How do we find the TOTAL energy of the system? We have to integrate in k. For this purpose use spherical symmetry and infinitesimal shells.

Vol. of a shell (octant; $4\pi/8=\pi/2$; area of sphere is $4\pi k^2$; dk is width)

$$\frac{2[(1/2)\pi k^2\, dk]}{(\pi^3/V)} = \frac{V}{\pi^2}k^2\, dk \qquad\qquad dE = \frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2}k^2\, dk$$

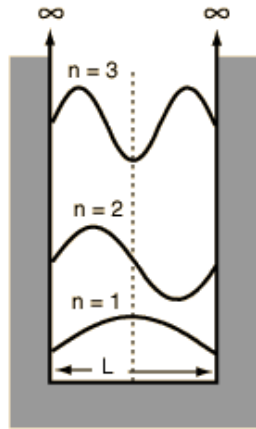2 electrons per point

Vol. of one elementary block

Energy at the shell

Number of states per shell

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m}\int_0^{k_F} k^4\, dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2(3\pi^2\, Nd)^{5/3}}{10\pi^2 m}V^{-2/3}$$

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

1D illustration for simplicity

n = 3

n = 2

n = 1

L

x = 0 at left wall of box.

As we move up in the well, the energy and momentum grows and the electron hits harder and harder the wall.

Similar to molecules hitting the walls in a perfect gas, but this happens in QM even at zero temperature!

Thus, the electrons exert a pressure on the walls. If the box expands by dV, the energy decreases.

$$dE_{\text{tot}} = -\frac{2}{3}\frac{\hbar^2(3\pi^2 \, Nd)^{5/3}}{10\pi^2 m}V^{-5/3}\,dV = -\frac{2}{3}E_{\text{tot}}\frac{dV}{V}$$
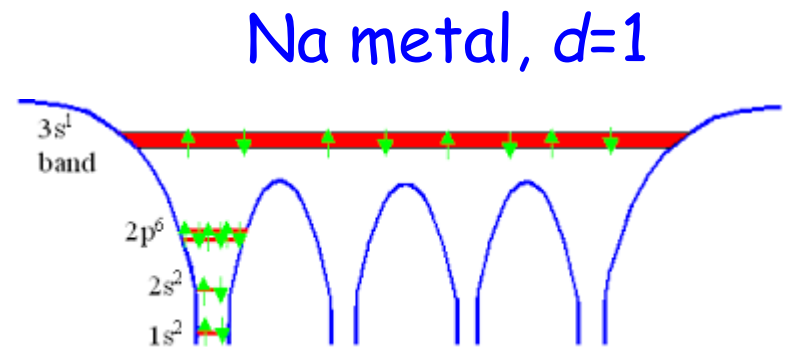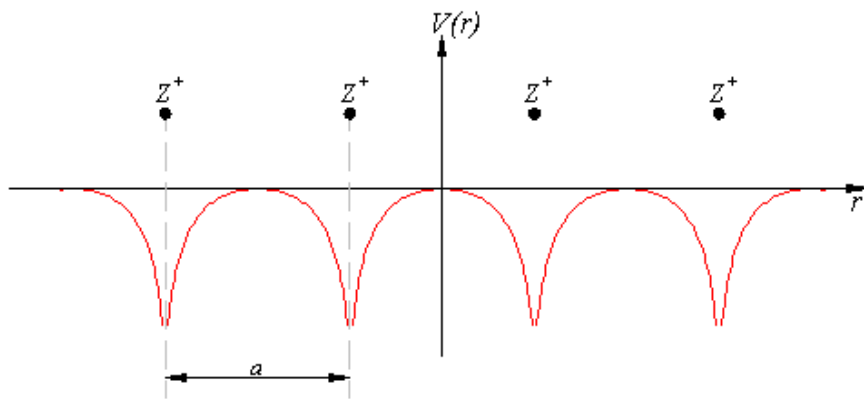
Finally, use dWork=PdV as for a gas in a cylinder. And dE$_{\text{tot}}$=-dW from thermodynamics.

$$P = \frac{2}{3}\frac{E_{\text{tot}}}{V} = \frac{2}{3}\frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\rho^{5/3}$$

2

5.3.2 Band Structure

This is an improvement on the free electron gas.

We will consider the same set of *Nd* electrons but now in a periodically-arranged positive charge potential, assumed rigid, that mimics the nuclei.


