CHM 3411 - Physical Chemistry II
Chapter 8 - Supplementary Material

1. Particle in a box - series solution

The general method that we wil use in studying systems in quantum mechanics is as follows:

1) Write down the TISE for the system

2) Solve the Schrodinger equation

3) Investigate the properties of the solutions

Note that the second step, solving the Schrodinger equation, is a mathematical problem. In fact, the solutions to the differential equations that turn up in Schrodinger equations were, for the most part, solved by 18^{th} and 19^{th} century mathematicians.

As chemists we are not as interested in solving the Schrodinger equation as we are in studying the properties of its solutions. However, it is useful to see the detailed solution of at least one Schrodinger equation. This will demonstrate that solving the Schrodinger equation, while tedious, is not particularly difficult. It will also give us an idea about how solutions for other Schrodinger equations are found.

As an example of solving the TISE we have chosen the particle in a one dimensional box. Recall that inside the box, the TISE is

$$- (\hbar^2/2m)\, d^2/dx^2\, \psi(x) = E\, \psi(x) \ , 0 < x < L \qquad (8.1.1)$$

an eigenvalue equation, as previously discussed.

If we represent $\psi(x)$ in terms of an expansion in powers of x

$$\psi(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + ... + a_nx^n + ... = \Sigma_{n=0}^{\infty}\, a_nx^n \qquad (8.1.2)$$

then

$$d/dx\, \psi(x) = a_1 + 2\, a_2x + 3\, a_3x^2 + ... + (n+1)\, a_{n+1}x^n + ... = \Sigma_{n=0}^{\infty}\, (n+1)\, a_{n+1}x^n \qquad (8.1.3)$$

and

$$d^2/dx^2\, \psi(x) = 2\, a_2 + 2\cdot3\, a_3x + 3\cdot4\, a_4x^2 + ... + (n+1)(n+2)\, a_{n+2}x^n + ...$$

$$= \Sigma_{n=0}^{\infty}\, (n+1)(n+2)a_{n+2}x^n \qquad (8.1.4)$$

If we substitute equn 8.1.2 and 8.1.4 into equn 8.1.1 we get

$$- (\hbar^2/2m)\, (2\, a_2 + 2\cdot3\, a_3x + 3\cdot4\, a_4x^2 + ... + (n+1)(n+2)\, a_{n+2}x^n + ...)$$

$$= E\, (a_0 + a_1x + a_2x^2 + a_3x^3 + ... + a_nx^n + ...) \qquad (8.1.5)$$

which, written using our summation notation, is

$$- (\hbar^2/2m)\, \Sigma_{n=0}^{\infty}\, (n+1)(n+2)a_{n+2}x^n = E\, \Sigma_{n=0}^{\infty}\, a_nx^n \qquad (8.1.6)$$

Equn 8.1.6 must be true for any value of x in the range $0 < x < L$. However, the rate at which x changes varies in each term in the summation based on the power of x for the term. The only way that the two sides of this equation can remain equal for all possible values for x is if terms on the left side and right side of equn 8.1.6 corresponding to the same power of x are equal. This condition leads to the following relationships

n = 0 term

$$- (\hbar^2/2m)\, 1 \cdot 2\, a_2 = E\, a_0 \qquad (8.1.7)$$

n = 1 term

$$- (\hbar^2/2m)\, 2 \cdot 3\, a_3 = E\, a_1 \qquad (8.1.8)$$

n = 2 term

$$- (\hbar^2/2m)\, 3 \cdot 4\, a_4 = E\, a_2 \qquad (8.1.9)$$

general term (corresponding to x^n)

$$- (\hbar^2/2m)\, (n+1)(n+2)\, a_{n+2} = E\, a_n \qquad (8.1.10)$$

We can rearrange each of these terms to solve for the coefficient on the left side. The result is

n = 0 term

$$a_2 = - (2mE/\hbar^2)\, (a_0/1 \cdot 2) \qquad (8.1.11)$$

n = 1 term

$$a_3 = - (2mE/\hbar^2)\, (a_1/2 \cdot 3) \qquad (8.1.12)$$

n = 2 term

$$a_4 = - (2mE/\hbar^2)\, (a_2/3 \cdot 4) \qquad (8.1.13)$$

general term (corresponding to x^n)

$$a_{n+2} = - (2mE/\hbar^2)\, a_n/(n+1)(n+2) \qquad (8.1.14)$$

Equn 8.1.14 is an example of a recursion relationship. It tells us that if we know the value of a_n, we can find the value of a_{n+2}.

