Schrödinger Eq. in 3D

Note Title

$$i\hbar\frac{\partial \Psi}{\partial t} = H\Psi = \left(\frac{p^2}{2m} + V\right)\Psi$$

$$p = \begin{cases} \frac{\hbar}{i}\frac{\partial}{\partial x} & ; 1D \\ \frac{\hbar}{i}\nabla & ; 3D \end{cases}$$

$$\nabla \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

In 3D: $i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$

, where $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

called Laplacian

* Normalization ; $\int |\Psi|^2 \underbrace{d^3\vec{r}}_{\text{|||} \; dx\,dy\,dz} = 1$

* Stationary states in 3D,

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

The time independent Schrödinger Eq, is

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

, where $\psi(\vec{r})$ are stationary states.

The general solution to the time dependent Schrödinger equation is

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

, where c_n are obtained from $\Psi(\vec{r},0)$.

* So if we obtain $\psi_n(\vec{r})$ and E_n by solving the eigenvalue problem of time independent Schrödinger Eq, we are basically done.

* So How do we solve

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

If $V(\vec{r}) = V(r)$, that is if it is independent of the orientation, using the spherical coordinates (r, θ, φ) simplifies the problem significantly.

* In spherical coordinates,

$$\nabla^2 = \frac{1}{r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2(\theta,\varphi)}{\hbar^2}\right)$$

, where

$$-\frac{L^2(\theta,\varphi)}{\hbar^2} \equiv \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

Now if we use the separation of variables method by

$$\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi),$$

Then the T. I. S. E. becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\,\psi = E\psi$$

$$\Rightarrow \nabla^2\psi - \frac{2m}{\hbar^2}(V-E)\,\psi = 0$$

$$\Rightarrow \frac{1}{r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2}\right)\psi - \frac{2m}{\hbar^2}(V-E)\,\psi = 0$$

$$\Rightarrow \left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V-E)\right]R\cdot Y$$

$$-\frac{L^2}{\hbar^2}R\cdot Y = 0$$

$$\Rightarrow \frac{1}{R}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V-E)\right]R$$

$$= \frac{1}{Y}\frac{L^2}{\hbar^2}Y \equiv \underbrace{l(l+1)}_{\text{some constant}}$$

So we have two equations

① $L^2(\theta,\varphi)\,Y(\theta,\varphi) = \hbar^2\, l(l+1)\,Y(\theta,\varphi)$

and ② $\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V-E)\right]R(r) = l(l+1) \times R(r)$

The first equation is called the angular equation and the second equation is called the radial equation.

We notice that the angular equation is completely independent of the potential energy, and can be completely solved on its own.

So we will handle the angular equation first, and then do the radial equation.

* Angular Equation

$$L^2(\theta, \varphi)\, Y(\theta, \varphi) = \hbar^2 \ell(\ell+1)\, Y(\theta, \varphi)$$

$$, \quad L^2(\theta, \varphi) \equiv -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$$

We will later find out that L^2 is the angular momentum squared. And ℓ is called azimuthal quantum number, which must be non-negative integers.

* Solving this eigenvalue problem again requires the separation of variable scheme.

Instead of going through the details, I will just cite the final answer for this.

The eigenstate of this angular equation is called "spherical harmonics"

$Y_\ell^m(\theta, \varphi)$, which are labeled by two quantum numbers ℓ and m.

See table 4.3 in the book for a list of spherical harmonics.

ℓ is called azimuthal quantum number
m the magnetic quantum number.

Generally, $Y_\ell^m(\theta, \varphi)$ looks like

$$Y_\ell^m(\theta, \varphi) = C_{\ell m} e^{im\phi} P_\ell^m(\cos\theta)$$

You should be able to handle the spherical harmonics proficiently.

Note: $Y(\theta, \varphi)$ is a two-dimensional function $\Leftrightarrow$ we need two quantum numbers to completely describe it. (ℓ, m)

Some comment on normalization

$$1 = \int |\psi|^2 d^3\vec{r} = \int |R|^2 |Y|^2 r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

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

$\Rightarrow$ We take $\int_{r=0}^{\infty} |R|^2 r^2 dr = 1$

and $\int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} |Y|^2 \sin\theta \, d\theta \, d\varphi = 1$

$Y_\ell^m(\theta,\varphi)$ satisfies the orthonormality such that

$$\langle Y_\ell^m | Y_{\ell'}^{m'} \rangle \equiv \iint (Y_\ell^m)^* Y_{\ell'}^{m'} \sin\theta \, d\theta \, d\varphi$$

$$= \delta_{\ell\ell'} \delta_{mm'}$$

* Radial Equation

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

With $u(r) \equiv rR(r)$

This equation reduces to

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

With $V_{eff}(r) \equiv V(r) + \dfrac{\hbar^2 l(l+1)}{2mr^2}$

[In classical mechanics,

$$V_{eff}(r) = V(r) + \frac{L^2}{2mr^2}$$]

$\dfrac{L^2}{2mr^2}$ is the so-called centrifugal term

$$* \quad -\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + V_{eff}(r)\,u(r) = E\,u(r)$$

is called the radial equation.

with $\int_0^\infty |u(r)|^2 dr = 1$ as the normalization condition.

→ This looks just like the 1D time-independent Schrödinger Eq.

* So the original 3D problem has now turned into a relatively simple 1D problem.

In other words, for any isotropic 3D problem, we have to solve only the radial equation, because the angular parts are just the spherical harmonics.