January 16

Energy Spectrum: Potentials with Rotational Symmetry

Up to this point in the course, we have only studied the Schrödinger equation in one dimension. In this lecture, I will discuss the Schrödinger eigenvalue problem in two and three dimensions. We will see some new features of the spectrum of eigenfunctions. The three-dimensional problems are obviously relevant to the study of atoms in the real world.

Before we begin to consider specific problems, I should point out that the structural results concerning the eigenvectors and eigenvalues of the Schrödinger equation that we proved in one dimension are equally true in two and three dimensions, and, in fact, the proofs go through unchanged. Thus, it is true that

1. A time independent potential $V(\vec{x})$ leads to solutions of the Schrödinger equation that have definite frequency

$$\psi(\vec{x},t) = e^{-i\frac{E}{\hbar}t}\,\psi(\vec{x})$$

with $\psi(\vec{x})$ an eigenfunction of the time-independent Schrödinger problem

$$E\,\psi(\vec{x}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})\right]\psi(\vec{x})$$

2. Eigenvalues E of the Schrödinger problem are real: $E = E^*$.

3. Eigenfunctions of the Schrödinger problem with different eigenvalues are orthogonal. In d dimensions,

$$\int d^dx\; \psi_i^*(\vec{x})\,\psi_j(\vec{x}) = 0 \qquad i \neq j$$

4. If $V(\vec{x})$ is symmetric under reflections

$$V(\vec{x}) = V(-\vec{x})$$

the eigenfunctions of the Schrödinger problem are either even or odd under reflections

$$\psi_j(\vec{x}) = \pm \psi_j(-\vec{x})$$

The last of these results generalizes to describe the properties of eigenfunctions for problems in which $V(\vec{x})$ is invariant under a larger set of symmetries. An important case is that in which V is rotationally invariant

$$V(\vec{x}) = V(r) \qquad r = |\vec{x}|$$

In this lecture, we will study the case of rotationally invariant potentials in detail. In the process, we will gain some data that we can use to formulate the needed generalization.

Begin in two dimensions. Consider the Schrödinger equation for a rotationally invariant V. The time-independent Schrödinger equation is

$$E\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi$$

It will be helpful to write ∇^2 in cylindrical coordinates

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

Then the equation becomes

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

Notice that this equation has no explicit dependence on ϕ. Then we can find solutions of the equation using the same trick that we used to solve for the time-dependence of the solutions to the Schrödinger equation: We can look for solutions of definite frequency in ϕ,

$$\psi(r,\phi) = e^{im\phi}\psi(r)$$

Essentially, we Fourier transform the wavefunction $\psi(\vec{x})$ in ϕ. Then we can notice that the Schrödinger equation does not mix these Fourier modes; rather, each leads to its own eigenvalue problem.

The original wavefunction $\psi(\vec{x})$ has a definite value at each point in space. However, the point $\vec{x}$ is not represented by a unique set of (r,ϕ) coordinates. The coordinates

$$(r,\phi) \qquad\qquad (r,\phi+2\pi)$$

represent the same point. So, ψ must have the same value at these two coordinate points. This implies

$$e^{2\pi im} = 1 \qquad \text{or} \qquad m = \text{integer}$$

This integer is called m by universal convention. Please do not confuse it with the mass m of the Schrödinger particle.

The radial function $\psi(r)$ then obeys the equation

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

which is an eigenvalue problem in one variable. Note that this equation depends on m. I will refer to the jth eigenfunction for the equation with given integer m as $\psi_{jm}(r)$. We can call the corresponding eigenvalue E_{jm}. Then a general solution of the Schrödinger equation will have the form

$$\psi(\vec{x},t) = \sum_{jm} c_{jm}\,\psi_{jm}(r)\,e^{im\phi}\,e^{-i\frac{E_{jm}}{\hbar}t}$$

