Angular motion in two-component systems

Notes on Quantum Mechanics

http://quantum.bu.edu/notes/QuantumMechanics/AngularMotionInTwoComponentSystems.pdf
Last updated Thursday, December 1, 2005 11:47:29-05:00

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The analysis of harmonic motion atoms in a diatomic molecule is an example of analyzing a two-component quantum system separately in terms of the relative motion of its parts and the motion of the system as a whole through space. We do this by transforming from coordinates centered in the laboratory to the coordinates (1) of the center of mass and (2) of each part of the system relative to the center of mass. In this way the motion of the system as a whole can be treated as (1) that of a mass equal to the total mass of the system moving freely through space and as (2) that of a mass equal to the reduce mass of the system moving with respect to a fixed center of mass in a potential energy that depends only on the internal, center of mass coordinates.

For example, if the system consists of the two atoms, A and B, of a diatomic molecule, then the free motion of the molecule through space is that of a mass $m_A + m_B$, and the internal, relative motion of the two atoms is that of a mass $\mu = m_A\, m_B / (m_A + m_B)$ in the inter-atom potential energy $V(r)$, where r is the atom-atom separation. Another example is a one-electron atom, consisting of an electron and a nucleus; the free motion of the atom through space is that of a combined mass of the electron and the nucleus, $m_e + m_N$, and the internal, relative motion of the electron and nucleus is that of mass $\mu = m_e\, m_N / (m_e + m_N)$ in the potential energy $V(r)$, where now r is the electron-nuclear separation.

In each of these examples, the potential energy depends only on the separation of the, r, of the two components of the system. Such a potential energy is call a *central potential*. Since the potential energy does not depend on the orientation of the system as a whole in space, it turns out that we can treat separately the internal motion in the r coordinate from the internal motion in the θ and ϕ coordinates. Further, while the wavefunction in the r coordinate depends on the details of the potential energy $V(r)$, the wavefunction in the θ and ϕ coordinates is independent of the potential energy $V(r)$. This means the wavefunctions in the θ and ϕ coordinates are *the same for any two component quantum system.*

Here we will fill in the details to learn about these angular wavefunctions.

■ Schrödinger equation for two-component systems

The Schrödinger equation for the internal, relative motion of a two-component quantum system is

$$\left\{ -\frac{\hbar^2}{2\,\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} \right) + V(r) \right\} \psi_{a\,b\,c}(x, y, z) = E_{a\,b\,c}\, \psi_{a\,b\,c}(x, y, z).$$

The mass of the "particle," μ, is the reduced mass of the internal motion of a system, as a result of transformation to center of mass coordinates. The particle is confined by a potential energy, $V(r)$, that depends only on the distance, r, from the center of mass. The kinetic energy has contributions from the motion of the particle along x, y, and z. The subscripts a, b and c, label the number of loops in the three cartesian coordinates.

Now, since the potential energy depends only on the distance, $r = \sqrt{x^2 + y^2 + z^2}$, from the coordinate center, cartesian coordinates, x, y and z, are not the most convenient way to express the kinetic energy. Rather, it is more natural to express the kinetic energy in terms of spherical polar

coordinates, r, θ, and ϕ, since in this way the potential energy will only influence the motion of the particle along the single coordinate r; the motion in θ and ϕ takes place at *constant* distance, r, from the coordinate center, and takes place at *constant* potential energy. This means that we can analyze the radial and angular motion using two *separate* Schrödinger equations, and so express the overall wavefunction as the *product* of the corresponding angular and radial wavefunctions.

■ Spherical polar coordinates: r, θ and ϕ

Let's first review the relation between spherical polar coordinates and cartesian coordinates.

Here is how to determine the spherical polar coordinates of a point. The first coordinate, r, is the distance of the point from the origin. The second coordinate, θ, is the angle between the positive z axis and the line from the origin to the point; θ is in the range 0 to π. The third coordinate, ϕ, is the angle between the positive x axis and the line from the origin to the location in the xy plane intercepted by the line perpendicular to the xy plane and passing through the point; ϕ is in the range 0 to 2π.

Using trigonometry and the three-dimensional Pythagorean theorem, it is not too hard to get the following expressions for the spherical polar coordinates in terms of the Cartesian coordinates.

$$r = \sqrt{x^2 + y^2 + z^2},$$

$$\theta = \text{ArcCos}(z/r), \text{ and}$$

$$\phi = \text{ArcTan}(y/x).$$

Here are some example points expressed in both Cartesian and spherical polar coordinates.

> What values of the spherical polar coordinate correspond to the xy plane? Answer: $\theta = \pi/2$ and all values of r and ϕ.

> What values of the spherical polar coordinates correspond to the yz plane? Answer: The positive y part of the yz plane corresponds to $\phi = \pi/2$ and all values of r and θ; the negative y part of the yz plane corresponds to $\phi = -\pi/2$ and all values of r and θ.

> What values of the spherical polar coordinates correspond to the zx plane? Answer: The positive x part of the zx plane corresponds to $\phi = 0$ and all values of r and θ; the negative x part of the zx plane corresponds to $\phi = \pi$ and all values of r and θ.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, 1, 1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(1/\sqrt{3}\right)$ and $\phi = \pi/4$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, 0, 0)$? Answer: $r = 1$, $\theta = \pi/2$ and $\phi = 0$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (0, -1, 0)$? Answer: $r = 1$, $\theta = \pi/2$ and $\phi = -\pi/2$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (0, -1, -1)$? Answer: $r = \sqrt{2}$, $\theta = 3\pi/4$ and $\phi = -\pi/2$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (-1, 1, -1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(-1/\sqrt{3}\right)$ and $\phi = 3\pi/4$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, 1, -1)$?
> Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(-1/\sqrt{3}\right)$ and $\phi = \pi/4$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, -1, 1)$?
> Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(1/\sqrt{3}\right)$ and $\phi = -\pi/4$.

> What values of the spherical polar coordinates correspond to the $(x, y, z) = (-1, -1, -1)$?
> Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(-1/\sqrt{3}\right)$ and $\phi = 5\pi/4$.

■ Transformation to spherical polar coordinates

The details of transforming the kinetic energy operator from cartesian coordinates to spherical polar coordinates are a little complicated, but the result is the Schrödinger equation

$$\left\{-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2\right) + V(r)\right\}\psi_{k\ell m}(r, \theta, \phi) = E_{k\ell m}\psi_{k\ell m}(r, \theta, \phi).$$

Here the angular part of the kinetic energy is expressed through the operator

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta},$$

and we use different subscripts, k, ℓ and m, to label the number of loops in the three spherical polar coordinates.

