Engineering Chemistry - 1
Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras
Lecture - 5
Module 1: Atoms and Molecules
Harmonic Oscillator (Continued)

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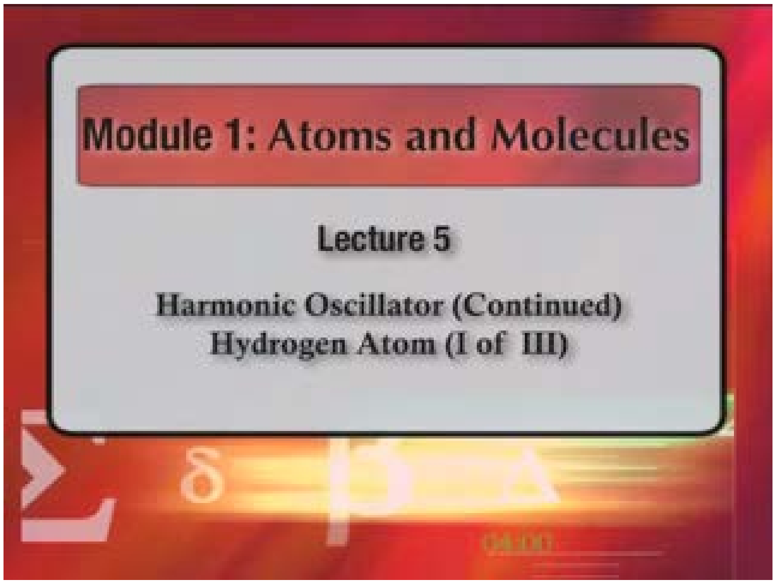

Module 1: Atoms and Molecules

Lecture 5

Harmonic Oscillator (Continued)
Hydrogen Atom (I of III)

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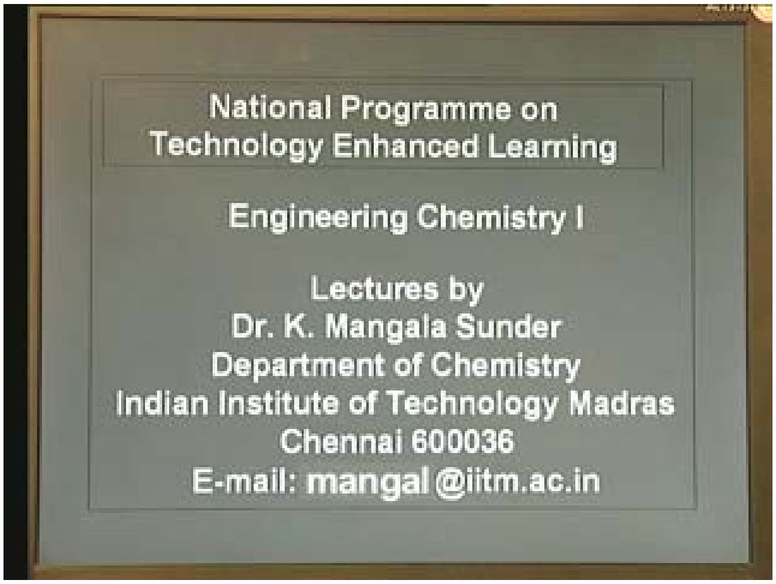

National Programme on
Technology Enhanced Learning

Engineering Chemistry I

Lectures by
Dr. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology Madras
Chennai 600036
E-mail: mangal @iitm.ac.in

Welcome back to the lecture series on the Engineering Chemistry. This is a series of lectures given on basic Chemistry under the auspices of the National Programme on Technology Enhanced Learning funded by the Ministry of Human Resource Development. Today we will continue with the lecture on Harmonic Oscillator, this is the 5th lecture. In the last lecture we talked about how to solve or how to study the solutions of Harmonic Oscillator from the point of view of Quantum Mechanics.

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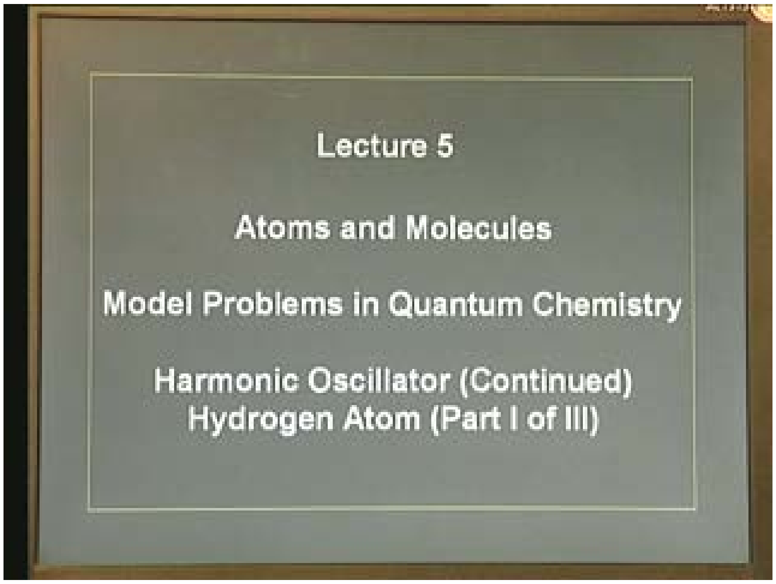

Lecture 5

Atoms and Molecules

Model Problems in Quantum Chemistry

Harmonic Oscillator (Continued)
Hydrogen Atom (Part I of III)

We will continue with the Harmonic Oscillator. We will look at the solutions and graphically we shall represent the functions that were written down in the last lecture. You might recall that these were written as Hermite polynomials multiplied by a Gaussian function that is an $\exp(-x^2)$ type functions. So graphically we will see how these functions are represented and the squares of these functions. We will also see what represents the probability densities.

