Lecture #17

<u>Quantum mechanics in three dimensions</u>

Schrödinger equation in spherical coordinates

How do we generalize Schrödinger equation to three dimensions?

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi$$

Hamiltonian in 3D is (from classical energy)

$$H = \frac{1}{2}mv^2 + V = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V$$

We previously used $p_x \to -i\hbar \frac{\partial}{\partial x}$.

Thus, $p_y \to -i\hbar \frac{\partial}{\partial y}, \quad p_z \to -i\hbar \frac{\partial}{\partial z}$.

$$\boxed{\vec{p} \to -i\hbar \nabla}$$

Therefore, Schrödinger equation in three dimensions is

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi + V\psi}$$

$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian in cartesian coordinates.

ψ and V are functions of $\vec{r} = (x, y, z)$ and t.

The probability to find particle in volume $d^3r = dx\,dy\,dz$ is $|\psi(\vec{r},t)|^2 d^3r$.

The normalization condition is $\boxed{\int |\psi|^2 d^3r = 1}$.

If potential V does not depend on time, we can define stationary states, just as in one dimension:

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar},$$

where functions $\psi_n(\vec{r})$ satisfy the time-independent Schrödinger equation in three dimensions:

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

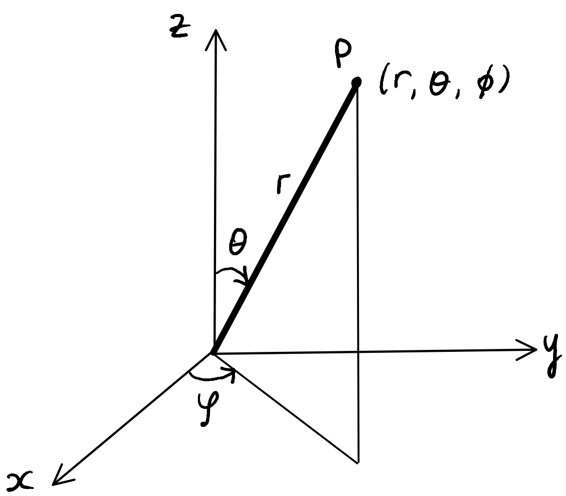
By complete analogy with one-dimensional case, the general solution of Schrödinger equation in three dimensions is

$$\boxed{\Psi(\vec{r},t) = \sum_n c_n \psi_n(\vec{r})\, e^{-iE_n t/\hbar}}.$$

Coefficients c_n are obtained as before from the wave function at t=0, $\Psi(\vec{r},0)$.
If the spectrum is continuous, sum in the above equation becomes an integral.

Separation of variables in spherical coordinates

In many important problems, potential V is spherically symmetric, i.e. depends only on distance r from the origin. It is convenient to use spherical coordinates in such cases.



$$\boxed{\begin{aligned} x &= r\sin\theta\cos\varphi \\ y &= r\sin\theta\sin\varphi \\ z &= r\cos\theta \end{aligned}}$$

We look for solutions that separate into the product of two functions: one that depends only on r and another that depends on ϕ and θ.

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

distance from the origin

The Laplacian in spherical coordinates is

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

Substituting ∇^2 and $\psi = RY$ into the Schrödinger equation, we get:

$$-\frac{\hbar^2}{2m}\left\{\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} + VRY = ERY$$

We want to separate this equation into two parts, one that depends only on r and another that depends only on ϕ and θ; hence the "separation of variables".

We multiply the equation by $-\dfrac{2mr^2}{\hbar^2 YR}$:

$$\underbrace{\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V-E)}}_{=\boxed{c}} + \underbrace{\boxed{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}}}_{=\boxed{-c}} = 0$$

This part only depends on r.

This part only depends on θ and ϕ.

Therefore, we can separate this equation into two with some separation constant c. For reasons that will eventually become clear, we will write this separation constant c as $c = \ell(\ell+1)$ (since it is a constant, we can write it any way we want.)

Radial equation:

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

Angular equation:

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

Since the angular equation does not depend on the potential and its solutions give angular functions Y for any spherically symmetric problem, we consider it first. To solve the radial equation, we need to know V.

Angular equation

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

We separate variables again and look for solutions in the form:

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

$$\Phi \sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\sin^2\theta\, \Theta\Phi + \Theta \frac{d^2\Phi}{d\phi^2} = 0$$

We divide this equation by $\Phi\Theta$ and separate parts that depend on ϕ and θ.

$$\underbrace{\boxed{\frac{1}{\Theta}\left\{\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right\} + \ell(\ell+1)\sin^2\theta}}_{=\, m^2} + \underbrace{\boxed{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}}_{=\, -m^2} = 0$$

Depends on θ.

Depends on ϕ.

This time we are going to call separation constant m^2.

$$\theta: \quad \frac{1}{\Theta}\left\{\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right\} + \ell(\ell+1)\sin^2\theta = \boxed{m^2}$$

$$\phi: \quad \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \boxed{-m^2}$$

Let's consider Φ equation first, since it is easy:

(1) $$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi = e^{im\phi} \text{ or } \Phi = e^{-im\phi}$$

We will allow m to be either positive or negative, so we can leave only solution

$$\boxed{\Phi = e^{im\phi}}$$

We require that $\Phi(\phi + 2\pi) = \Phi(\phi)$ since ϕ and $\phi+2\pi$ correspond to the same point in space.

$$e^{im[\phi+2\pi]} = e^{im\phi} \Rightarrow e^{im2\pi} = 1$$

Therefore, m has to be an integer.

$$\left\{ e^{2\pi i m} = \cos(2\pi m) + i\sin(2\pi m) = 1 \text{ if } m \text{ is integer.} \right\}$$

Summary: $$\boxed{\Phi = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots}$$

(2) We now consider equation for Θ:

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

The solutions of this equation are $\Theta(\theta) = A P_\ell^m(\cos\theta)$, where P_ℓ^m is the associated Legendre function, ℓ is positive integer.

$$\boxed{P_\ell^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_\ell(x) \quad \text{and}}$$

$P_\ell(x)$ is the ℓ^{th} Legendre polynomial.

