Free Electron Gas in Solids

Suppose that we model the electrons in a solid by the potential

$$V(x,y,z) = 0 \; , \text{ if } x \in [0, l_x] \\ y \in [0, l_y] \text{ and} \\ z \in [0, l_z]$$

$$= \infty \; , \text{ otherwise}$$

Then we need to solve

$$\hat{H}\Psi = E\Psi$$

$$\Rightarrow \quad \nabla^2 \Psi = -k^2 \Psi, \text{ where } k = \left[\frac{2mE}{\hbar^2}\right]^{1/2}$$

By separation of variables we may solve to get

$$\Psi_{n_x n_y n_z}(\bar{x}) = \left[\frac{8}{l_x l_y l_z}\right]^{1/2} \sin(k_x x)\sin(k_y y)\sin(k_z z) \rightarrow \text{5.38}$$

where $\bar{k} = \left(\frac{n_x}{l_x}, \frac{n_y}{l_y}, \frac{n_z}{l_z}\right)\pi$

and n_x, n_y, n_z are positive integers.

$$E_{n_x n_y n_z} = \frac{\hbar^2 \bar{k}^2}{2m} = \frac{\pi^2 \hbar^2}{2m}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right] \longrightarrow \text{5.39}$$

Now let us constuct a space with Cartesian axes along k_x, k_y and k_z as in Fig 5.3.

Each point P in this space defined by integers $(n_x, n_y, n_z) \ni$

$$\bar{r}_p = \pi \left[\frac{n_x}{l_x}, \frac{n_y}{l_y}, \frac{n_z}{l_z} \right]$$ will correspond

to a single electron state $\Psi_{n_x n_y n_z}(\bar{r})$ with

energy $E_{n_x n_y n_z}$ of Eq. (5-38) and (5-39).

So in one rectangular parallelopiped of volume $\frac{\pi^3}{V}$ where $V \equiv l_x l_y l_z$

there can be $(2S+1)$ states where S = spin of the particles under study. For us $S = \frac{1}{2}$

because we have electrons in the solid.

So volume per state $V_S = \frac{\pi^3}{(2S+1)V}$

Let there be N atoms in the solid each with valency q. This gives Nq electrons that are free.

Due to the fact that electrons are fermions these Nq electrons will occupy states within ~~the~~ a sphere of radius k_F. Only states in the first octant are used. Hence we get

$$\underbrace{\frac{1}{8}}_{\text{for octant}} \underbrace{\left(\frac{4\pi k_F^3}{3}\right)}_{\text{volume of a sphere}} = \underbrace{(Nq)}_{\text{total \# of free electrons}} \times \underbrace{\frac{\pi^3}{(2S+1)V}}_{\text{volume per state}}$$

