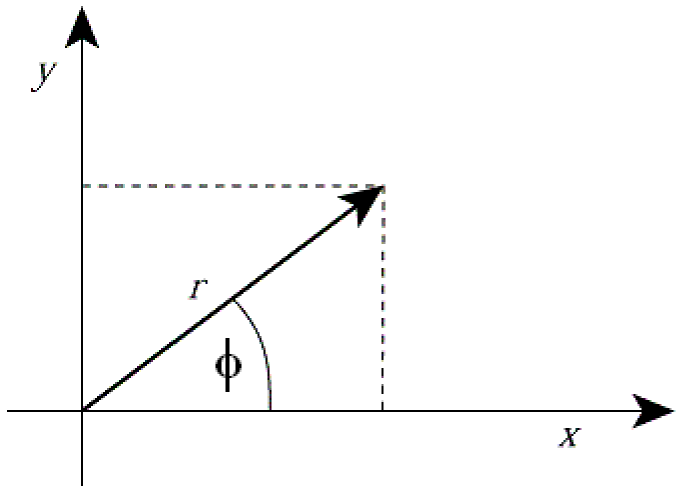
CHM 3411 - Physical Chemistry II
Handout 4

1. Polar coordinates

The relationship between Cartesian (rectangular) and polar coordinates is shown below



. The two coordinate systems are related by the expressions

$x = r\cos\phi$ $\qquad$ $r = (x^2 + y^2)^{1/2}$

$y = r\sin\phi$ $\qquad$ $\phi = \arctan(y/x)$

Based on the above we can show the following:

$$\partial/\partial x = \cos\phi\ \partial/\partial r - (\sin\phi/r)\ \partial/\partial\phi \qquad (4.1.1)$$

$$\partial/\partial y = \sin\phi\ \partial/\partial r + (\cos\phi/r)\ \partial/\partial\phi \qquad (4.1.2)$$

Also

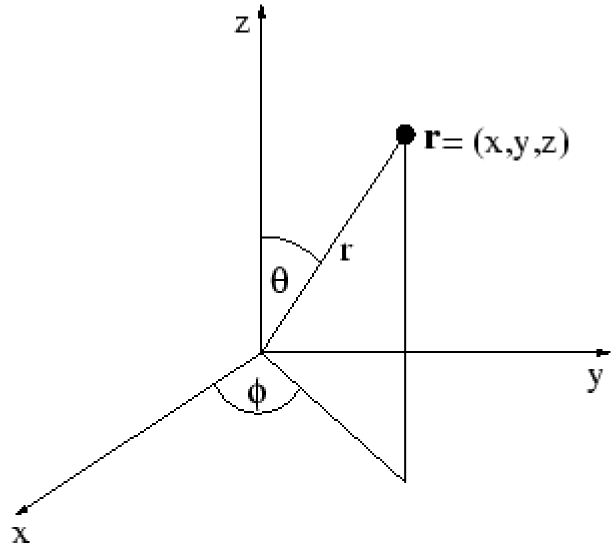
$$\partial^2/\partial x^2 + \partial^2/\partial y^2 = \partial^2/\partial r^2 + (1/r)\ \partial/\partial r + (1/r^2)\ \partial^2/\partial\phi^2 \qquad (4.1.3)$$

Note that for a particle on a ring, where r = constant, eq. 4.1.3 reduces to the expression

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 = (1/r^2)\ \partial^2/\partial\phi^2 \qquad \text{(for } r = \text{constant)} \qquad (4.1.4)$$

2. Spherical polar coordinates

The relationship between Cartesian (rectangular) and spherical polar coordinates is shown below