The form of the radial eigenvalue problem suggests an interpretation of the integer m. In classical mechanics, the Hamiltonian of a radially symmetric problem can be written

$$H = \frac{p_r^2}{2m} + V(r) + \frac{L^2}{2mr^2}$$

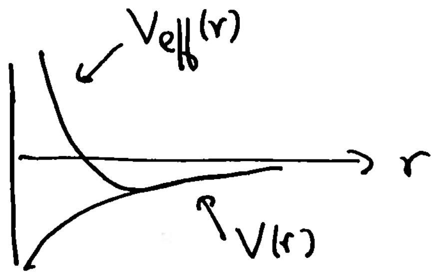
where p_r is the momentum conjugate to r and $\vec{L}$ is the angular momentum. The term

$$\frac{L^2}{2mr^2}$$

is called the *centrifugal potential barrier*. For an attractive potential, the typical form of

$$V_{eff}(r) = V(r) + \frac{L^2}{2mr^2}$$

is



A particle with nonzero angular momentum cannot travel all of the way in from large r to $r = 0$. When we convert from a problem in two dimensions to a problem for the radial coordinate $r(t)$, it is the centrifugal potential barrier that encodes the effect of angular momentum and keeps the particle away from $r = 0$. This strongly suggests that we should identify

$$L = \hbar m$$

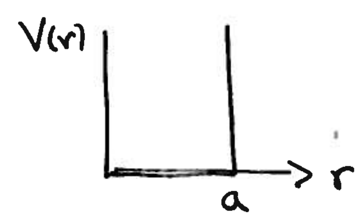
The identification makes sense, because the units of $\hbar$ are

$$\mathrm{kg}\,\mathrm{m}^2/\mathrm{sec}$$

which are exactly the units of angular momentum. I will prove this relation between L and m later in the course.

A relatively simple two-dimensional Schrödinger problem is that of the cylindrical infinite square well,

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



The eigenfunctions $\psi_{jm}(r)$ must be smooth functions of r that vanish at $r = a$. They obey the equation

$$E_{jm}\psi_{jm}(r) = \left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}\right)+\frac{\hbar^2 m^2}{2mr^2}\right)\psi_{jm}(r)$$

or

$$\left(\frac{d^2}{dr^2}+\frac{1}{r}\frac{d}{dr}+k_{jm}^2-\frac{m^2}{r^2}\right)\psi_{jm}(r)$$

where

$$k_{jm} = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$$

If we let $z = kr$, the equation becomes

$$\left[z^2\frac{d^2}{dz^2}+z\frac{d}{dz}+(z^2-m^2)\right]\psi_{jm}(z) = 0$$

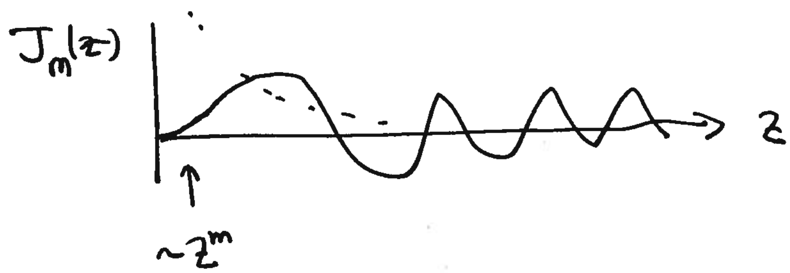
This is called *Bessel's equation.* Its solution are called *Bessel functions.* Bessel's equation arises in many contexts in mathematical physics, but this is the most characteristic application. Bessel's equation has two independent solutions, one of which is regular and the other singular at $z = 0$. These are called $J_m(z)$ and $Y_m(z)$, respectively:

$$J_m(z) \sim \left(\tfrac{1}{2}z\right)^m \quad \text{as } z \to 0$$

$$Y_m(z) \sim -\frac{1}{\pi}\left(\tfrac{1}{2}z\right)^{-m}$$

$$\left(Y_0(z) \sim \frac{2}{\pi}\log z\right) \quad \text{as } z \to 0$$

It is not difficult to guess what these functions look like. Bessel's equation becomes similar to the wave equation for large values of z. So, the Bessel functions start from the appropriate forms near $z = 0$, tunnel out of the angular momentum barrier, and then begin to oscillate



Bessel functions, like Hermite polynomials, are a type of function called *special functions*. When ordinary and partial differential equations began to be studied seriously in the nineteenth century, there were no computers, and so it was very important to work out the properties of the solutions of important differential equations by analytical methods. A mathematician would spend a decade completely characterizing the solutions of a given equation, working out Taylor series and asymptotic representations, integral representations, transformations of the solutions and, of course, tables of values. If the equation turned out to be an important one with many physical applications, the mathematician would thereby become immortal. Mathematicians and physicists who were interested in the solutions of problems involving particles and waves would need to have this information at their fingertips, and so they would spend many years becoming familiar with the detailed properties of the major classes of special functions.

