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Fri. Sept. 14

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- Our goal is to improve upon the free electron model by considering the quantum makeup of electrons
- We first would like to review some results from QM
- a particle obeying the time-ind. SE in a 1D "box" with potential

$$V(x) = \begin{cases} 0 & ; 0 \leq x \leq a \\ \infty & ; \text{otherwise} \end{cases}$$

- the solution of the SE gives (with b.c.'s)

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

with energy eigenstates  $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$

- we see that for some  $n$ , the value of  $E_n$  increases with decreasing  $a$ , or smaller box  $\rightarrow$  larger energy

(2)

- let's assume we have 2 particles in a system, the wave function is simply a product

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi_a(\vec{r}_1) \Psi_b(\vec{r}_2)$$

where we assign  $\Psi_a$  to one particle +  $\Psi_b$  to the other.

- the problem with such a formulation is that it assumes the particles are "distinguishable"
- electrons, photons, etc. are however not distinguishable
- this is counterintuitive, but accurate
- if we put two particles in a box, say electrons, once they are in there we cannot tell them apart
- Why? We would need to precisely measure the positions of each, which we cannot (+ trajectories)

$$\Delta x \propto p^2 \hbar / 2$$



(3)

- We can write down the equation for ind. particles as

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) =$$

$$A[\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) \pm \Psi_b(\vec{r}_1)\Psi_a(\vec{r}_2)]$$

- for bosons (spin: integer) we use the (+) sign
- for Fermions (spin: half-int.) we use the (-) sign
- let's assume the two example particles are in the same state or

$$\Psi_a = \Psi_b$$

- we see that for Fermions

$$\Psi_{-}(\vec{r}_1, \vec{r}_2) = A[\Psi_a(\vec{r}_1)\Psi_a(\vec{r}_2)$$

$$- \Psi_a(\vec{r}_1)\Psi_a(\vec{r}_2)]$$

$$= 0$$

- or, Fermions cannot occupy the same state (this is the Pauli exc. principle)

(4)

- back to the particle in a box, but now add 2 particles

- $\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), E_n = n^2 K$

$$K = \frac{\pi^2 \hbar^2}{2ma^2}$$

- if distinguishable

$$\Psi_n, \Psi_{n_2} = \Psi_{n,n_2}, E_{n,n_2} = (n_1^2 + n_2^2)K$$

grand state:

$$\Psi_{11} = \frac{2}{a} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right); E_{11} = 2K$$

- first excited state:  $E_{12} = 5K \quad \left. \begin{matrix} \\ E_{21} = 5K \end{matrix} \right\}$  degenerate

- for indistinguishable (electrons, say)

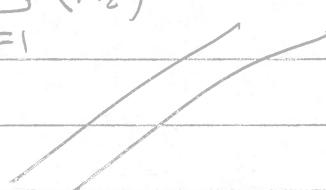
ground state:  $E = 5K$

$$\frac{2}{a} \left[ \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{2\pi}{a}x_2\right) - \sin\left(\frac{2\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) \right]$$

(5)

- so we see that as we add more particles to the box, we find the ground state energy increases
- however, we are assuming the box stays the same size ( $a$  in our example)
- with a solid, each atom donates say 1 electron to the box (with box = solid) so grand state increases with more electrons, but box gets larger, decreasing energy
- recall  $E_n \propto \frac{1}{a^2}$  but  $E_n \propto n^2$
- for  $N$  atoms donating 1 e<sup>-</sup> each

ground state  $E_g = \frac{\pi^2 \hbar^2}{2ma^2} \sum_{i=1}^N (n_i)^2$



(6)

- as a solid conductor is really a large molecule with atoms metallically bonded, the electrons (valence) are spread throughout the solid (free electron gas)
- Consider a rectangular solid with edges  $l_x, l_y, l_z$
- assume no potential inside box

$$V(x, y, z) = \begin{cases} 0 & ; 0 < x < l_x, \dots \\ \infty & ; \text{otherwise} \end{cases}$$

• solving for  $-\frac{\hbar^2}{2m} \nabla^2 \Psi = E\Psi$

• gives  $\Psi(x, y, z) = X(x) Y(y) Z(z)$

• boundary cond. etc.

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

• just a 3D box



(7)

- allowed energies :

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

$$= \frac{\hbar^2 k^2}{2m}$$

where  $k = |\vec{k}|$ ,  $\vec{k}$  is wave vector

- in 3D  $k$ -space, each point represents a stationary state
- the volume of a cube (block) in  $k$ -space with 8 points as corners has volume

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

- Next time we will see quantum mechanical energy shows up as a quantum pressure

$$P \propto \rho^{5/3} \text{ or } N^{5/3}$$

degeneracy pressure