. The two coordinate systems are related by the expressions

$x = r \sin\theta \cos\phi$ $r = (x^2 + y^2 + z^2)^{1/2}$

$y = r \sin\theta \sin\phi$ $\theta = \arccos(z/r)$

$z = r \cos\theta$ $\phi = \arctan(y/x)$

Based on the above we can show the following:

$$\partial/\partial x = \sin\theta \cos\phi\ \partial/\partial r + (1/r) \cos\theta \cos\phi\ \partial/\partial\theta - \sin\phi/(r \sin\theta)\ \partial/\partial\phi \quad (4.2.1)$$

$$\partial/\partial y = \sin\theta \sin\phi\ \partial/\partial r + (1/r) \cos\theta \sin\phi\ \partial/\partial\theta + \cos\phi/(r \sin\theta)\ \partial/\partial\phi \quad (4.2.2)$$

$$\partial/\partial z = \cos\theta\ \partial/\partial r - (1/r) \sin\theta\ \partial/\partial\theta \quad (4.2.3)$$

Also

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

$$= \partial^2/\partial r^2 + (2/r)\ \partial/\partial r + 1/(r^2 \sin\theta)\ \partial/\partial\theta \sin\theta\ \partial/\partial\theta + (1/r^2 \sin^2\theta)\ \partial^2/\partial\phi^2 \quad (4.2.4)$$

$$= \partial^2/\partial r^2 + (2/r)\ \partial/\partial r + (1/r^2)\Lambda^2 \quad (4.2.5)$$

where

$$\Lambda^2 = (1/\sin\theta)\ \partial/\partial\theta \sin\theta\ \partial/\partial\theta + (1/\sin^2\theta)\ \partial^2/\partial\phi^2 \quad (4.2.6)$$

Note that for a particle on a sphere, where r = constant, eq. 4.2.4 reduces to the expression

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 = (1/r^2)\Lambda^2 \quad \text{(for r = constant)} \quad (4.2.7)$$

3. Angular momentum operators in spherical polar coordinates

The angular momentum operators in spherical polar coordinates are

$$L_x = (y\,p_z - z\,p_y) = i\hbar\,[\,\sin\phi\,\partial/\partial\theta + \cot\theta\cos\phi\,\partial/\partial\phi\,] \qquad (4.3.1)$$

$$L_y = (z\,p_x - x\,p_z) = -\,i\hbar\,[\,\cos\phi\,\partial/\partial\theta - \cot\theta\sin\phi\,\partial/\partial\phi\,] \qquad (4.3.2)$$

$$L_z = (x\,p_y - y\,p_x) = -\,i\hbar\,\partial/\partial\phi \qquad (4.3.3)$$

and

$$L^2 = -\,\hbar^2\,\Lambda^2 \qquad (4.3.4)$$

Note that L^2 commutes with L_x, L_y and L_z, but L_x, L_y, and L_z do not commute with one another.

4. Spherical harmonics

The spherical harmonics are the functions that are the solutions to the TISE for any one particle central potential problem. Recall that a central potential is a potential in three dimensions where the potential energy depends only on the distance of the particle from the center of the coordinate system, that is

$$V(x,y,z) = V(r) \qquad (4.4.1)$$

where r is as previously defined in the discussion of spherical polar coordinates. For particles in a central potential, a separation of variables can be carried out and the angular portion of the TISE solved to find the general solutions for the angular dependence of the wavefunction. The results are the spherical harmonic functions

$$Y_{\ell,m}(\theta,\phi) = \Theta_{\ell,|m|}(\theta)\,\Phi_m(\phi) \qquad \ell = 0, 1, 2, \ldots \quad m = 0, \pm1, \pm2, \ldots, \pm\ell \qquad (4.4.2)$$

where $\Theta_{\ell,|m|}(\theta)$ and $\Phi_m(\phi)$ are the solutions to the θ and ϕ portions of the overall wavefunction, and ℓ and m are quantum numbers with restrictions as given.

