

Q.M 2

Chapter 1

1-1 The Shrödinger Equation and some simple equation applications:

Shrödinger equation was regarded as to be a fundamental postulate, or axiom of quantum and atomic physics, Just as Newton's laws are fundamental postulates of classical mechanics . The solutions to the Shrödinger equation are called the *wave function*. The Shrödinger Equation that does not contain time as a variable is called the time independent Shrödinger Equation and the solutions of such equation are called the *stationary state wave function*.

As well as matters have a particle like character, matter has a wave like character. Since then there must be a wave equations that governs them.

For simplicity let us start with the classical one-dimensional wave equation

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2} \quad 1)$$

Equation (1) can be solved by the method of separation of variables and that $u(x, t)$ can be written as the product of a function of x and a harmonic or sinusoidal function of time.

$$u(x, t) = \psi(x) \cos \omega t \quad 2)$$

$\psi(x)$ is called the spatial amplitude of the wave. Substituting (2) into(1)we obtain

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\omega^2}{v^2} \psi(x) = 0 \quad 3)$$

We now introduce the idea of de Broglie mater waves, the wavelength associated with the momentum of the particle

$$\lambda = \frac{h}{P} \quad 4)$$

where h is Planck's constant. Substituting for the momentum from the law of the total energy $E = \frac{p^2}{2m} + U(x)$ into (4) we obtain

$$\lambda = \frac{h}{P} = \frac{h}{\{2m[E - U(x)]\}^{1/2}} \quad 5)$$

since $\omega = 2\pi\nu$ and $\nu\lambda = v$ the term $\frac{\omega^2}{v^2}$ in equation (3) can be written in the form

$$\frac{\omega^2}{v^2} = \frac{4\pi^2\nu^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m[E - U(x)]}{\hbar^2} \quad 6)$$

where $\hbar = \frac{h}{2\pi}$ and so equation 3 can be written as

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2} [E - U(x)]\psi(x) = 0 \quad 7)$$

This is the famous Schrodinger equation, a differential equation for $\psi(x)$ for a particle of mass m moving in a potential field described by $U(x)$. The exact nature of $\psi(x)$ is vague at this point, but in some sense it is a measure of the amplitude of the matter wave and is called the wave function of the particle. Equation (7) does not contain time and is called the time-independent Schrödinger equation.

The wave functions obtained from Eq. (7) are called stationary-state wave functions. Although there is a more general Schrödinger

equation that contains a time dependence, we shall see throughout the course that a great number of problems of atomic and molecular interest can be described in terms of stationary-state wave functions. Equation (7) can be written in the form

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x)\psi(x) = E\psi(x) \quad 8)$$

1-2 The Schrödinger Equation Can Be Formulated as an Eigenvalue Problem.

An operator is a simple that tells you to do something to whatever follows the symbol. For example, we can consider $\partial y / \partial x$ to be the $\partial / \partial x$ operator operating in the function $y(x)$. some other examples are SQRT (take the square root of what follows), \int_0^1 , 3 (multiply by 3), and $\partial / \partial \gamma$. Clearly the operator and the operand (the function on which the operator acts) must be compatible; the operation and the result must be mathematically well-defined. We shall usually denote an operator by a capital letter with a carat over it. Thus we write

$$g(x) = \hat{A} f(x)$$

to indicate that the operator \hat{A} operates on $f(x)$ to give a new function $g(x)$.

In quantum mechanics, we deal only with linear operators. An operator is said to be linear if

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

where c_1 and c_2 are (possibly imaginary or complex) constants. Clearly the “differentiate” and “integrate” operators are linear while “square” and the “square root” operators are non linear (prove).

A problem that occurs frequently is the following: Given \hat{A} , find a function $\phi(x)$ and a constant a such that

$$\hat{A}\phi(x) = a\phi(x)$$

Note that the result of operating on the function $\phi(x)$ by \hat{A} is a simply to give $\phi(x)$ back again, only multiplied by a constant factor. Clearly \hat{A} and $\phi(x)$ have a very special relationship with respect to each other. The function $\phi(x)$ is called an *eigenfunction* of the operator \hat{A} , and a is called an *eigenvalue* problem.

If we go back to equation (8) and we rearrange it in form the

$$\left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi(x) = E \psi(x) \quad 9)$$

if we denote the operators in the brackets by \hat{H} then equation (9) can be written in the form

$$\hat{H} \psi(x) = E \psi(x) \quad 10)$$

Here we have formulated the Schrödinger equation by an eigenvalue problem where \hat{H} is called the *Hamiltonian operator*. This suggests a correspondence between the Hamiltonian operator and the energy.

The wave function is an eigenvalue of the Hamiltonian operator and the energy is the eigenvalue of it.

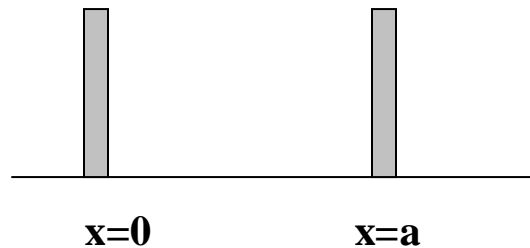
1-3 Classical-Mechanical Quantities Are Represented by Linear Operators in Quantum Mechanics.

To every observable in classical mechanics there corresponds an operator in quantum mechanics. These correspondence are collected in Table 1

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x r	\hat{X} \hat{R}	Multiply by x Multiply by r
Momentum	p_x \mathbf{p}	\hat{p}_x $\hat{\mathbf{p}}$	$-i\hbar \frac{\partial}{\partial x}$ $-i\hbar \left(i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \right)$
Kinetic energy	k_x \mathbf{k}	\hat{p}_x $\hat{\mathbf{k}}$	$-\frac{\hbar^2}{2m} \left(i \frac{\partial^2}{\partial x^2} \right)$ $-\frac{\hbar^2}{2m} \left(i \frac{\partial^2}{\partial x^2} + j \frac{\partial^2}{\partial y^2} + k \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$U(x)$ $U(x,y,z)$	$U(\hat{x})$ $U(\hat{x}, \hat{y}, \hat{z})$	Multiply by $U(x)$ Multiply by $U(x)$
Total Energy	E	\hat{H}	$-\frac{\hbar^2}{2m} \left(i \frac{\partial^2}{\partial x^2} + j \frac{\partial^2}{\partial y^2} + k \frac{\partial^2}{\partial z^2} \right)$ $+ U(x,y,z)$
Angular momentum ($r \times p$)	$l_x = yp_z - zp_y$ $l_y = zp_x - xp_z$ $l_z = xp_y - yp_x$	\hat{L}_x \hat{L}_y \hat{L}_z	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$ $-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$ $-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

1-4 Wave Function for A particle in one-dimensional box

For a free particle (the particle experiences no potential energy i.e. $U(x)=0$) of mass m constrained to lie along the x -axis between $x=0$ and $x=a$ the Schrödinger Equation will be defined as



$$\frac{\partial^2}{\partial x^2} \psi(x) + \frac{2mE}{\hbar^2} \psi(x) = 0 \quad 0 \leq x \leq a \quad (11)$$

here $\psi(0) = \psi(a) = 0$. The general solution of equation (11) is

$$\psi(x) = A \cos kx + B \sin kx \quad , \quad k = \frac{(2mE)^{\frac{1}{2}}}{\hbar} \quad (12)$$

$\psi(0) = 0 \Rightarrow A = 0$ then

$$\psi(a) = B \sin ka = 0 \quad (13)$$

since $B \neq 0$ then

$$ka = n\pi \quad n=1,2,3,\dots \quad (14)$$

Substituting for k from (12) into (14), we find that

$$E_n = \frac{\hbar^2 n^2}{8ma^2} \quad n=1,2,3,\dots \quad (15)$$

Thus, the energy of a particle is said to be quantized and the integer n is called the quantum number. The wave function that associated with E_n is

$$\psi_n(x) = B \sin kx = B \sin \frac{n\pi x}{a} \quad n=1,2,3,\dots \quad (16)$$

Max Born found that the probability of finding a particle located between x and $x+dx$ can be calculated by

$$\text{Prob}\{x_1 \leq x \leq x_2\} = \int_x^{x+dx} \psi^*(x)\psi(x)dx = \begin{cases} 1 & 0 \leq x \leq a \\ 0 & \text{Otherwise} \end{cases}$$

Substituting from 16 into 17 we find

$$|B|^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1 \quad (18)$$

Let $\frac{n\pi x}{a} = z$ then

$$\int_0^a \sin^2 \frac{n\pi x}{a} dx = \frac{a}{n\pi} \int_0^{n\pi} \sin^2 z dz = \frac{a}{n\pi} \left(\frac{n\pi}{2} \right) = \frac{a}{2} \quad (19)$$

Therefore, $B^2 \left(\frac{a}{2} \right) = 1$, $B = \left(\frac{2}{a} \right)^{1/2}$ and

$$\psi_n(x) = \left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \quad 0 \leq x \leq a \quad n=1,2,3,\dots \quad (20)$$