It is natural, based on equn 8.1.14, to divide our power series expansion for $\psi(x)$ into terms in even powers of x and terms in odd powers of x.

$$\psi(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots + a_n x^n + \ldots$$

$$= (a_0 + a_2 x^2 + a_4 x^4 + \ldots a_{2n} x^{2n} + \ldots) + (a_1 x + a_3 x^3 + a_5 x^5 + \ldots + a_{2n+1} x^{2n+1} + \ldots) \qquad (8.1.15)$$

$$= (\Sigma_{n=0}^{\infty}\, a_{2n} x^{2n}) + (\Sigma_{n=0}^{\infty}\, a_{2n+1} x^{2n+1}) \qquad (8.1.16)$$

Now consider the terms in even powers of x. Equn 8.1.11 gives the value of a_2 in terms of a_0, and equn 8.1.13 gives the value of a_4 in terms of a_2. But we can use equn 8.1.11 to substitute into equn 8.1.13, to get

$$a_4 = (-1)^2 (2mE/\hbar^2)^2 (a_0/1\cdot 2\cdot 3\cdot 4) = (-1)^2 (2mE/\hbar^2)^2 (a_0/4!) \quad (8.1.17)$$

We can therefore write a_4 in terms of a_0.

If we continue this process the next term gives a_6 in terms of a_4. But since equn 8.1.17 gives a_4 in terms of a_0, we can express a_6 in terms of a_0. In fact, every even coefficient can be written in terms of a_0.

$$a_{2n} = (-1)^n (2mE/\hbar^2)^n [a_0/(2n)!] \quad (8.1.18)$$

Therefore, the first summation on the right in equn 8.1.16 can be written as

$$\Sigma_{n=0}^{\infty} a_{2n}x^{2n} = \Sigma_{n=0}^{\infty} (-1)^n (2mE/\hbar^2)^n [a_0/(2n)!]\, x^{2n} \quad (8.1.19)$$

Similarly, the second summation on the right in equn 8.1.16 can be written as

$$\Sigma_{n=0}^{\infty} a_{2n+1}x^{2n+1} = \Sigma_{n=0}^{\infty} (-1)^n (2mE/\hbar^2)^n [a_1/(2n+1)!]\, x^{2n+1} \quad (8.1.20)$$

Now recall the Taylor series expansions for cos(kx) and sin(kx)

$$\cos(kx) = 1 - k^2x^2/2! + k^4x^4/4! + ... = \Sigma_{n=0}^{\infty} (-1)^n [k^{2n}/(2n)!]\, x^{2n} \quad (8.1.21)$$

$$\sin(kx) = kx - k^3x^3/3! + k^5x^5/5! + ... = \Sigma_{n=0}^{\infty} (-1)^n [k^{2n+1}/(2n+1)!]\, x^{2n+1} \quad (8.1.22)$$

If we compare equn 8.1.19 to equn 8.1.21, and equn 8.1.20 to equn 8.1.22, with $k = (2mE/\hbar^2)^{1/2}$, it is clear that equn 8.1.19 and 8.1.20 are simply cos(kx) and sin(kx) written as Taylor series. Substitution into equn 8.1.16 gives

$$\psi(x) = a_0 \cos(kx) + a_1 \sin(kx) \ , \ k = (2mE/\hbar^2)^{1/2} \quad (8.1.23)$$

the general solution to the differential equation corresponding to the TISE for the particle in a box.