This operator Λ^2, known as the *Legendrian*, determines the contribution to the kinetic energy of motion at constant distance from the coordinate center. Because in this form of the Schrödinger equation the potential energy affects motion in only the radial coordinate, the wavefunction can be written as a product

$$\psi_{k\ell m}(r, \theta, \phi) = R_{k\ell}(r)\, Y_{\ell m}(\theta, \phi)$$

of two probability amplitudes. The amplitude $R_{k\ell}(r)$ is called the radial wavefunction, since depends only on the distance from the center of mass; the amplitude $Y_{\ell m}(\theta, \phi)$ is called the angular wavefunction, or *spherical harmonic*, and it depends only on the coordinates θ and ϕ.

Two quantum numbers, one for each coordinate, are needed to specify the spherical harmonic. (We'll see in a moment why *two* labels, k and ℓ, are also need on the radial wavefunction, even though it pertains to only a *one* coordinate.) The quantum number for motion in θ is called ℓ; it can have the values 0, 1, 2, …; the quantum number for motion in ϕ is called m_ℓ; it can have the values $-\ell,\ -\ell+1,\ \ldots,\ \ell-1,\ \ell$. The effect of the operator Λ^2 on spherical harmonics is very simple,

$$\Lambda^2\, Y_{\ell m}(\theta, \phi) = -\ell(\ell+1)\, Y_{\ell m}(\theta, \phi).$$

Using this relation, we can rewrite the Schrödinger equation as

$$\left\{-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\ell(\ell+1)}{r^2}\right) + V(r)\right\}R_{k\ell}(r)\, Y_{\ell m}(\theta, \phi) = E_{k\ell m}\, R_{k\ell}(r)\, Y_{\ell m}(\theta, \phi)$$

In this equation the spherical harmonic appears as a common multiplicative factor (since the differentiations in the Legendrian have been carried out) on both sides and so we can cancel it out altogether! The Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2\mu}\,\frac{1}{r}\,\frac{\partial^2}{\partial r^2}\,r + V_{\text{eff},\ell}(r)\right) R_{k\ell}(r) = E\,R_{k\ell}(r)$$

in terms of an *effective potential energy function*

$$V_{\text{eff},\ell}(r) = \frac{\hbar^2\,\ell\,(\ell+1)}{2\,\mu\,r^2} + V(r).$$

This potential energy expression contains, in addition to the contribution from radial potential energy, $V(r)$, a repulsive term due to the angular motion of the particle. The repulsive contribution is different for different values of the quantum number ℓ. This means that radial wavefunctions with a given number of loops will be different for different values of ℓ. It is for this reason that the radial wavefunctions are labeled by both the radial loop index, k, and the θ loop index ℓ. In this context, k is a quantum number but ℓ is instead a *parameter* characterizing the repulsive component of the effective potential energy due to angular motion. In this way we see that the radial wavefunction properly is labeled by just one quantum number.

To analyze radial motion further, we must specify the radial potential energy, $V(r)$. Let's defer this for now, and instead turn our attention to learning about angular motion and its wavefunctions, $Y_{\ell m}(\theta, \phi)$.

■ Schrödinger equation for motion on the surface of a sphere

A way to do this is to assume that the particle is first confined to move just in θ and ϕ, that is on the surface of a sphere or radius r_0. For example, we can imagine a potential energy function, $V(r)$, that has value 0 at $r = r_0$ and value ∞ otherwise. The consequence is that the radial wavefunction then must be zero except on the surface of the sphere, that is, except when $r = r_0$, for otherwise it would diverge to infinity in the infinite potential present when $r \neq r_0$. The net effect is that angular motion then takes place at the single, fixed value $r = r_0$, and so the Schrödinger equation

$$\left\{-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\,\frac{\partial^2}{\partial r^2}\,r + \frac{1}{r^2}\,\Lambda^2\right) + V(r)\right\} R_{k\ell}(r)\,Y_{\ell m}(\theta, \phi) = E_{k\ell m}\,R_{k\ell}(r)\,Y_{\ell m}(\theta, \phi)$$

becomes

$$-\frac{\hbar^2}{2\mu}\,\frac{1}{{r_0}^2}\,\Lambda^2\,Y_{\ell m}(\theta, \phi) = E_{\ell m}\,Y_{\ell m}(\theta, \phi).$$

Using the equation for the effect of the Legendrian on the spherical harmonic, we can rewrite the equation as

$$\frac{\hbar^2\,\ell\,(\ell+1)}{2\,\mu\,{r_0}^2}\,Y_{\ell m}(\theta, \phi) = E_{\ell m}\,Y_{\ell m}(\theta, \phi).$$

and so determine the energies of a particle confined to the surface of a sphere of radius r_0 are

$$E_{\ell m} = \frac{\hbar^2\,\ell\,(\ell+1)}{2\,\mu\,{r_0}^2}.$$

■ Angular kinetic energy

In classical physics, angular kinetic energy is given by

$$\frac{1}{2} I \omega^2 = \frac{J^2}{2 I}$$

in terms of the moment of inertia, $I = m r^2$, and the angular velocity, ω.

Moment of inertia and angular velocity are the angular equivalents of mass and velocity that appear in the expressions $m v^2 / 2 = p^2 / 2 m$ for translation kinetic energy. I find that this correspondence between the formulas for angular and translational kinetic energy helps me to remember them.

Comparing the expression for angular kinetic energy to the repulsive term in the effective potential energy, we can identify the quantal angular momentum to be

$$J \to \hbar \sqrt{\ell(\ell + 1)}$$

This correspondence is the reason ℓ is called the orbital momentum quantum number.

A key result of the Bohr model was the angular momentum of the electron is quantized in integer multiples of $\hbar$. Here, in the Schrödinger treatment, the angular momentum is still quantized, but the multiple is no longer integer, since $\sqrt{\ell(\ell + 1)}$ is somewhat larger than ℓ. This indicates that the picture of angular momentum in the Bohr model is not complete.

> Use the relation between classical and quantal angular momentum to derive an expression for the angular velocity, ω, of an electron in a one electron atom as a function of the nuclear charge, Z, orbital momentum quantum number, ℓ, and Bohr model quantum number, n. Use your expression to show that an electron with $\ell = 1$ in a hydrogen atom has an angular velocity of about 6×10^{16} radians per second for $n = 1$ and about 6 radians per second for $n = 10^4$. The average value of r of an electron in a one-electron atom is $n^2 a_0 / Z$.

> What is the angular velocity of an electron with $\ell = 0$ in a one-electron atom? How do you interpret your answer?

