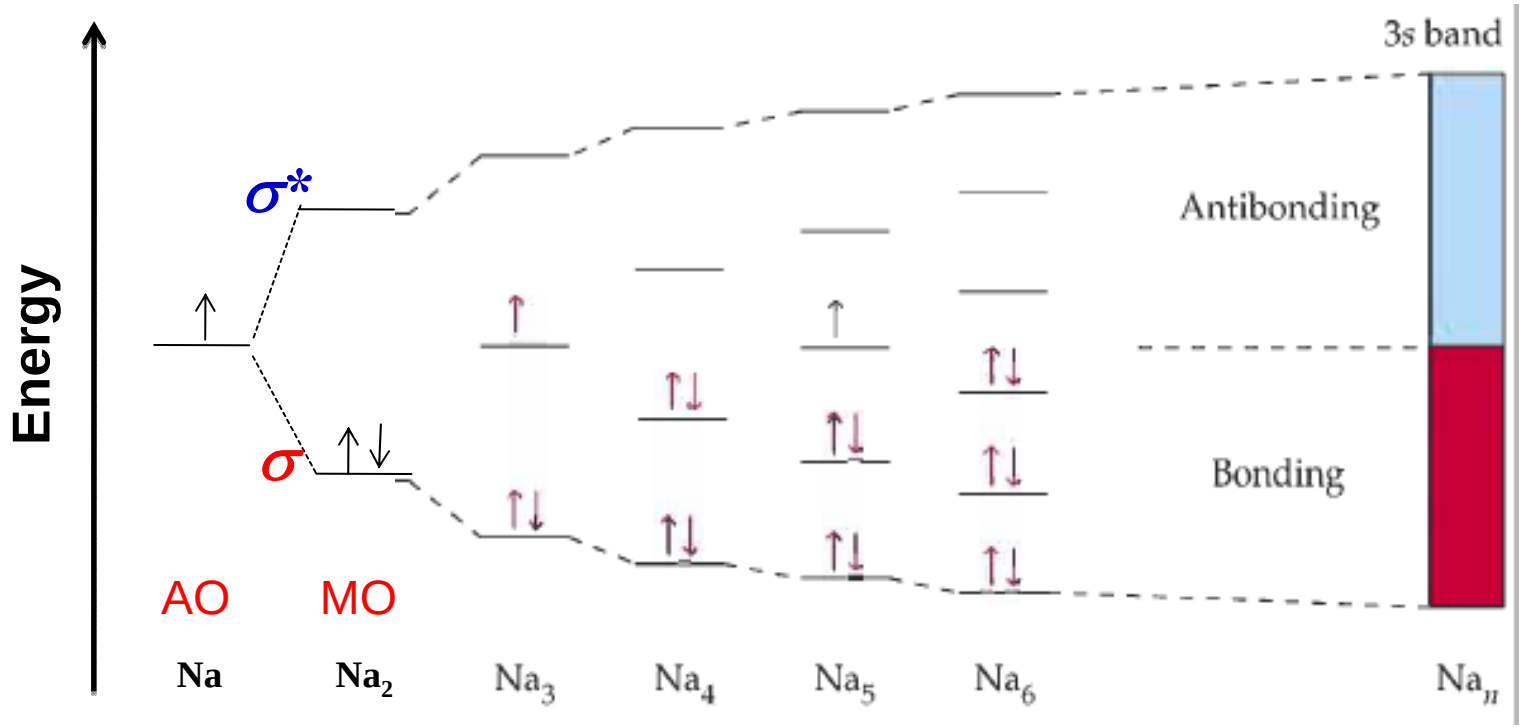
In solid-state physics, the tight binding model is an approach to the calculation of electronic band structure using an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site. In this approach, interactions between different atomic sites are considered as perturbations, i.e. correction to the atomic potential ΔU is small.

