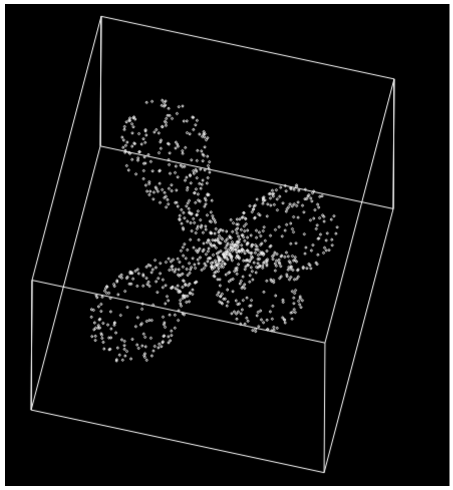
Quantum Mechanics

3D box



Problem 1.- Solve the Schrodinger equation for a particle in a three-dimensional box:

$$V(x,y,z) = \begin{cases} 0, & for\ 0 < x < a\ and\ 0 < y < a\ and\ 0 < z < a \\ \infty, & otherwise \end{cases}$$

Find the wave functions and energies.

Solution: In this case, it is easier to solve the Schrödinger equation in Cartesian coordinates:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + V\psi(x,y,z) = E\psi(x,y,z)$$
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) + V\psi(x,y,z) = E\psi(x,y,z)$$

We will assume that the solutions are the product of three functions that depend on x, y and z:

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

In which case the equation looks like:

$$-\frac{\hbar^2}{2m}YZ\frac{\partial^2 X}{\partial x^2} - \frac{\hbar^2}{2m}XZ\frac{\partial^2 Y}{\partial y^2} - \frac{\hbar^2}{2m}XY\frac{\partial^2 Z}{\partial z^2} + VXYZ = EXYZ$$

The potential is infinite at the walls of the box, so the wave function will have to be zero at those walls. On the other hand, inside the box, the potential is zero, so we can simplify the equation to:

$$-\frac{\hbar^2}{2m}YZ\frac{\partial^2 X}{\partial x^2}-\frac{\hbar^2}{2m}XZ\frac{\partial^2 Y}{\partial y^2}-\frac{\hbar^2}{2m}XY\frac{\partial^2 Z}{\partial z^2}=EXYZ \qquad \text{Inside the box}$$

Now, let us divide the equation by XYZ:

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\partial^2 X}{\partial x^2}-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=E$$

Now, the first term depends only on x, the second term on y and the third on z, so each of these terms has to be equal to a constant, that we can call E_x, E_y and E_z:

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\partial^2 X}{\partial x^2}=E_x \qquad -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=E_y \qquad -\frac{\hbar^2}{2m}\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=E_z$$

$$E_x+E_y+E_z=E$$

The solutions of these equations are sine and cosine functions. For X we get:

$$X = A_x\sin\left(\frac{\sqrt{2mE_x}}{\hbar}x\right)+B_x\cos\left(\frac{\sqrt{2mE_x}}{\hbar}x\right)$$

Similarly for Y and Z.

The boundary condition at x = 0 eliminates the cosine, so only the sine function will be a solution. The other boundary condition when x = a means that:

$$X(a)=A_x\sin\left(\frac{\sqrt{2mE_x}}{\hbar}a\right)=0\rightarrow \quad \frac{\sqrt{2mE_x}}{\hbar}a=n_x\pi \quad n_x=1,2,3...$$

This gives us the energy $E_x=n_x^2\frac{\hbar^2\pi^2}{2ma^2}$

Similarly, with the other two functions:

$$Y(y)=A_y\sin\left(\frac{\sqrt{2mE_y}}{\hbar}y\right) \quad \text{and} \quad Z(z)=A_z\sin\left(\frac{\sqrt{2mE_z}}{\hbar}z\right)$$

The eigen energies will be: $E_y=n_y^2\frac{\hbar^2\pi^2}{2ma^2}$ and $E_z=n_z^2\frac{\hbar^2\pi^2}{2ma^2}$

Using these eigenvalues, the solution becomes

$$\psi(x,y,z) = A\sin\left(\frac{\pi n_x}{a}x\right)\sin\left(\frac{\pi n_y}{a}y\right)\sin\left(\frac{\pi n_z}{a}z\right)$$

Next, we normalize the wave function to find A

$$\int_0^a\int_0^a\int_0^a |\psi|^2\,dxdydz = 1 \rightarrow \int_0^a\int_0^a\int_0^a \left|A\sin\left(\frac{\pi n_x}{a}x\right)\sin\left(\frac{\pi n_y}{a}y\right)\sin\left(\frac{\pi n_z}{a}z\right)\right|^2 dxdydz = 1$$

$$\rightarrow A^2(a/2)^3 = 1 \rightarrow A = \sqrt{\frac{8}{a^3}}$$

The solution including the normalizing factor is

$$\psi(x,y,z) = \sqrt{\frac{8}{a^3}}\sin\left(\frac{\pi n_x}{a}x\right)\sin\left(\frac{\pi n_y}{a}y\right)\sin\left(\frac{\pi n_z}{a}z\right)$$

The total energy is:

$$E = (n_x^2 + n_y^2 + n_z^2)\frac{\hbar^2\pi^2}{2ma^2}$$

Evidently, the minimum energy happens when $n_x = n_y = n_z = 1$, which is the ground state.

$$E_1 = (1^2 + 1^2 + 1^2)\frac{\hbar^2\pi^2}{2ma^2} = 3\frac{\hbar^2\pi^2}{2ma^2} = 3E_o \qquad where \quad E_o = \frac{\hbar^2\pi^2}{2ma^2}$$

This is a unique state, so the degeneracy is 1. Although, considering spin, electrons would have degeneracy 2.

To get the excited states we should look at combinations of integers:

Second state: (first excited state): Combinations 112, 121 and 211 for the three quantum numbers give energy $6E_o$ and a degeneracy of 3.

Third state: (second excited state): Combinations 122, 212 and 221 for the three quantum numbers give $9E_o$ and a degeneracy of 3.

Fourth state: Combinations 311, 131 and 113 give $11E_o$ and a degeneracy of 3.

Fifth state: The combination 222 gives $12E_o$ and a degeneracy of 1.
Sixth state: Combinations 123, 231, 312, 132, 321, 213 give $14E_o$ and a degeneracy of 6.

Bonus: The 14th state is the first time that two different kind of combinations give the same energy. That is, one combination is not a permutation of the quantum numbers of the other. The combinations are 333, 511, 151 and 115.