Quantum Mechanics In 3D: Particle in 3D Box

Extension of a Particle In a Box with rigid walls
1D $\rightarrow$ 3D
$\Rightarrow$ Box with Rigid Walls ($U = \infty$) in X,Y,Z dimensions

Ask same questions:
- Location of particle in 3d Box
- Momentum
- Kinetic Energy, Total Energy
- Expectation values in 3D

To find the Wavefunction and various expectation values, we must first set up the appropriate TDSE & TISE
The Schrödinger Equation in 3 Dimensions: Cartesian Coordinates

Time Dependent Schrödinger Eqn:

\[-\frac{\hbar^2}{2m} \nabla^2 \psi(x,y,z,t) + U(x,y,z)\psi(x,y,z) = i\hbar \frac{\partial \psi(x,y,z,t)}{\partial t}\]

\[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\]

So \[-\frac{\hbar^2}{2m} \nabla^2 = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) + \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \right) + \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \right) = [K]

so \[H\psi(x,y,z,t) = [E]\psi(x,y,z,t)\] is still the Energy Conservation Eq

Stationary states are those for which all probabilities are constant in time and are given by the solution of the TDSE in separable form:

\[\psi(x,y,z,t) = \psi(r,t) = \psi(r)e^{i\omega t}\]

This statement is simply an extension of what we derived in case of 1D time-independent potential

Particle in 3D Rigid Box: Separation of Orthogonal Spatial (x,y,z) Variables

TISE in 3D: \[-\frac{\hbar^2}{2m} \nabla^2 \psi(x,y,z) + U(x,y,z)\psi(x,y,z) = E\psi(x,y,z)\]

x,y,z independent of each other, write \[\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z)\]

and substitute in the master TISe, after dividing through by \[\psi = \psi_1(x)\psi_2(y)\psi_3(z)\]

and noting that \[U(r) = 0\] for \[0 < x, y, z < a\] ⇒

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2(y)}{\partial y^2} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi_3(z)}{\partial z^2} = E = \text{Const}\]

This can only be true if each term is constant for all x,y,z ⇒

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_1(x)}{\partial x^2} = E\psi_1(x), \quad \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2(y)}{\partial y^2} = E\psi_2(y), \quad \frac{\hbar^2}{2m} \frac{\partial^2 \psi_3(z)}{\partial z^2} = E\psi_3(z)\]

With \[E_1 + E_2 + E_3 = E = \text{Constant}\] (Total Energy of 3D system)

Each term looks like particle in 1D box (just a different dimension)

So wavefunctions must be like \[\psi_1(x) \approx \sin k_1 x, \quad \psi_2(y) \approx \sin k_2 y, \quad \psi_3(z) \approx \sin k_3 z\]
Particle in 3D Rigid Box: Separation of Orthogonal Variables

Wavefunctions are like \( \psi_1(x) \propto \sin k_1x \), \( \psi_2(y) \propto \sin k_2y \), \( \psi_3(z) \propto \sin k_3z \)

Continuity Conditions for \( \psi_i \) and its first spatial derivatives \( \Rightarrow n_x = k_1L \)

Leads to usual Quantization of Linear Momentum \( \hat{p} = \hbar \frac{\partial}{\partial x} \) in 3D

\[
p_x = \left( \frac{\pi \hbar}{L} \right) n_x ; \quad p_y = \left( \frac{\pi \hbar}{L} \right) n_y ; \quad p_z = \left( \frac{\pi \hbar}{L} \right) n_z, \quad (n_x, n_y, n_z = 1, 2, 3, \ldots \infty)
\]

Note: by usual Uncertainty Principle argument neither of \( n_x, n_y, n_z = 0 \) (!why?)