Since we do not at this point know the values for a_0, a_1, and E, we generally rewrite equn 8.1.23 as

$$\psi(x) = C \sin(kx) + D \cos(kx) \quad (8.1.24)$$

where C, D, and k are constants. If we insert this equation into our original TISE (equn 8.1.1) and use our boundary conditions (normalization and the fact that $\psi(0) = \psi(L) = 0$), as discussed in class, we get our final result

$$\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L) \quad (8.1.25)$$

$$E_n = n^2 E_0 \ , \ E_0 = h^2/8mL^2 \quad n = 1, 2, 3, ... \quad (8.1.26)$$

2. Even and odd functions

A function is classified as an <u>even function</u> if f(-x) = f(x) for all values of x. A function is classified as an <u>odd function</u> if f(-x) = - f(x) for all values of x. For example

$f(x) = x^2$	$f(x) = \cos(x)$	$f(x) = \exp(ax^2)$	are even functions
$f(x) = x$	$f(x) = \sin(x)$	$f(x) = \sin(x)\cos(x)$	are odd functions
$f(x) = x^2 + x$	$f(x) = \exp(ax)$	$\ln(x)$	are neither even nor odd

There are general properties of even and odd functions that are sometimes useful. In particular, if we consider the product of two functions

(even) · (even) = even (even) · (odd) = odd

(odd) · (odd) = even (odd) · (even) = odd

For example, f(x) = sin(x) cos(x) is an odd function times an even function, and so is an odd function.

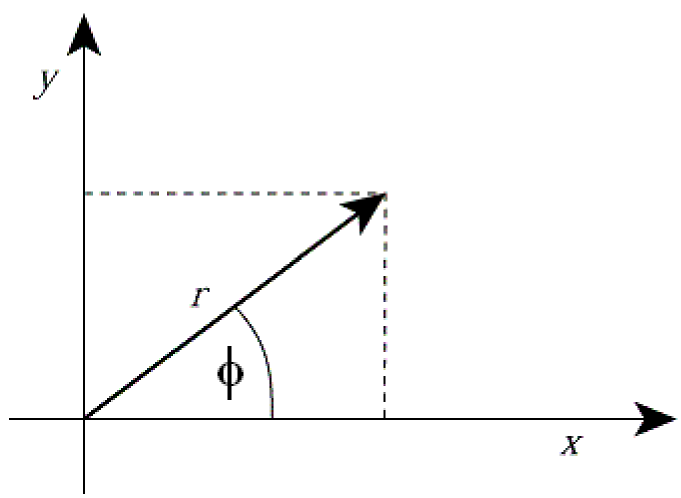
Finally, if we consider the integral of a function about symmetric limits, we may say the following

$$\int_{-a}^{a} f(x)\,dx = 2\int_{0}^{a} f(x)\,dx \quad \text{if } f(x) \text{ is even} \qquad (8.2.1)$$

$$\int_{-a}^{a} f(x)\,dx = 0 \quad \text{if } f(x) \text{ is odd} \qquad (8.2.2)$$

3. Polar coordinates

The relationship between Cartesian (rectangular) and <u>polar coordinates</u> is shown below



. The two coordinate systems are related by the expressions

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

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

Based on the above we can show the following:

$$\partial/\partial x = \cos\phi \, \partial/\partial r - (\sin\phi/r) \, \partial/\partial\phi \qquad (8.3.1)$$

$$\partial/\partial y = \sin\phi \, \partial/\partial r + (\cos\phi/r) \, \partial/\partial\phi \qquad (8.3.2)$$

Also

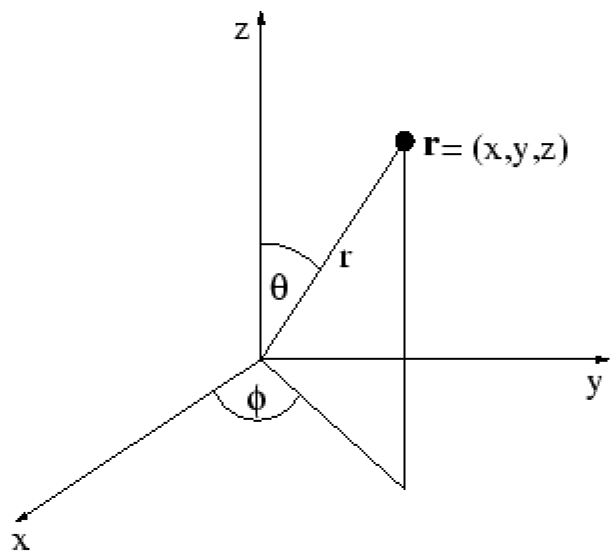
$$\partial^2/\partial x^2 + \partial^2/\partial y^2 = \partial^2/\partial r^2 + (1/r) \, \partial/\partial r + (1/r^2) \, \partial^2/\partial\phi^2 \qquad (8.3.3)$$

