Class 22: Schrödinger equation in spherical polar coordinates

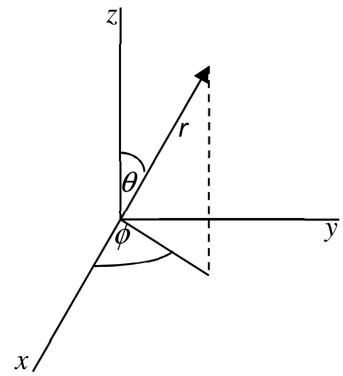
The Schrödinger equation in three dimensions is

$$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\Psi+V(\mathbf{r})\Psi. \tag{22.1}$$

Here use has been made of the momentum operator

$$\hat{\mathbf{p}}=-i\hbar\nabla, \tag{22.2}$$

which is a straightforward generalization of the one-dimensional case. The wave function Ψ is a function of position $\mathbf{r}$ and time t.



For a central force law, the potential energy will depend only on the distance from the force center. It is then convenient to use spherical polar coordinates (r,θ,ϕ).

In these coordinates, the Laplacian operator is

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \tag{22.3}$$

and the time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V(r)\psi=E\psi. \tag{22.4}$$

Making use of the angular momentum operator, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{2mr^2}\hat{L}^2\psi+V(r)\psi=E\psi. \tag{22.5}$$

Since the angular momentum is a conserved quantity, the Hamiltonian operator and $\hat{L}^2$ commute and have a complete set of common eigenfunctions. Thus the angular dependence of the eigenfunctions of the Hamiltonian operator will be described by a spherical harmonic, $Y_l^m(\theta,\phi)$ for which

$$\hat{L}^2Y_l^m(\theta,\phi)=\hbar^2l(l+1)Y_l^m(\theta,\phi). \tag{22.6}$$

The radial part of the eigenfunction will then be a solution of

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\hbar^2}{2mr^2}l(l+1)R+V(r)R=ER, \tag{22.7}$$

which can be simplified, by changing to a new dependent variable $u(r) = rR(r)$, to

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + V(r)\right]u = Eu. \tag{22.8}$$

This is identical to the one dimensional Schrödinger equation, except that the potential is replaced by an effective potential

$$V_{eff}(r) = \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + V(r). \tag{22.9}$$

For $l \neq 0$, the first term in the effective potential results in a ***centrifugal barrier*** which tends to push the particle away from the force center.

The normalization condition is obtained from

$$\begin{aligned}\int_0^\infty\int_0^{2\pi}\int_0^\pi |\psi(r,\theta,\phi)|^2 r^2 \sin\theta d\theta d\phi dr &= \int_0^\infty\int_0^{2\pi}\int_0^\pi R^2 |Y_l^m|^2 r^2 \sin\theta d\theta d\phi dr = \int_0^\infty R^2 r^2 dr \\ &= \int_0^\infty u^2 dr = 1.\end{aligned} \tag{22.10}$$

The infinite spherical well

Consider a particle confined inside a sphere of radius a, by a potential

$$V(r) = \begin{cases} 0, & r < a, \\ \infty, & r > a. \end{cases} \tag{22.11}$$

The radial function is then a solution of

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2\right]u, \tag{22.12}$$

where $k^2 = 2mE/\hbar^2$. The boundary conditions are that $u = 0$ at $r = a$, and R is non-singular at $r = 0$. The solutions of equation (22.12) that satisfy these boundary conditions are

$$u = Arj_l(kr), \tag{22.13}$$

where j_l is a spherical Bessel function of the first kind, and k satisfies $j_l(ka) = 0$.