■ Motion confined to a ring

Using the explicit expression for the Legendrian, the Schrödinger equation for motion on the surface of a sphere is

$$-\frac{\hbar^2}{2\mu} \frac{1}{r_0^2} \left(\frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} \right) Y_{\ell m}(\theta, \phi) = E_{\ell m} Y_{\ell m}(\theta, \phi).$$

We can simplify things further by confining the particle to move only on a great circle of the sphere. We can again do that by adjusting the potential energy so that it is infinite for positions off the great circle. Let's specify the great circle along the equator, and so that $\theta = \pi / 2$. (Strictly, to do this we must make the potential energy dependent on both r and θ, with infinite value except for $r = r_0$ and $\theta = \pi / 2$.) The result is the Schrödinger equation for motion on a ring in the xy plane,

$$-\frac{\hbar^2}{2 \mu r_0^2} \frac{d^2}{d \phi^2} \Phi_m(\phi) = E_m \Phi_m(\phi).$$

> Carry out the steps leading to this equation form the Schrödinger equation for motion on the surface of a sphere.

In this equation we have introduced a new wavefunction, $\Phi_m(\phi)$, for motion in the ϕ coordinate.

A way to determine what the explicit form of the wavefunctions, $\Phi_m(\phi)$, is to note that when they are differentiated twice, the result is proportional to $-\Phi_m(\phi)$. This means the wavefunctions are proportional to $e^{i a \phi}$, $\sin(a\,\phi)$, or $\cos(a\,\phi)$, where m is a constant to be determined. Let's assume the complex exponential form, $\Phi_m(\phi) = N\, e^{i m \phi}$, where N is a normalization constant. Substituting this into the Schrödinger equation, we get

$$-\frac{\hbar^2}{2\,\mu\,{r_0}^2}\,\frac{d^2}{d\phi^2}\,N\,e^{i m \phi} = -\frac{\hbar^2}{2\,\mu\,{r_0}^2}\,(i\,m)^2\,N\,e^{i m \phi}$$
$$= \frac{\hbar^2\,m^2}{2\,\mu\,{r_0}^2}\,N\,e^{i m \phi} = E_m\,N\,e^{i m \phi}$$

From the last equality, we see that

$$E_m = \frac{\hbar^2\,m^2}{2\,\mu\,{r_0}^2}.$$

To proceed further, we need to determine the possible values of m. The way to do this is to use the fact that $\Phi_m(\phi = 0) = \Phi_m(\phi = 2\,\pi)$ to obtain the equality

$$e^0 = 1 = e^{i m 2 \pi} = \cos(m\,2\,\pi) + i \sin(m\,2\,\pi).$$

The most general solution to this equality is that m is an integer or 0, $m = 0, \pm 1, \pm 2, \ldots$, since then $\sin(m\,2\,\pi) = 0$ and $\cos(m\,2\,\pi) = 1$.

With the possible values of m determined, we can finally evaluate the normalization constant. The total probability evaluates to

$$\int_0^{2\pi} \Phi_m(\phi)^*\,\Phi_m(\phi)\,d\phi = N^2 \int_0^{2\pi} e^{-i m \phi}\,e^{i m \phi}\,d\phi = N^2 \int_0^{2\pi} e^0\,d\phi = N^2\,2\,\pi.$$

Since this must be equal to 1, we see that $N = 1\,/\,\sqrt{2\,\pi}$, and so that the normalized wavefunction of a particle on a ring is

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\,\pi}}\,e^{i m \phi},\ m = 0, \pm 1, \pm 2, \ldots$$

> Show that the operator for the component of angular momentum perpendicular the a ring is $L_z = -i\,\hbar\,d/d\phi$. Hint: Show that the particle on a ring wavefunction, $\Phi_m(\phi) = 1/\sqrt{2\,\pi}\;e^{i\,m\,\phi}$ is an eigenfunction of the operator, with eigenvalue $m\,\hbar$.

> Show that the operator for the kinetic energy on the right is $L_z^2/2\,I = -\hbar^2/(2\,\mu\,r_0^2)\,d^2/d\phi^2$.

> Show that the probability density of the ring wavefunction $\Phi_m(\phi)$ is constant, and so there is complete delocalization in ϕ. This is a consequence of the angular momentum about the z axis having the precise value $m\,\hbar$.

> Show that
>
> $\Phi_{c,|m|}(\phi) = 1/\sqrt{2}\;\{\Phi_{|m|}(\phi) + \Phi_{-|m|}(\phi)\} = 1/\sqrt{\pi}\;\cos(m\,\phi)$
>
> is an eigenfunction of the angular kinetic energy operator, $-\hbar/(2\,I)\,d^2/d\phi^2$ but that it does *not* have a well defined angular momentum component perpendicular to the ring.

> Show that the probability density of the ring wavefunction $\Phi_{c,|m|}(\phi)$ is *not* constant, but instead localized along $\pm x$. This is a consequence of the angular momentum about the z axis *not* having a precise value, but rather equal contributions of $\pm m\,\hbar$.

> Show that $\Phi_m(\phi, t) = 1/\sqrt{2\,\pi}\;e^{i\,m\,\phi}\,e^{-i\,E_m\,t/\hbar}$ corresponds to a particle "moving" counter clockwise when $m > 0$ and clockwise when $m < 0$. Use this result to explain why $\Phi_{c,|m|}(\phi)$ does not have a well defined angular momentum component perpendicular to the ring.

Motion around a ring

We can localize a particle on a ring and so follow its motion by constructing a wavepacket. The time factors of each wavepacket component are

$$e^{-i\,E\,t/\hbar} = e^{-i\,m^2\,\nu\,t},$$

in terms of the characteristic frequency

$$\nu = \frac{\hbar}{2\,\mu\,r^2}.$$

> Show that these two expression are correct.

If we express time as $t = \tau\,t_0$, in terms of dimensionless multiples, τ, of the reciprocal of the characteristic frequency,

$$t_0 = 1/\nu = 1\Big/\frac{\hbar}{2\,\mu\,r^2},$$

then the time factor becomes

$$e^{-i\,m^2\,\nu\,t} = e^{-i\,m^2\,\tau}.$$

> Show that this result is correct.

As example, for $^1H^{35}Cl$, the characteristic frequency is

$$\frac{1.99564\times 10^{12}}{\text{Second}}$$

and so the unit of time is

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5.01092 × 10^-13 Second
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> Use the reduced mass of $^1H^{35}Cl$ and the its internuclear distance, 127.45 pm, to confirm these results.

