Chapter One

Lecture One

Quantum mechanics in three dimensions

I will attempt in this chapter to extend the Schrödinger equation, which we studied in Course 301, from one dimension to three dimensions (x, y, z) and also express it in spherical coordinates r, ϑ, φ.

Let us begin with the Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\,\psi \qquad (1)$$

Here, H represents the Hamiltonian (the sum of kinetic and potential energy), and ψ is the wave function that describes the moving particle.

$$H = \frac{1}{2}m\,v^2 + U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + U$$

We previously defined the momentum components as operators as follows:

$$p_x = -i\hbar\frac{\partial}{\partial x} \quad , p_y = -\,i\hbar\frac{\partial}{\partial y} \quad , p_z = -\,i\hbar\frac{\partial}{\partial z}$$

Thus, the total momentum operator can be expressed concisely as:

$$\vec{P} = -i\hbar\vec{\nabla}$$

Accordingly, the Schrödinger equation in three dimensions becomes:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U\psi \qquad (2)$$

Here, ∇^2 represents the Laplacian operator in Cartesian coordinates.

Since ψ,U are functions of position and time, the spherical coordinate r can be written as a vector in terms of Cartesian coordinates r=(x,y,z).

The probability of a particle is

$$|\psi(r,t)|^2 \mathrm{d}^3\mathrm{r}$$

Normalization is

$$\int |\psi(r,t)|^2 d^3 r = 1$$

This means the particle is guaranteed to exist within the specified range (probability = 100%).

If U (the potential) is time-independent, we can define the stationary state (ground state) just as in the one-dimensional case—by separating the wave function into two parts: one dependent on position and the other on time.

$$\psi_n(r,t) = \psi_n(r)\exp(-iE_n)\mathrm{t}/\hbar \qquad (3)$$

Here, the functions ψn(r) satisfy the time-independent Schrödinger equation in three dimensions:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi \qquad (4)$$

Comparing this to the one-dimensional Schrödinger equation, the general solution to (4) in three dimensions is:

$$\psi(r,t) = \sum_n C_n \psi_n(r)\exp(-iE_n t/\hbar) \qquad (5)$$

The constants Cn can be determined as before from the initial wave function at t=0. If the energy spectrum is continuous, the summation becomes an integral.

Separation of Variables in Spherical Coordinates

In many important problems, the potential energy *U* is **spherically symmetric** (i.e., it depends only on the distance *r* from a central point). In such cases, it is convenient to use **spherical coordinates**.

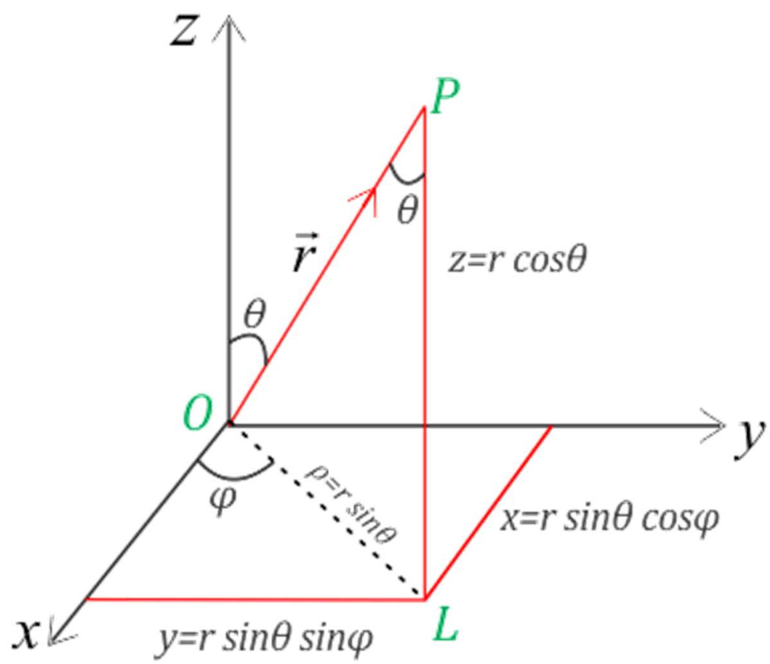
The following coordinate relationships:

$$x = rsin(\vartheta)\cos(\varphi)$$

$$y = rsin(\vartheta)\sin(\varphi)$$

$$z = rcos(\vartheta)$$

$$\rho = rsin(\vartheta)$$



We are looking for solutions that can be separated into the product of two functions, where one depends on the variable *r* and the other depends on the angles ϑ and φ:

$$\psi(r, \vartheta, \varphi) = R(r)Y(\vartheta, \varphi) \qquad (6)$$

It is known that the Laplacian ∇^2 in spherical coordinates has the following form:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\vartheta)}\frac{\partial}{\partial\vartheta}\left(\sin(\vartheta)\frac{\partial}{\partial\vartheta}\right) + \frac{1}{r^2 sin^2(\vartheta)}\left(\frac{\partial^2}{\partial\varphi^2}\right) \qquad (7)$$

We substitute equations (6) and (7) into the Schrödinger equation (equation (4)) and then multiply both sides of the equation by $(-\frac{2mr^2}{\hbar^2 RY})$.

We obtain:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(U-E) + \frac{1}{Y}\left\{\frac{1}{\sin(\vartheta)}\frac{\partial}{\partial\vartheta}\left(\sin(\vartheta)\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{sin^2(\vartheta)}\frac{\partial^2 Y}{\partial\varphi^2}\right\} = 0$$

This equation consists of two parts: the first depends on the radial distance *r*, and the second depends on the angles ϑ and φ. For the equation to hold, each part must equal a constant. Therefore, we can separate this equation into two equations using a **separation constant** *C*.

Based on our knowledge of this constant and its relationship to the **angular momentum** of the moving particle, we assume its value to be $C = l(l+1)$**.** Since it is an arbitrary constant, we can choose its form as needed. Thus, we obtain:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(U-E) = C = l(l+1) \qquad (8)$$

$$\frac{1}{Y}\left\{\frac{1}{\sin(\vartheta)}\frac{\partial}{\partial\vartheta}\left(\sin(\vartheta)\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{sin^2(\vartheta)}\frac{\partial^2 Y}{\partial\varphi^2}\right\} = -C = -l(l+1) \qquad (9)$$

Equation (8) represents the **radial part** of the Schrödinger equation, while **Equation (9)** represents the **angular part**.

From **Equation (9)**, we observe that it **does not depend on the potential energy *U***. Therefore, its solution, *Y*(ϑ,φ), is a **general solution** applicable to all problems with **spherical symmetry**. Thus, we will focus on it first.

On the other hand, solving **Equation (8)** requires knowledge of the **potential energy function *U*(*r*)**, which is **specific to each quantum system** (e.g., an atom, a molecule, or any other system).

The Angular Equation (Separation of Variables)

The angular part of the equation is given by:

$$\frac{1}{Y}\left\{\frac{1}{\sin(\vartheta)}\frac{\partial}{\partial\vartheta}\left(\sin(\vartheta)\frac{\partial Y}{\partial\vartheta}\right)+\frac{1}{\sin(\vartheta)^2}\frac{\partial^2 Y}{\partial\varphi^2}\right\}=-l(l+1)$$

This can be rewritten as:

$$\sin(\vartheta)\frac{\partial}{\partial\vartheta}\left(\sin(\vartheta)\frac{\partial Y}{\partial\vartheta}\right)+\frac{\partial^2 Y}{\partial\varphi^2}=-l(l+1)\ \sin(\vartheta)^2\,Y \qquad (10)$$

