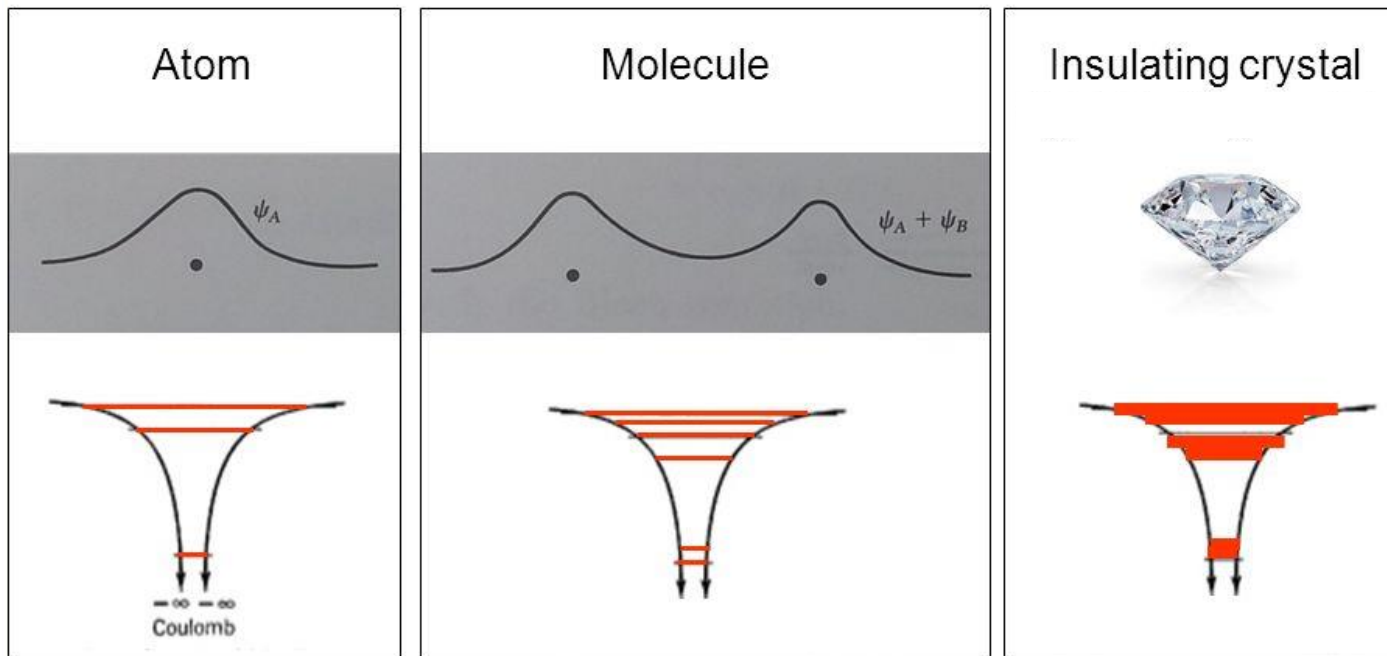


5.3 Solids

When atoms are brought together, the wave functions start overlapping.

When that happens, energy levels split by small amounts, keeping the total number of levels constant.



Example: 3 levels

6 levels

3N levels
"bands" are formed

The **inner electrons**, like those in (1s), remain trapped near its original nucleus. But the **outer electrons**, with more extended wave functions, can move from atom to atom.

Depending on how the bands are formed, and how many electrons you have, you may have a **metal** or **insulator**.

We will consider two crude approximations:

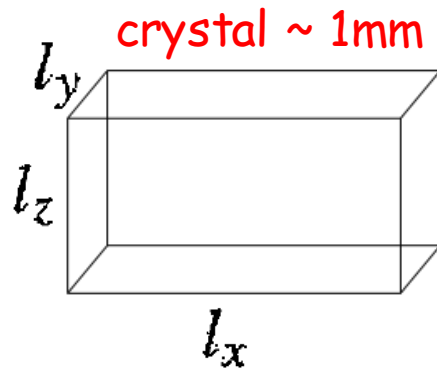
(a) **Non-interacting electrons in a giant box**
(such as a cubic well)

(b) **Non-interacting electrons in a periodic potential**
produced by nuclei.