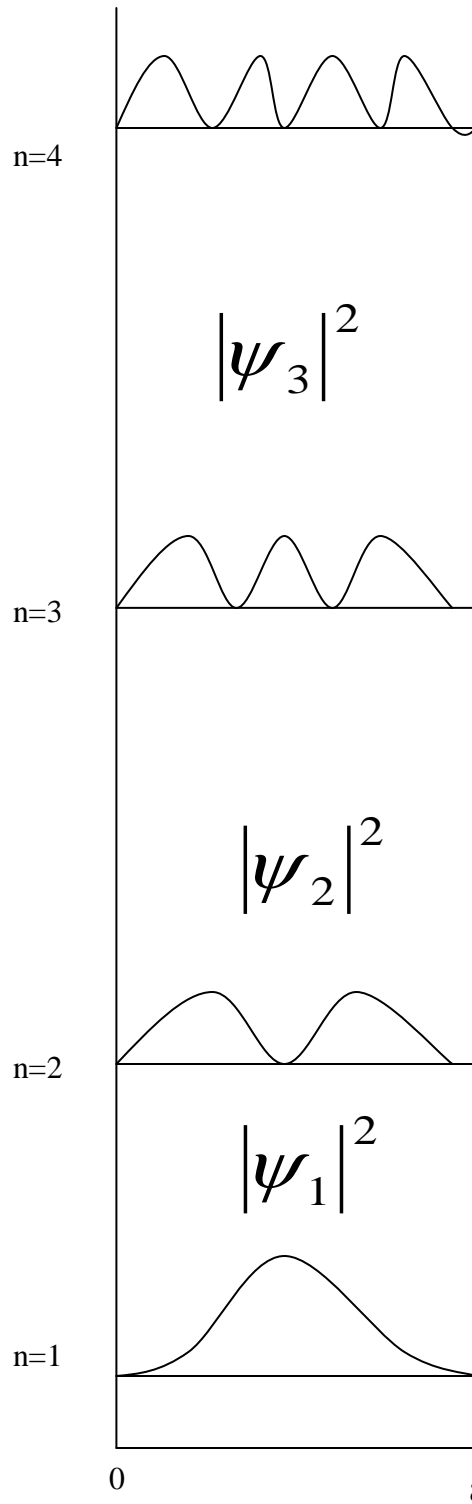
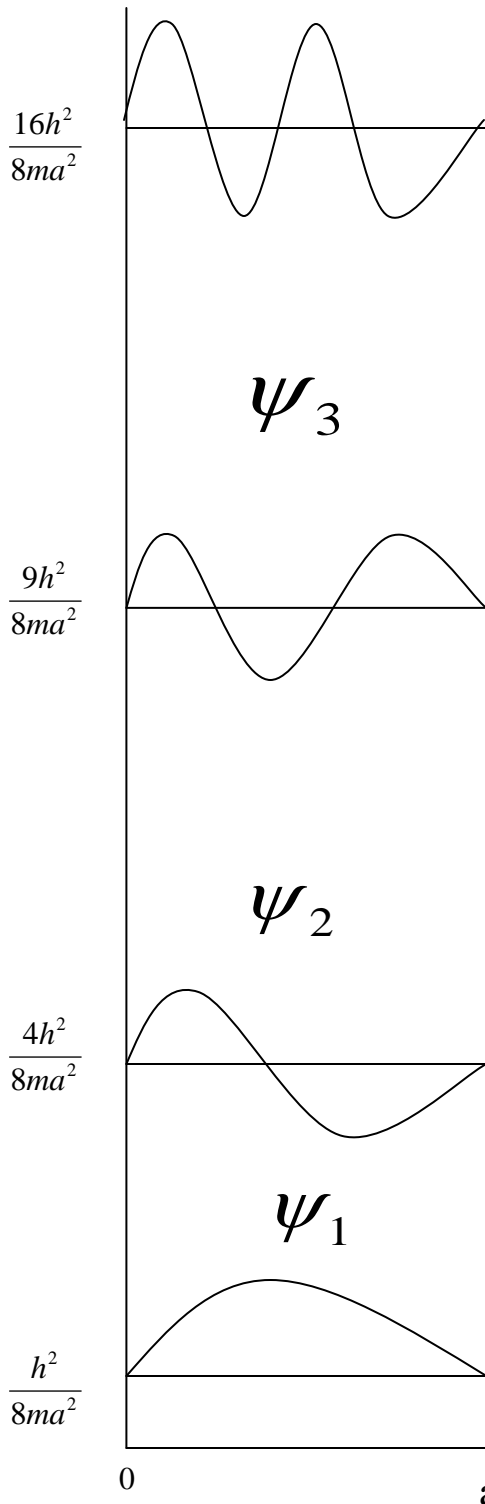
- A wave function that satisfied (17) and given by (20), is said to be *normalized*.
- when constant that multiplies a wave function(e.g B) is adjusted to assure that the wave function is normalized ,then this constant is called the *normalization constant*.
- because Hamiltonian operator is a linear operator, if ψ is a solution to Schrödinger equation $\hat{H}\psi = E\psi$ then $A\psi$ is also a solution to the Schrödinger equation where A is any constant and A can always be chosen to normalize the equation.

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a}$$

$$E_n = \frac{h^2 n^2}{8ma^2}$$

ψ_4

$|\psi_4|^2$



Example 1:

Find the energy of the first excited state in the linear butadiene molecule $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ (model of free particle (electron) in a one dimensional box). Given that the $\text{C}=\text{C}$ bond length is 1.35 \AA and the $\text{C}-\text{C}$ bond length is 1.54 \AA .

Solution:

For simplicity we shall assume that the four electrons is moving along the straight line whose length can be estimated by

$$a = 2 \times (1.35) + 1.54 + 1.54 = 2 \times (\text{C}=\text{C} \text{ bond length}) + \text{C}-\text{C} \text{ bond length} + \text{the distance of carbon atom radius at each end} = 5.78.$$

The energy of the first excited state of this system of four electrons is that having one electron elevated from $n=2$ to $n=3$ state see figure below The from the energy equation obtained

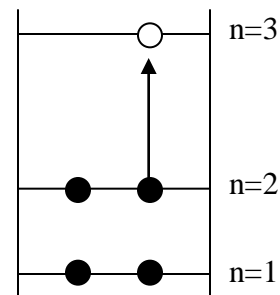
before $E_n = \frac{h^2 n^2}{8ma^2}$ we find that

$$\Delta E = \frac{h^2}{8ma^2} (3^2 - 2^2), \text{therefore}$$

$$\begin{aligned} \Delta E &= \frac{(6.626 \times 10^{-34} \text{ J.s})^2 \times 5}{8 \times (9.110 \times 10^{-31} \text{ Kg})(5.78 \times 10^{-10} \text{ m})^2} \\ &= 9.02 \times 10^{-19} \text{ J} \end{aligned}$$

The frequency of the electron is given by

$$v = \frac{p}{h} = \frac{(2mE)^{1/2}}{h} = 4.54 \times 10^4 \text{ cm}^{-1}$$



1-5 The Average momentum of a particle in a box is Zero:

Suppose that some number x_j is associated with the out come j (e.g tossing a die has 6 possible outcomes and $j=1,2,\dots,6$) and let $f(x_j)$ represent the probability of realizing the number x_j then we define the *average of x* or the *expectation value of x* to be

$$\bar{x} \equiv \langle x \rangle = \sum_{j=1}^n x_j f(x_j)$$

and the *second moment* to be

$$\langle x^2 \rangle = \sum_{j=1}^n x_j^2 f(x_j)$$

another quantity of importance is the *second central moment*, or the *variance*, defined by

$$\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle = \sum_{j=1}^n (x_j - \langle x \rangle)^2 f(x_j)$$

For the case of the **particle in a box** where $0 \leq x \leq a$

$$f(x)dx = \begin{cases} \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx & 0 \leq x \leq a \\ 0 & \text{Otherwise} \end{cases} \quad (21)$$

the average value of x or the mean position of the particle, is

$$\langle x \rangle = \frac{2}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} dx = \frac{a}{2} \quad (\text{for all } n)$$

To calculate the spread about $\langle x \rangle$ we calculate

$$\begin{aligned}\sigma_x^2 &= \langle x^2 \rangle - \langle x \rangle^2 = \frac{2}{a} \int_0^a x^2 \sin^2 \frac{n\pi x}{a} dx - \left(\frac{2}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} dx \right)^2 \\ &= \left(\frac{a}{2\pi n} \right) \left(\frac{\pi^2 n^2}{3} - 2 \right)\end{aligned}\quad 22)$$

For the case of the position it is quite simple, but the problem arises if we want to find the expectation or variance values for a differential equations operators such as Hamiltonian or momentum operators. Then the only way to solve such problem is to sandwich the operator between ψ^* and ψ in order to calculate the average value associated with that operator.

$$\int \psi_n^*(x) \hat{H} \psi_n(x) dx = E_n \int \psi_n^*(x) \psi_n(x) dx = E_n \quad 23)$$

$$\langle p \rangle = \int_0^a \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] \left(-i\hbar \frac{d}{dx} \right) \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] dx \quad 24)$$

$$\langle p \rangle = -i\hbar \frac{2\pi n}{a^2} \int_0^a \sin \frac{n\pi x}{a} \cos \frac{n\pi x}{a} dx = 0 \quad 25)$$

1-6 The Werner Heisenberg (1927) Uncertainty Principle

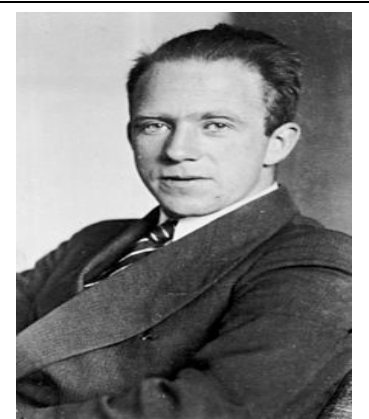
Says That $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

Now let us calculate the variance of the momentum

$$\sigma^2 = \langle p^2 \rangle - \langle p \rangle^2$$

To calculate $\langle p^2 \rangle$ we use

Werner Heisenberg, Germany
Nobel Prize in Physics (1932)
"for the creation of quantum mechanics"



$$\langle p^2 \rangle = \int_0^a \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] \left(-\hbar^2 \frac{d^2}{dx^2} \right) \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] dx \quad (26)$$

$$= \frac{2\pi^2 n^2 \hbar^2}{a^3} \int_0^a \sin \frac{n\pi x}{a} \sin \frac{n\pi x}{a} dx = 0$$

$$= \frac{\pi^2 n^2 \hbar^2}{a^3}$$

$$\text{Then } \sigma_p^2 = \frac{\pi^2 n^2 \hbar^2}{a^3}$$

$$\text{and } \sigma_p = \frac{\pi n \hbar}{a} \quad (27)$$

Because σ ,is a measure of the spread of a distribution about its mean value, we can interpret σ as a measure of the uncertainty involved in any measurement. The above equation shows that the uncertainty in a measurement of particle momentum is inversely proportional to a .While the uncertainty in the position of a particle is directly proportional to a (Eq.22). Thus ,the more we try to localize the particle (definite short area of movement) the greater is the uncertainty in its momentum.

$$\sigma_x \sigma_p = \frac{\hbar}{2} \left(\frac{\pi^2 n^2}{3} - 2 \right)^{1/2}$$

then since the value of the square root term here is greater than the unity for all n

$$\sigma_x \sigma_p \succ \frac{\hbar}{2} \quad (28)$$

Thus, we see that there is a reciprocal relation between the uncertainty of the position and in momentum. and that a free particle has a definite momentum but its position is completely undefined.