Particle Energy \( E = K + U = K + 0 = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \)

Energy is again quantized and brought to you by integers \( n_x, n_y, n_z \) (independent) and \( \psi(\vec{r}) = A \sin k_x x \sin k_y y \sin k_z z \) \( (A = \text{Overall Normalization Constant}) \)

\[
\Psi(\vec{r}, t) = \psi(\vec{r}) \ e^{iEt} = A \left[ \sin k_x x \sin k_y y \sin k_z z \right] \ e^{\frac{i E t}{\hbar}}
\]

Particle in 3D Box: Wave Function Normalization Condition

\[
\Psi(\vec{r}, t) = \psi(\vec{r}) \ e^{\frac{i E t}{\hbar}} = A \left[ \sin k_x x \sin k_y y \sin k_z z \right] \ e^{\frac{i E t}{\hbar}}
\]

\[
\Psi^* (\vec{r}, t) = \psi^* (\vec{r}) \ e^{\frac{i E t}{\hbar}} = A \left[ \sin k_x x \sin k_y y \sin k_z z \right] \ e^{\frac{i E t}{\hbar}}
\]

\[
\Psi^* (\vec{r}, t) \Psi(\vec{r}, t) = A^2 \left[ \sin^2 k_x x \sin^2 k_y y \sin^2 k_z z \right]
\]

Normalization Condition: \( 1 = \iiint P(\vec{r}) \ dx \ dy \ dz \Rightarrow \)

\[
l = A^2 \int_{x=0}^{L} \sin^2 k_x x \ dx \int_{y=0}^{L} \sin^2 k_y y \ dy \int_{z=0}^{L} \sin^2 k_z z \ dz = A^2 \left( \frac{L}{2} \right) \left( \frac{L}{2} \right) \left( \frac{L}{2} \right)
\]

\[
\Rightarrow A = \left[ \frac{2}{L} \right]^\frac{3}{2} \quad \text{and} \quad \Psi(\vec{r}, t) = \left[ \frac{2}{L} \right]^\frac{3}{2} \left[ \sin k_x x \sin k_y y \sin k_z z \right] \ e^{\frac{i E t}{\hbar}}
\]
Particle in 3D Box: Energy Spectrum & Degeneracy

\[ E_{n_1,n_2,n_3} = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2); \quad n_i = 1, 2, 3 \ldots \infty, n_i \neq 0 \]

Ground State Energy \[ E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2} \]

Next level \( \Rightarrow 3 \) Excited states \[ E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2mL^2} \]

Different configurations of \( \psi(r) = \psi(x,y,z) \) have same energy \( \Rightarrow \) degeneracy

**Degenerate States**

\[ E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2mL^2} \]
Probability Density Functions for Particle in 3D Box

Same Energy → Degenerate States
Can't tell by measuring energy if particle is in 211, 121, 112 quantum state

Source of Degeneracy: How to “Lift” Degeneracy

• Degeneracy came from the threefold symmetry of a CUBICAL Box (L_x = L_y = L_z = L)

• To Lift (remove) degeneracy → change each dimension such that CUBICAL box → Rectangular Box
  • (L_x ≠ L_y ≠ L_z)
  • Then

\[ E = \frac{n_x^2 \pi^2}{2mL_x^2} + \frac{n_y^2 \pi^2}{2mL_y^2} + \frac{n_z^2 \pi^2}{2mL_z^2} \]

\[ \begin{align*}
E_1 & = E_{121} \\
E_2 & = E_{122} \\
E_3 & = E_{211} \\
E_4 & = E_{212} \\
E_5 & = E_{221}
\end{align*} \]
The Hydrogen Atom In Its Full Quantum Mechanical Glory

\[ U(r) = \frac{kZe^2}{r} \]

The Coulomb Attractive Potential That Binds the electron and Nucleus (charge +Ze) into a Hydrogenic atom

\[ U(r) \approx \frac{1}{r} = \frac{1}{\sqrt{x^2 + y^2 + z^2}} \Rightarrow \text{More complicated form of U than box} \]

By example of particle in 3D box, need to use separate variables \((x,y,z)\) to derive 3 independent differential eqns.

This approach will get very ugly since we have a "conjoined triplet"

To simplify the situation, use appropriate variables

Independent Cartesian \((x,y,z) \rightarrow \text{Inde. Spherical}\ (r,\theta,\phi)\)

Instead of writing Laplacian \( \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \), write

\[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \]

TISE for \( \psi(x,y,z) = \psi(r,\theta,\phi) \) becomes

\[ \frac{1}{r^2} \left( r^2 \frac{\partial}{\partial r} \right) \psi + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \psi + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \psi = \frac{2m}{\hbar^2} (E - U(r)) \psi = 0 \]