5.3.1 The Free Electron Gas

Considering the enormity of the problem, we need to start making **crude approximations** and see how they work, and refine accordingly.

We will first assume that the "**conduction electrons**" -- those that can jump from atom to atom -- are totally free inside a giant box (i.e. a 3D well) the size of the crystal.



$$V = l_x \cdot l_y \cdot l_z$$

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < l_x, \quad 0 < y < l_y, \text{ and } 0 < z < l_z \\ \infty, & \text{otherwise.} \end{cases}$$

This is the plan within this very crude approximation:

(1) We will solve the Sch Eq for **ONE PARTICLE**, i.e. a particle in a big box. Very easy! It was already done in a HW problem.

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

(2) After solving this problem, we will simply start filling levels with 2 electrons per state (1 up, 1 down), until we have the (large) number of electrons we want. The e-e repulsion will be neglected.

(3) Conceptually, it is the analog of using the exact solution of the H atom, but for a much heavier element like Cu (29) or Au (79).

So let us recall fast the steps to solve the "cubic well":

(a) Use "separation of variables" $\psi(x, y, z) = X(x)Y(y)Z(z)$ plug into Sch Eq, divide by XYZ, and find the equation is written as 3 independent pieces.

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X; \quad -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y; \quad -\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z$$

$$E = E_x + E_y + E_z$$

(b) Introduce standard "k" notation:

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}; \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}; \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar}$$

(c) Solutions are:

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x)$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y)$$

$$Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z)$$

(d) Boundary conditions $X(0) = Y(0) = Z(0) = 0$
lead to cancellations

$$B_x = B_y = B_z = 0$$

(e) Other boundary conditions are $X(l_x) = Y(l_y) = Z(l_z) = 0$

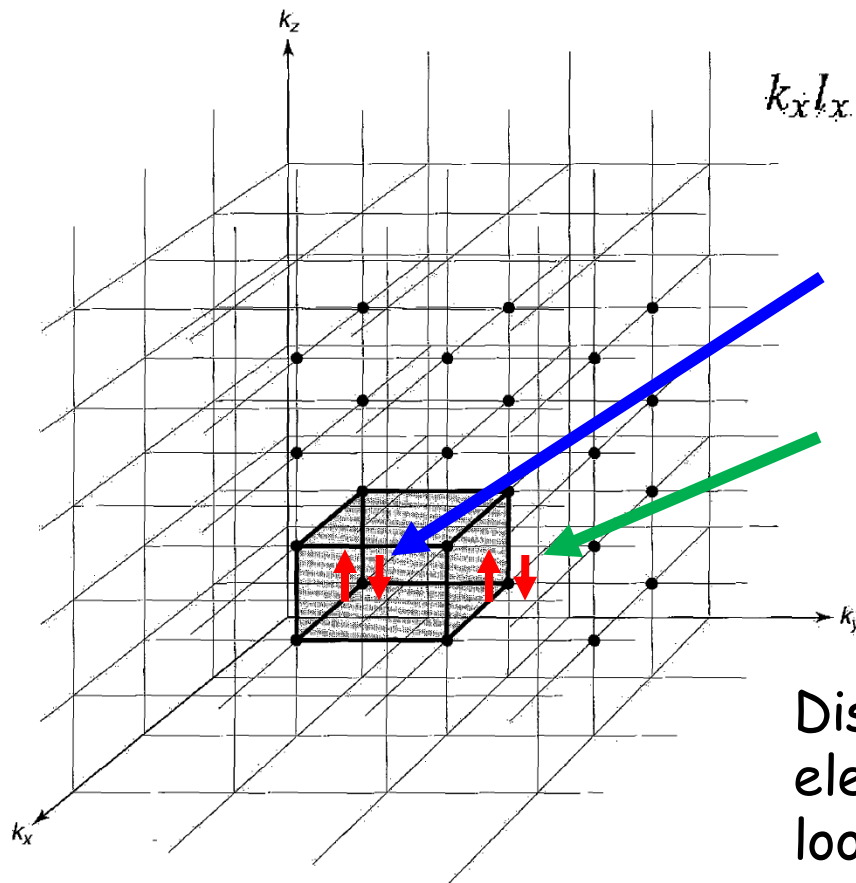
lead to $k_x l_x = n_x \pi$, $k_y l_y = n_y \pi$, $k_z l_z = n_z \pi$.