Today, this kind of knowledge is more and more rare. Today, a physicist who wants to solve a differential equation can put it on a computer and easily find a graph or a set of numerical values. However, it is sometimes useful to have an analytic understanding of the solutions. Fortunately, some excellent references have been created where it is possible to look up the properties of the major special functions. Two web sites that are very useful for this purpose are:

- the NIST Digital Library of Mathematical Functions: dlmf.nist.gov/
- Wolfram MathWorld: mathworld.wolfram.com/

The NIST reference is also available in less technologically advanced form called a "book". The computer application Mathematica directly computes many special functions. For example, the Bessel function $J_m(z)$ is called in Mathematica as *BesselJ[m,z]*.

We have now almost completed the solution for the eigenfunctions of the cylindrical square well. All that remains is to satisfy the boundary condition $\psi_{jm}(r) = 0$ at

$r = a$. To do this, we adjust k so that the value $z = ka$ corresponds to a zero of the Bessel function. Let

$$z_{jm}$$

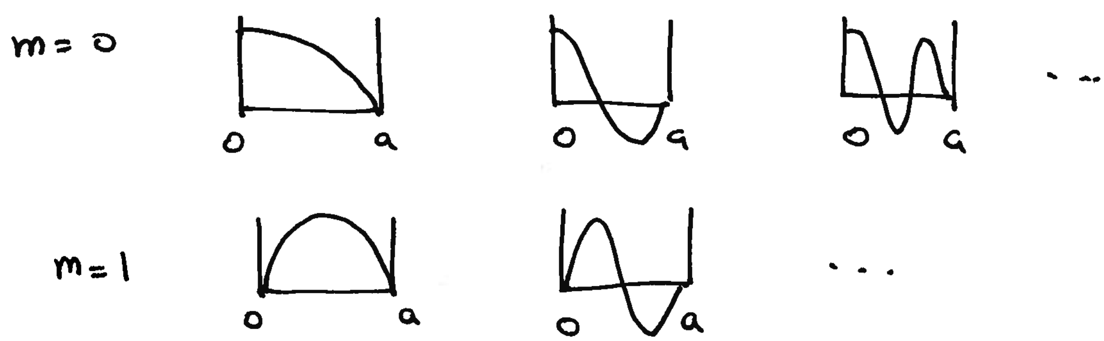
be the jth zero of $J_m(z)$. Then the most general eigenfunction has the form

$$\psi_{jm}(r,\phi) = N_{jm} \, e^{im\phi} \, J_m\!\left(z_{jm} \frac{r}{a} \right)$$

The corresponding energy is

$$E = \frac{\hbar^2 k_{jm}^2}{2m} = \frac{\hbar^2}{2ma^2} z_{jm}^2$$

Here are sketches of the radial part of the eigenfunctions:



The details of these solutions are developed further in the problem set.

The eigenfunctions we have found obey the orthogonality relation

$$\int d^2x \; \psi^*_{jm}(r,\phi) \, \psi_{j'm'}(r,\phi) = 0 \qquad j \neq j' \text{ or } m = m'$$

In cylindrical coordinates, this takes the form

$$\int_0^\infty dr\, r \int_0^{2\pi} d\phi \, \left(e^{-im\phi} J_m(z_{jm}\tfrac{r}{a})\right)\left(e^{im'\phi} J_{m'}(z_{j'm'}\tfrac{r}{a})\right)$$

Notice that this expression involves

$$\int_0^{2\pi} d\phi \quad e^{-i(m-m')\phi}$$

which integrates to zero when $m \neq m'$. Thus eigenfunctions with different m are automatically orthogonal. When $m = m'$, eigenfunctions built from different zeros of $J_m(z)$ obey the relation

$$\int_0^a dr\, r \quad J_m(z_{jm}\tfrac{r}{a})\, J_m(z_{j'm}\tfrac{r}{a}) = 0 \qquad j \neq j'$$

That is, the various functions

$$J_m(z_{jm}\tfrac{r}{a})$$

are orthogonal with respect to the measure

$$\int d\mu = \int_0^a dr\, r$$

This relation can be proved directly from Bessel's equation by a method similar to the one we used with the Hermite polynomials.