In terms of the dimensionless unit of time, τ, we can write a general wavepacket for a particle on a ring as

$$\Phi(\phi, \tau) = \frac{1}{\sqrt{\sum_m g_m{}^2}} \sum_m g_m \Phi_m(\phi)\, e^{-i\, m^2\, \tau}.$$

A simple example is a two component wavepacket consisting of equal contributions of $m = 1$ and $m = 2$,

$$\Phi(\phi, \tau) = \frac{1}{\sqrt{2}} (\Phi_1(\phi)\, e^{-i\,\tau} + \Phi_2(\phi)\, e^{-i\,4\,\tau}) = \frac{1}{2\sqrt{\pi}} (e^{i\,\phi}\, e^{-i\,\tau} + e^{i\,4\,\phi}\, e^{-i\,4\,\tau})$$

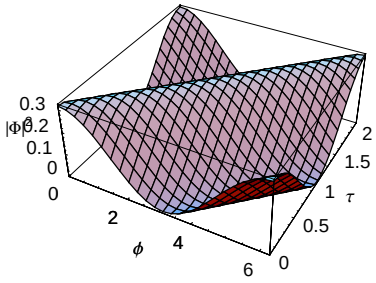
> Show that this wavepacket is normalized to 1, independently of the value of τ.

The probability density evaluates to

$$\Phi(\phi, \tau)^* \Phi(\phi, \tau) = \frac{1}{\pi} \cos[(3\,\tau - \phi)/2]^2.$$

> Verify this result.

The period of the time variation of the probability density is determined from $3\,\tau/2 = \pi$ (π rather the $2\,\pi$ since the density is given by the square of the cosine), and so is $4\,\pi/3 = 2.09$ units of dimensionless time τ. The wavelength of the ϕ variation is determined from $\phi/2 = \pi$, and so is π units of ϕ. Here is a plot of the wavepacket from one cycle of time variation.



Particle on a ring wavepacket probability density, composed of equal contributions of $m = 1$ and $m = 2$. Time is in dimensionless units of $\hbar/(2\,\mu\,r^2)$.

The figure shows that the point of maximum localization starts at $\phi = 0$ and returns there in dimensionless time $\tau = 2\,\pi/3$.

To make a more highly localized packet, we would need to combine ring wavefunctions with more different values of m.

Here is the expression for the probability amplitude at $\phi = 0$ or a packet composed of five values $m = 8 – 12$.

```
0.01 (Cos[64. τ]^2 + 20. Cos[81. τ]^2 + 55. Cos[100. τ]^2 + 66. Cos[100. τ] Cos[120. τ] +
   20. Cos[120. τ]^2 + 15. Cos[100. τ] Cos[140. τ] + 9. Cos[120. τ] Cos[140. τ] +
   Cos[140. τ]^2 + 9. Cos[81. τ] (7.4 Cos[100. τ] + 4.5 Cos[120. τ] + Cos[140. τ]) +
   2. Cos[64. τ] (4.5 Cos[81. τ] + 7.4 Cos[100. τ] + 4.5 Cos[120. τ] + Cos[140. τ]) +
   Sin[64. τ]^2 + 9. Sin[64. τ] Sin[81. τ] + 20. Sin[81. τ]^2 + 15. Sin[64. τ] Sin[100. τ] +
   66. Sin[81. τ] Sin[100. τ] + 55. Sin[100. τ]^2 + 9. Sin[64. τ] Sin[120. τ] +
   40. Sin[81. τ] Sin[120. τ] + 66. Sin[100. τ] Sin[120. τ] +
   20. Sin[120. τ]^2 + 2. Sin[64. τ] Sin[140. τ] + 9. Sin[81. τ] Sin[140. τ] +
   15. Sin[100. τ] Sin[140. τ] + 9. Sin[120. τ] Sin[140. τ] + Sin[140. τ]^2)
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The packet was constructed with the following relative weights of the different *m* values.

```
{0.101656, 0.455589, 0.751139, 0.455589, 0.101656}
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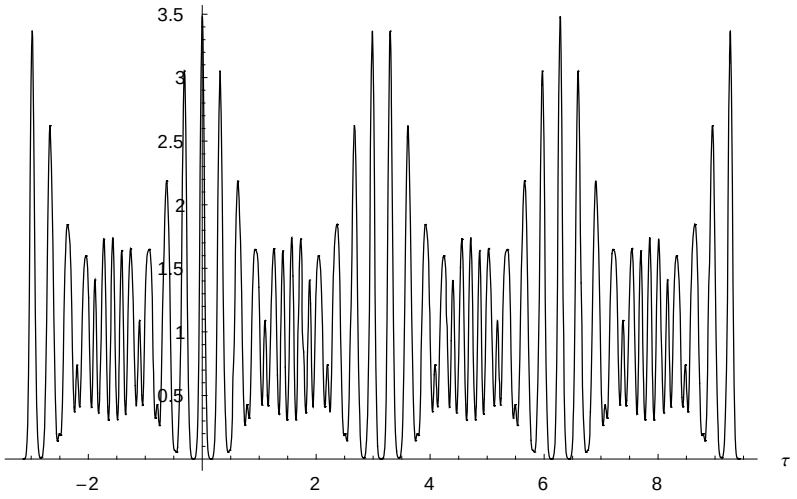
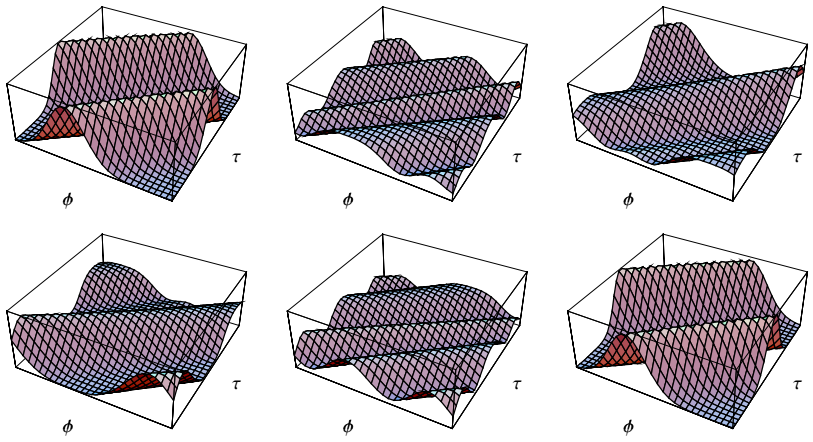
Since each term of this wavepacket contains cosine or sine factors or their products, the shortest time over which every term in this expression repeats is 2π. We can see this explicitly by plotting the probability amplitude versus dimensionless time for $\phi = 0$.



Probability amplitude $|\Theta(\phi = 0, \tau)|^2$ for a five component particle of a ring wavepacket with *m* values 8, 9, 10, 11, and 12.