$$n_x = 1, 2, 3, \dots, \quad n_y = 1, 2, 3, \dots, \quad n_z = 1, 2, 3, \dots$$

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m}$$

$$\mathbf{k} \equiv (k_x, k_y, k_z)$$

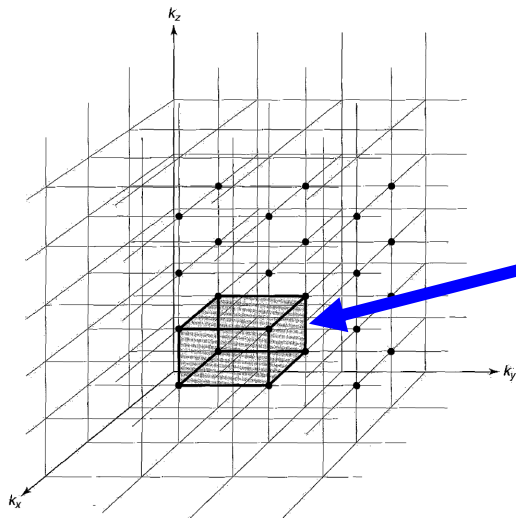


$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi$$

Each point is an eigenstate.
Lowest energy is $(n_x, n_y, n_z) = (1, 1, 1)$

Next levels are $(n_x, n_y, n_z) = (1, 2, 1) \dots$
deg=3 $\rightarrow (2, 1, 1), (1, 2, 1), (1, 1, 2)$

Discrete but there are so many electrons that from far away it looks like a continuum ...

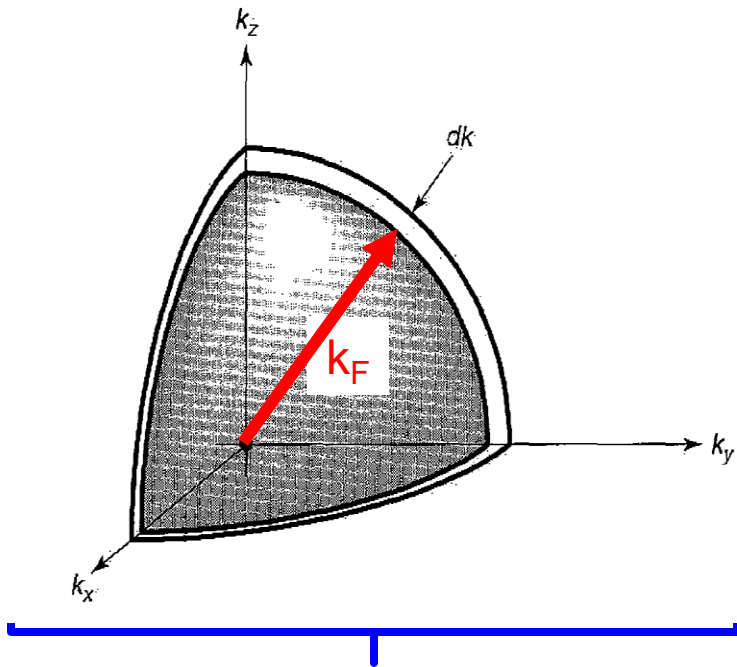


Each shaded block in this grid occupies a volume:

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

Most electrons in atoms are trapped near the nucleus, but some ($q=1,2,3,\dots$) are free to move long distances: the conduction electrons.

There is a huge number of atoms N even in a small crystal $(1\text{mm})^3$



The ground state is an octant with a high density of points

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right)$$

Octant vol. in the "continuum"

Number of blocks needed

Vol. of a block

Repeating:
$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right)$$

Now define the density of electrons:

$$\rho \equiv \frac{Nq}{V}$$

The Fermi wavevector is:

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

The Fermi energy is:
This in practice is a key number!

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

The Fermi energy is NOT the ground state energy but the energy of the electrons with the individual highest energy.