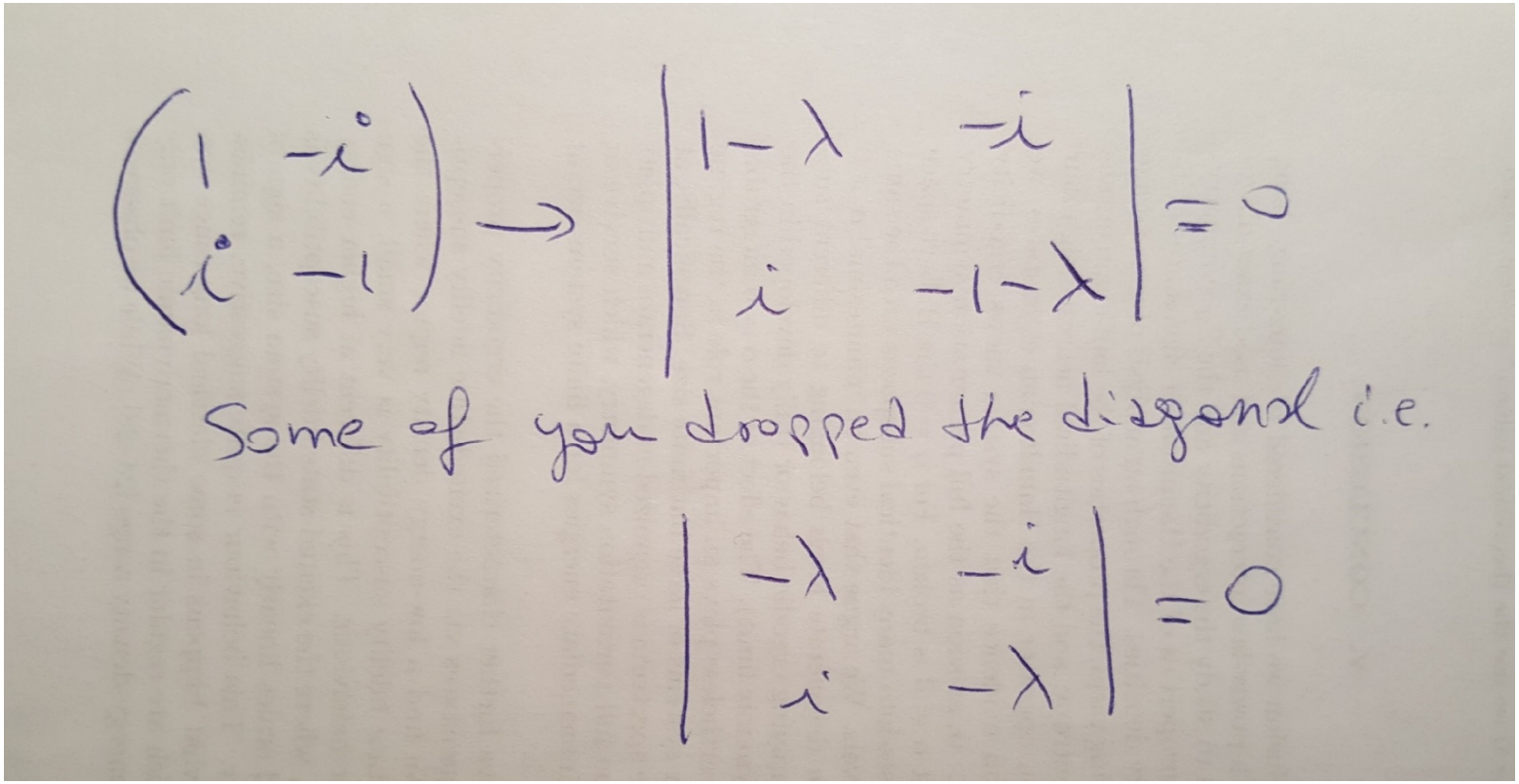
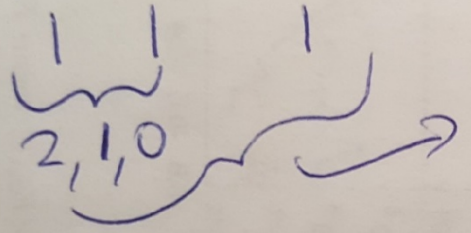
Test 1: common errors.



Probabilities must be real numbers between 0 and 1.
If you find P=0.5i or P=-2, they are wrong.