Chapter 2

2-The Postulates and General principles of Quantum Mechanics

In this Chapter We shall formalize a set of wave mechanics postulates and then discuss some general theorems that follow from this postulates.

2-1 The State of a system is completely Specified by its wave function

The position of the particle depends not only on the time but also on the initial conditions

$$x(t) = x(t; x_o, y_o, x_o, v_{x_o}, v_{y_o}, v_{z_o})$$

$$y(t) = y(t; x_o, y_o, x_o, v_{x_o}, v_{y_o}, v_{z_o})$$

$$z(t) = z(t; x_o, y_o, x_o, v_{x_o}, v_{y_o}, v_{z_o})$$

we can write these three equations in a vector notation

$$r(t) = r(t; r_o, v_o)$$

The vector $r(t)$ describes the position of the particle as a function of time; $r(t)$ is called the trajectory of the particle.

In classical mechanics, if there are N particles in the system, then it takes 3N coordinates and 3N velocities to specify the state of the system. Then the trajectory of the system is the position of each of the N particles in the system as a function of time and as a function of the initial conditions. We should suspect immediately that this is not going to be so in quantum mechanics because the Uncertainty Principle tells us that we cannot specify or determine the position and momentum of a particle simultaneously with finite precision. Thus we see that in classical mechanics (the mechanics of macroscopic bodies) the Uncertainty Principle is of no practical importance.

This leads us to the **first postulate of Quantum Mechanics**

The state of quantum mechanics system is completely specified by a function

$\Psi(\mathbf{r}, t)$ that depends on the coordinates of the particle and on the time. This function, called the wave function or the state function, has the important property that $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) dx dy dz$ is the probability that the particle lies in the volume element $dx dy dz$, located at r , at time t .

If there is more than one particle, say two, then we write

$$\Psi^*(r_1, r_2, t)\Psi(r_1, r_2, t) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

For the probability that particle 1 lies in the volume element $dx_1 dy_1 dz_1$ at r_1 and that particle 2 lies in the volume element $dx_2 dy_2 dz_2$ at r_2 at the time t .

Because the square of the wave function has probabilistic interpretation, it must satisfy certain physical requirements. For example a wave function must be normalized, so that for the case of one particle we have

$$\int_{-\infty}^{\infty} \int \int \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) dx dy dz = 1 \quad 1)$$

It is convenient to abbreviate Eq. 1 by letting $dx dy dz = d\tau$ and we write

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) d\tau = 1$$

with the understanding that this is really a triple integral.

Postulate 2

To every observable in classical mechanics there corresponds an operator in quantum mechanics.(table1.chapter1)

In other words Quantum-Mechanical Operators Represents Classical –Mechanical variables

Postulate 3

In any measurement of the observable associated with the operator \hat{A} , the only value that will ever be observed are the eigen value a , which satisfy the eigen value equation

$$\hat{A}\Psi = a\Psi \quad 2)$$

Generally, an operator will have asset of eignfunctions and eignvalues

$$\hat{A}\Psi_n = a_n\Psi_n$$

So in any experiment designed to measure the observable corresponding to \hat{A} , the only values we find are a_1, a_2, a_3, \dots . The set of eignvalues $\{a_n\}$ of operator \hat{A} is called the spectrum of \hat{A} .

As a specific example, consider the measurement of energy. The operator corresponding to the energy is the Hamiltonian operator, and it is eign value equation is given by

$$\hat{H}\Psi_n = E_n\Psi_n$$

The solution to this equation gives the Ψ_n and E_n for the case of the particle

in a box $E_n = \frac{n^2 h^2}{8ma^2}$. Postulate 3 says that if we measure the energy of a particle in a box, we shall find one of these energies and no others.

(no such energies will founded $E_n = \frac{(n+1)^2 h^2}{8ma^2}$).

Postulste 4

If system is in state described by a normalized wave function Ψ then the average value of the observable corresponding to is given by

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi \, d\tau$$

Suppose that Ψ just happens to be an eigenfunction of \hat{A} ; that is, suppose that $\Psi = \Psi_n$ where

$$\hat{H} \Psi_n = E_n \Psi_n$$

then

$$\begin{aligned} \langle a \rangle &= \int_{-\infty}^{\infty} \Psi_n^* \hat{A} \Psi_n d\tau = \int_{-\infty}^{\infty} \Psi_n^* a_n \Psi_n d\tau = \\ &a_n \int_{-\infty}^{\infty} \Psi_n^* \Psi_n d\tau = a_n \end{aligned} \quad 5)$$

Further more

$$\begin{aligned} \langle a^2 \rangle &= \int_{-\infty}^{\infty} \Psi_n^* \hat{A}^2 \Psi_n d\tau = \int_{-\infty}^{\infty} \Psi_n^* \hat{A} \left(\hat{A} \Psi_n \right) d\tau = \\ &\int_{-\infty}^{\infty} \Psi_n^* \hat{A} (a_n \Psi_n) d\tau = \int_{-\infty}^{\infty} \Psi_n^* a_n \left(\hat{A} \Psi_n \right) d\tau = \\ &\int_{-\infty}^{\infty} \Psi_n^* a_n^2 \Psi_n d\tau = a_n^2 \end{aligned} \quad 6)$$

From Eq. 5 and Eq.6 we see that the variance of the measurements gives

$$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = 0 \quad (\text{i.e they are the same})$$

Thus as postulate 3 says that the only value that we measure is the value a_n .

2-3 The Time-Dependence Schrödinger Equation

Postulate 5

The wave function or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$\hat{H} \Psi(x, t) = i\hbar \frac{\partial \Psi}{\partial t} \quad 7)$$

again here with the use of method of separation of variables we reach to the interesting solution of Eq.7

$$\Psi(x, t) = \psi(x) e^{\frac{-iEt}{\hbar}} \quad 8)$$

So if we use the relation $E = h\nu = \hbar\omega$

$$\Psi(x, t) = \psi(x) e^{-i\omega t} \quad 9)$$

As the time independent Schrödinger equation has a harmonic oscillation with time, the time-dependent Schrödinger equation has a harmonic oscillation with time Yet the time-dependent Schrödinger equation does not have the same form as classical wave equation. Schrödinger equation has a first derivative of time, while the classical wave equation has a second derivative in time. Nevertheless the Schrödinger equation does have a wavelike solution which is one reason why quantum mechanics is some times called the *wave mechanics*.

There is asset of solutions to Eq. 7

$$\Psi_n(x, t) = \psi_n(x) e^{\frac{-iE_n t}{\hbar}} \quad (10)$$

If the system happens to be in one of the eigenstates given by 10 then

$$\Psi_n^*(x, t) \Psi_n(x, t) = \psi_n^*(x) \psi_n(x) dx$$

Thus the probability density and the averages calculated from Eq.10 are independent of time, and the $\psi_n(x)$ are called the *stationary state wave function*

The stationary state wave function are of central importance in atomic and molecular physics. and in later chapters we shall represent an atom or molecule by asset of stationary energy states and express the spectroscopic properties of the system in terms of transitions from one of the stationary state to another. The Bohr model of the hydrogen atom a simple illustration of this idea.

A system is not generally in a state described by a wave function of Eq.10. And the general solution of the time-dependent Schrödinger equation is a superposion of it Eq.10

$$\Psi_n(x, t) = \sum_n C_n \psi_n(x) e^{\frac{-iE_n t}{\hbar}} \quad (11)$$

$$\Psi_n(x, t) = C_1 \psi_1(x) e^{\frac{-iE_1 t}{\hbar}} + C_2 \psi_2(x) e^{\frac{-iE_2 t}{\hbar}}$$

and the probability density in this case is

$$\Psi_n^*(x,t)\Psi_n(x,t) = \left[C_1^* \psi_1^*(x) e^{\frac{-iE_1 t}{\hbar}} + C_2^* \psi_2^*(x) e^{\frac{-iE_2 t}{\hbar}} \right] \left[C_1 \psi_1(x) e^{\frac{-iE_1 t}{\hbar}} + C_2 \psi_2(x) e^{\frac{-iE_2 t}{\hbar}} \right]$$

$$= |C_1|^2 \psi_1^*(x)\psi_1(x) + |C_2|^2 \psi_2^*(x)\psi_2(x) + c_1^* c_2 \psi_1^*(x)\psi_2(x) \exp\left[\frac{i(E_1 - E_2)t}{\hbar}\right] + c_2^* c_1 \psi_2^*(x)\psi_1(x) \exp\left[\frac{i(E_2 - E_1)t}{\hbar}\right]$$

The third and fourth terms here contain time explicitly, so that $\Psi_n^*(x,t)\Psi_n(x,t)$ is not independent of time.