This means that the period of the probability amplitude variation is 2π. Here are plots of the wavepacket evolution for six portions of one time period. Each portion is 0.4 dimensionless time units. Successive plots are centered at τ equal to 0, $2\pi/5$, $4\pi/5$, $6\pi/5$, $8\pi/5$ and 2π.



Probability amplitude $|\Theta(\phi, \tau)|^2$ for a five component particle of a ring wavepacket with *m* values 8, 9, 10, 11, and 12. Clockwise The dimensionless time, τ, varies over a 0.4 unit range centered at 0, $2\pi/5$, $4\pi/5$, (upper row, from left) $6\pi/5$, $8\pi/5$ and 2π (lower row, from left).

■ Schrödinger equation for motion on the surface of a sphere, again.

We can use what we have learned about the wavefunctions and energies of a particle on a ring to get further insight into the wavefunctions, $Y_{\ell m}(\theta, \phi)$, and energies of a particle on a sphere. We do this by expressing the sphere surface wavefunction as the product

$$Y_{\ell m}(\theta, \phi) = \Phi_m(\phi)\,\Theta_\ell(\theta)$$

of the ring wavefunction, $\Phi_m(\phi)$, and a new wavefunction, $\Theta_\ell(\theta)$, for the θ coordinate. Using this product wavefunction in the particle on a sphere surface Schrödinger equation, we get the following:

$$\begin{aligned}
&-\frac{\hbar^2}{2\,\mu\,{r_0}^2}\left(\frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right)Y_{\ell m}(\theta,\phi)\\
&\quad=-\frac{\hbar^2}{2\,\mu\,{r_0}^2}\left(\frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right)\Phi_m(\phi)\,\Theta_\ell(\theta)\\
&\quad=-\frac{\hbar^2}{2\,\mu\,{r_0}^2}\left(-\frac{m^2}{\sin^2\theta}+\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right)\Phi_m(\phi)\,\Theta_\ell(\theta)\\
&\quad=\frac{\hbar^2\,\ell\,(\ell+1)}{2\,\mu\,{r_0}^2}\,\Phi_m(\phi)\,\Theta_\ell(\theta).
\end{aligned}$$

where we have used the effect of the Legendrian on the spherical harmonic express the eigenvalue, $E_{l,m}$, in terms of ℓ.

> Verify that $E_{l,m} = \hbar^2\,\ell(\ell+1)/(2\,\mu\,{r_0}^2)$.

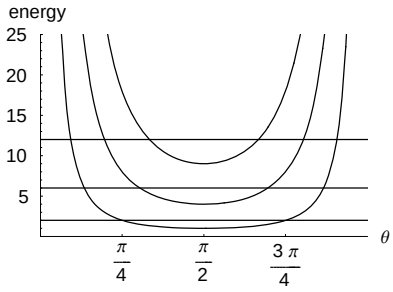
In the last equality, the ring wavefunction, Φ_m, appears as a multiplicative factor in each term and so we can cancel it out to get the Schrödinger equation for the θ coordinate,

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

where the common energy unit, $\hbar^2/(2\,\mu\,{r_0}^2)$, has been divided out. While this equation pertains only to the θ coordinate, there is a residue of the ϕ coordinate through the term $m^2/\sin^2(\theta)$. This factor depends on the square of the ϕ quantum number, m, and so in independent of the sign of m. It acts as a "polar" potential energy, in units $\hbar^2/(2\,\mu\,{r_0}^2)$, for the θ coordinate.

The potential energy rises to infinity at the poles, $\theta = 0$ and $\theta = \pi$. This means we can anticipate that the wavefunction $\Theta_\ell(\theta)$ must vanish at these poles, since otherwise it would diverge to infinite values, and also that it must be concentrated nearer the equator ($\theta = \pi/2$) the greater the magnitude of m. To make explicit this dependence of the wavefunction in the θ coordinate on the polar repulsive potential, it is conventionally written as $\Theta_{\ell,|m|}(\theta)$. This notation reminds us that ℓ by itself is not sufficient to determine the number of loops; we must also know the potential energy.

Here is a sketch of the this potential energy for values of m from 1 to 3, together with the energies for $\ell = 1,\ 2$ and 3.



Polar potential energy, $m^2 / \sin^2(\theta)$, for values of m from 1 (widest well) to 3 (narrowest well). The horizontal lines are the energies of motion on a sphere for $\ell = 1,\ 2$ and 3. Energies are in units $\hbar^2 m^2 / (2 \mu r_0^2)$.

For $m = 0$ there is no polar potential energy. Since the small ℓ can be is m, the energy for $\ell = 3$ is the lowest energy possible for $m = 3$, the second lowest for $m = 2$, the third lowest for $m = 1$, and the fourth lowest for $m = 0$ (for $m = 0$ there is no polar potential energy). From what we know about wavefunctions, this means we can anticipate that $\Theta_{3,|m|}(\theta)$ will have three loops for $m = 1$, two loops for $m = 2$, one loop for $m = 3$, and four loops for $m = 0$.

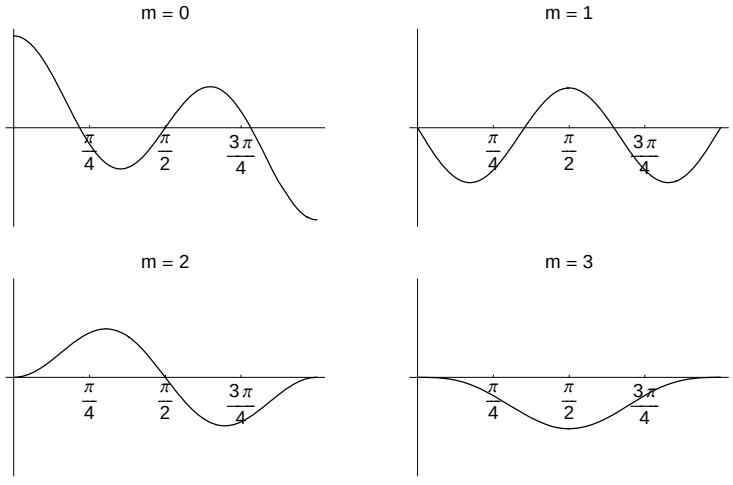
Further, because the polar potential energy is more confining the higher the value of m, we expect the polar wavefunction with the highest m to be most localized about $\theta = \pi / 2$, that is, near the equator. We can think of m measuring angular motion in the plane perpendicular to the z axis. The greater this motion the more the particle should be held away from the poles. This is analogous to how we would expect the water of a flooded planet to be distributed: The more rapidly the planet spins about its polar axes, the more the water will move away from the poles and bulge at the equator.