!!!! fun!!!
Spherical Polar Coordinate System

\[ r = \sqrt{x^2 + y^2 + z^2} \]
\[ \theta = \cos^{-1} \left( \frac{z}{r} \right) \text{ (Polar angle)} \]
\[ \phi = \tan^{-1} \left( \frac{y}{x} \right) \text{ (Azimuthal angle)} \]

Volume Element \( dV \)
\[ dV = (r \sin \theta dr d\theta)(dr) = r^2 \sin \theta dr d\theta d\phi \]

\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) - \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) - \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} = \frac{2m}{\hbar^2} (E-U(r)) \psi(r, \theta, \phi) = 0 \]

Try to free up last term from all except \( \phi \)
This requires multiplying thruout by \( r^2 \sin^2 \theta \) \( \Rightarrow \)
\[ \sin^2 \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} = \frac{2m \sin^2 \theta}{\hbar^2} (E + \frac{ke^2}{r}) \psi = 0 \]

For Separation of Variables, Write \( \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \)
Plug it into the TISE above & divide thruout by \( \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \)

Note that:
\[ \frac{\partial \psi(r, \theta, \phi)}{\partial r} = \Theta(\theta) \Phi(\phi) \frac{\partial R(r)}{\partial r} \]
\[ \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} = R(r) \Phi(\phi) \frac{\partial \Theta(\theta)}{\partial \theta} \]
\[ \frac{\partial \psi(r, \theta, \phi)}{\partial \phi} = R(r) \Theta(\theta) \frac{\partial \Phi(\phi)}{\partial \phi} \]

\[ \sin^2 \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{2m \sin^2 \theta}{\hbar^2} (E + \frac{ke^2}{r}) = 0 \]

Rearrange by taking the \( \phi \) term on RHS
\[ \frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2m \sin^2 \theta}{\hbar^2} (E + \frac{ke^2}{r}) = \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \]

LHS is fn. of \( r, \theta \) & RHS is fn of \( \phi \) only, for equality to be true for all \( r, \theta, \phi \)
\[ \Rightarrow \text{LHS} = \text{constant} = \text{RHS} = m^2 \]
Now go break up LHS to separate the \( r \) & \( \theta \) terms:

\[
\text{LHS: } \frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2m^2 \sin^2 \theta}{\hbar^2} \frac{(E - \frac{\mathbf{k}^2}{r})}{r} = m^2
\]

Divide throughout by \( \sin^2 \theta \) and arrange all terms with \( r \) away from \( \theta \) ⇒

\[
\frac{1}{r} \frac{d}{dr} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2m^2}{\hbar^2} \frac{\left( E - \frac{\mathbf{k}^2}{r} \right)}{r} = \frac{m^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right)
\]

Same argument: LHS is fn of \( r \), RHS is fn of \( \theta \), for them to be equal for all \( r, \theta \)

⇒ \[ \text{LHS} = \text{const} = \text{RHS} = l(l+1) \] What do we have after shuffling!

\[
\frac{d}{d\phi} \Phi + m_\phi \Phi = 0 \tag{1}
\]

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0 \tag{2}
\]

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m^2}{\hbar^2} \left( \frac{E - \frac{\mathbf{k}^2}{r}}{r} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0 \tag{3}
\]

These 3 "simple" diff. eqn describe the physics of the Hydrogen atom.

All we need to do now is guess the solutions of the diff. equations.
Each of them, clearly, has a different functional form.

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**Solutions of The S. Eq for Hydrogen Atom**

The Azimuthal Diff. Equation

\[ \frac{d}{d\phi} \Phi + m_\phi \Phi = 0 \tag{1} \]

Solution : \( \Phi(\phi) = A e^{im_\phi \phi} \) but need to check "Good Wavefunction Condition" 
Wave Function must be Single Valued for all \( \phi \) ⇒ \( \Phi(\phi) = \Phi(\phi + 2\pi) \)

⇒ \( \Phi(\phi) = A e^{im_\phi \phi} = A e^{in_\phi (2\pi + \phi)} \Rightarrow m_\phi = 0, \pm 1, \pm 2, \pm 3, \ldots \) (Magnetic Quantum \( n \))

The Polar Diff. Eq

\[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0 \tag{2} \]

