Quantum Mechanics in Three Dimensions

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Overview

Schrödinger's Equation in 3 Dimensions

- To begin converting Schrödinger 's wave equation to 3-dimensions, we start with a generalized wave function:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{1}$$

- H is the Hamiltonian operator and from Chpt. 2 it is defined as:

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2) + V \tag{2}$$

- Where:

$$P_x = \frac{\hbar}{i}\frac{\partial}{\partial x}; P_y = \frac{\hbar}{i}\frac{\partial}{\partial y}; P_z = \frac{\hbar}{i}\frac{\partial}{\partial z} \tag{3}$$

Schrödinger Equation in 3 Dimensions

- p can be simplified to:

$$\mathbf{p} = \frac{\hbar}{i}\nabla \tag{4}$$

- Plugging this back into the generalized Schrödinger , we get:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \tag{5}$$

- And

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{6}$$

- Equation 6 represents the Laplacian in cartesian coordinates.

Schrödinger Equation in 3 Dimensions

- V and Ψ are now functions of r and time, where r is:

$$r = (x, y, z) \tag{7}$$

- The volume of the square well is:

$$d^3r = dx \cdot dy \cdot dz \tag{8}$$

- The probablity of finding a particle in this volume is

$$P = |\Psi(r,t)|^2 d^3r \tag{9}$$

- Therefore, the normalizing follows:

$$\int |\Psi|^2 d^3r = 1 \tag{10}$$

Schrödinger Equation in 3 Dimensions

- There should be a complete set of stationary states when the potential is independent of time. Therefore :

$$\Psi_n(r,t) = \psi_n(r)e^{-iE_nt/\hbar} \tag{11}$$

- which satisfies the time-independent Schrödinger wave-equation and becomes:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{12}$$

- This has the general solution:

$$\Psi(r,t) = \Sigma c_n\psi_n(r)e^{-iE_nt/\hbar} \tag{13}$$

- $\Psi(r,0)$ yields the constant c_n

Spherical Coordinates

- Now, we can can rewrite the Laplacian in spherical coordinates knowing that:

$$x = rsin(\theta)cos(\phi)$$

$$y = rsin(\theta)sin(\phi)$$

$$z = rcos(\theta)$$

- This obtains:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin(\theta)}\frac{\partial}{\partial \theta}\left(sin(\theta)\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 sin^2(\theta)}\left(\frac{\partial^2}{\partial \phi^2}\right) \tag{14}$$

Spherical Coordinates

- This new laplacian can be plugged into Schrödinger 's Time-Independent wave-equation.

$$-\frac{\hbar^2}{2m}\Big[\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big)+\frac{1}{r^2 sin(\theta)}\frac{\partial}{\partial\theta}\Big(sin(\theta)\frac{\partial}{\partial\theta}\Big)+\frac{1}{r^2 sin^2(\theta)}\Big(\frac{\partial^2}{\partial\phi^2}\Big)\Big] \tag{15}$$

$$+V\psi=E\psi$$

- To solve this in spherical coordinates, we need to use seperation of variables:

$$\psi(r,\theta,\phi)=R(r)Y(\theta,\phi) \tag{16}$$

- Plugging this into (15) yields:

$$-\frac{\hbar^2}{2m}\Big[\frac{Y}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R}{\partial r}\Big)+\frac{R}{r^2 sin(\theta)}\frac{\partial}{\partial\theta}\Big(sin(\theta)\frac{\partial Y}{\partial\theta}\Big)+\frac{R}{r^2 sin^2(\theta)}\Big(\frac{\partial^2 Y}{\partial\phi^2}\Big)\Big]$$

$$+VRY=ERY$$

Seperation of Variables

- Dividing by RY and then multiplying by $\frac{-2mr^2}{\hbar^2}$ yields:

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r) - E)\right] + \frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0 \tag{17}$$

- In this form, the first term depends on r only and the second term depends on θ and ϕ only.
- Now we can seperate the two terms and set them equal to $l(l+1)$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r) - E) = l(l+1) \tag{18}$$

$$\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -l(l+1) \tag{19}$$

The Angular Equation

- By using Equation (20) and multiplying through by $Y sin^2\theta$, we obtain:

$$sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)sin^2(\theta)Y \tag{20}$$