2-4 Hermitian Quantum-Mechanical Operators

All Quantum-Mechanical Operators Must Be Hermitian

Postulate 6

To every observable in classical mechanics there corresponds a linear Hermitian operator in quantum mechanics.

All the operators in table 1 are Hermitian and that they satisfy the following condition

12)

$$\int_{-\infty}^{\infty} f^* \hat{A} f dx = \int_{-\infty}^{\infty} f \hat{A}^* f^* dx$$

Example1

Prove that the kinetic energy operator is Hermitian

Solution:

~~$$\int_{-\infty}^{\infty} f^* \frac{-\hbar^2 d^2}{2m dx^2} f dx = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} f^* \frac{df}{dx} dx + \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{df^*}{dx} \frac{df}{dx} dx =$$~~

$$\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{df^*}{dx} f dx - \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{d^2 f^*}{dx^2} f dx = \int_{-\infty}^{\infty} f \frac{-\hbar^2 d^2}{2m dx^2} f^* dx = \int_{-\infty}^{\infty} f \left(\frac{-\hbar^2 d^2}{2m dx^2} \right)^* f^* dx$$

Example2:

Prove

$$\int_{-\infty}^{\infty} f^* \hat{A} f dx = \int_{-\infty}^{\infty} f \hat{A}^* f^* dx .$$

Proof

In quantum mechanics the wave functions and operators generally are complex, but certainly the eigenvalues must be real quantities if they are corresponds to the result of experimental measurements.

As from Eq.2 we have

$$\hat{A}\psi = a\psi$$

multiply from left by ψ^* and integrate we find that

$$\int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx = a \int_{-\infty}^{\infty} \psi^* \psi dx = a \quad (13)$$

Now we take the complex conjugate of Eq.2

$$\hat{A}^* \psi^* = a^* \psi^* = a \psi^*$$

recognize that a is real . Multipling from the left by ψ and integrating

$$\int_{-\infty}^{\infty} \psi \hat{A} \psi^* dx = a \int_{-\infty}^{\infty} \psi \psi^* dx = a \quad (14)$$

then from Eq.13 and Eq.14

$$\int_{-\infty}^{\infty} f^* \hat{A} f dx = \int_{-\infty}^{\infty} f \hat{A}^* f^* dx \quad (15)$$

Prove:

Amore general definition of a Hermitian operator is

$$\int_{-\infty}^{\infty} g^* \hat{A} f dx = \int_{-\infty}^{\infty} f \hat{A}^* g^* dx$$

where g and f are any two wave function.

2-5 The Eigenfunctions of Hermitian Operators are Orthogonal

Consider the two eigenvalue equations

$$\hat{A}\psi_n = a_n\psi_n \quad , \quad \hat{A}\psi_m = a_m\psi_m$$

We multiply the first by ψ_m^* and integrate and then we take the complex conjugate of the second and multiply it by ψ_n , then

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx = a_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx$$

$$\int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx = a_m^* \int_{-\infty}^{\infty} \psi_n \psi_m^* dx$$

By subtracting the two equations

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx - \int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx = (a_n - a_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx$$

because \hat{A} is Hermitian ,the left hand side here is zero and so we have

$$(a_n - a_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad 16)$$

If n=m

The integral is unity by normalization and so we have

$$a_n = a_n^*$$

which is just another proof that the eigenvalues are real

if n ≠ m we have

$$(a_n - a_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0$$

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad 17)$$

A set of eigenvalues that satisfies Eq.17 is said to be *orthogonal*

A set of functions that are both normalized and orthogonal to each other is called an *orthonormal* set and is expressed by

$$\int_{-\infty}^{\infty} \psi_j^* \psi_i dx = \delta_{ij} \quad 18)$$

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$

The symbol δ_{ij} is called *Kronecher delta*

So by now we come to the summery that: the quantum mechanics operators are Hermitian and the Eigenvalues of that Hermitian operators must be real and the corresponding wave functions are orthogonal.

Example 3:

Prove that the wave function for a particle in a box is orthonormal.

Proof:

The wave function for a particle in a box is given by

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a} \quad n=1,2,3,\dots$$

from the trigonometric identity, $\sin \alpha \sin \beta = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)$

then

$$\left(\frac{2}{a}\right) \int_0^a \sin \frac{n\pi x}{a} \sin \frac{m\pi x}{a} dx = \left(\frac{1}{a}\right) \int_0^a \cos \frac{(n-m)\pi x}{a} dx - \left(\frac{1}{a}\right) \int_0^a \cos \frac{(n+m)\pi x}{a} dx$$

Because n and m are integers so both integrands of the right-hand side are of the form $\cos \frac{N\pi x}{a}$ where N is an integer, both integrals are equal to zero if $m \neq n$. **If $m = n$ then**

$$\left(\frac{2}{a}\right) \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1$$

there for the wave function of the particle in the box it is orthonormal.

Chapter 3

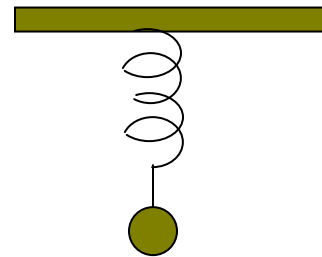
The Harmonic Oscillator

For a mass m connected to a wall by spring of equilibrium length l_o . A force was then applied to the spring to pull the mass to some displacement x , so $x = z - l_o$. The Newton's equation with Hooks law define the equitation of motion to be

$$m \frac{d^2 z}{dt^2} = -k(z - l_o)$$

then since $\frac{d^2 z}{dt^2} = \frac{d^2 x}{dt^2}$

$$m \frac{d^2 x}{dt^2} + kx = 0 \quad 1)$$



The solution to this equation is given by

$$x(t) = A \sin \omega t + B \cos \omega t$$

where $\omega = \left(\frac{k}{2m} \right)^{1/2} = 2\pi\nu \quad 2)$

the initial velocity in this case is zero and so

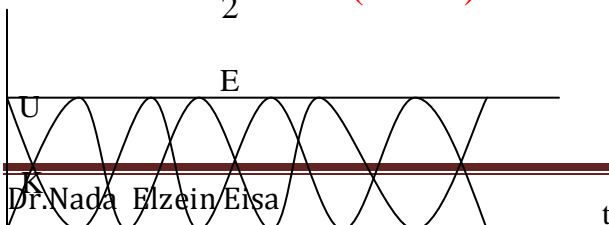
$$x(0) = B \quad \text{and} \quad \left(\frac{dx}{dt} \right)_{t=0} = A \cos \omega t = 0$$

And so

$$x(t) = B \cos \omega t$$

From classical mechanics we know that the total energy of harmonic oscillator is conserved and that

$$E = K + U = \frac{B^2 k}{2} \quad \text{(Prove)}$$



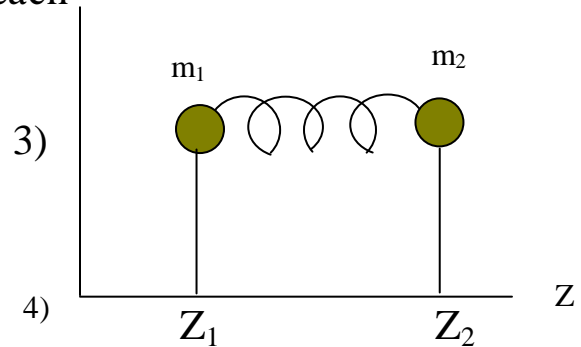
3-1 The Equation of a Harmonic-Oscillator is a Model of a Diatomic Molecule contains the reduced mass of the molecule

We are going to see later that the simple harmonic oscillator is a good model for a vibrating diatomic molecule. The vibrating diatomic molecule can be pictured by the system of two masses connected by spring as shown in the Fig below

The two equation of motion, one for each mass

$$m_1 \frac{d^2 z_1}{dt^2} = k(z_2 - z_1 - l_0) \quad 3)$$

$$m_2 \frac{d^2 z_2}{dt^2} = -k(z_2 - z_1 - l_0) \quad 4)$$



Note that if $z_2 - z_1 > l_0$, the spring is stretched and so the force on mass m_1 is toward the right and that on mass m_2 is toward the left. This is why the term in Eq.3 is positive and that in Eq. 4 is negative.

* If we add Eq.3 to Eq.4

$$m_1 \frac{d^2 z_1}{dt^2} + m_2 \frac{d^2 z_2}{dt^2} = 0 \quad \text{or} \quad \frac{d^2}{dt^2}(m_1 z_1 + m_2 z_2) = 0 \quad 5)$$

This last term suggest that we introduce the center of mass coordinate

$$Z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2} = \frac{m_1 z_1 + m_2 z_2}{M}$$

Substituting in Eq.5 we get

$$M \frac{d^2 Z}{dt^2} = 0$$

This show that the center of mass moves uniformly in time with constant momentum

*If we divide Eq.3 by m_1 and Eq.4 by m_2 and then subtract them we find

$$\frac{d^2 z_1}{dt^2} - \frac{d^2 z_2}{dt^2} = -\frac{k}{m_2}(z_2 - z_1 - l_0) - \frac{k}{m_1}(z_2 - z_1 - l_0)$$

$$\frac{d^2(z_2 - z_1)}{dt^2} = -k \left(\frac{1}{m_1} + \frac{1}{m_2} \right) (z_2 - z_1 - l_0)$$

If we recognize that $\left(\frac{1}{m_1} + \frac{1}{m_2} \right) = \frac{m_1 + m_2}{m_1 m_2} = \frac{1}{\mu}$

where μ is the reduced mass and let $x = z_2 - z_1 - l_0$, then we have

$$\mu \frac{d^2 x}{dt^2} + kx = 0 \quad (6)$$

If we compare Equation 6 to equation 1 we find that the only difference is that the mass is expressed once as m and then as μ which means that the two body system can be treated as easily as the one body problem by using the reduced mass of the two body system μ .