Here are the five polar functions, $\Theta_{\ell,|m|}(\theta, \phi)$, for $\ell \le 2$.

ℓ	m	Label	Polar Wavefunction
0	0	Θ_{s}	$\frac{1}{\sqrt{2}}$
1	0	Θ_{p0}	$\sqrt{\frac{3}{2}}$ Cos[Θ]
1	1	Θ_{p1}	$-\frac{1}{2}\sqrt{3}$ Sin[Θ]
2	0	Θ_{d0}	$\frac{1}{2}\sqrt{\frac{5}{2}}$ (−1 + 3 Cos[Θ]^2)
2	1	Θ_{d1}	$-\frac{1}{2}\sqrt{15}$ Cos[Θ] Sin[Θ]
2	2	Θ_{d2}	$\frac{1}{4}\sqrt{15}$ Sin[Θ]^2

Polar functions, $\Theta_{\ell,|m|}(\theta, \phi)$, for $\ell = 0$, 1 and 2, and $m = 0, 1, \ldots, \ell$.

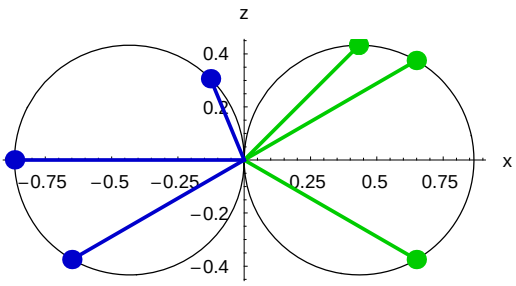
Here are plots of the $\ell = 3$ polar wavefunctions.



Polar wavefunction $\Theta_{3,|m|}(\theta)$.

The plots confirm our expectations. The polar wavefunction is more confined the higher the value of m. At the opposite extreme, when $m = 0$, the particle does not experience an infinite potential at the poles and so is able to have amplitude there. Indeed, *only* the $m = 0$ polar function has amplitude at the poles.

An alternative way to visualize the polar functions is by means of a polar plot. A polar plot is the locus of points whose distance from the origin in the direction θ is the value of the function at θ. Here is a polar plot of the function $\Theta_{1,1}(\theta)$.



Polar plot of $\Theta_{1,1}(\theta)$ in the x y plane. The length of each line is the magnitude of the function in that direction. The right lobe (green lines) corresponds to positive values, and the left lobe (blue lines) corresponds to negative values.

■ Orthonormality of spherical harmonics

Spherical harmonics are products of a ring function, $\Phi_m(\phi)$, and a polar function, $\Theta_{\ell,|m|}(\theta)$,

$$Y_{\ell\, m}\,(\theta,\,\phi)\;=\Phi_m\,(\phi)\,\Theta_{\ell,|m|}\,(\theta).$$

Ring functions for different values of m are orthogonal,

$$\int_0^{\pi}\Phi_m\,(\phi)^*\,\Phi_m\,(\phi)\,d\!\!\!^{-}\phi=\delta_{m\,m'}.$$

Polar functions for different values of ℓ and the *same* values of $|\,m\,|$ are orthogonal,

$$\int_0^{\pi}\Theta_{\ell,|m|}\,(\theta)^*\,\Theta_{\ell',|m|}\,(\theta)\sin(\theta)\,d\!\!\!^{-}\theta=\delta_{\ell\,\ell'}.$$

The combined consequence is that the integral

$$\int_0^{2\,\pi}\left(\int_0^{\pi}Y_{\ell\,m}\,(\theta,\,\phi)^*\,Y_{\ell'\,m'}\,(\theta,\,\phi)\sin(\theta)\,d\!\!\!^{-}\theta\right)d\!\!\!^{-}\phi$$

vanishes if $m \neq m'$, owing to the ring function orthogonality, and if $m = m'$, then it vanishes if $\ell \neq \ell'$, owing to the polar function orthogonality. This means that in general,

$$\int_0^{2\,\pi}\left(\int_0^{\pi}Y_{\ell\,m}\,(\theta,\,\phi)^*\,Y_{\ell'\,m'}\,(\theta,\,\phi)\sin(\theta)\,d\!\!\!^{-}\theta\right)d\!\!\!^{-}\phi=\delta_{\ell\,\ell'}\,\delta_{m\,m'}.$$

For example,

$$\int_0^{2\,\pi}\left(\int_0^{\pi}Y_{4,4}\,(\theta,\,\phi)^*\,Y_{3,-2}\,(\theta,\,\phi)\sin(\theta)\,d\!\!\!^{-}\theta\right)d\!\!\!^{-}\phi=0,$$

since the m values are different, and

$$\int_0^{2\pi} \left(\int_0^{\pi} Y_{4,3}(\theta, \phi)^* \, Y_{3,3}(\theta, \phi) \sin(\theta) \, d\theta \right) d\phi = 0,$$

since the m values are the same but the ℓ values are different.

■ Wavefunctions for motion on a sphere

The wavefunctions for motion on a sphere are the spherical harmonics,

$$Y_{\ell m}(\theta, \phi) = \Phi_m(\phi) \, \Theta_\ell(\theta).$$

Here are the nine spherical harmonics functions for $\ell \leq 2$.

ℓ	m	Label	Angular Wavefunction
0	0	s	$\frac{1}{2\sqrt{\pi}}$
1	0	p_0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\,\mathrm{Cos}[\theta]$
1	1	p_1	$-\frac{1}{2}e^{i\phi}\sqrt{\frac{3}{2\pi}}\,\mathrm{Sin}[\theta]$
1	−1	p_{-1}	$\frac{1}{2}e^{-i\phi}\sqrt{\frac{3}{2\pi}}\,\mathrm{Sin}[\theta]$
2	0	d_0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\,(-1+3\,\mathrm{Cos}[\theta]^2)$
2	1	d_1	$-\frac{1}{2}e^{i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]$
2	−1	d_{-1}	$\frac{1}{2}e^{-i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta]$
2	2	d_2	$\frac{1}{4}e^{2i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Sin}[\theta]^2$
2	−2	d_{-2}	$\frac{1}{4}e^{-2i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Sin}[\theta]^2$

Spherical harmonics, $Y_{\ell m}(\theta, \phi)$, for $\ell = 0$, 1 and 2, and $m = -\ell, -\ell+1, \ldots, \ell$.