We can further **separate the variables** ϑ and φ by assuming:

$$Y(\vartheta,\varphi)=\theta(\vartheta)\emptyset(\varphi) \qquad (11)$$

Substituting **(11)** into the angular equation and dividing by θ(ϕ) $\Phi(\varphi)$, we obtain:

$$\frac{1}{\theta(\vartheta)}\left\{\sin(\vartheta)\frac{d}{d\vartheta}\left(\sin(\vartheta)\frac{d\theta(\vartheta)}{d\vartheta}\right)\right\}+l(l+1)sin^2(\vartheta)+\frac{1}{\emptyset(\varphi)}\frac{d^2\emptyset(\varphi)}{d\varphi^2}=0$$

Since the equation must hold for all θ and ϕ, each part must equal a **constant**. Let this separation constant be m^2 (it does not necessarily have to be m^2, but this choice is conventional). Thus, we split the equation into two independent parts:

1. **The θ-dependent equation:**

$$\frac{1}{\theta(\vartheta)}\left\{\sin(\vartheta)\frac{d}{d\vartheta}\left(\sin(\vartheta)\frac{d\theta(\vartheta)}{d\vartheta}\right)\right\}+l(l+1)sin^2(\vartheta)=m^2 \qquad (12)$$

2. **The ϕ-dependent equation:**

$$\frac{1}{\emptyset(\varphi)}\frac{d^2\emptyset(\varphi)}{d\varphi^2}=-m^2 \qquad (13)$$

The solution to **(13)** is **well known and straightforward**, so we will proceed with it first.

Solution to the Azimuthal Equation (ϕ-part)

The differential equation for $\Phi(\varphi)$ is:

$$\frac{d^2\emptyset(\varphi)}{d\varphi^2} = -m^2\emptyset(\varphi)$$

Its general solutions are complex exponentials:

$$\emptyset(\varphi) = e^{im\varphi} \quad \text{or} \quad \emptyset(\varphi) = e^{-im\varphi}$$

For simplicity, we choose:

$$\emptyset(\varphi) = e^{im\varphi} \qquad (14)$$

Boundary Condition: Since φ and (φ+2π) represent the same point in space, the solution must satisfy:

$$e^{im(\varphi+2\pi)} = e^{im\varphi} \implies e^{2im\pi} = 1$$

This implies:

$$\cos(2m\pi) + i\sin(2m\pi) = 1$$

Which holds **only if *m* is an integer**. Thus:

$$\Phi(\varphi) = e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

Solution to the Polar Equation (θ-part)

The equation for $\Theta(\vartheta)$ is:

$$\frac{1}{\theta(\vartheta)}\left\{\sin(\vartheta)\frac{d}{d\vartheta}\left(\sin(\vartheta)\frac{d\theta(\vartheta)}{d\vartheta}\right)\right\} + l(l+1)sin^2(\vartheta) = m^2$$

Or

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

This is a well-known equation in mathematics, solvable using **associated Legendre polynomials** P_l^m. The solution is:

$$\theta(\vartheta)=AP_l^m(\cos(\vartheta) \qquad (15)$$

where:

- $P_l^m(cos\theta)$ are the **associated Legendre functions**.
- l is a **positive integer** (quantum number linked to angular momentum).
- m is an integer constrained by $|\ m\ |\leq l$.

Associated Legendre Polynomials

The associated Legendre polynomials $P_l^m(x)$ are defined as:

$$P_l^m(x)=(1-x^2)^{\frac{|m|}{2}}(\frac{d}{dx})^{|m|}P_l(x)$$

where:

- $P_l(x)$ is the **Legendre polynomial of degree *l***.
- $P_l(x)$ is given by the **Rodrigues formula**:

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

Examples of Legendre Polynomials

$l = 0$	$P_0(x)$=1
$l = 1$	$P_1(x) = \frac{1}{2*1}\frac{d}{dx}(x^2-1) = \frac{1}{2}(2x) = x$
$l = 2$	$P_l(x) = \frac{1}{2^2*2}(\frac{d}{dx})^2(x^2-1)^2 = \frac{1}{8}\frac{d}{dx}\{2(x^2-1)*2x\}$ $= \frac{1}{2}\frac{d}{dx}(x^3-x) = \frac{1}{2}(3x^2-1)$