3-2 The Schrödinger equation of motion of harmonic oscillator (harmonic oscillator in Quantum Physics)

The Schrödinger equation for harmonic oscillator is

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi}{\partial x^2} + U(x)\psi(x) = E\psi(x)$$

With $U(x) = \frac{1}{2}kx^2$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2}kx^2 \right] \psi(x) = 0 \quad (7)$$

This differential equation, however, doesn't have constant coefficients and so we cannot use the method of separation of variables. In fact when a differential equation doesn't have constant

coefficients there is no simple general technique for solving it and each case must be studied individually. The wave functions of the harmonic oscillator is given by

$$\psi_n(x) = N_n H_n\left(\alpha^{1/2} x\right) e^{-\alpha x^2/2} \quad 8)$$

$$\text{Where } \alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2} \quad 9)$$

$$\text{And the normalization constant } N_n = \frac{1}{(2^n n!)^{1/2}} \left(\frac{\alpha}{\pi}\right)^{1/4} \quad 10)$$

And the $H_n\left(\alpha^{1/2} x\right)$ are polynomials called the *Hermite polynomials* where

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} \quad 11)$$

The first few Hermit polynomials are listed below in table 1

$H_0(\xi) = 1$	$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$	$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

The solution of the harmonic oscillator given by equation 8) is associated with the energy restricted by the quantized value

$$E_n = \hbar \left(\frac{k}{\mu}\right)^{1/2} \left(n + \frac{1}{2}\right) = \hbar \omega \left(n + \frac{1}{2}\right) = h\nu \left(n + \frac{1}{2}\right) \quad 12)$$

$$n = 0, 1, 2, 3, ..$$

$$\text{Where } \omega = \left(\frac{k}{\mu}\right)^{1/2} \text{ and } \nu = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} \quad 13)$$

Example 1

Find ψ_0 and

a) prove that it satisfy the quantum harmonic oscillator equation of motion

b) prove that it is a normal wave functions

solution:

Substituting for n=0 into equation 8

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \text{Then}$$

a) by substituting into equation 7) with $E_0 = \frac{1}{2}\hbar\omega$ to obtain

$$\frac{\partial^2 \psi_0}{\partial x^2} + \frac{2\mu}{\hbar^2} \left[E_0 - \frac{1}{2} kx^2 \right] \psi_0(x) = 0$$

$$\left(\frac{\alpha}{\pi}\right)^{1/4} \left(\alpha^2 x^2 e^{-\alpha x^2/2} - \alpha e^{-\alpha x^2/2} \right) + \frac{2\mu}{\hbar^2} \left(\frac{\hbar\omega}{2} - \frac{kx^2}{2} \right) \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} = 0$$

$$(\alpha^2 x^2 - \alpha) + \left(\frac{\mu\omega}{\hbar} - \frac{\mu kx^2}{\hbar} \right) = 0$$

Using the fact that $\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$ and $\omega = \left(\frac{k}{\mu}\right)^{1/2}$, we see that every thing cancel in the above expression.

$$\text{b) } \int_{-\infty}^{\infty} \psi_0^2(x) dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{\pi}{\alpha}\right)^{1/2} = 1$$

3-3 The Harmonic oscillator accounts for the infrared spectrum

According to Eq.12 the vibrational energy levels of a diatomic molecule are given by

$$E_n = \hbar \left(\frac{k}{\mu} \right)^{1/2} \left(n + \frac{1}{2} \right) = \hbar \omega \left(n + \frac{1}{2} \right) = h\nu \left(n + \frac{1}{2} \right) \quad n=0,1,2,\dots$$

A diatomic molecule can make a transition from one vibrational state to another (model allows transition between adjacent energy states only) by absorbing or emitting electromagnetic radiation whose observed frequency satisfied the Bohr frequency condition

$$\Delta E = E_{N+1} - E_N = \hbar \left(\frac{k}{\mu} \right)^{1/2} = h\nu_{obs}$$

$$\text{Thus } \nu_{obs} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \quad \text{OR} \quad \bar{\nu}_{obs} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2}$$

Where

$$\bar{\nu}_{obs} = \frac{1}{\lambda} \quad \text{and} \quad \nu_{obs} = \frac{c}{\lambda}$$

Example 2

The infrared spectrum of the molecule $^{75}\text{Br}^{19}\text{F}$ consists of an intense line at 380 cm^{-1} . Calculate the force constant of the molecule.

Solution

$$k = (2\pi c \bar{\nu}_{obs})^2 \mu$$

And so

$$k = (2\pi(3.0 \times 10^8 \text{ m.s}^{-1})(3.8 \times 10^4 \text{ m}^{-1}))^2 \left[\frac{75 \times 19}{75 + 19} \right]$$

$$= 129 \text{ kg.s}^{-2} = 129 \text{ N.m}^{-1}$$

3-4 Hermit polynomials are either Even or Odd functions

Recall that an even function is a function that satisfy the following equation

$$f(x) = f(-x) \quad \text{(even)} \quad 14)$$

And an odd function is the function that satisfy the following equation

$$f(x) = -f(-x) \quad \text{(odd)} \quad 15)$$

The even-odd property of a function is very important and special property and that

- 1)the product of two even or two odd functions is an even function
- 2)the product of an even function with an odd function is odd function.
- 3)The derivative of odd (even) function is even (odd) function.

$$4) \int_{-A}^A f(x)dx = 0 \quad \text{for odd f(x)} \quad 16)$$

$$\psi_n(x) = N_n H_n \left(\alpha^{1/2} x \right) e^{-\alpha x^2 / 2}$$

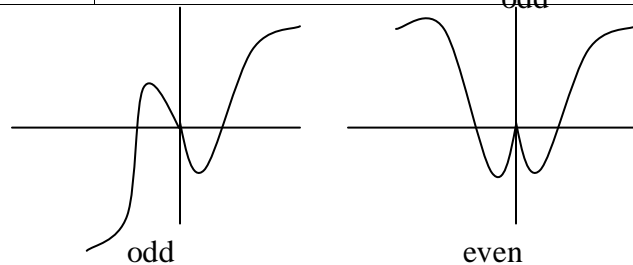
Applying this properties to the harmonic oscillator wave function

$$\psi_n(x) = N_n H_n \left(\alpha^{1/2} x \right) e^{-\alpha x^2 / 2}$$

A) $\psi_n(x)$ is even when n is even number and odd when n is odd number, Since

$H_0(\xi) = 1$ even	$H_1(\xi) = 2\xi$ odd
$H_2(\xi) = 4\xi^2 - 2$ even	$H_3(\xi) = 8\xi^3 - 12\xi$ odd
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$ even	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$ odd

And $e^{-\alpha x^2}$ is even function.
(the properties 1 and 2)



B) $\psi_n^2(x)$ is an even function for all values of n.

$$\text{C) } \int_{-\infty}^{\infty} \psi_n x \psi_n dx = 0 \quad (\text{property 4})$$

$$\text{D) } \int_{-\infty}^{\infty} \psi_m \psi_n dx = 0 \quad \text{or more explicitly}$$

$$\int_{-\infty}^{\infty} H_m \left(\alpha^{1/2} x \right) H_n \left(\alpha^{1/2} x \right) e^{-\alpha x^2 / 2} dx = 0 \quad m \neq n$$

From which we can show that $\psi_0(x)$ and $\psi_1(x)$ are orthogonal

3-4 The average kinetic Energy is equal to the average potential energy of a harmonic oscillator

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n(x) x \psi_n(x) dx = 0 \quad \text{according to the property 4}$$

Which say that the average internuclear separation is the equilibrium bond length l_o .

