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

$$\Psi(\vec{r}, t) = \sum_n{}' c_n \psi_n(\vec{r})\, e^{-\frac{iE_n t}{\hbar}}$$

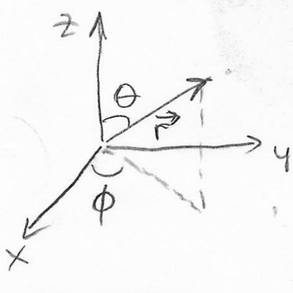
where ψ_n are the solutions of the stationary SE

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

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:

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



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

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

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:

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

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 representing $Y(\theta,\phi)$ as $Y = \Theta(\theta)\,\Phi(\phi)$. After putting this in the above equation and dividing by $\Theta\Phi$ we will obtain

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

The resulting equation for Φ is very simple

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0$$

Its solution is $\Phi(\phi) = e^{\pm im\phi}$. Rather than having a sum of two exponents we will leave just one, but we will let m run over both positive and negative values. There may also be a constant in front of the remaining exponent, but we let it be absorbed into $\Theta(\theta)$ or $R(r)$. Thus, $\Phi(\phi) = e^{im\phi}$. In order to determine what values of m are possible (allowed) we must apply the boundary condition $\Phi(\phi+2\pi) = \Phi(\phi)$

$$e^{im(\phi+2\pi)} = e^{im\phi} \Longrightarrow e^{2\pi im} = 1$$

From here it follows that m must be an integer,

$$m = 0, \pm1, \pm2, \ldots$$

The equation for Θ is more complicated

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

When we make a substitution $\cos\theta = q$ it becomes (after dividing by $1-q^2$)

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

In the theory of special functions this equation is known as the equation for the associated Legendre polynomials (general Legendre equation). The general Legendre equation has two solutions: regular and singular. As we require the square integrability and finiteness of the wave function in quantum mechanics we will only use physically acceptable (i.e. finite) solution, which is given by associated Legendre polynomials

$$P_e^m(q) = (1-q^2)^{\frac{|m|}{2}} \left(\frac{d}{dq}\right)^{|m|} P_e(q)$$

Sometimes an additional factor of $(-1)^m$ is included here, but we will skip it.

Here $P_e(q)$ are Legendre polynomials given by

$$P_e(q) = \frac{1}{2^e e!} \left(\frac{d}{dq}\right)^e (q^2-1)^e$$

The first few polynomials $P_e(q)$ are:

$$P_0(q) = 1 \qquad P_1(q) = q \qquad P_2(q) = \frac{1}{2}(3q^2-1)$$

The first few associated Legendre polynomials are:

$$P_0^0(q) = 1 \qquad P_1^{\pm 1}(q) = \sqrt{1-q^2} \qquad P_1^0 = q$$

$$P_2^{\pm 2}(q) = 3(1-q^2) \qquad P_2^{\pm 1} = 3q\sqrt{1-q^2} \qquad P_2^0(q) = \frac{1}{2}(3q^2-1)$$

or, if we substitute $q = \cos\theta$

$$P_0^0 = 1 \qquad P_1^{\pm 1} = \sin\theta \qquad P_1^0 = \cos\theta$$

$$P_2^{\pm 2} = 3\sin^2\theta \qquad P_2^{\pm 1} = 3\sin\theta\cos\theta \qquad P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$$

The solution of the general Legendre equation is finite (i.e. polynomial) only when l is an integer:

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

Moreover $|m| \leq l$, 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

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

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: $Y_0^0 = \frac{1}{\sqrt{4\pi}}$

$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\phi}$ $\qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$