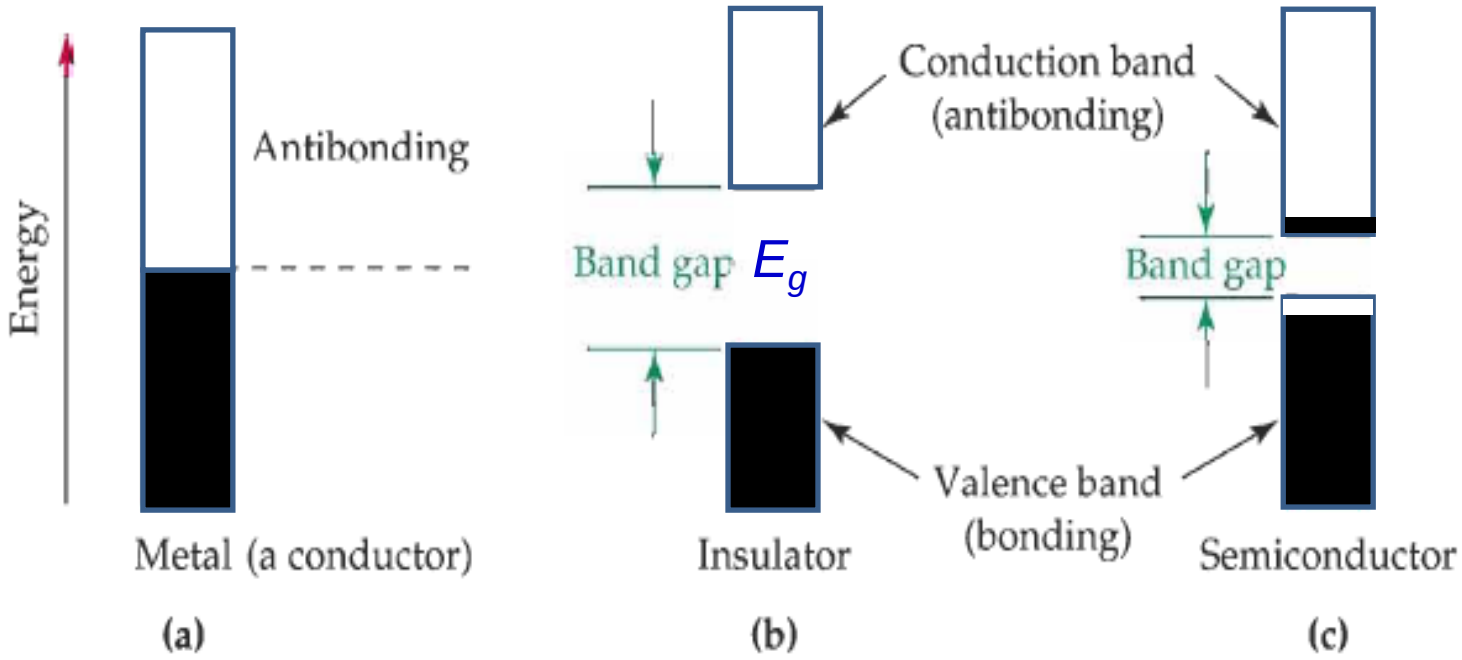
$$H(\boldsymbol{r}) = \sum_{\boldsymbol{R_n}} H_{\mathrm{at}}(\boldsymbol{r} - \boldsymbol{R_n}) + \Delta U(\boldsymbol{r}) \ .$$

A solution ϕ (***r***) to the time-independent single electron Schrödinger equation is then approximated as a linear combination of atomic orbitals $\varphi_{\mathrm{m}}(\boldsymbol{r} - \boldsymbol{R_n})$:

$$\psi(\boldsymbol{r}) = \sum_{m,\boldsymbol{R_n}} b_m(\boldsymbol{R_n})\ \varphi_m(\boldsymbol{r} - \boldsymbol{R_n})$$

where *m* refers to the *m-th* atomic energy level and $\boldsymbol{R_n}$ locates an atomic site in the crystal lattice.