The average momentum

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_n(x) \left(-i\hbar \frac{d}{dx} \right) \psi_n(x) dx = 0$$

according to the properties 3 and 4

$$\langle x^2 \rangle = \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \left(\frac{\alpha}{\pi} \right)^{1/2} \left[\frac{1}{2\alpha} \left(\frac{\pi}{\alpha} \right)^{1/2} \right] = \frac{1}{2\alpha} = \frac{\hbar}{2(\mu k)^{1/2}}$$

$$\begin{aligned}
\langle p^2 \rangle &= \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \left(-\hbar^2 \frac{d^2}{dx^2} \right) e^{-\alpha x^2/2} dx = \\
&= \left(\frac{\alpha}{\pi} \right)^{1/2} \hbar^2 \int_{-\infty}^{\infty} (\alpha - \alpha^2 x^2) e^{-\alpha x^2} dx = \left(\frac{\alpha}{\pi} \right)^{1/2} \hbar^2 \left\{ \alpha \left(\frac{\alpha}{\pi} \right)^{1/2} - \alpha^2 \left[\frac{1}{2\alpha} \left(\frac{\alpha}{\pi} \right)^{1/2} \right] \right\} \\
&= \frac{\hbar^2 \alpha}{2} = \frac{\hbar(\mu k)^{1/2}}{2}
\end{aligned}$$

For the case of n=1 $\psi_1(x) = \left(\frac{\alpha}{4\pi} \right)^{1/4} \left(2\alpha^{1/2} x \right) e^{-\alpha x^2/2}$

and $\langle x^2 \rangle = \frac{3\hbar}{2(\mu k)^{1/2}}$

the two results for $\langle x^2 \rangle$ suggest that

$$\langle x^2 \rangle = \frac{\hbar}{2(\mu k)^{1/2}} \left(n + \frac{1}{2} \right)$$

Also for $\langle p^2 \rangle = \hbar(\mu k)^{1/2} \left(n + \frac{1}{2} \right)$

Then $\sigma_p^2 \sigma_x^2 = \langle p^2 \rangle \langle x^2 \rangle = \hbar \left(n + \frac{1}{2} \right) \geq \frac{\hbar}{2}$

Which is in accord to the Uncertainty principle of Heisenberg

$$\langle K \rangle = \left\langle \frac{p^2}{2\mu} \right\rangle = \frac{1}{2\mu} \langle p^2 \rangle = \left(\frac{\hbar}{2} \right) \left(\frac{k}{\mu} \right)^{1/2} \left(n + \frac{1}{2} \right) = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) = \frac{E_n}{2}$$

$$\langle U(x) \rangle = \left\langle \frac{kx^2}{2} \right\rangle = \frac{k}{2} \langle x^2 \rangle = \frac{\hbar}{2} \left(\frac{k}{\mu} \right)^{1/2} \left(n + \frac{1}{2} \right) = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) = \frac{E_n}{2}$$

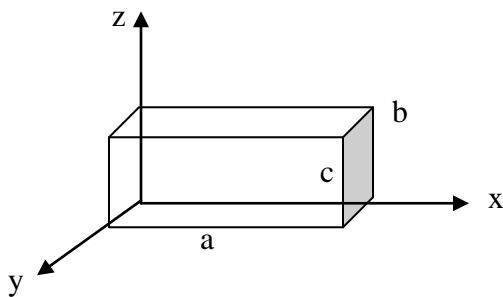
Then we can say that the total energy is equally distributed between the Kinetic and the potential energy.

Chapter 4

Three Dimensional systems

4-1 The Problem of a Particle in a Three-dimensional Box is a simple Extension of the One- dimensional Case

For the case of a three-dimensional version of a particle in a box the particle is confined to lie within a rectangular parallelepiped with sides of lengths a, b, c. The shrodinger equation is given by



$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E \psi(x, y, z) \quad \begin{array}{l} 0 \leq x \leq a \\ 0 \leq y \leq b \\ 0 \leq z \leq c \end{array} \quad 1)$$

The wave function $\psi(x, y, z)$ satisfies the boundary condition that it vanishes at the walls of the box, and so

$$\begin{aligned} \psi(0, y, z) = \psi(a, y, z) &= 0 && \text{For all } y \text{ and } z \\ \psi(x, 0, z) = \psi(x, b, z) &= 0 && \text{For all } x \text{ and } z \\ \psi(x, y, 0) = \psi(x, y, c) &= 0 && \text{For all } x \text{ and } y \end{aligned}$$

With the use of method of separation of variables

$$\psi(x, y, z) = X(x)Y(y)Z(z) \quad \text{A)}$$

to solve Eq.1 we write

$$-\frac{\hbar^2}{2m} \frac{X''}{X} - \frac{\hbar^2}{2m} \frac{Y''}{Y} - \frac{\hbar^2}{2m} \frac{Z''}{Z} = E$$

the three terms of the equation is a function of only x,y,z. Therefore, where each term must be a constant to be valid for all values of x, y, or z. Thus

$$E_x + E_y + E_z = E$$

Where E_x, E_y, E_z are constants given by

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{X''}{X} &= E_x \\ -\frac{\hbar^2}{2m} \frac{Y''}{Y} &= E_y \\ -\frac{\hbar^2}{2m} \frac{Z''}{Z} &= E_z \end{aligned} \quad 2)$$

Satisfying the boundary conditions

$$X(0) = X(a) = 0$$

$$Y(0) = Y(b) = 0$$

$$Z(0) = Z(c) = 0$$

Following the same development as in the one dimensional case

$$\begin{aligned} X(x) &= A_x \sin \frac{n_x \pi x}{a} & n_x &= 1, 2, 3, \dots \\ Y(y) &= A_y \sin \frac{n_y \pi y}{b} & n_y &= 1, 2, 3, \dots \\ Z(z) &= A_z \sin \frac{n_z \pi z}{c} & n_z &= 1, 2, 3, \dots \end{aligned} \quad 3)$$

According to the Eq.A the solution of Eq.1 is given by

$$\psi(x, y, z) = A_x A_y A_z \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

The normalization constant $A_x A_y A_z$ is found from

$$\int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x, y, z) \psi(x, y, z) = 1$$

$$A_x A_y A_z = \left(\frac{8}{abc} \right)^{1/2} \quad \text{one particle in a box}$$

Thus the wave function of a particle in three-dimensional box is given by

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{8}{abc} \right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad 4)$$

If we substitute Eq.4 into Eq.1 we can find

$$E_{n_x n_y n_z} = \left(\frac{h^2}{8m} \right) \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad 5)$$

4-2 The average position of a particle in a three dimensional box is at the center of the box

The position operator in three dimensions is

$$\hat{\mathbf{R}} = \hat{X} \mathbf{i} + \hat{Y} \mathbf{j} + \hat{Z} \mathbf{k}$$

and the average position is given by

$$\langle \mathbf{r} \rangle = \int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x, y, z) \hat{\mathbf{R}} \psi(x, y, z) = \mathbf{i} \langle x \rangle + \mathbf{j} \langle y \rangle + \mathbf{k} \langle z \rangle$$

Let us evaluate $\langle x \rangle$ first using Eq.4 we have

$$\langle x \rangle = \left[\left(\frac{2}{a} \right) \int_0^a x \sin^2 \frac{n_x \pi x}{a} dx \right] \left[\left(\frac{2}{b} \right) \int_0^b \sin^2 \frac{n_y \pi y}{b} dy \right] \left[\left(\frac{2}{c} \right) \int_0^c \sin^2 \frac{n_z \pi z}{c} dz \right]$$

The second and the third integrals are unity by normalization conditions of a particle in one-dimensional box. The first integral is just $\langle x \rangle$ for a particle in

one dimensional box $\langle x \rangle = \frac{a}{2}$. The calculations for $\langle y \rangle$ and $\langle z \rangle$ are similar and

we see that

$$\langle \mathbf{r} \rangle = \frac{a}{2} \mathbf{i} + \frac{b}{2} \mathbf{j} + \frac{c}{2} \mathbf{k}$$

Thus The average position of a particle in a three dimensional box is at the center of the box.

4-3 The average momentum of a particle in a three-dimensional box is zero (prove)

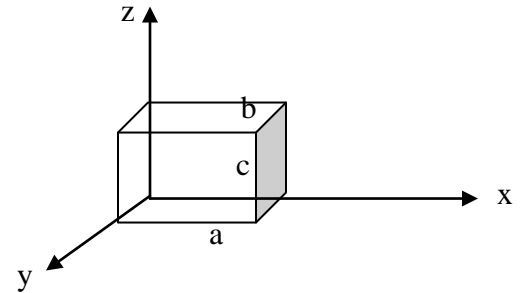
$$\hat{\mathbf{P}} = -i\hbar \left(\frac{\partial}{\partial x} \mathbf{i} + \frac{\partial}{\partial y} \mathbf{j} + \frac{\partial}{\partial z} \mathbf{k} \right)$$

$$\langle \mathbf{P} \rangle = \int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x, y, z) \hat{\mathbf{P}} \psi(x, y, z) = 0$$

4-4 Degeneracies of the energy levels for a particle in a three-dimensional box

An interesting feature of a particle in a three-dimensional box Occurs when the sides of the box is equal such that a=b=c. In such case

$$E_{n_x n_y n_z} = \left(\frac{h^2}{8ma^2} \right) (n_x^2 + n_y^2 + n_z^2)$$



And so the lowest level here is nondegenerate

$$E_{111} = \frac{3h^2}{8ma^2} \neq E_{222} = \frac{12h^2}{8ma^2}$$

but the second level is threefold degenerate (degeneracy arises because of symmetry)

$$E_{112} = E_{121} = E_{211} = \frac{6h^2}{8ma^2}$$

	(n_x, n_y, n_z)	Degeneracy
19	_____	
18	_____	
16	_____	
14	_____	(321)(312)(231)(132)(123)(213) 6
12	_____	(222) 1
11	_____	(311)(131)(113) 3
9	_____	(221)(212)(122) 3
6	_____	(211)(121)(112) 3
3	_____	(111) 1
0	_____	

It is a general theorem in quantum mechanics. That degeneracies are the results of underlying symmetry and that degeneracies are lifted when the symmetry is broken.