The spherical Bessel functions of the first kind are given by

$$j_l(x) = (-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x}. \tag{22.14}$$

Hence

$$j_0(x) = \frac{\sin x}{x}. \tag{22.15}$$

Useful recursion relations are

$$j_{l+1}(x) = \frac{l}{x} j_l(x) - j_l'(x). \tag{22.16}$$

and

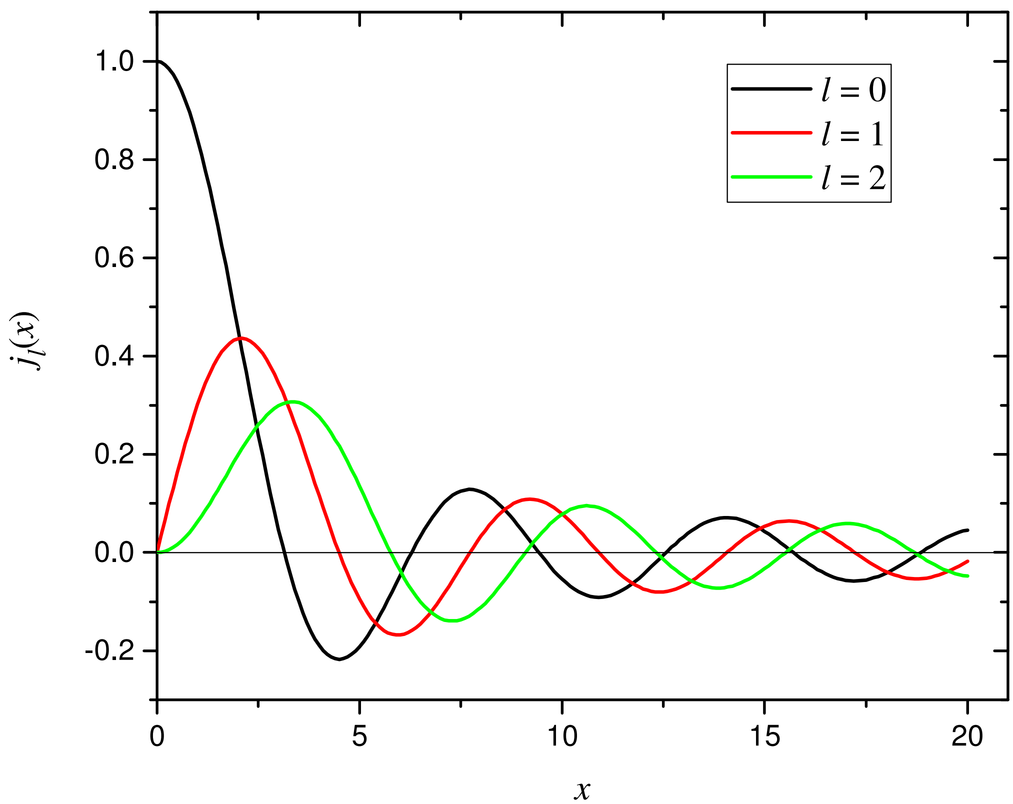
$$j_{l+1}(x) = \frac{2l+1}{x} j_l(x) - j_{l-1}(x). \tag{22.17}$$

This gives

$$\begin{aligned}
j_1(x) &= -j_0'(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}, \\
j_2(x) &= \frac{1}{x} j_1(x) - j_1'(x) = 3\frac{\sin x}{x^3} - 3\frac{\cos x}{x^2} - \frac{\sin x}{x}, \\
j_3(x) &= \frac{5}{x} j_2(x) - j_1(x) = 15\frac{\sin x}{x^4} - 15\frac{\cos x}{x^3} - 6\frac{\sin x}{x^2} + \frac{\cos x}{x},
\end{aligned} \tag{22.18}$$

etc.

The spherical Bessel functions of the first kind are shown below for $l = 0$, 1, and 2.



Because of their dependence on sin x and cos x, the spherical Bessel functions have multiple zeros. If β_{nl} is the n^{th} zero of $j_l(x)$, the energy eigenvalues are

$$E_{nl} = \frac{\hbar^2 \beta_{nl}{}^2}{2ma^2}. \tag{22.19}$$

We see that the energy levels depend on two quantum numbers n and l. The eigenfunctions

$$\psi_{nlm}(r,\theta,\phi) = A_{nl}\, j_l\left(\beta_{nl}\frac{r}{a}\right) Y_l^m(\theta,\phi) \tag{22.20}$$

depend on the magnetic quantum number m, and so the energy levels are degenerate. Since for given l, m can take the values $-l$, $-l+1$, …, $l-1$, l, we see that there are $2l+1$ states with the same energy.