Energy
3s band
σ*
σ
Antibonding
Bonding
AO
MO
Na
Na2
Na3
Na4
Na5
Na6
Nan



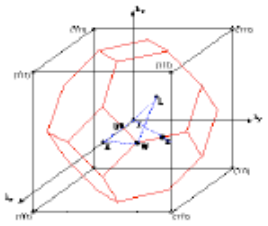
$E_g = 0$

$E_g > 3$ eV

$E_g < 3$ eV

Examples

Free electron bands for fcc structure

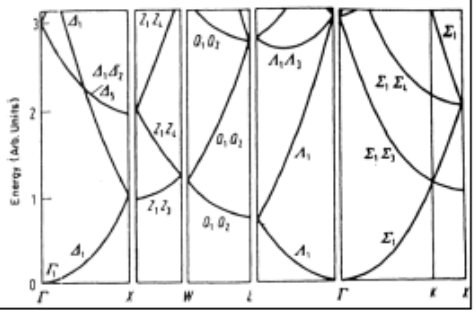


Γ – center of the BZ

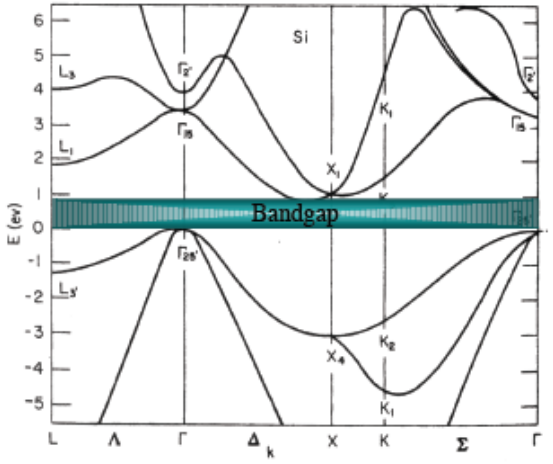
X – [100] intercept; Γ – X path Δ

K – [110] intercept; Γ – K path Σ

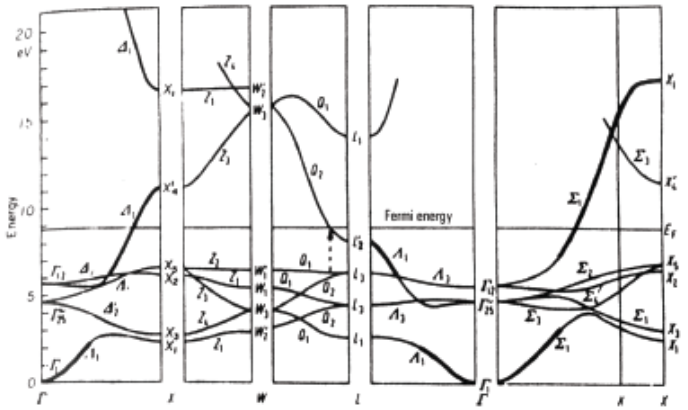
L – [111] intercept; Γ – L path Λ



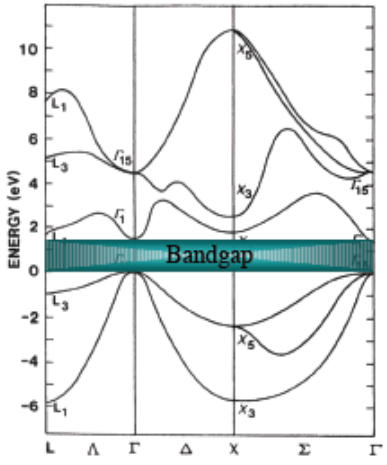
Band structure of Si (diamond)



Band structure of Cu (fcc)



Band structure of GaAs (zb)



Homework#7 (Dec. 14, 2009):

(a)Construct the third Brillouin zone for a simple square lattice in both the extended- and reduced-zone representations.
(b)Find the expressions of the density of states for free electron gas in one dimension (1D) and 2D.