Now let's go on to three dimensions. Again, I will study potentials of the form

$$V(\vec{x}) = V(r)$$

We now need the Laplacian in spherical coordinates

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

The eigenvalue problem for a spherically symmetric potential is then

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

We can simplify this problem by looking for solutions of the form

$$\psi(r,\theta,\phi) = e^{im\phi}\,\psi_m(r,\theta)$$

as we did in two dimensions. It is less clear what to do about θ.

I propose that we treat the entire piece of ∇^2 involving angular derivatives as a special eigenvalue problem for eigenfunctions $\psi(\theta,\phi)$

$$\Lambda\,\psi(\theta,\phi) = \left(-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi)$$

For the moment, I will call the eigenvalues Λ. The corresponding eigenfunctions $\psi_\Lambda(\theta,\phi)$ play the same role on the sphere as the sine and cosine functions play on a one-dimensional interval—they provide a basic set of functions in which any other function can be expanded

$$f(\theta,\phi) = \sum_{\Lambda} c_\Lambda \psi_\Lambda(\theta,\phi)$$

A general function of (r, θ, ϕ) can then be represented as a sum of terms of the form

$$\psi_\Lambda(\theta,\phi) \cdot \psi(r)$$

Thus, we can then look for eigenfunctions of the complete Schrödinger problem of the form

$$\psi(r,\theta,\phi) = \psi_\Lambda(\theta,\phi) \cdot \psi_{j\Lambda}(r)$$

where $\psi_{j\Lambda}(r)$ solves the eigenvalue problem

$$E\,\psi_{j\Lambda}(r) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + V(r) + \frac{\hbar^2\Lambda}{2mr^2}\right)\psi_{j\Lambda}(r)$$

The second term in parentheses again can be interpretated as a centrifugal potential barrier for this three-dimensional problem. It is thus tempting to identify

$$L^2 = \hbar^2\Lambda$$

I will give a derivation of this connection later in the course.

The eigenfunctions $\psi_\Lambda(\theta, \phi)$ have the form

$$\psi_\Lambda(\theta,\phi) = e^{im\phi}\,\psi_{\Lambda m}(\theta)$$

Before studying the general case, I would like to spend some time on the important special case of cylindrically symmetric functions, that is, the case $m = 0$.

For $m = 0$, the eigenvalue problem for $\psi_{\Lambda m}(\theta)$ simplifies to

$$\Lambda\,\psi_{\Lambda m}(\theta) = -\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\,\psi_{\Lambda m}(\theta)$$

To solve this equation, let

$$z = \cos\theta$$

Then

$$\frac{d}{dz} = -\frac{1}{\sin\theta}\frac{d}{d\theta} \qquad \sin^2\theta = 1 - z^2$$

and the eigenvalue problem becomes

$$\Lambda\,\psi_{\Lambda 0}(z) = -\frac{d}{dz}(1-z^2)\frac{d}{dz}\,\psi_{\Lambda 0}(z)$$

where $\psi(z)$ a function on the interval $(-1,1)$. We can try to guess some solutions to this equation. Two easy cases are

$$\psi_{\Lambda 0}(z) = 1 \qquad \Lambda = 0$$

and

$$\psi_{\Lambda 0}(z) = z \qquad \Lambda = 2$$

This problem is thus similar to the problem of solving Hermite's equation. If we try a polynomial solution, the polynomial structure is preserved by the equation. So we can propose a solution of the form

$$\psi_{\Lambda 0}(z) = z^{\ell} + a z^{\ell-2} + \cdots$$

The equation is symmetric under $z \to -z$, so the eigenfunctions are alternatively even and odd. Plugging this into the equation and matching terms of order z^{ℓ}, we can compute the corresponding value of Λ. Then the terms of lower polynomial order can be solved for the coefficients a, b, ... The terms of order z^{ℓ} are

$$\Lambda z^{\ell} = (\ell+1) \cdot \ell \cdot z^{\ell}$$

so

$$\Lambda = \ell(\ell+1)$$

The next two polynomial solutions are then

$$\psi_{\Lambda 0}(z) = z^2 - \frac{1}{3} \qquad \psi_{\Lambda 0} = z^3 - \frac{3}{5} z$$

$$\Lambda = 6 \qquad \Lambda = 12$$

Note that

$$\int_{-1}^{1} dz \left(z^2 - \frac{1}{3}\right) = 0 \qquad \int_{-1}^{1} dz\, z \left(z^3 - \frac{3}{5}\right) = 0$$

This is not an accident. These polynomials are orthogonal on the interval $(-1, 1)$, as we will see below.