Probability of $+\frac{\hbar}{2}$ along x is <u>not</u> $|a|^2$ if $\chi = \begin{pmatrix} a \\ b \end{pmatrix}$

3 particles with $\ell = 1$



$(2,1) \rightarrow 3,2,1$

$(1,1) \rightarrow 2,1,0$

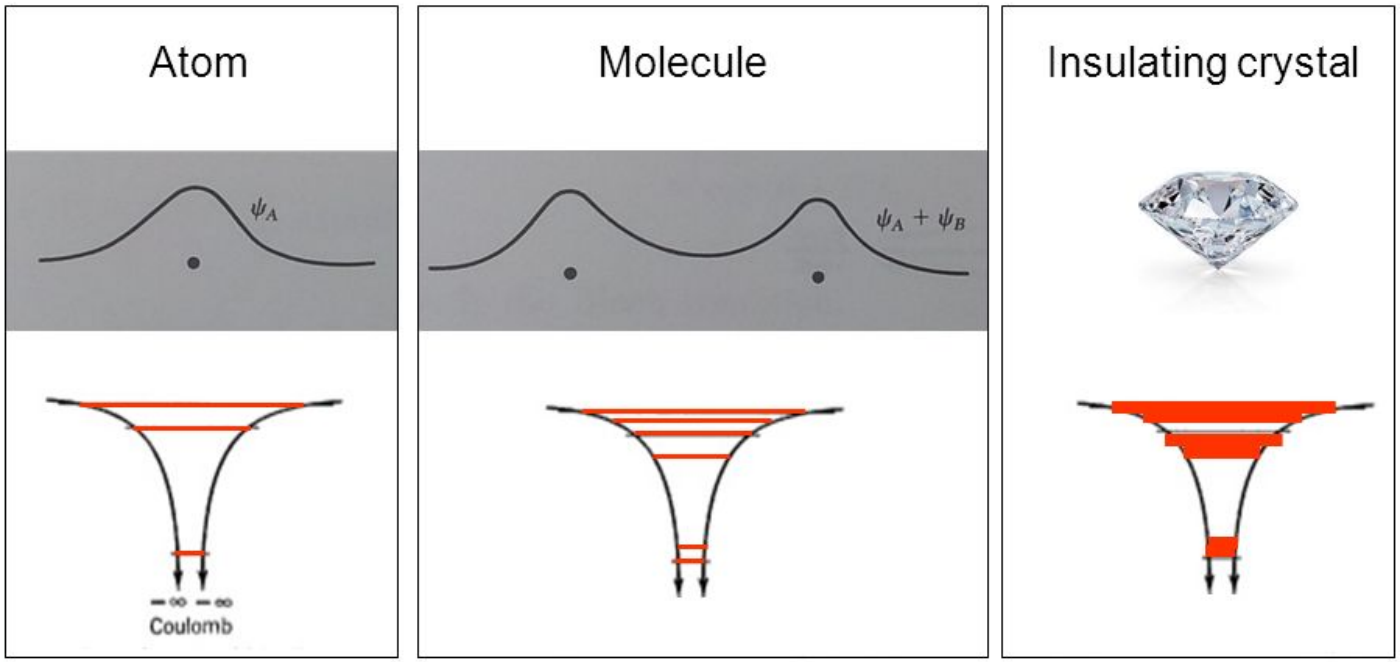
$(0,1) \rightarrow 1$

Most of you simply said $L = 0,1,2,3$

5.3 Solids

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

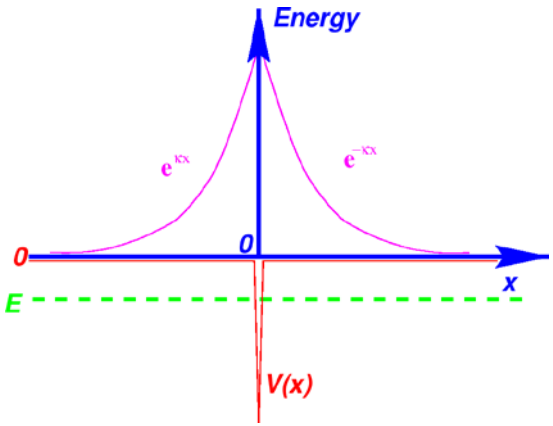
When that happens, energy levels split by small amounts, keeping the total number of levels constant.