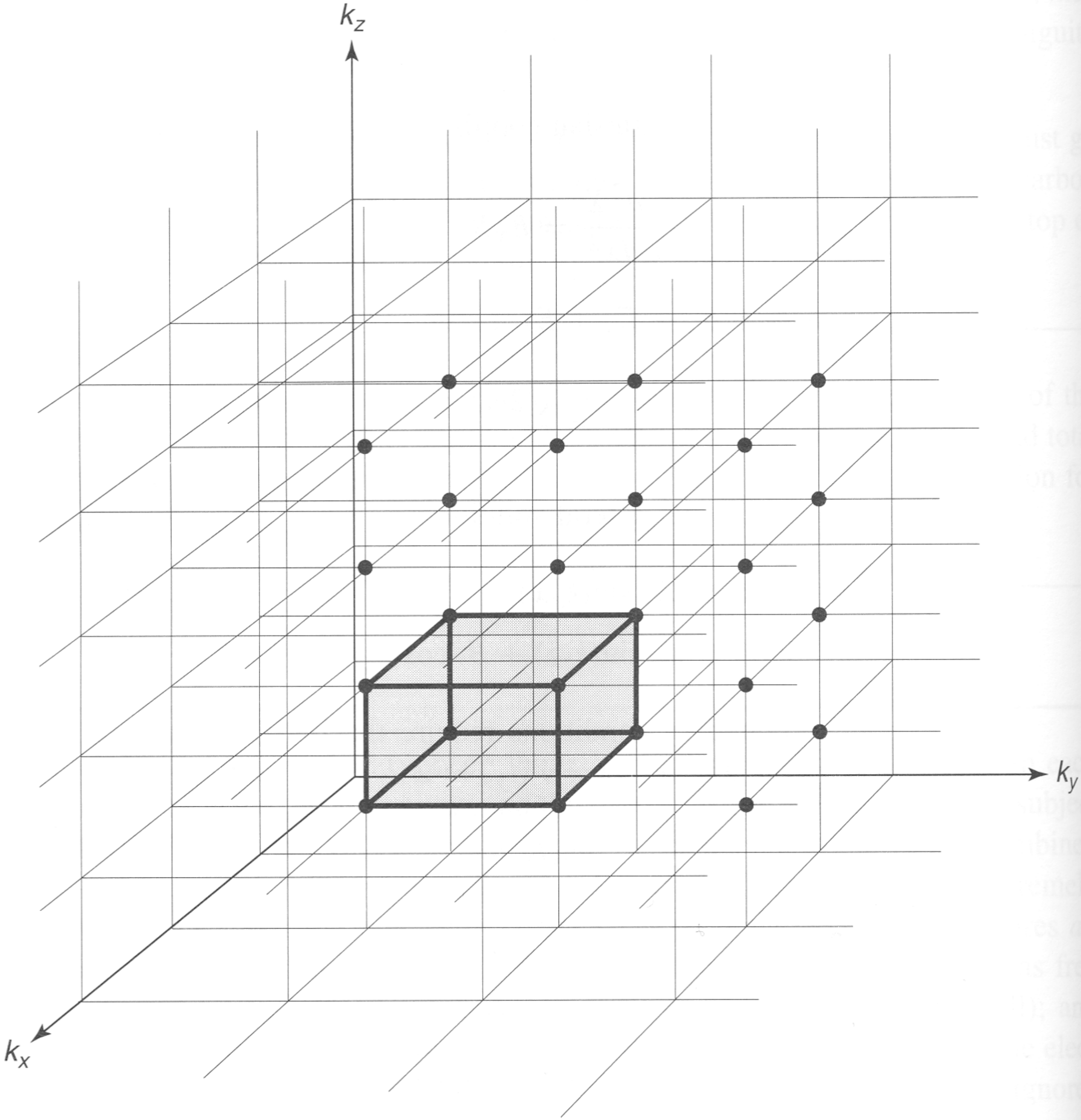

FIGURE 5.3: Free electron gas. Each intersection on the grid represents a stationary state. Shading indicates one “block”; there is one state for every block.