Na metal, *d*=1

Qualitatively, the new key property is the periodicity, not the details of the potential used.

Because the periodicity is the key aspect, the book uses a 1D "**Dirac comb**" as example (Fig. 5.4).
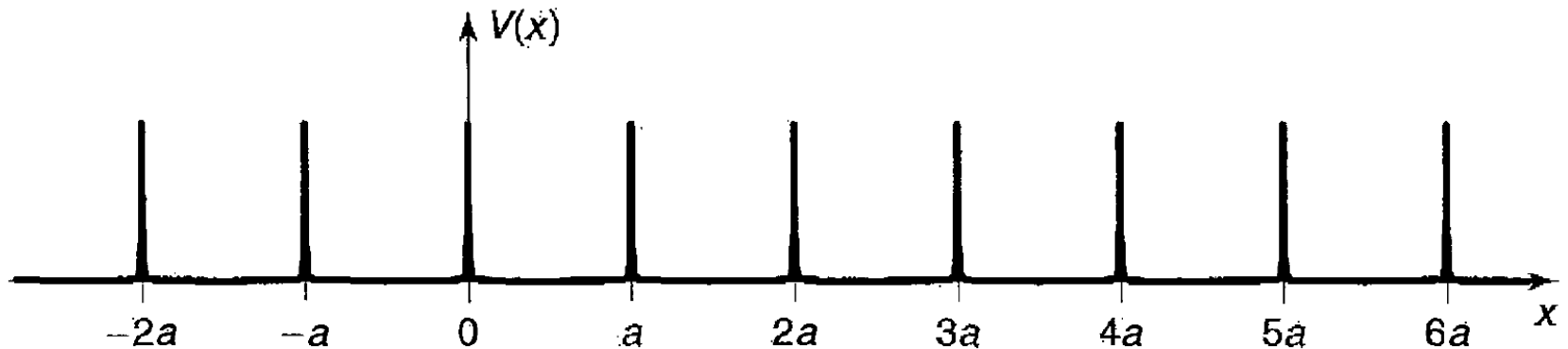
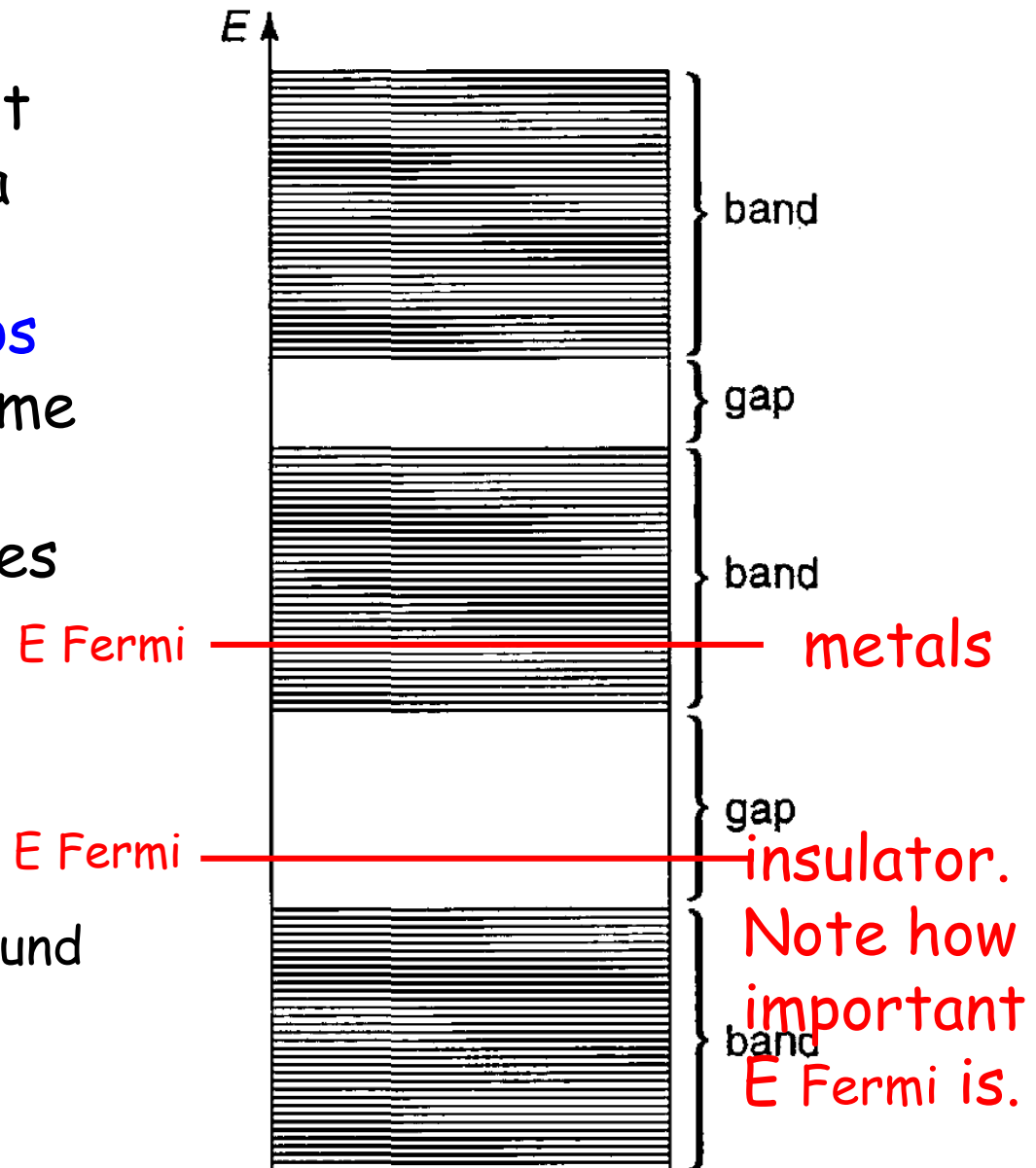It is a periodic positive potential for simplicity to avoid the bound states that make more difficult the math.

