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Fri. Sept. 14

- 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 $E_n = \dfrac{n^2 \pi^2 \hbar^2}{2ma^2}$

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

- 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 ψ_a to one particle + ψ_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)

$$\Delta x \Delta p \geq \hbar/2$$

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

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

$$A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right]$$

- 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

$$\psi_-(\vec{r}_1,\vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_1)\psi_a(\vec{r}_2)\right]$$

$$= 0$$

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

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

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

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

- if distinguishable

$$\psi_{n_1} \psi_{n_2} = \psi_{n_1 n_2} \quad , \quad E_{n_1 n_2} = (n_1^2 + n_2^2) K$$

ground 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: $\left.\begin{array}{l} E_{12} = 5K \\ E_{21} = 5K \end{array}\right\}$ degenerate

- for indistinguishable (electrons, say)

ground state: $E = 5K$

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

- 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 ground 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 $1\ e^-$ each

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

- 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 the 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 $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$

$\vdots$ 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

$\longrightarrow$

- 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