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 straitforward. We just change $V(x) \to V(\vec{r})$ and also modify the kinetic energy in the Hamiltonian

$$\frac{\hat{p}_x^2}{2m} \longrightarrow \frac{|\hat{\vec{p}}|^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

where as usual $p_x \equiv -i\hbar \frac{\partial}{\partial x}$; $p_y = -i\hbar \frac{\partial}{\partial y}$; $p_z = -i\hbar\frac{\partial}{\partial z}$, or $\vec{p} = -i\hbar \vec{\nabla}$. The Schrödinger equation then looks as follows

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

The general solution to the Schrödinger equation can be represented as

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

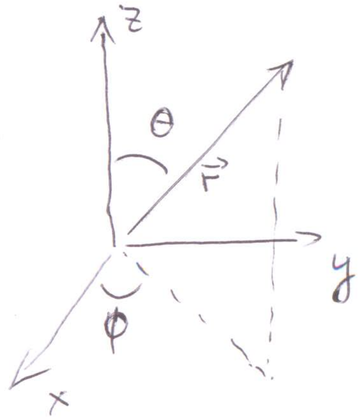
Where ψ_n are the solutions of the stationary SE:

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

Separation of variables for spherically symmetric potentials

The interaction between particles often depends only on the distance between them (e.g. ~~two~~ charged particles). In other words $V = V(|\vec{r}|)$. In this case it is natural to introduce spherical coordinates:

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



$r = |\vec{r}|$

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 SE 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 equation above yields

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

When we divide everything by RY and by $-\frac{\hbar^2}{2mr^2}$ we will get:

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

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

Next we will focus on the equation that involves 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

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

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 let m ~~take~~ over 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 ever $R(r)$. Thus $\Phi(\phi) = e^{im\phi}$. In order to determine what values of m are possible (allowed) we must apply the boundary condition $\Phi(\phi+2\pi) = \Phi(\phi)$:

$$e^{im(\phi+2\pi)} = e^{im\phi} \implies e^{2\pi i m} = 1$$

From here it follows that m must be an integer,

$$m = 0, \pm 1, \pm 2 \ldots$$

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 $1-q^2$)

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

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 pick physically acceptable (finite) solution, which is associated Legendre polynomials

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

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

$P_\ell(q)$ are Legendre polynomials:

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

A few polynomials $P_\ell(q)$ for small ℓ:

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

and

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

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

or if we substitute $q = \sin\theta$

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

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

The solution of the general Legendre equation is finite (e.g. 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} are normalization constants

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 SE 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 number