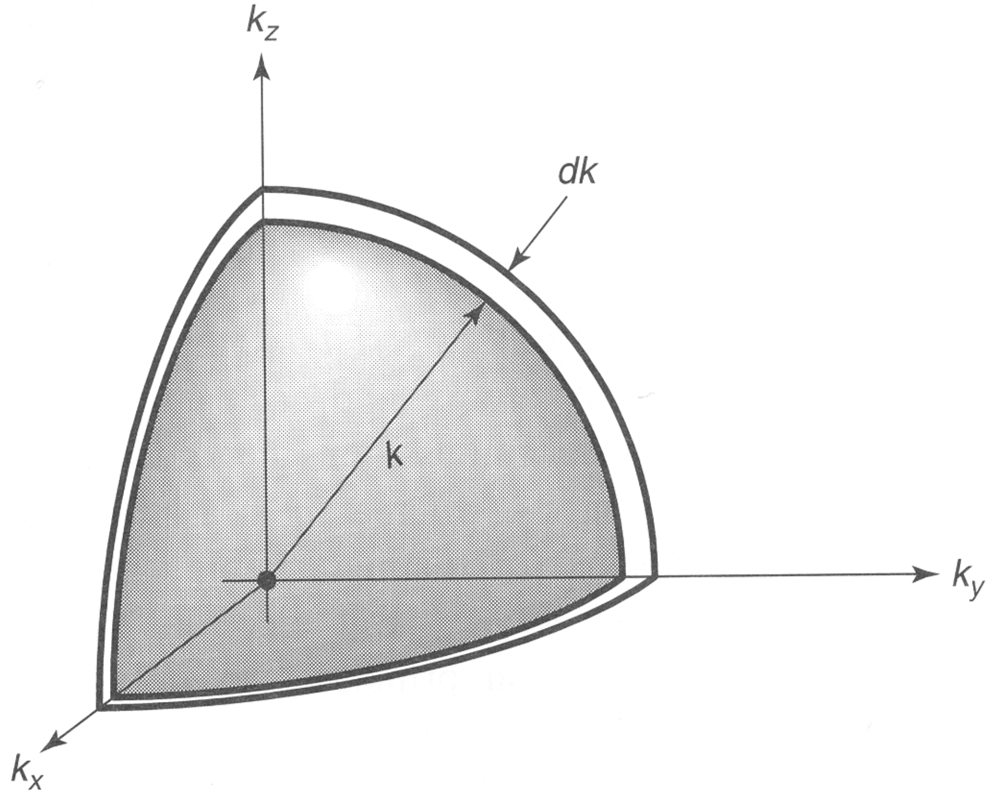

FIGURE 5.4: One octant of a spherical shell in *k*-space.

Let $\rho \equiv \left(\frac{Nq}{V}\right)$ = free electron density

$$\Rightarrow \quad k_F = (3\rho\pi^2)^{1/2}$$

Energy of the highest occupied state

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2\rho)^{1/2}.$$

Energy of an arbitrary state is

$$E_a = \frac{\hbar^2 k^2}{2m} \Rightarrow dE_a = \frac{\hbar^2}{m} k\,dk$$

Consider a shell as shown in Fig. 5.4.
Its volume is $\left(\frac{1}{8}\right)(4\pi k^2 dk)$

So # of electrons in the shell is

$$\frac{4\pi k^2 dk}{8\,\frac{\pi^3}{(2s+1)V}} = \frac{V k^2 dk (2s+1)}{2\pi^2}, \quad s = 1/2 \text{ for electrons}$$

$$= \frac{V k^2}{\pi^2} dk$$

So total energy of all states in the shell is

$$dE = E_a \frac{Vk^2}{\pi^2} dk = \frac{\hbar^2 V}{2m\pi^2} k^4 dk$$

Total electronic energy of the solid

$$E_{tot} = \int_0^{E_F} dE = \frac{\hbar^2 V}{2m\pi^2} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10 m \pi^2}$$

$$\Rightarrow E_{tot} = \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-2/3}$$

$\Rightarrow$ the pressure P of this electron gas on the external walls would be

$$P = -\frac{dE_{tot}}{dV} = -\frac{2}{3V} E_{tot} = (3\pi^2)^{2/3} \frac{\hbar^2}{5m} \rho^{5/3}$$

This is a purely quantum mechanical pressure from postulate VI as applied to electrons. It keeps the solid from collapsing. It is called the degeneracy pressure. Also found in neutron stars.

Band Structure:

We now consider a new model for electrons in a solid. Consider a 1D solid of length Na with a potential

$V(x+a) = V(x)$, where a is the periodic length = the inter-nuclear distance
N = # of atoms $\sim 10^{23}$.
We want to solve

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_E(x)}{dx^2} + V(x)\psi_E(x) = E\psi_E(x),$$