4-5 If the Hamiltonian is separable then its Eigenfunction is a product of simpler Eigenfunctions

Consider the simple case in which we say that the Hamiltonian is separable in the case of two coordinates

$$\hat{H} = \hat{H}_1(x) + \hat{H}_2(y) \quad 6)$$

with

$$\hat{H} \psi(x, y) = E \psi(x, y) \quad 7)$$

$$\hat{H}_1 \psi_1(x) = E_1 \psi_1(x) \quad 8)$$

$$\hat{H}_2 \psi_2(y) = E_2 \psi_2(y)$$

Substitute Eq.8 into Eq.7 to obtain

$$\hat{H} \psi(x, y) = \left(\hat{H}_1 + \hat{H}_2 \right) \psi_1(x) \psi_2(y) = \left(\hat{H}_1 \right) \psi_1(x) \psi_2(y) + \left(\hat{H}_2 \right) \psi_1(x) \psi_2(y)$$

Because $\hat{H}_1(x)$ operates only upon $\psi_1(x)$ and $\hat{H}_2(y)$ operates only upon $\psi_2(y)$, we can write

$$\begin{aligned} & \hat{H} \psi(x, y) \\ &= \psi_2(y) \hat{H}_1 \psi_1(x) + \psi_1(x) \hat{H}_2 \psi_2(y) \\ &= E_1 \psi_2(y) \psi_1(x) + E_2 \psi_1(x) \hat{H}_2 \psi_2(y) \\ &= (E_1 + E_2) \psi_2(y) \psi_1(x) \\ &= E \psi(x, y) \end{aligned} \quad 9)$$

Thus we reach that if \hat{H} is separable, that is, if \hat{H} can be written as a sum of independent terms involving separate coordinates, then the eigenfunction of

\hat{H} is a product of the Eigenfunctions of \hat{H}_1 and \hat{H}_2 and the eigenvalues is the sums of the eigenvalues of \hat{H}_1 and \hat{H}_2 .

Example 1

Consider a two dimensional harmonic oscillator whose potential energy is given by

$$U(x, y) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2$$

Derive the wave functions and the energy levels of the system.

Solution

The Hamiltonian for this system is

$$\hat{H} = \frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2$$

And so \hat{H} is of the form

$$\hat{H} = \hat{H}_x + \hat{H}_y$$

$$\left(\frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} \right) + \frac{1}{2}k_x x^2 \right) + \left(\frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial y^2} \right) + \frac{1}{2}k_y y^2 \right)$$

Since the Hamiltonian is separable then

$$\psi(x, y) = \psi_x(x)\psi_y(y) \quad \text{And} \quad E = E_x + E_y$$

using the results of the harmonic oscillator in the last chapter then

$$E = h\nu_x \left(n_x + \frac{1}{2} \right) + h\nu_y \left(n_y + \frac{1}{2} \right)$$

Where

$$\nu_x = \frac{1}{2\pi} \left(\frac{k_x}{\mu} \right)^{1/2} \quad \text{and} \quad \nu_y = \frac{1}{2\pi} \left(\frac{k_y}{\mu} \right)^{1/2}$$

and the wave functions are

$$\psi_{n_x n_y}(x, y) = \psi_{n_x}(x)\psi_{n_y}(y) \quad \text{Where}$$

$$\psi_{n_x}(x) = \left[\frac{1}{(2^{n_x} n_x!)^{1/2}} \left(\frac{\alpha_x}{\pi} \right) \right]^{1/2} H_{n_x}(\alpha_x^{1/2} x) e^{-\alpha_x x^2/2}$$

$$\psi_{n_y}(y) = \frac{1}{(2^{n_y} n_y!)^{1/2}} \left(\frac{\alpha_y}{\pi} \right)^{1/4} H_{n_y}(\alpha_y^{1/2} y) e^{-\alpha_y y^2/2}$$

4-6 System of two particles

For a system of two particles that interacting through a potential energy that depends only on their relative separation. If we let X,Y and Z be the center of mass coordinates and x,y and z be the relative coordinates , then the total energy of the system is given by

$$E = \frac{M}{2} \left(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2 \right) + \frac{\mu}{2} \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2 \right) + U(x, y, z) \quad (10)$$

this equation can be written in terms of momenta rather than velocities

$$E = \frac{1}{2M} (P_x^2 + P_y^2 + P_z^2) + \frac{1}{2\mu} (P_x^2 + P_y^2 + P_z^2) + U(x, y, z) \quad (11)$$

The quantum mechanical Hamiltonian operator corresponding to it is given by

$$\hat{H} = \frac{-\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x, y, z) \quad (12)$$

and we can see that this equation is separable and can be written as

$$\hat{H} = \hat{H}_1(X, Y, Z) + \hat{H}_2(x, y, z) \quad (13)$$

where

$$\hat{H}_1 = \frac{-\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) \quad \text{and} \quad \hat{H}_2 = \frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x, y, z)$$

Consequently, the total wave function for this motion factors into

$$\psi(X, Y, Z, x, y, z) = \psi_{trans}(X, Y, Z)_{rel} \psi(x, y, z) \quad (14)$$

and the total energy is

$$E = E_{trans} + E_{rel} \quad (15)$$

trans stand for translation of the center of mass and *rel* stands for relative motion. The transnational motion represents just the rectilinear motion of the center of mass and is of no interest. The interesting part is the relative motion which is governed by the potential energy $U(x, y, z)$.

The shrodinger equation for the relative motion is given by

$$\left(\frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x, y, z) \right) \psi(x, y, z) = E \psi(x, y, z)$$

or

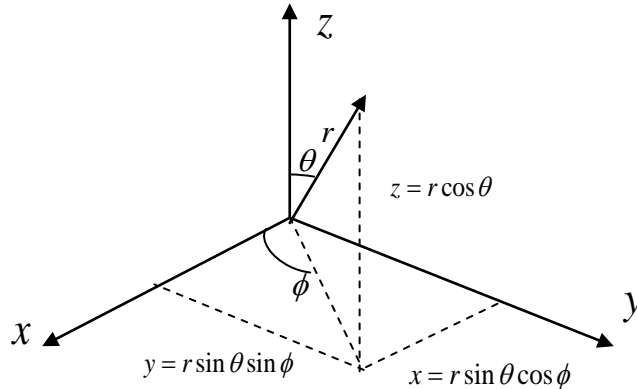
$$\frac{-\hbar^2}{2\mu} \nabla^2 \psi + U \psi = E \psi \quad (16)$$

Where the $\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$ is the Laplacian operator To convert ∇^2 in spherical coordinates we need the equations that relates Cartesian coordinates and spherical coordinates

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

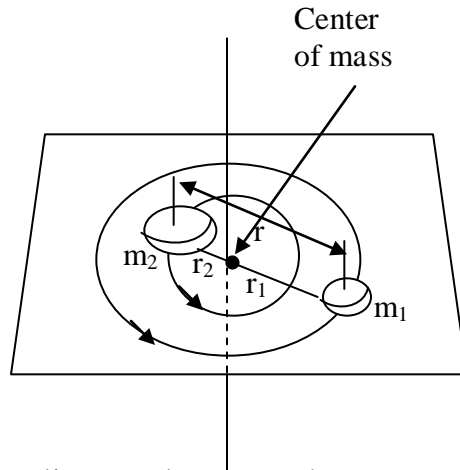
$$z = r \cos \theta$$



$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)_{r, \theta} \quad (17)$$

4-7 Rotating diatomic molecule

The model of rotating diatomic molecule is represented by two point masses m_1 and m_2 at fixed distances r_1 and r_2 from their center of masses,



Because the distance between the two masses is fixed, this model is referred to as rigid rotator model. Although the diatomic molecule vibrates as it rotates, the vibrational amplitude is small compared to the bond length, and so it is a good approximation to consider the bond length to be fixed.

According to the theorem concerning center of mass and relative coordinates, we can treat a rigid rotator as having one mass fixed at the origin with another mass (the reduced mass μ) rotating about the origin at affixed distance r .

$$m_1 r_1 = m_2 r_2 \quad (18)$$

$$r = r_1 + r_2 \quad (19)$$

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{And} \quad r_2 = \frac{m_1}{m_1 + m_2} r \quad (20)$$

The kinetic energy of the rigid rotator is

$$K = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \quad (21)$$

$$\text{Where } v_1 = r_1 \omega \quad \text{and} \quad v_2 = r_2 \omega \quad (22)$$

where ω is the angular velocity.

$$\begin{aligned} K &= \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2 \\ &= \frac{1}{2} \left(m_1 r_1^2 + m_2 r_2^2 \right) \omega^2 \end{aligned}$$

Substituting for r_1 and r_2 from above and with the use of the

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Then the kinetic energy can be written as

$$k = \frac{1}{2} I \omega^2 \quad (23)$$

Where $I = \mu r^2$ is the moment of inertia.

The angular momentum is given by

$$L = I \omega \quad (24)$$

And then we can write the kinetic energy in terms of the angular momentum is given by

$$k = \frac{L^2}{2I} \quad (25)$$

The Hamiltonian operator of a rigid rotator is just the kinetic energy operator

$$\hat{H} = \frac{-\hbar^2}{2I} \nabla^2 \quad (26)$$

Because one of the two masses of a rigid rotator is fixed at the origin we shall express ∇^2 in spherical coordinate

$$\hat{H} = \frac{-\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] \quad (27)$$

As we can see that there is no term in the Laplacian operator involving the partial derivative with respect to r. This is because r is fixed in the rigid rotator model.

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] \quad (28)$$

The orientation of a rigid rotator is completely specified by the two angles θ and ϕ , and so the rigid rotator wave function depend on these two variables.

The rigid rotator wave function are customarily denoted by $Y(\theta, \phi)$, and so the shrödinger equation for a rigid rotator reads

$$\hat{H} Y(\theta, \phi) = E Y(\theta, \phi)$$

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] Y(\theta, \phi) = EY(\theta, \phi) \quad (29)$$

If we multiply the equation by $\sin^2 \theta$ and let $\beta = \frac{2IE}{\hbar^2}$ we find the partial differential equation

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \left(\frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) + \beta \sin^2 \theta Y(\theta, \phi) = 0 \quad (30)$$

To solve the partial differential equation we use the method of separation of variables

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad (31)$$

If we substitute into Eq.30 Above and then divide by $\Theta(\theta)\Phi(\phi)$, we find

$$\frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2 \theta + \frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} = 0 \quad (32)$$

Because θ and ϕ are independent variables, we must have that

$$\frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2 \theta = m^2 \quad (33)$$

$$\text{Where } \frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad (34)$$

and m^2 is a constant.