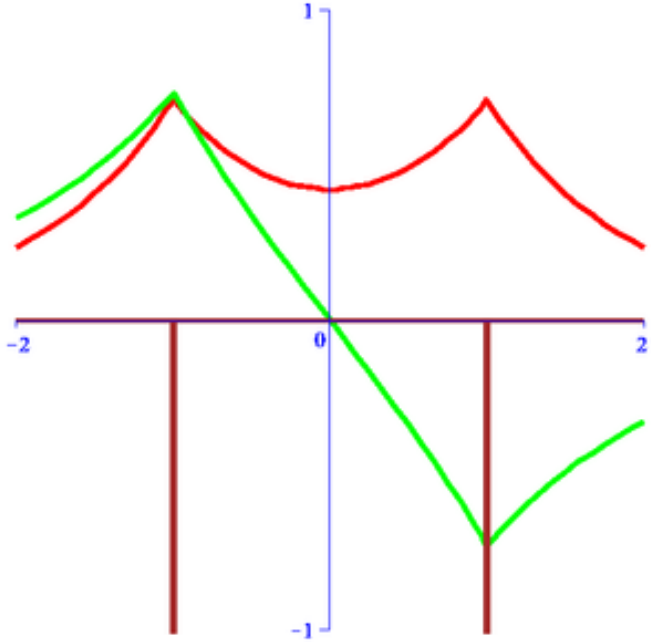
Example: 3 levels 6 levels 3N levels
"bands" are formed

Reminder from Ch 2, 2020: In the delta function potential the (only) bound state and its energy is:

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \qquad E = -\frac{m\alpha^2}{2\hbar^2}.$$



NOTE (not in book):
Generalization to two deltas will have **two solutions (even and odd)** with slightly different energies.



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)

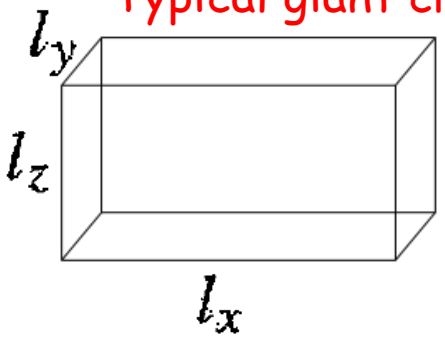
(b) Non-interacting electrons in a periodic potential
produced by nuclei.

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.

Typical giant crystal ~ 1mm^3 ☺



$$V = l_x \; l_y \; l_z$$

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

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 in P411.

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

(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). Not a bad approximation. But here we go all the way to cover the whole crystal.

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 realize the equation is written as 3 independent pieces.

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

$$E = E_x + E_y + E_z$$

(b) Introduce standard "*k*" notation, but now 3 of them:

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

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

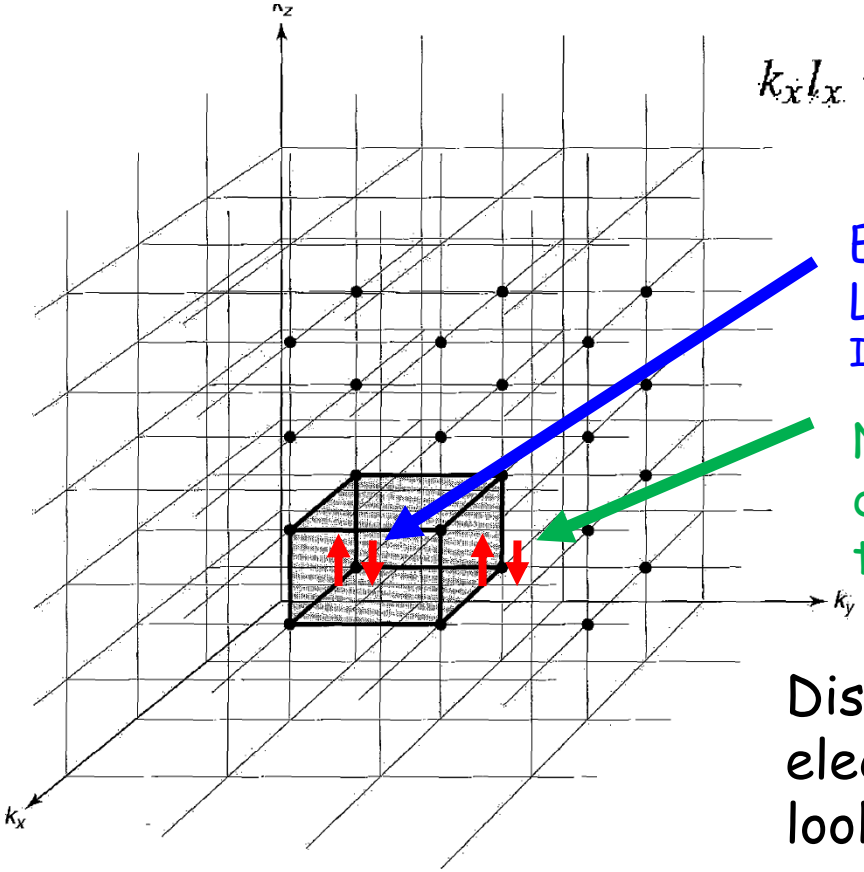
$$n_x = 1, 2, 3, \ldots, \quad n_y = 1, 2, 3, \ldots, \quad n_z = 1, 2, 3, \ldots.$$