Consider the operator $\hat{D} \ni \hat{D} f(x) = f(x+a)$

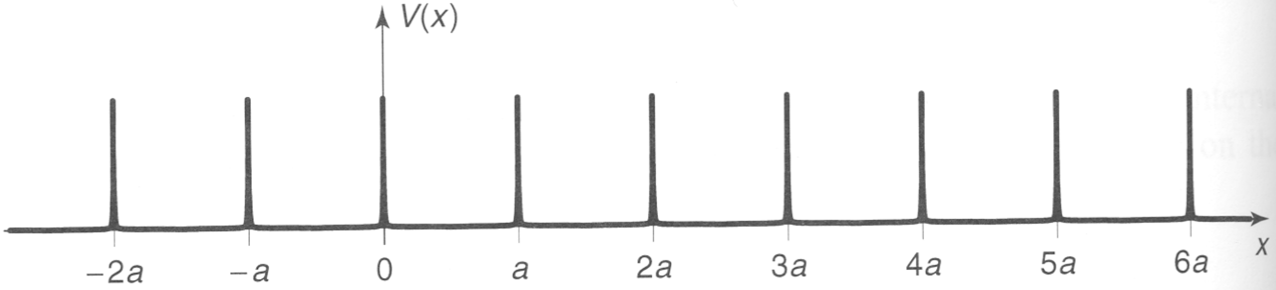

FIGURE 5.5: The Dirac comb, Equation 5.57.

$\hat{D}$ is the translation operator. For our periodic potential then

$$\hat{D}\hat{H} = \hat{H}\hat{D} \Rightarrow [\hat{D}, \hat{H}] = 0$$

$\Rightarrow$ we can choose $\psi_E(x)$ which satisfies

$$\hat{D}\psi_E(x) = \lambda \psi_E(x)$$

$$\Rightarrow \quad \psi_E(x+a) = \lambda \psi_E(x)$$

$$\Rightarrow \quad \psi_E(x+Na) = \lambda^n \psi_E(x).$$

Now we impose the boundary condition

$$\psi_E(x+Na) = \psi_E(x) \Rightarrow \lambda^N = 1$$

$$\Rightarrow \lambda^N = e^{2\pi i} \Rightarrow \lambda = e^{\frac{2\pi i n}{N}}, \ \forall n = 0,1,2,\ldots (N-1).$$

Define $K = \dfrac{2\pi n}{Na} \Rightarrow \lambda = e^{iKa}$

$\Rightarrow$ $Ka \in [0, 2\pi]$ is a continuous variable because $N \sim 10^{23} \gg 1$

Now consider the potential called a Dirac comb of the form

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$$ as shown in Fig 5.5.

Now due to the fact that

$$\psi_E(x+a) = \lambda \psi_E(x) = e^{iKa} \psi_E(x)$$

we need to solve for $\psi_E(x)$ only in $0<x<a$.

For $0<x<a$ we get

$$\psi_E''(x) = -k^2 \psi_E(x) \text{ , where } k \equiv \sqrt{\frac{2mE}{\hbar^2}} .$$

$$\Rightarrow \psi_E(x) = A \sin(kx) + B \cos(kx) \text{ , } \forall\, 0<x<a$$

$$= e^{-iKa}\left[A \sin[k(x+a)] + B \cos[k(x+a)]\right] \text{ , } \forall\, -a<x<0$$

Continuity of $\psi_E(x)$ at $x=0 \Rightarrow$

$$B = e^{-iKa}\left[A \sin(ka) + B \cos(ka)\right] \quad \rightarrow (5.61)$$

Also $$\left.\frac{d\psi_E}{dx}\right|_{x=0+} - \left.\frac{d\psi}{dx}\right|_{x=0-} = \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon} V(x)\psi(x)\,dx$$

$$\Rightarrow kA - e^{-iKa} k\left[A \cos(ka) - B \sin(ka)\right] = \frac{2m\alpha B}{\hbar^2} \quad \rightarrow (5.62)$$

Eliminating A and B from Eqs. (5.61) and (5.62) gives

$$\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)$$

This may be rewritten as shown below by using $z \equiv ka$, $\beta = \frac{m\alpha a}{\hbar^2}$,

to give

$$f(z) = \cos(Ka)$$

where $f(z) = \cos(z) + \beta \dfrac{\sin(z)}{z}$

Note $Ka = \dfrac{2\pi n}{N} \in [0, 2\pi]$

$\Rightarrow -1 \leq \cos(Ka) \leq 1$

$\Rightarrow |f(z)| \leq 1$ are the only values of k for which TISE may be solved
But $k = \sqrt{\dfrac{2mE}{\hbar^2}}$ $\Rightarrow$ quantization of energy E in solids!
See Figs 5.6 and 5.7.