The equation

$$\left((z^2-1)\frac{d^2}{dz^2} + 2z\frac{d}{dz}\right) P_\ell(z) = \ell(\ell+1) P_\ell(z)$$

is called the *Legendre equation.* The polynomial solutions $P_\ell(z)$ are the *Legendre polynomials.* The standard convention for these polynomials chooses a different normalization from that given above.

You have already met the Legendre polynomials in another context. In electrostatics, a key problem is to solve Laplace's equation

$$-\nabla^2 \phi = 0$$

to find the potential $\varphi(\vec{x})$ due to a point charge located at $\vec{y}$. The solution is of course

$$\phi(\vec{x}) = \frac{1}{|\vec{x}-\vec{y}|} = \frac{1}{\left[x^2+y^2-2xy\cos\theta\right]^{\frac{1}{2}}}$$

For $|\vec{y}| \ll |\vec{x}|$, we can expand in $y = |\vec{y}|$, and we find

$$\phi(\vec{x}) = \frac{1}{x} + \frac{y\cos\theta}{x^2} + \frac{y^2\left(\frac{3}{2}\cos^2\theta - 1\right)}{x^3} + \cdots$$

The standard way to write this expansion is

$$\frac{1}{|\vec{x}-\vec{y}|} = \sum_{\ell=0}^{\infty} \frac{y^\ell}{x^{\ell+1}} P_\ell(\cos\theta)$$

The Legendre polynomials appear because we analyze the Laplace operator in spherical coordinates as above. Each term is a solution to

$$\nabla^2\phi = 0 \quad \text{or} \quad \left(\frac{1}{x^2}\frac{\partial}{\partial x} x^2 \frac{\partial}{\partial x} + \frac{1}{x^2 \sin\theta}\frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}\right)\phi = 0$$

For the term with $P_\ell(\cos\theta)$, you can check that

$$\left[\left(\frac{1}{x^2}\frac{\partial}{\partial x} x^2 \frac{\partial}{\partial x}\right) - \frac{\ell(\ell+1)}{x^2}\right]\frac{1}{x^{\ell+1}} = 0$$

This expansion gives the standard normalization of $P_\ell(z)$. The first few Legendre polynomials are

$$P_0(z) = 1 \qquad P_1(z) = z$$

$$P_2(z) = \frac{1}{2}(3z^2-1) \qquad P_3(z) = \frac{1}{2}(5z^3 - 3z)$$

Setting $x = 1$, $\cos\theta = z$ in the above expansion, we have

$$\frac{1}{[1+y^2-2y\cos\theta]^{1/2}} = \sum_{\ell=0}^{\infty} y^\ell P_\ell(\cos\theta)$$

This function $T(z, y)$ is a *generating function* for the Legendre polynomials.

$$T(z,y) = \frac{1}{[1+y^2-2yz]^{1/2}} = \sum_{\ell=0}^{\infty} y^\ell P_\ell(z)$$

Though it is not very obvious, you can show by working out sufficiently many cases that the expansion of $T(z,y)$ gives the following explicit expression for the Legendre polynomials:

$$P_\ell(z) = \sum_{\substack{r\geq 0 \\ \ell-2r\geq 0}} (-1)^r \frac{(2\ell-2r)!}{2^\ell\, r!\,(\ell-r)!\,(\ell-2r)!}\, z^{\ell-2r}$$

This series expansion is also the series expansion of the expression

$$P_\ell(z) = \frac{1}{2^\ell\,\ell!}\frac{d^\ell}{dz^\ell}(z^2-1)^\ell$$

which is called *Rodrigues' formula* for the Legendre polynomials. A nicer derivation of the Rodrigues' formula—which, however, requires some complex variable theory—can be found in Setion 15.1 of the classic (1902) textbook on special functions, *A Course of Modern Analysis*, by Whittaker and Watson.