The first few normalized spherical harmonics are given in a table on the next page. There are several things to notice about the spherical harmonics. First, the spherical harmonics are in general complex functions (the exceptions are functions where m = 0). Second, for a particular value for the ℓ, the $\pm$m spherical harmonics are similar, differing only by a sign in the normalization constant and the exponential term involving ϕ. Finally, since linear combinations of degenerate solutions to a TISE are also solutions to the TISE, linear combinations of the $\pm$m spherical harmonics for a particular value of ℓ can be used to construct new wavefunctions that are entirely real. This procedure is used to construct atomic orbitals (such as the set of p-orbitals) which simplifies visualizing the wavefunctions for the hydrogen atom and in the calculations involved in molecular orbital theory.

The spherical harmonics for larger values of ℓ may be found by using the generating function for $\Theta_{\ell,|m|}(\theta)$, a set of functions related to the associated Legengre polynomials. The ϕ dependence of the spherical harmonics has a more simple form, with

$$\Phi_m(\phi) = (1/2\pi)^{1/2}\,e^{im\phi} \qquad (4.4.3)$$

Note that the functions in 4.4.3 represent the solutions to the TISE for a particle on a ring, that is, a particle constrained to move in a circle. This TISE has many similarities to the TISE for the particle in an infinite box.

Table of spherical harmonics		
ℓ	m	$Y_{\ell,m}(\theta,\phi)$
0	0	$(1/4\pi)^{1/2}$
1	1	$-(3/8\pi)^{1/2}\sin\theta\, e^{i\phi}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	-1	$(3/8\pi)^{1/2}\sin\theta\, e^{-i\phi}$
2	2	$(15/32\pi)^{1/2}\sin^2\theta\, e^{2i\phi}$
2	1	$-(15/8\pi)^{1/2}\sin\theta\cos\theta\, e^{i\phi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta - 1)$
2	-1	$(15/8\pi)^{1/2}\sin\theta\cos\theta\, e^{-i\phi}$
2	-2	$(15/32\pi)^{1/2}\sin^2\theta\, e^{-2i\phi}$

5. Integration in two and three dimensions

We will often solve the TISE for systems of two or three (or more!) dimensions. Because of this, we need a general procedure for finding normalization constants, probabilities, expectation values, and so forth, for multidimensional systems.

The general form for an integral of a function in two or three dimensions in Cartesian coordinates is

two dimensions: $\int dx \int dy\, f(x,y) = \int\int d\sigma\, f(x,y)$ (4.5.1)

where $d\sigma$ represents an area element (with $d\sigma = dx\,dy$ in Cartesian coordinates), and

three dimensions: $\int dx \int dy \int dz\, f(x,y,z) = \int\int\int d\tau\, f(x,y,z)$ (4.5.2)

where $d\tau$ represents a volume element (with $d\tau = dx\,dy\,dz$ in Cartesian coordinates).

To carry out integrals in other coordinate systems requires finding the value for the area element or volume element in the new coordinate system. For polar coordinates (two dimensions) $d\sigma = (dr)\,(r\,d\phi) = r\,dr\,d\phi$, so that the integral of a function of r and ϕ becomes

$$\int r\,dr \int d\phi\, f(r,\phi) \qquad (4.5.3)$$

and for spherical polar coordinates (three dimensions) $d\tau = (dr)\,(r\,d\theta)\,(r\sin\theta\,d\phi) = r^2\,dr\,\sin\theta\,d\theta\,d\phi$, so that the integral of a function of r, θ, and ϕ becomes

$$\int r^2\,dr \int \sin\theta\,d\theta \int d\phi\, f(r,\theta,\phi) \qquad (4.5.4)$$

As an example of how the above procedure works in practice, consider the following definite integral

$\int_0^1 dx \int_0^4 dy\ (x^2 + xy)$

$= \int_0^1 dx \int_0^4 \ (x^2 + xy)\ dy$

$= \int_0^1 dx\ (x^2y + xy^2/2)\ |_0^4$

$= \int_0^1 (4x^2 + 8x)\ dx$

$= (4x^3/3 + 4x^2)\ |_0^1 = 16/3$

Notice the procedure we use. We integrate over each variable, one at a time. When we are integrating over one variable, all other variables are treated as constants (the same procedure used for partial derivatives of functions of several variables).