SCHRÖDINGER EQUATION IN THREE DIMENSIONS - SPHERICAL HARMONICS

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Sec 4.1.

Although some physical systems can be described in one or two dimensions, the most general problems require the solution of the Schrödinger equation in three dimensions. Recall that in one dimension, the equation reads

$$\frac{p^2}{2m}\Psi+V\Psi=i\hbar\frac{\partial\Psi}{\partial t} \tag{1}$$

where the momentum p is given by the differential operator

$$p=-i\hbar\frac{\partial}{\partial x} \tag{2}$$

To generalize this to three dimensions, we can give the momentum its three components in each of the three spatial dimensions, so we get

$$\begin{aligned}
p_x &= -i\hbar\frac{\partial}{\partial x} && (3)\\
p_y &= -i\hbar\frac{\partial}{\partial y} && (4)\\
p_z &= -i\hbar\frac{\partial}{\partial z} && (5)\\
p^2 &= -\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) && (6)\\
&= -\hbar^2\nabla^2 && (7)
\end{aligned}$$

where the differential operator ∇^2 is defined by this equation.

The Schrödinger equation in three dimensions can therefore be written as

$$-\frac{\hbar^2}{2m}\nabla^2\Psi+V\Psi=i\hbar\frac{\partial\Psi}{\partial t} \tag{8}$$

If we assume that the potential $V=V(x,y,z)$ is independent of time, we can use the same separation of variables method that we used in one dimension to split off the time part of the solution to get

$$\Psi(x,y,z,t)=\psi(x,y,z)e^{-iEt/\hbar} \tag{9}$$

where, as before, the energy E takes on a set of discrete values for the bound states and a set of continuous values for the scattering, or unbound, states. The spatial wave function ψ satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi \tag{10}$$

So far, the analysis is the same as that for one dimension.

Things get interesting when we consider the analysis relating to the three spatial dimensions. A common situation is that where the potential is spherically symmetric; it depends only on the radial distance r for the origin (the electrostatic potential is one such case). In this case, it makes more sense to use spherical coordinates, so we need to rewrite 10 in spherical coordinates. We'll just quote the result in spherical coordinates (r,θ,ϕ) (general formulas for div, grad, curl and Laplacian operators in spherical and cylindrical coordinates are given in Griffiths's *Introduction to Electrodynamics* inside the front cover, but you should be able to find these on many web sites), where r is the distance from the origin (so $r\geq0$), θ is the angle from the positive z axis (so $0\leq\theta\leq\pi$), and ϕ is the azimuthal angle measured from the x axis (so $0\leq\phi\leq2\pi$) :

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{11}$$

Given this, the time-independent portion of the Schrödinger equation satisfies

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right]+V\psi=E\psi \tag{12}$$

At this point, we try separation of variables again, initially by just peeling off the dependence on r. We propose $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$. Plugging this in, we get

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]+VRY=ERY \quad (13)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{Rr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{Yr^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Yr^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]+(V-E)=0 \quad (14)$$

$$\left[\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2mr^2}{\hbar^2}(V-E)\right]+\left[\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]=0 \quad (15)$$

In the second line, we divided through by RY and in the third line, we multiplied through by $-2mr^2\hbar^2$, and regrouped the terms. We can see that in the last line, the terms in the first square brackets depend only on r, while those in the second square brackets depend only on θ and ϕ. Thus each term must be equal to some constant, which is written in the curious form of $l(l+1)$. The reason for this will appear when we consider the angular equation in more detail in a minute. So we write:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2mr^2}{\hbar^2}(V-E) = l(l+1) \quad (16)$$

$$\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right) = -l(l+1) \quad (17)$$

There isn't much more we can do with the first equation (the one in R) until we specify what the potential is. However, the angular equation does not depend on r and the differential equation as written is fully specified, so we should be able to solve it. We can try separation of variables yet again, and propose that

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \quad (18)$$

This gives

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi\sin^2\theta}\left(\frac{\partial^2\Phi}{\partial\phi^2}\right) = -l(l+1) \quad (19)$$

$$\left[\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)\sin^2\theta\right]+\frac{1}{\Phi}\left(\frac{\partial^2\Phi}{\partial\phi^2}\right) = 0 \quad (20)$$

Again, we have split the equation into two parts, the first of which depends only on θ and the second of which depends only on ϕ, so each part must again be equal to a constant, which we'll call m^2 this time.

$$\begin{aligned}
\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)\sin^2\theta &= m^2 && (21)\\
\frac{1}{\Phi}\left(\frac{\partial^2\Phi}{\partial\phi^2}\right) &= -m^2 && (22)
\end{aligned}$$

The second equation is easily solved to give

$$\Phi(\phi)=Ae^{im\phi} \tag{23}$$

where A is some constant to be determined by normalization. If we allow m to be negative or positive, we can merge the other solution $Ae^{-im\phi}$ with the one just given.

If we rewrite the first equation by multiplying through by $\Theta/\sin^2\theta$ we get

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m^2}{\sin^2\theta}\right]\Theta=0 \tag{24}$$

which turns out to be the general Legendre equation which we've analyzed in other posts, and also reveals why we chose the constant above to be $l(l+1)$. That is, its solutions are given by the associated Legendre functions $P_l^m(\cos\theta)$. Thus the complete angular part of the wave function can be written as

$$Y_l^m(\theta,\phi)=Ae^{im\phi}P_l^m(\cos\theta) \tag{25}$$

The combined functions Y_l^m are known as *spherical harmonics*.

We've already established the orthogonality of the associated Legendre functions. The orthogonality of the ϕ part of the spherical harmonics is fortunately much easier to show:

$$\begin{aligned}
\int_0^{2\pi}e^{-im'\phi}e^{im\phi}d\phi &= \left.\frac{1}{i(m-m')}e^{i(m-m')\phi}\right|_0^{2\pi} && (26)\\
&= 0 && (27)
\end{aligned}$$

provided $m'\neq m$. If $m'=m$ then the integral is simply

$$\int_0^{2\pi} d\phi = 2\pi \tag{28}$$

When we examined the orthogonality properties of the associated Legendre functions we found that

$$\int_{-1}^{1} P_p^m P_q^m dx = \frac{2}{2p+1}\frac{(p+m)!}{(p-m)!}\delta_{pq} \tag{29}$$

If we require the spherical harmonics to be normalized, we therefore need to define the normalization constant A as

$$A = \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} \tag{30}$$

so the spherical harmonics, properly normalized, are:

$$Y_l^m(\theta,\phi) = \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} e^{im\phi}P_l^m(\cos\theta) \tag{31}$$

They obey the normalization condition

$$\int_0^{2\pi}\int_0^{\pi} (Y_l^m)^* Y_{l'}^{m'} \sin\theta d\theta d\phi = \delta_{ll'}\delta_{mm'} \tag{32}$$

Note that the orthogonality with respect to the upper index m comes from the integral over ϕ. The associated Legendre functions are *not* orthogonal with respect to their upper indexes.

This is as far as we can go in solving the spherically symmetric equation without specifying the potential $V(r)$.

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