For values of the quantum number m equal to zero, the spherical harmonics are cylindrically symmetric about the z axis; these are the functions p_z, d_{z^2}, etc. For values of the quantum number m different from 0, they contain imaginary parts and so are not readily visualized. We can eliminate these imaginary parts by using combinations of the functions for m and $-m$. These combinations are the angular functions that are not cylindrically symmetric about the z axis, namely the functions p_x, p_y, d_{xy}, etc. Here is a *Mathematica* expression for these real (non-imaginary) angular wavefunctions.

```
YReal[ℓ_, m_] := ComplexExpand[
   Which[
    m == 0, Y[ℓ, m],
    m > 0, (-1)^(m+1) i^m (Y[ℓ, m] + Y[ℓ, -m]) / √2,
    m < 0, (-1)^(m+1) i^(m+1) (Y[ℓ, m] - Y[ℓ, -m]) / √2
   ]] // Simplify
```

Here are the nine real spherical harmonics for $\ell \leq 2$.

ℓ	m	Label	Angular Wavefunction
0	0	s	$\frac{1}{2\sqrt{\pi}}$
1	0	p_z	$\frac{1}{2}\sqrt{\frac{3}{\pi}}$ Cos[θ]
1	±1	p_x	$\frac{1}{2}\sqrt{\frac{3}{\pi}}$ Cos[ϕ] Sin[θ]
1	±1	p_y	$\frac{1}{2}\sqrt{\frac{3}{\pi}}$ Sin[θ] Sin[ϕ]
2	0	d_{z^2}	$\frac{1}{8}\sqrt{\frac{5}{\pi}}$ (1 + 3 Cos[2 θ])
2	±1	d_{yz}	$\frac{1}{2}\sqrt{\frac{15}{\pi}}$ Cos[θ] Sin[θ] Sin[ϕ]
2	±1	d_{zx}	$\frac{1}{2}\sqrt{\frac{15}{\pi}}$ Cos[θ] Cos[ϕ] Sin[θ]
2	±2	d_{xy}	$\frac{1}{4}\sqrt{\frac{15}{\pi}}$ Sin[θ]^2 Sin[2 ϕ]
2	±2	$d_{x^2-y^2}$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}$ Cos[2 ϕ] Sin[θ]^2

Real spherical harmonics for $\ell = 0$, 1 and 2, and $m = -\ell, -\ell+1, \ldots, \ell$.

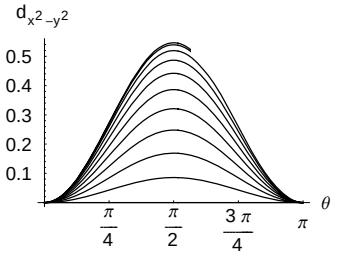
■ Visualization of real spherical harmonics

Since spherical harmonics depend on two variables, there are various ways to visualize them. Let's look at some of these, for the example of the real spherical harmonic $d_{x^2-y^2}$,

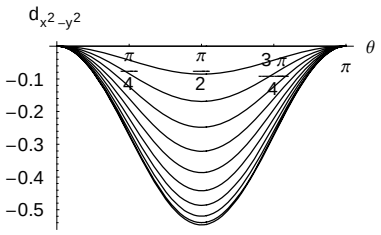
$$d_{x^2-y^2} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\,\cos(2\phi)\sin^2(\theta).$$

Since this function is a mixture of $m = \pm 2$ for $\ell = 2$, it must vanish at the poles and have its maximum values in the x y plane; the factor $\sin^2(\theta)$ accounts for this. The factor $\cos(2\phi)$ means that the function will have maximum positive values along $\pm x$ and maximum negative values along $\pm y$.

Here are plots of the function for $0 \le \theta \le \pi$ for ranges of ϕ between 0 and $\pi/4$ and between $\pi/4$ and $\pi/2$.



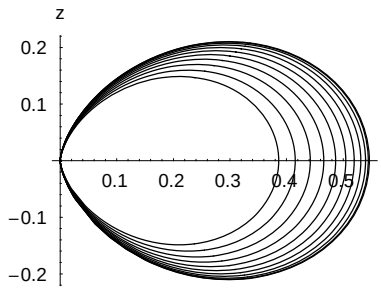
Plot of the function $d_{x^2-y^2}$ for $0 \le \theta \le \pi$ for ranges of ϕ between 0 (curve with greatest magnitude) and $\pi/4$ (zero line) and between $\pi/4$ and $\pi/2$.



Plot of the function $d_{x^2-y^2}$ for $0 \le \theta \le \pi$ for ranges of ϕ between $\pi/4$ (zero line) and $\pi/2$ (curve with greatest magnitude).

The plots show the change from maximum positive amplitude along $+x$ to maximum negative amplitude along $+y$.

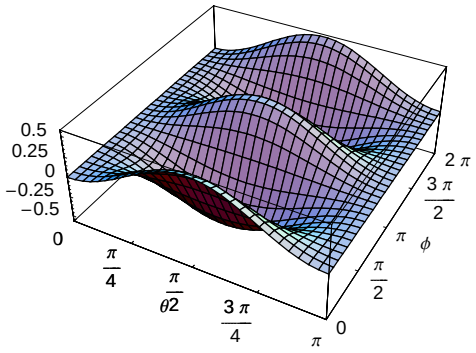
Here are polar plots of the function for $0 \le \theta \le \pi$ for ranges of ϕ between 0 and $\pi/8$.



Polar plots of the function $d_{x^2-y^2}$ for $0 \le \theta \le \pi$ for values of ϕ between 0 (largest locus) and $\pi/8$ (smallest locus).

The polar plots show that the amplitude is greatest along $+x$.

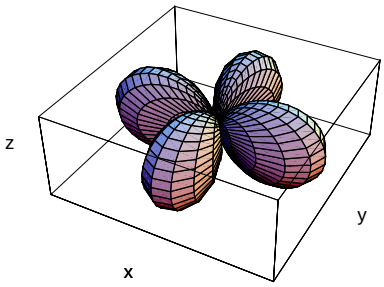
Here is a surface plot of the function, for the full range of θ and ϕ.



Surface plot of the function $d_{x^2-y^2}$.

The surface shows that the greatest magnitude is at $\theta = \pi/2$ (in the $x\,y$ plane), with largest positive amplitude along $\phi = 0$ $(+x)$ and π $(-x)$ and with largest negative amplitude along $\phi = \pi/2$ $(+y)$ and $-\pi/2$ $(-y)$.

Finally, here is a three dimensional polar plot.

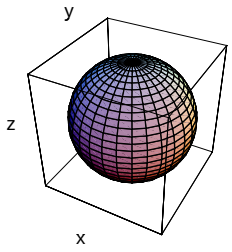


Three dimensional polar plot of the function $d_{x^2-y^2}$. The distance from the origin to the surface is the magnitude of the function in that direction. The lobes along $\pm x$ correspond to positive values, and the lobes along $\pm y$ correspond to negative values.