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

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

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

$k^2 = \mathbf{k}.\mathbf{k}$
dot product

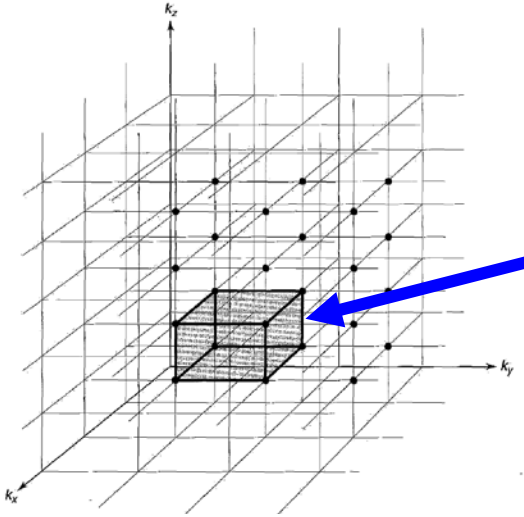


$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi$$

Each point is an eigenstate.
Lowest energy is $(n_x, n_y, n_z)=(1,1,1)$.
In Figure the origin is (0,0,0) which has no state.

Next levels are $(n_x, n_y, n_z)=(1,2,1)$ …
deg=3 for (2,1,1),(1,2,1),(1,1,2) if this is a cube. You can assume that.

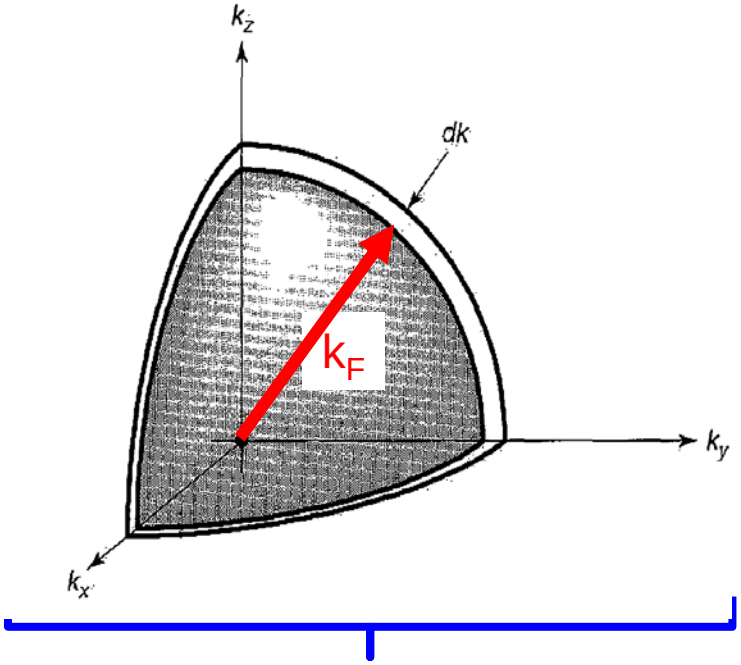
Discrete but there are **so many** electrons that from "far away" it looks like a continuum …



Each shaded block in this grid occupies a little 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 (d=1,2,3,…) are free to move long distances: the conduction electrons.



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

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

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

Octant vol. in the "continuum"

Number of blocks needed (2 from Pauli)

Vol. of a tiny block

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

Now define the density of electrons: $$\rho \equiv \frac{N\,d}{V}$$

Then, 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 total ground state energy but the energy of the electrons with the individual highest energy.