- We can use seperation of variables again,where:

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \tag{21}$$

- Plugging in and dividing through by $\Theta\Phi$:

$$\left\{\frac{1}{\Theta}\left[sin\theta\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)\right]+l(l+1)sin^2\theta\right\}+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=0 \tag{22}$$

The Angular Equation

- Now each term can be set equal to its "seperation constant", m^2

$$\frac{1}{\Theta}\left[sin\theta\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)\right]+l(l+1)sin^2\theta=m^2 \tag{23}$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2 \tag{24}$$

- Equation (24) can be simplified to:

$$\Phi(\phi)=e^{im\phi} \tag{25}$$

- So

$$\Phi(\phi+2\pi)=\Phi(\phi) \tag{26}$$

$$e^{im\phi}=e^{im(\phi+\pi)} \tag{27}$$

The Legendre Function

- Therefore, m must be an integer:

$$m = 0, \pm 1, \pm 2, \ldots \tag{28}$$

- For the θ equation:

$$sin\theta \frac{d}{d\theta}\left(sin\theta \frac{d\Theta}{d\theta}\right) + [l(l+1)sin^2\theta - m^2]\Theta = 0 \tag{29}$$

- Which has the solution:

$$\Theta(\theta) = AP_l^m(cos\theta) \tag{30}$$

The Legendre Function

- P_l^m is the asscociated Legendre function. It is defined as:

$$P_l^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x) \tag{31}$$

- The Rodrigues formula defines P_l using the lth Legendre polynomial:

$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l \tag{32}$$

- l must be a non-negative integer for the Rodrigues formula to work.

$$l = 0, 1, 2, \ldots \tag{33}$$

- For any l, there are $(2l+1)$ possibilities for m

$$m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l \tag{34}$$

The Legendre Function

- Polynomial Examples for P_l:

$$P_0 = 1$$

$$P_1 = x$$

$$P_2 = \frac{1}{2}(3x^2 - 1)$$

$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$

Spherical Harmonics

- Now the volume written in spherical coordinates is:

$$d^3r = r^2 sin\theta dr d\theta d\phi \tag{35}$$

- This makes the normalization:

$$\int |\psi|^2 r^2 sin\theta dr d\theta d\phi = 1 \tag{36}$$

- Then using the fact that $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, we get:

$$\int |R|^2 r^2 dr \int |Y|^2 sin\theta d\theta d\phi = 1 \tag{37}$$

Spherical Harmonics

- Sperating to normalize, we get:

$$\int_0^\infty |R|^2 r^2 dr = 1 \tag{38}$$

$$\int_0^{2\pi} \int_0^\pi |Y|^2 sin\theta d\theta d\phi = 1 \tag{39}$$

- When normalized, these angular wave functions are called Spherical Harmonics.

$$Y_l^m(\theta,\phi) = \in \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|!)}} e^{im\phi} P_l^m(cos\theta) \tag{40}$$

- Here; when $m \geq 0$ then$\in = (-1)^m$ and for $m \leq 0$ then $\in = 1$.

Spherical Harmonics

- Spherical Harmonic Examples

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1) e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

The Radial Equation

- We can see that the angular component $Y(\theta, \phi)$ does not change for spherically symmetric potentials
- The shape of the potential $V(r)$ only affects the radial component $R(r)$ and is determined by (18)

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = l(l+1)R \tag{41}$$

- To simplify this equation we can define the variables as such:

$$u(r) \equiv rR(r) \tag{42}$$

- Then $R = u/r$, $dR/dr = [r(dr/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = rd^u/dr^2$ and

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu \tag{43}$$

The Radial Equation

- Equation 43 is the radial equation
- One-dimensional Schrödinger equation is identical in form
- In this case, however, a centrifugal term is present in our new effective potential term

$$V_{eff} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} \tag{44}$$

- Similar to the pseudo-force in classical mechanics, this centrifugal component tends to send particles away from the origin
- The normalization term becomes

$$\int_0^\infty |u|^2 dr = 1 \tag{45}$$

- This is as far as we can go until we supply a specific potential $V(r)$

The End

Thanks for listening!