Rodrigues' formula is a very useful starting point for the derivation of many properties of the Legendre polynomials. One of these is their orthogonality relation. The solutions of the three-dimensional Schrödinger equation from which we started obey orthogonality

$$\int d^3x\; \psi_j^*(\vec{x})\,\psi_{j'}(\vec{x}) = 0 \qquad j\neq j'$$

by our general proof. If we write the eigenfunctions as products of functions of r, θ and ϕ, as we did above, this relation becomes

$$\left(\int_0^\infty dr\, r^2 \;\psi^*_{j\Lambda}(r)\,\psi_{j'\Lambda'}(r)\right)\left(\int_0^\pi d\theta \sin\theta \;\psi^*_{\Lambda m}(\theta)\,\psi_{\Lambda' m'}(\theta)\right)\cdot\left(\int_0^{2\pi} d\phi\, e^{-im\phi} e^{im'\phi}\right)$$
$$= 0 \quad (j\Lambda m \neq j'\Lambda' m')$$

We might expect that each factor reflects an orthogonality relation in its subspace. We already saw that

$$\int_0^{2\pi} d\phi \quad e^{-im\phi}\, e^{im'\phi} = 0 \quad \text{for} \quad m \neq m'$$

For the θ eigenfunctions, we would expect the relation

$$\int_0^\pi d\theta \sin\theta \quad \psi^*_{\Lambda m}(\theta)\,\psi_{\Lambda' m'}(\theta) = 0 \quad \text{for} \quad m = m' \text{ but } \Lambda \neq \Lambda'$$

or, setting $z = \cos\theta$,

$$\int_{-1}^{1} dz \quad \psi^*_{\Lambda m}(z)\,\psi_{\Lambda' m}(z) = 0 \quad \text{for} \quad \Lambda \neq \Lambda'$$

For $m = 0$, this relation reads

$$\int_{-1}^{1} dz \quad P_\ell(z)\, P_{\ell'}(z) = 0 \quad \text{for} \quad \ell \neq \ell'$$

I will prove this relation directly from the Rodrigues formula.

Begin with the integral

$$\int_{-1}^{1} dz \left(\frac{d^\ell}{dz^\ell}(z^2-1)^\ell \right) \left(\frac{d^{\ell'}}{dz^{\ell'}}(z^2-1)^{\ell'} \right)$$

Consider the case $\ell > \ell'$. Integrate by parts from left to right. The surface terms vanish; the function

$$\frac{d^m}{dz^m}(z^2-1)^\ell$$

vanishes at $z = \pm 1$ for $m < \ell$, since $(z^2-1)^\ell$ has ℓ zeros at each endpoint, and differentiation removes only m of them. Finally, we find

$$\int_{-1}^{1} dz \ (-1)^\ell \ (z^2-1)^\ell \ \frac{d^{\ell+\ell'}}{dz^{\ell+\ell'}}(z^2-1)^{\ell'}$$

but

$$\frac{d^{\ell+\ell'}}{dz^{\ell+\ell'}}(z^2-1)^{\ell'} = 0 \qquad \text{for } \ell > \ell'$$

since $\ell + \ell' > 2\ell$. The case $\ell = \ell'$ gives the normalization of the Legendre polynomials. The same integration by parts procedure gives

$$\int_{-1}^{1} dz \left(\frac{d^\ell}{dz^\ell}(z^2-1)^\ell \right) \left(\frac{d^\ell}{dz^\ell}(z^2-1)^\ell \right) = \int_{-1}^{1} dz \ (1-z^2)^\ell \cdot (2\ell)!$$