■ Gallery of three-dimensional polar plots of real spherical harmonics

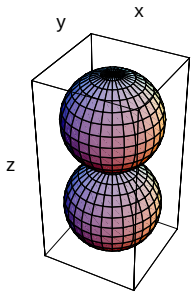
The three-dimensional polar plot is the visualization that is most often used in textbooks. Here are these plot for the s, p, and d real spherical harmonics, together with a description of their main features.

s angular function: $\frac{1}{2\sqrt{\pi}}$



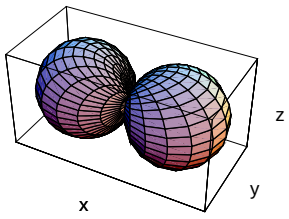
Visualization of the angular function *s*. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive. The function does not depend on either θ or ϕ and so is the same in all directions; that is, the function is *spherically symmetric*.

p_z angular function: $1/2\sqrt{3/\pi}$ Cos[θ]



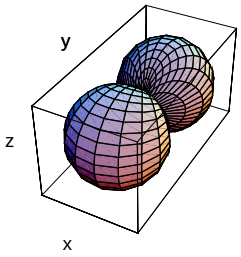
Visualization of the angular function p_z. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobe along *z* and negative in the lobe along $-z$. The function does not depend on ϕ and so is the same for all values of ϕ; that is, the function is *cylindrically symmetric* about the *z* axis. The function has maxima in its magnitude at $\theta = 0$ (along *z*) and $\theta = \pi$ (along $-z$), and vanishes at $\theta = \pi/2$ (in the *x y* plane).

p_x angular function: $1/2\sqrt{3/\pi}$ Cos[ϕ] Sin[θ]



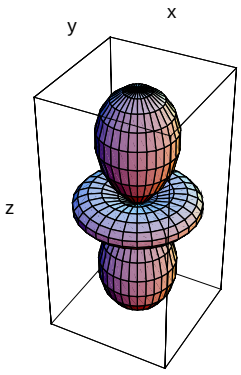
Visualization of the angular function p_x. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobe along *x* and negative in the lobe along $-x$. The function is *cylindrically symmetric* about the *x* axis. The function vanishes in the *y z* plane and has maxima in magnitude at $\theta, \phi = \pi/2, 0$ (along $+x$) and $\theta, \phi = \pi/2, \pi$ (along $-x$).

p_y angular function: $1/2\sqrt{3/\pi}$ Sin[θ] Sin[ϕ]



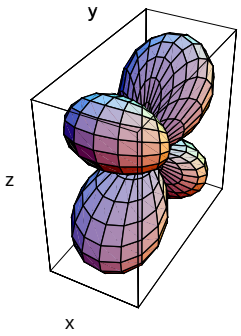
Visualization of the angular function p_y. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobe along y and negative in the lobe along $-y$. The function is *cylindrically symmetric* about the y axis. The function vanishes in the $z\,x$ plane and has maxima in magnitude at $\theta, \phi = \pi/2, \pi/2$ (along $+y$) and $\theta, \phi = \pi/2, 3\pi/2$ (along $-y$).

d_{z^2} angular function: $1/8\sqrt{5/\pi}$ $(1 + 3\,\text{Cos}[2\,\theta])$



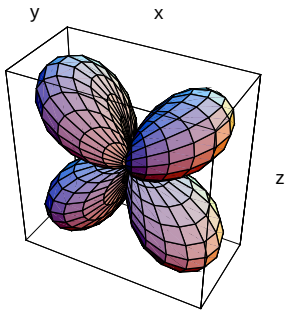
Visualization of the angular function d_{z^2}. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobes along z and $-z$ and negative in the lobe centered in the $x\,y$ pnae. The function does not depend on ϕ and so is the same for all values of ϕ; that is, the function is *cylindrically symmetric* about the z axis. The function has maxima in its magnitude at $\theta = 0$ (along z), $\theta = \pi/2$ (in the $x\,y$ plane), and $\theta = \pi$ (along $-z$), and vanishes at $\theta = 54.7°$ and $180° - 54.7° = 125.3°$ (in cones at ±35.3° to the $x\,y$ plane).

d_{yz} angular function: $1/2\sqrt{15/\pi}$ Cos[θ] Sin[θ] Sin[ϕ]



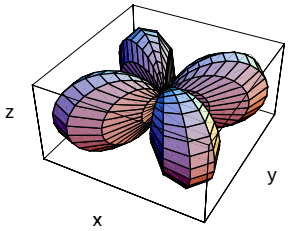
Visualization of the angular function d_{yz}. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobes between $\pm z$ and $\pm y$, and negative in the lobes between $\pm z$ and $\mp y$. The function has maxima in its magnitude along directions at 45° to the $\pm y$ and $\pm z$ zxes. It vanishes on the $x\,y$ and $z\,x$ planes.

d_{zx} angular function: $1/2\sqrt{15/\pi}$ Cos[θ] Cos[ϕ] Sin[θ]



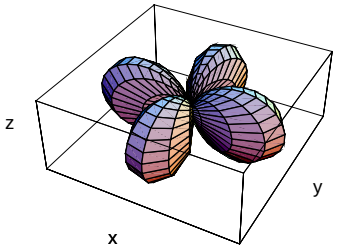
Visualization of the angular function d_{zx}. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobes between $\pm z$ and $\pm x$, and negative in the lobes between $\pm z$ and $\mp x$. The function has maxima in its magnitude along directions at 45° to the $\pm z$ and $\pm x$ axes. It vanishes on the $x\,y$ and y z planes.

d_{xy} angular function: $1/4\sqrt{15/\pi}$ Sin[θ]^2 Sin[2 ϕ]



Visualization of the angular function d_{xy}. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobes between $\pm x$ and $\pm y$, and negative in the lobes between $\pm x$ and $\mp y$. The function has maxima in its magnitude along directions at 45° to the $\pm x$ and $\pm y$ axes. It vanishes along the $z\,x$ and $y\,z$ planes.

$d_{x^2-y^2}$ angular function: $1/4\sqrt{15/\pi}$ Cos[2 ϕ] Sin[θ]^2



Visualization of the angular function $d_{x^2-y^2}$. The distance from the origin to the surface is the value of the function along the corresponding direction. The sign of the function is positive in the lobes along $\pm x$ and negative in the lobes along $\pm y$. The function has maxima in its magnitude along the $\pm x$ and $\pm y$ axes. It vanishes in the planes perpendicular to the $x\,y$ plane that are at 45° to the $\pm x$ and $\pm y$ axes.