Schrödinger equation in 3D

So far we have studied quantum systems in 1D. The generalization of the Schrödinger equation to the case of 3D is straightforward. We just change $V(x) \to V(\vec{r})$ and also modify the kinetic energy in the Hamiltonian:

$$\frac{\hat{p}_x^2}{2m} \longrightarrow \frac{|\hat{\vec{p}}|^2}{2m} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m}$$

where, as usual,

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \qquad \hat{p}_y = -i\hbar\frac{\partial}{\partial y} \qquad p_z = -i\hbar\frac{\partial}{\partial z}$$

or simply

$$\hat{\vec{p}} = -i\hbar\nabla$$

The Schrödinger equation then looks as follows

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\vec{r})\Psi$$

When the potential V does not depend on time explicitly then the general solution of the Schrödinger equation can be written as

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

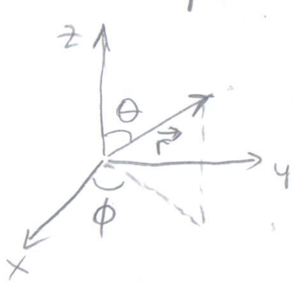
where ψ_n are the solutions of the stationary SE

$$\hat{H}\psi_n(\vec{r}) = E_n\psi_n(\vec{r})$$

Separation of variables for spherically symmetric potentials

In many practical cases the interaction between particles depends only on the distance between them. In other words, $V = V(|\vec{r}|)$. It is natural to use spherical coordinates then:

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned} \quad \Longleftrightarrow \quad \begin{aligned} r &= \sqrt{x^2+y^2+z^2} \\ \theta &= \arctan\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right) \\ \phi &= \arctan\left(\frac{y}{x}\right) \end{aligned}$$



In the new (spherical) coordinates we can separate variables, much in the same way as we did when we had $V \neq V(t)$ and we separated x and t.

The Laplacian in spherical coordinates is:

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

The time-independent Schrödinger equation is then

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

We look for solutions in the form $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$

Plugging this product in the above equation yields

$$-\frac{\hbar^2}{2m}\left(\frac{Y}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial R}{\partial r} + \frac{R}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]\right) + V(r)RY = ERY$$

If we now divide everything by RY and by $-\frac{\hbar^2}{2mr^2}$

we get:

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r} r^2 \frac{\partial R}{\partial r} - \frac{2mr^2}{\hbar^2}V(r) + \frac{2mr^2E}{\hbar^2}}_{\text{independent of } \theta,\phi \text{ so must be a constant } = \ell(\ell+1)} + \underbrace{\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]}_{\text{independent of } r\text{, so must be a constant } = -\ell(\ell+1)} = 0$$

The choice of the constant in the form of $\ell(\ell+1)$ is made purely for convenience (we will see later that ℓ will only take integer values) and is not restrictive.

Next, we will focus on the equation that contains θ and ϕ variables. This equation occurs in many problems that have spherical symmetry (not only in quantum mechanics)

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

Here we can, again, separate variables (θ and ϕ) by

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

Moreover $|m| \le l$, otherwise $P_l^m = 0$

Thus, for each l value m ranges from $-l$ to l.

Functions $Y(\theta, \phi)$ then have the following form:

$$Y_l^m(\theta, \phi) = C_{lm} P_l^m(\cos\theta) e^{im\phi}$$

where C_{lm} is a normalization constant

Remember that the element of volume in spherical coordinates is $d\vec{r} = dx\,dy\,dz = r^2 \sin\theta\, dr\, d\theta\, d\phi$. The normalization condition for Y_l^m looks as follows:

$$\int_0^{2\pi}\int_0^{\pi} |Y_l^m(\theta,\phi)|^2 \sin\theta\, d\theta\, d\phi = 1$$

[r^2 goes to the normalization integral for $R(r)$]

Any general solution of the angular part of the Schrödinger equation can be represented as a linear combination of $Y_l^m(\theta,\phi)$ and

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

Functions $Y_l^m(\theta,\phi)$ are called spherical harmonics

Quantum numbers l and m are called the azimutal and magnetic quantum numbers.

The complete expression for Y_l^m (including the normalization factor is

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

The first few Y_l^m's are: $Y_0^0 = \frac{1}{\sqrt{4\pi}}$

$Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\phi}$ $\qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$