The solution to the Eq.34 is relatively easy

$$\Theta(\phi) = A_m e^{im\phi} \quad \text{and} \quad (35)$$

$$\Theta(\phi) = A_{-m} e^{-im\phi}$$

The requirement that $\Phi(\phi)$ is continuous

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

By substituting into the above two equations we find that

$$A_m e^{im(\phi+2\pi)} = A_m e^{im\phi}$$

$$A_{-m} e^{-im(\phi+2\pi)} = A_{-m} e^{-im(\phi)}$$

From the two equations, it implies that

$$e^{-i2\pi m} = 1$$

In terms of sine and cos

$$\cos(2\pi m) \pm i \sin(2\pi m) = 1$$

Then it implies that $m = 0, \pm 1, \pm 2, \pm 3, \dots$, because $\cos(2\pi m) = 1$ and $\sin(2\pi m) = 0$ for $m = 0, \pm 1, \pm 2, \pm 3, \dots$

The two equations above can be written in the form

$$\Phi(\phi) = A_m e^{im\phi} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \quad (36)$$

Example:

Prove that the normalization constant $A_m = \frac{1}{(2\pi)^{1/2}}$

When Eq.33 is solved it turns out

$$\beta = l(l-1) \quad l = 0, 1, 2, \dots \quad (37)$$

Using the definition of $\beta = \frac{2IE}{\hbar^2}$ then

$$E_l = \frac{\hbar^2}{2I} l(l-1) \quad l = 0, 1, 2, \dots \quad (38)$$

The differential equation (Eq.33) for $\Theta(\theta)$ is not easy to solve and like the solution of vibrating molecule (Hermite's equation), the solution is obtained by power series method. To solve Eq.33 it is convenient to let $x = \cos \theta$ and let $\Theta(\theta) = P(x)$. Eq.33 then becomes

$$(1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2} \right] P(x) = 0 \quad (39)$$

We have used the fact that $\beta = l(l+1)$. The above equation is known as *Legendre's Equation*. The solution to this equation is determined according to the value of m

If $m=0$

The solutions are known as Legendre's polynomials and are denoted by $P_l(x)$ The first few Legendre Polynomials,

$P_0(x) = 1$
$P_1(x) = x$

$P_2(x) = \frac{1}{2}(3x^2 - 1)$
$P_3(x) = \frac{1}{2}(5x^3 - 3x)$
$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$

Example

Prove that the first Legendre polynomials satisfy Eq.39.

Example

Prove that the Legendre polynomials are normalized by the general relation

$$\int_{-1}^1 dx p_l(x) p_n(x) = \int_0^\pi d\theta \sin \theta p_l(\cos \theta) p_n(\cos \theta) = \frac{2}{2l+1} \delta_{ln}$$

As you see the factor $d\theta \sin \theta$ is the “ θ ” part of the spherical $d\tau = r^2 \sin \theta dr d\theta d\phi$
And that the normalization constant of $p_l(x)$

$$N_l = \left(\frac{2l+1}{2} \right)^{1/2} \quad 40)$$

If $m \neq 0$

The solution is known as the associated legendre functions denoted by

$$P_l^{|m|}(x) = (1-x^2)^{|m|/2} \frac{d^m}{dx^m} P_l(x) \quad 41)$$

The first few associated legendre functions are listed below

$P_0^0(x) = 1$
$P_1^0(x) = x = \cos \theta$
$P_1^1(x) = \frac{1}{2}(1-x^2)^{1/2} = \sin \theta$
$P_2^0(x) = \frac{1}{2}(3x^2 - 1) = \frac{1}{2}(3 \cos^2 \theta - 1)$
$P_2^1(x) = 3x(1-x^2)^{1/2} = 3 \cos \theta \sin \theta$
$P_2^2(x) = 3(1-x^2) = 3 \sin^2 \theta$
$P_3^0(x) = \frac{1}{2}(5x^3 - 3x) = \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta)$
$P_3^1(x) = \frac{3}{2}(5x^2 - 1)(1-x^2)^{1/2} = \frac{3}{2}(5 \cos^2 \theta - 1) \sin \theta$
$P_3^2(x) = 15x(1-x^2) = 15 \cos \theta \sin^2 \theta$
$P_3^3(x) = 15(1-x^2)^{3/2} = 15 \sin^3 \theta$

Example

Prove that P_1^1 and P_2^1 are orthogonal.

Example

Prove that the Legendre polynomials are normalized by the general relation

$$\int_{-1}^1 dx p_l^{|m|}(x) p_n^{|m|}(x) = \int_0^\pi d\theta \sin \theta p_l^{|m|}(\cos \theta) p_n^{|m|}(\cos \theta) = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ln}$$

As you see the factor $d\theta \sin \theta$, is the “ θ ” part of the spherical $d\tau = r^2 \sin \theta dr d\theta d\phi$

And that the normalization constant of $p_l(x)$

$$N_{lm} = \left[\left(\frac{2l+1}{2} \right) \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \quad (42)$$

Returning to the original problem now, Eq.31 the rigid rotator wave function

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) = P_l^{|m|}(\cos \theta)\Phi(\phi)$$

$$Y_l^m(\theta, \phi) = \left[\left(\frac{2l+1}{4\pi} \right) \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{im\phi} \quad (43)$$

The first few spherical harmonics rotators is listed in the table below. In summary the shrodinger equatoion for a rigid rotator is

$$\hat{H} Y_l^m(\theta, \phi) = \frac{\hbar^2 l(l+1)}{2I} Y_l^m(\theta, \phi) \quad (44)$$

With \hat{H} given by Eq.27. Since from Eq.28 \hat{L}^2 differs from \hat{H} by the constant factor $2I$ only then

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi) \quad (45)$$

That is to say the square of the angular momentum can have only the values given by

$$\hat{L}^2 = \hbar^2 l(l+1) \quad l = 0,1,2,3,\dots \quad (46)$$

$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$
$Y_1^0 = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$
$Y_1^1 = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{i\phi}$

$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1)$
$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi}$
$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi}$
$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{2i\phi}$
$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi}$

Rigid rotator angular momentum

	Classical definition	Quantum operators	Quantum definition
Angular momentum (r x p)	$l_x = yp_z - zp_y$	\hat{L}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$l_y = zp_x - xp_z$	\hat{L}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$l_z = xp_y - yp_x$	\hat{L}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

It is straightforward to convert the partial differentiation into spherical coordinates to obtain

$$\begin{aligned} \hat{L}_x &= -i\hbar \left(-\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_y &= -i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial \phi} \end{aligned} \quad 47)$$

The last one of equation 47 is simple and applying the equation 45 we find

$$\hat{L}_z (e^{im\phi}) = -i\hbar \frac{\partial e^{im\phi}}{\partial \phi} = m\hbar e^{im\phi} \quad (48)$$

$$\hat{L}_z \Phi_m(\phi) = m\hbar \Phi_m(\phi) \quad (49)$$

$$\hat{L}_z Y_l^m(\theta, \phi) = N_{lm} \hat{L}_z P_l^{|m|}(\cos \theta) e^{im\phi} = N_{lm} P_l^{|m|}(\cos \theta) \hat{L}_z e^{im\phi} = \hbar m Y_l^m(\theta, \phi) \quad (50)$$

This Equation shows that the only possible values that L_z can be observed to have are integral multiples of \hbar . It also shows that $Y_l^m(\theta, \phi)$ are eigenfunctions of \hat{L}_z as well as \hat{L}^2 (see Eq. 45), which implies that the two operators commute or

$$\left[\hat{L}^2, \hat{L}_z \right] = 0 \quad (\text{Prove})$$

It follows from Eq.50 that

$$\hat{L}_z^2 Y_l^m(\theta, \phi) = m^2 \hbar^2 Y_l^m(\theta, \phi)$$

And because

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

And

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

then

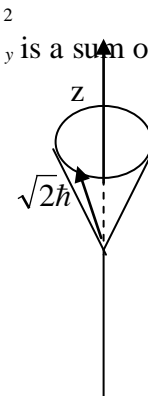
$$\left(\hat{L}^2 - \hat{L}_z^2 \right) Y_l^m(\theta, \phi) = \left(\hat{L}_x^2 + \hat{L}_y^2 \right) Y_l^m(\theta, \phi) = [l(l+1) - m^2] \hbar^2 Y_l^m(\theta, \phi) \quad (51)$$

Thus, the observed values of $L_x + L_y$ are $[l(l+1) - m^2] \hbar^2$, and since $L_x + L_y$ is a sum of two squared terms, it cannot be negative

$$[l(l+1) - m^2] \hbar^2 \geq 0$$

$$\text{or that } l(l+1) \geq m^2$$

$$\text{and } |m| \leq l \quad \longrightarrow \quad m = 0, \pm 1, \pm 2, \pm 3, \dots, l \quad (52)$$



For the case of $l=1$, $m=0,\pm 1$ and so

$$\hat{L}^2 Y_l^m(\theta, \phi) = 2\hbar^2 Y_l^m(\theta, \phi) \Rightarrow |L| = (L^2)^{1/2} = \sqrt{2}\hbar \quad 53)$$

$$\hat{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi) \Rightarrow L_z = -\hbar, 0, +\hbar$$

Note that the maximum value of L_z is less than $|L|$, which implies that L_z cannot point in

the same direction as L . This is illustrated in the above figure which shows $L_z = \hbar$ and $|L| = \sqrt{2}\hbar$. This result might be familiar with the condition of the magnetic quantum number of the hydrogen atom.