Note that for a particle on a ring, where r = constant, eq. 8.3.3 reduces to the expression

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 = (1/r^2) \, \partial^2/\partial\phi^2 \qquad \text{(for r = constant)} \qquad (8.3.4)$$

4. Spherical polar coordinates

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



. The two coordinate systems are related by the expressions

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

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

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

Based on the above we can show the following:

$$\partial/\partial x = \sin\theta \cos\phi \, \partial/\partial r + (1/r) \cos\theta \cos\phi \, \partial/\partial\theta - \sin\phi/(r \sin\theta) \, \partial/\partial\phi \qquad (8.4.1)$$

$$\partial/\partial y = \sin\theta \sin\phi \, \partial/\partial r + (1/r) \cos\theta \sin\phi \, \partial/\partial\theta + \cos\phi/(r \sin\theta) \, \partial/\partial\phi \qquad (8.4.2)$$

$$\partial/\partial z = \cos\theta \, \partial/\partial r - (1/r) \sin\theta \, \partial/\partial\theta \qquad (8.4.3)$$

Also

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

$$= \partial^2/\partial r^2 + (2/r)\ \partial/\partial r + 1/(r^2 \sin\theta)\ \partial/\partial\theta \sin\theta\ \partial/\partial\theta + (1/r^2 \sin^2\theta)\ \partial^2/\partial\phi^2 \quad (8.4.4)$$

$$= \partial^2/\partial r^2 + (2/r)\ \partial/\partial r + (1/r^2)\Lambda^2 \quad (8.4.5)$$

where

$$\Lambda^2 = (1/\sin\theta)\ \partial/\partial\theta \sin\theta\ \partial/\partial\theta + (1/\sin^2\theta)\ \partial^2/\partial\phi^2 \quad (8.4.6)$$

Note that for a particle on a sphere, where r = constant, eq. 8.4.4 reduces to the expression

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 = (1/r^2)\Lambda^2 \quad \text{(for r = constant)} \quad (8.4.7)$$

5. Angular momentum operators in spherical polar coordinates

The angular momentum operators in spherical polar coordinates are

$$L_x = (y\ p_z - z\ p_y) = i\hbar\ [\ \sin\phi\ \partial/\partial\theta + \cot\theta \cos\phi\ \partial/\partial\phi\ ] \quad (8.5.1)$$

$$L_y = (z\ p_x - x\ p_z) = -\ i\hbar\ [\ \cos\phi\ \partial/\partial\theta - \cot\theta \sin\phi\ \partial/\partial\phi\ ] \quad (8.5.2)$$

$$L_z = (x\ p_y - y\ p_x) = -\ i\hbar\ \partial/\partial\phi \quad (8.5.3)$$

and

$$L^2 = -\ \hbar^2\ \Lambda^2 \quad (8.5.4)$$

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.

6. 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

$$\text{two dimensions: } \int dx \int dy\ f(x,y) = \int\int d\sigma\ f(x,y) \quad (8.6.1)$$

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

$$\text{three dimensions: } \int dx \int dy \int dz\ f(x,y,z) = \int\int\int d\tau\ f(x,y,z) \quad (8.6.2)$$

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

$$\int r\, dr \int d\phi\, f(r,\phi) \qquad (8.6.3)$$

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

$$\int r^2\, dr \int \sin\theta\, d\theta \int d\phi\, f(r,\theta,\phi) \qquad (8.6.4)$$

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

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

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

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

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

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

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 procedure used for partial derivatives of functions of several variables).