Alternatively, think of the space in between the deltas as the "nuclei" potential
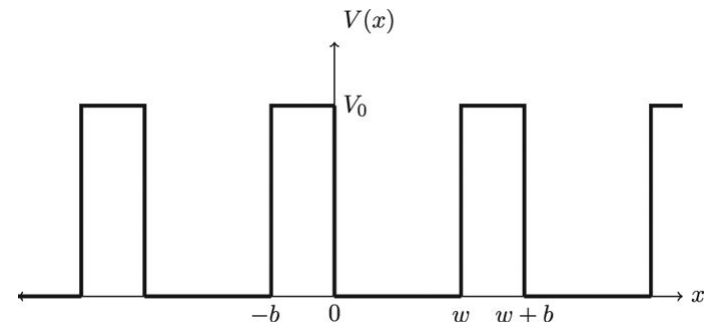
The remarkable result we will find by using a periodic potential is that there will be gaps (i.e. no solutions in some energy ranges) in between allowed states bands.

Energy gaps cannot be found with just the "free electrons in a box" approximation. Periodic potential needed.

E ↑

band

gap

band

E Fermi ——————— metals

gap

E Fermi ———————

insulator.
Note how important
E Fermi is.

band

5

The key aspect to emphasize is the periodicity:

$$V(x + a) = V(x)$$

Sch Eq same as usual: $\quad -\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} + V(x)\psi = E\psi$

For a periodic potential, we will prove the Bloch's theorem:

Consider the displacement operator D. It takes any function or operator and changes x to $x+a$:

$$Df(x) = f(x + a)$$

6

$$D \frac{d}{dx} = \frac{d}{d(x+a)} = \frac{d\,x}{d(x+a)}\frac{d}{dx} = \frac{d}{dx}$$

$$D \, V(x) = V(x+a) = V(x)$$

if periodic

Then $[D, H] = 0$ and the eigenfunctions can also be eigenfunctions of D: $\quad D\psi = \lambda\psi \quad i.e. \ \psi(x+a) = \lambda\psi(x)$

So far this seems "trivial": naively for a periodic potential, the solutions of the Sch Eq should be periodic. However, "physics" tells us that actually it is the probability that should be periodic by "common sense", not the wave functions:

$$|\psi(x+a)|^2 = |\psi(x)|^2$$

The statement $\psi(x + a) = \lambda\psi(x)$ considering the only constraint $|\psi(x + a)|^2 = |\psi(x)|^2$ becomes less trivial and gives:

$$\lambda = e^{iqa}$$

Thus, the Bloch's theorem says:

$$\psi(x + a) = e^{iqa}\,\psi(x)$$

So the wave functions are more complicated than the probabilities …