Associated Legendre Polynomials

$$P_l^m(x) = (1-x^2)^{\frac{|m|}{2}}(\frac{d}{dx})^{|m|}P_l(x) \quad , x = \cos(\vartheta)$$

$l = 0 \ , m = 0 \qquad P_0^0(x) = 1$

$l = 0, \quad m = \pm 1 \qquad P_0^{\pm 1} = P_0^1 = (1-x^2)^{\frac{1}{2}}\frac{d}{dx}P_0(x) = 0$

General Property:

If | m |> l, then **all $P_l^m(x)$=0**.

l	m	$P_l(x)$	$P_l^m(x)$
0	0	1	1
1	0 $+1$ -1 ± 2	x x x x	$x = \cos(\vartheta)$ $\sqrt{1-\cos(\vartheta)^2}$ = $\sin(\vartheta)$ $\sin(\vartheta)$ 0

Summary:

The solutions take the form:

$$\theta(\vartheta) = AP_l^m(\cos(\vartheta))$$
$$l = 0, 1, 2, \ldots.$$
$$|m| < l$$

where:

- $l = 0,1,2, \ldots$ (orbital quantum number)
- For each l, the magnetic quantum number mm satisfies $| \; m \; | \leq l$:

$$m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l$$

Normalization Condition in Spherical Coordinates

The volume element in spherical coordinates is:

$$d^3r = r^2 \sin(\vartheta) \, d\vartheta d\varphi dr$$

The normalization condition becomes:

$$\int |\psi(r,t)|^2 d^3r = \int |\psi(r,t)|^2 \, r^2 \sin(\vartheta) \, d\vartheta d\varphi dr$$

$$= \int |R(r)|^2 r^2 dr \int |Y(\vartheta, \varphi)|^2 \sin(\vartheta) \, d\vartheta d\varphi$$

The last equation is suitable for performing the integration over the variables separately as follows:

$$\int_0^\infty |R(r)|^2 \, r^2 \, dr = 1 \quad (16)$$

Normalization Condition for the Angular Part of the Schrödinger Equation Solution

The normalization condition for the angular part of the wavefunction is given by:

$$\int_0^{2\pi} \int_0^{\pi} |Y(\vartheta, \varphi)|^2 \sin(\vartheta)\, d\vartheta\, d\varphi = 1 \qquad (17)$$

Here, the angular variables span the ranges:

$$\begin{gathered} 0 \leq \varphi \leq 2\pi \quad (\text{azimuthal angle}) \\ 0 \leq \vartheta \leq \pi \quad (\text{polar angle}) \end{gathered}$$

Spherical Harmonics: The Angular Solution

The angular part of the wavefunction is expressed in terms of **spherical harmonics** $Y_l^m(\vartheta, \varphi)$:

$$Y_l^m(\vartheta, \varphi) = \epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\varphi}\, P_l^m(\cos(\vartheta)) \qquad (18)$$

where:

- ϵ is a phase factor:

$$\epsilon = \begin{cases} (-1)^m & \text{if } m \geq 0, \\ 1 & \text{if } m \leq 0. \end{cases}$$

- $P_l^m(\cos\vartheta)$ are the **associated Legendre polynomials**.
- l and m are the **orbital** and **magnetic quantum numbers**, respectively, with $|m| \leq l$.

Orthonormality Condition

The spherical harmonics satisfy the **orthonormality** condition:

$$\int_0^{2\pi} \int_0^{\pi} [Y_l^m(\vartheta, \varphi)]^* \left[Y_{l'}^{m'}(\vartheta, \varphi)\right] \sin(\vartheta)\, d\vartheta\, d\varphi = \delta_{ll'}\, \delta_{mm'} \qquad (19)$$

Here:

- $\delta_{ll'}$ and $\delta_{mm'}$ are **Kronecker deltas**, ensuring orthogonality unless $l = l'$ and $m = m'$.
- The * denotes the **complex conjugate**.