Using the (somewhat nontrivial) integral

$$\int_{-1}^{1} dz\,(1-z^2)^{\ell} = 2\,\frac{(\ell!)^2}{(2\ell+1)!}$$

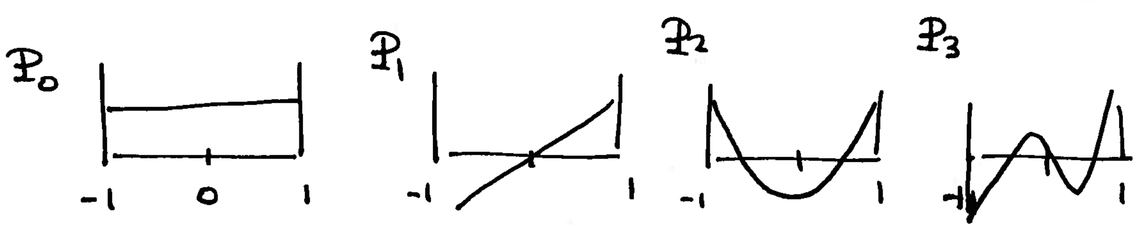
we find

$$\int_{-1}^{1} dz\, P_\ell^2(z) = \frac{2}{2\ell+1}$$

Combining these results,

$$\int_{-1}^{1} dz\, P_\ell(z)\, P_{\ell'}(z) = \delta_{\ell\ell'}\,\frac{2}{2\ell+1}$$

The first four Legendre polynomials have the form



With this knowledge in hand, we can go back to the general case $m \neq 0$. The generalization of the Legendre equation is

$$\left(-\frac{d}{dz}(1-z^2)\frac{d}{dz} + \frac{m^2}{1-z^2}\right) P_\ell^m(z) = \Lambda\, P_\ell^m(z)$$

Some regular solutions of this equation for $m = 1$ are

$$(1-z^2)^{1/2} \qquad \Lambda = 2$$

$$z(1-z^2)^{1/2} \qquad \Lambda = 6$$

and for $m = 2$,

$$(1-z^2) \qquad \Lambda = 6$$

These solutions are called *associated Legendre functions.* The general formula for these functions, for $m > 0$, is

$$P_\ell^m(z) = (1-z^2)^{m/2} \frac{d^m}{dz^m} P_\ell(z)$$

The solutions for $(-m)$ obey the same equation as the solutions for m, so, by convention, we set

$$P_\ell^{-m}(z) = P_\ell^m(z)$$

The corresponding eigenvalues take the form

$$\Lambda = \ell(\ell+1)$$

just as for $P_\ell(z)$.

The complete eigenfunctions of the (θ, ϕ) problem are called the *spherical harmonics*, notated $Y_{\ell m}(\theta, \phi)$. These have the form

$$Y_{\ell m}(\theta,\phi) = N_{\ell m} \cdot e^{im\phi} \cdot P_\ell^m(\cos\theta)$$

They obey the eigenvalue equation

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

By convention, the $Y_{\ell m}$ are normalized to

$$\int d\Omega\, |Y_{\ell m}|^2 = \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, |Y_{\ell m}|^2 = 1$$

The first few spherical harmonics are: for $\ell = 0$,

$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

for $\ell = 1$,

$$Y_{1-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{-i\phi} \qquad Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \qquad Y_{11} = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\phi}$$

for $\ell = 2$,

$$Y_{2-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{-2i\phi} \qquad Y_{2-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{-i\phi}$$

$$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_{21} = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{i\phi} \qquad Y_{22} = +\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{2i\phi}$$

The spherical harmonics obey the orthogonality relation

$$\int d\Omega \; Y^{*}_{\ell m}(\theta,\phi) \, Y_{\ell' m'}(\theta,\phi) = \delta_{\ell\ell'} \delta_{mm'}$$

These can be shown to be a complete set of indepedent functions on the sphere. Then any function of (θ, ϕ) can be written in the form

$$f(\theta,\phi) = \sum_{\ell m} c_{\ell m} \, Y_{\ell m}(\theta,\phi)$$

where, as with Fourier series, the function on the left is approximated to arbitrary accuracy as more terms are included. The orthogonality relation gives the formula for the coefficient functions

$$c_{\ell m} = \int d\Omega \; Y^{*}_{\ell m}(\theta,\phi) \, f(\theta,\phi)$$

Notice that, for each discrete value of the eigenvalue Λ, that is, for each value of ℓ, there are $(2\ell + 1)$ independent spherical harmonics.

We can summarize this discussion as follows: Each eigenfunction of the Schrödinger equation for a rotationally symmetric potential in three dimensions can be written in the form

$$\psi(\vec{x}) = \psi_{j\ell}(r) \cdot Y_{\ell m}(\theta,\phi)$$

where $\psi_{j\ell}(r)$ is an eigenfunction of the equation

$$E\,\psi_{j\ell}(r) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + V(r) + \frac{\hbar^2\,\ell(\ell+1)}{2mr^2}\right)\psi_{j\ell}(r)$$

We will study solutions of this equation in the next lecture.