Solutions: go by the name of "Associated Legendre Functions"

only exist when the integers \( l \) and \( m_\phi \) are related as follows

\( m_\phi = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l \); \( l \) is positive number

**I: Orbital Quantum Number**

For \( l = 0 \), \( m_\phi = 0 \) ⇒ \( \Theta(\theta) = \frac{1}{\sqrt{2}} \)

For \( l = 1 \), \( m_\phi = 0, \pm 1 \) ⇒ Three Possibilities for the Orbital part of wavefunction

\[ l = 1, m_\phi = 0 \Rightarrow \Theta(\theta) = \frac{\sqrt{3}}{2} \cos \theta \]

\[ l = 1, m_\phi = \pm 1 \Rightarrow \Theta(\theta) = \frac{\sqrt{3}}{2} \sin \theta \]

\[ l = 2, m_\phi = 0 \Rightarrow \Theta(\theta) = \frac{1}{4} (3\cos^2 \theta - 1) \ldots \text{and so on and so forth (see book)} \]
Radial Wave Functions & Radial Prob Distributions

\begin{align*}
\text{Radial Wave Functions:} & & R_n(r) \\
\text{Solutions:} & & \Psi(r, \theta, \phi) = R_n(r) \cdot \Theta_m(\theta) \cdot \Phi_{\ell_m}(\phi) = R_{\ell_m} Y_{\ell m} \quad (\text{Spherical Harmonics})
\end{align*}

\begin{align*}
n=1 & \rightarrow \text{K shell} & \ell=0 & \rightarrow \text{s(harp) sub shell} \\
n=2 & \rightarrow \text{L Shell} & \ell=1 & \rightarrow \text{p(principal) sub shell} \\
n=3 & \rightarrow \text{M Shell} & \ell=2 & \rightarrow \text{d(iffuse) sub shell} \\
n=4 & \rightarrow \text{N Shell} & \ell=3 & \rightarrow \text{f(undamental) ss} \\
\text{......} & & \ell=4 & \rightarrow \text{g sub shell} \\
\text{......} & & & \text{......}
\end{align*}
Symbolic Notation of Atomic States in Hydrogen

\[
\begin{array}{cccccc}
1 & \text{s} & (l = 0) & \text{p} & (l = 1) & \text{d} & (l = 2) & \text{f} & (l = 3) & \text{g} & (l = 4) \\
\downarrow \\
1 & \text{1s} \\
2 & \text{2s} & \text{2p} \\
3 & \text{3s} & \text{3p} & \text{3d} \\
4 & \text{4s} & \text{4p} & \text{4d} & \text{4f} \\
5 & \text{5s} & \text{5p} & \text{5d} & \text{5f} & \text{5g}
\end{array}
\]

Note that:

- \( n = 1 \) non-degenerate system
- \( n > 1 \) are all degenerate in \( l \) and \( m_l \)

All states have same energy
But different spatial configuration

\[
E = -\frac{\hbar^2}{2\alpha_0^2} \left( \frac{1}{n^2} \right)
\]

Facts About Ground State of H Atom

\( n = 1, \ l = 0, \ m_l = 0 \Rightarrow R(r) = \frac{2}{\alpha_0} \ e^{-r}; \ \Theta(\theta) = \frac{1}{\sqrt{2\pi}}; \ \Phi(\phi) = \frac{1}{\sqrt{2}} \)

\[
\Psi_{100}(r, \theta, \phi) = \frac{1}{\alpha_0 \sqrt{\pi}} e^{-r} \quad \text{....look at it carefully}
\]

1. Spherically symmetric \( \Rightarrow \) no \( \theta, \phi \) dependence (structure)
2. Probability Per Unit Volume: \( |\Psi_{100}(r, \theta, \phi)|^2 = \frac{1}{\pi \alpha_0^2} e^{-2r} \)

Likelihood of finding the electron is same at all \( \theta, \phi \) and depends only on the radial separation \( (r) \) between electron & the nucleus.

3. Energy of Ground State \( -\frac{\hbar^2}{2\alpha_0} = -13.6eV \)

Overall The Ground state wavefunction of the hydrogen atom is quite boring
Not much chemistry or Biology could develop if there was only the ground state of the Hydrogen Atom!  

We need structure, we need variety, we need some curves!