The Legendre polynomial P_ℓ is defined by the Rodrigues formula:

$$P_\ell(x) \equiv \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell .$$

Let's get a few first functions to see how these formulas work:

$$\ell=0 \Rightarrow P_0(x) = 1$$

$$\ell=1 \Rightarrow P_1(x) = \frac{1}{2\cdot 1}\frac{d}{dx}(x^2-1) = \frac{1}{2}(2x) = x$$

$$\ell=2 \Rightarrow P_2(x) = \frac{1}{2^2\cdot 2}\left(\frac{d}{dx}\right)^2 (x^2-1)^2$$

$$= \frac{1}{8}\frac{d}{dx}\left\{2(x^2-1)\cdot 2x\right\} = \frac{1}{2}\frac{d}{dx}(x^3-x) = \frac{1}{2}(3x^2-1)$$

Now on to associated Legendre functions:

$$\boxed{P_\ell^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x)} \qquad x=\cos\theta$$

$\boxed{\ell=0}$ $P_0(x) = 1$

$\boxed{m=0}$ $\Rightarrow$ $P_0^0 = 1$

$\boxed{m=\pm 1}$ $\Rightarrow$ $P_0^1 = (1-x^2)^{1/2}\dfrac{d}{dx}\overbrace{P_0(x)}^{1} = 0$

This is general property, if $\boxed{|m| > \ell \Rightarrow P_\ell^m = 0}$.

Thus, if $\ell=0 \Rightarrow m=0$ $P_0^0 = 1$.

$\boxed{\ell = 1}$ $P_1 = x$

$\boxed{m=0}$ $\Rightarrow$ $P_1^0 = P_1 = x = \cos\theta$

$\boxed{m = 1 \quad [\text{or } m = -1]}$ $P_1^1 = (1-x^2)^{1/2} \frac{d}{dx}(x) = \sqrt{1-\cos^2\theta}$

$P_1^1 = \sin\theta$

$\boxed{m = \pm 2}$ $P_1^2 = 0$ $\left[\frac{d^2}{dx^2} x = 0\right]$ as we noted above ...

Thus, $\ell = 1$ $m = 0$ $P_1^0 = \cos\theta$

$m = 1$ $P_1^1 = \sin\theta$.

same for $m = -1$

Summary: $\Theta(\theta) = A P_\ell^m(\cos\theta)$

$\ell = 0, 1, 2 \ldots$

$|m| < \ell \Rightarrow$

For each ℓ, there are $2\ell + 1$ possible values of m.

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

We still need to find out A from normalization condition.

In spherical coordinates volume element is $d^3\mathbf{r} = r^2 \sin\theta \, dr \, d\theta \, d\phi$

Normalization gives: $\int |\Psi(\bar{r}, t)|^2 d^3 r = \int |\Psi|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$

$$= \underbrace{\int |R|^2 r^2 dr}_{1} \underbrace{\int |Y|^2 \sin\theta \, d\theta \, d\phi}_{1} = 1$$

$\Leftarrow$ Convenient to normalize R and Y separately.

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

Normalization condition for radial function R.

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

Normalization condition for Y.

Note that $0 \le \phi \le 2\pi$ and $0 \le \theta \le \pi$.

The normalized angular wave functions are called **spherical harmonics**:

$$\boxed{Y_\ell^m(\theta,\phi) = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, e^{im\phi} P_\ell^m(\cos\theta)}$$

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

These functions are orthogonal:

$$\int_0^{2\pi}\int_0^{\pi} [Y_\ell^m(\theta,\phi)]^* Y_{\ell'}^{m'}(\theta,\phi) \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'}\delta_{mm'}$$

Summary

The general solution of Schrödinger equation in three dimensions (if V does not depend on time)

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi} \qquad H = -\frac{\hbar^2}{2m}\nabla^2 + V$$

is

$$\psi(\vec{r},t) = \sum_n c_n \psi_n(\vec{r})\, e^{-iE_n t/\hbar},$$

where functions $\psi_n(\vec{r})$ are solutions of time-independent Schrödinger equation

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}. \qquad [H\psi = E\psi]$$

If potential V is spherically symmetric, i.e. only depends on distance to the origin r, then the separable solutions are

$$\boxed{\psi(r,\theta,\phi) = R(r)\, Y_\ell^m(\theta,\phi)},$$

where $R(r)$ are solutions of radial equation

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

with normalization condition $\int_0^\infty |R|^2 r^2\, dr = 1$

The spherical harmonics are

$$Y_\ell^m(\theta,\phi) = \epsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, e^{im\phi}\, \underbrace{P_\ell^m(\cos\theta)}_{\text{associated Legendre functions}}$$

$$\epsilon = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m \leq 0 \end{cases} \qquad \boxed{\begin{array}{l} \ell = 0, 1, 2, \ldots \\ m = -\ell, -\ell+1, \ldots 0, 1, \ldots \ell \end{array}}$$