Now each band of allowed E values contains $2N$ states to be filled where $2 = (2s+1)$ coming from spin degrees of freedom. Suppose each atom contains q valence electrons then they will fill $\dfrac{Nq}{2N} = \dfrac{q}{2}$ bands.

If $q = 1$ or ~~and~~ any odd value $= 3, 5, 7, \ldots$ then the top bands will be half filled making the solid a metal. If $q = 2$ or an even integer $= 2, 4, 6, \ldots$ then the top filled band would be completely filled making the solid an insulator.

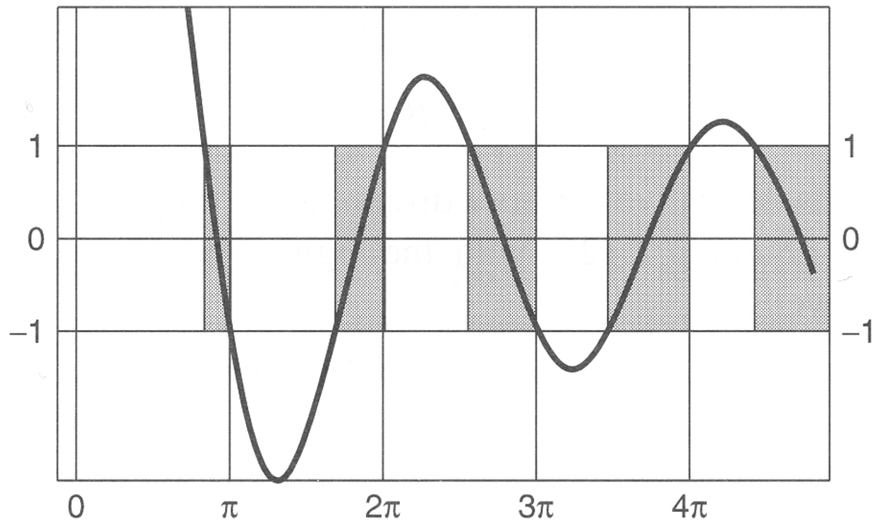

FIGURE 5.6: Graph of $f(z)$ (Equation 5.66) for $\beta = 10$, showing allowed bands (shaded) separated by forbidden gaps (where $|f(z)| > 1$).

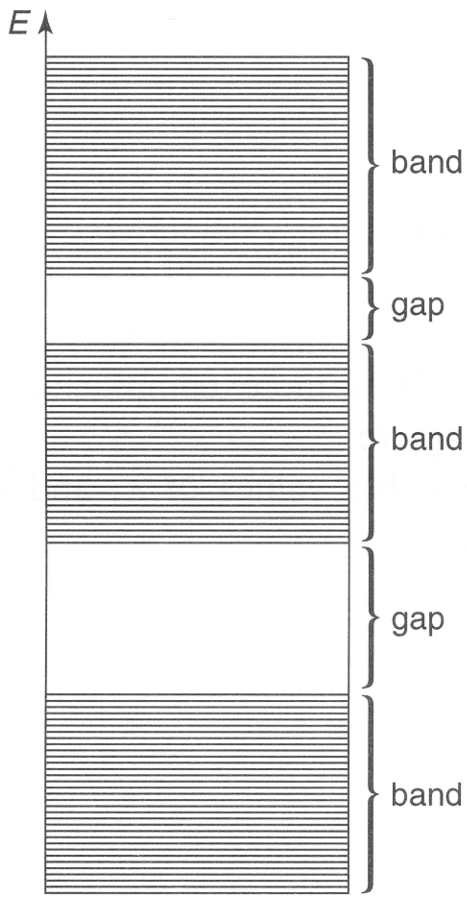

FIGURE 5.7: The allowed energies for a periodic potential form essentially continuous bands.