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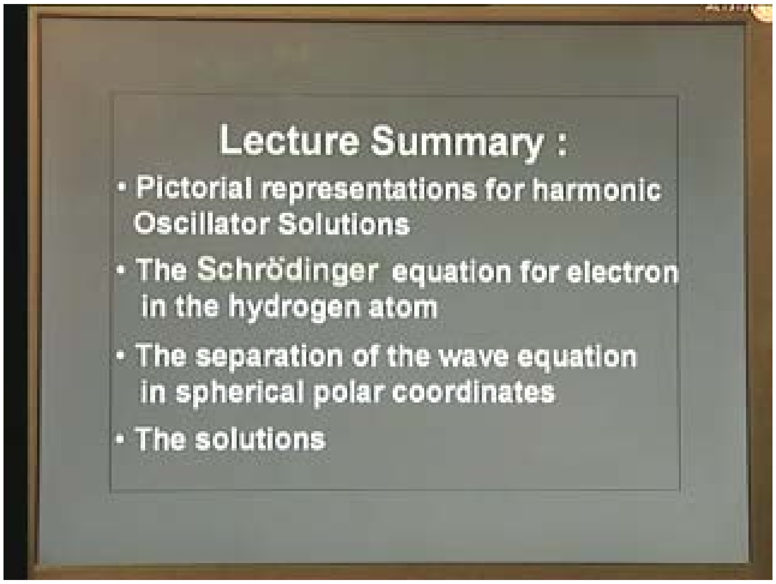

Lecture Summary :

- Pictorial representations for harmonic Oscillator Solutions
- The Schrödinger equation for electron in the hydrogen atom
- The separation of the wave equation in spherical polar coordinates
- The solutions

The summary of today's lecture as organized for the rest of this lecture is like this: We shall discuss pictorial representation of the Harmonic Oscillator solutions and then we shall introduce the Schrödinger equation for electron in the hydrogen atom. This is of fundamental interest to chemist. Depending on the time we will try and see if we can proceed towards the separation of the wave equation in spherical polar coordinates. And the solutions of course will not be done today but will be a part of a series of lectures on the hydrogen atom. Let me continue with the Harmonic Oscillator.

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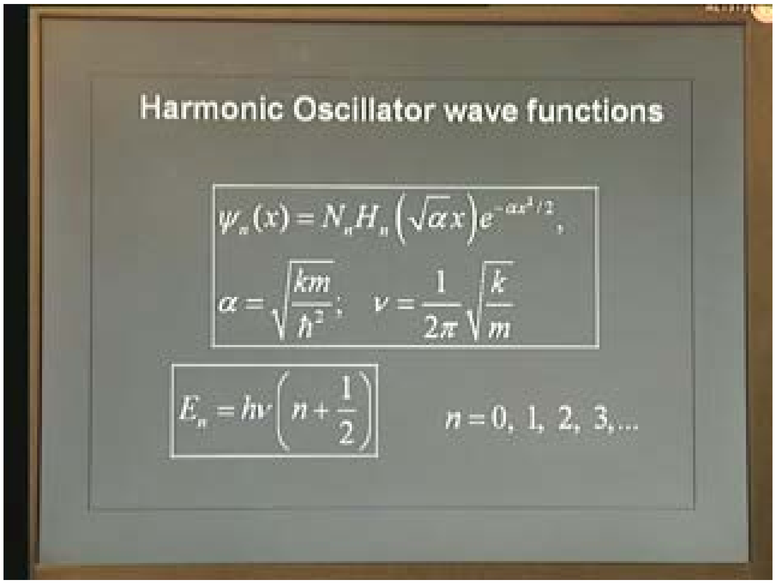

Harmonic Oscillator wave functions

$$\boxed{\begin{array}{l}\psi_n(x) = N_n H_n\left(\sqrt{\alpha}x\right)e^{-\alpha x^2/2}, \\ \alpha = \sqrt{\dfrac{km}{\hbar^2}}; \quad \nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}\end{array}}$$

$$\boxed{E_n = h\nu\left(n + \frac{1}{2}\right)} \qquad n = 0, 1, 2, 3, \ldots$$

Recollect from the last lecture that we wrote the Harmonic Oscillator solutions $\psi_n(x)$ as a normalization constant N_n and the Hermite polynomial $H_n(\sqrt{\alpha}\, x)$ where the α was defined in terms of the constants which appear in the Hamiltonian $\sqrt{km/\hbar^2}$ where k is the force constant and m is the mass of the oscillator, ħ is the Planck's constant/2π that is h/2π and $\exp(-\alpha x^2/2)$ here. So the whole equation is $\psi_n(x) = N_n\, H_n(\sqrt{\alpha}\, x) \exp(-\alpha x^2/2)$. And remember the solutions for this problem, the quantized solutions or the energy levels which are quantized are given by the formula $h\upsilon(n + ½)$ and υ was given as $½\pi\sqrt{k/m}$. The quantum numbers, n were given from the solutions as having the possible values of 0, 1, 2, 3, etc including the value 0.

The simplest of these solutions when we did $\psi_0(x)$ excluding the normalization constant right now and including the Hermite polynomial and the $\exp(-\alpha x^2/2)$. The Hermite polynomial for the 0th order which is a constant so you recall that the ground state Harmonic Oscillator solution was $\exp(-\alpha x^2/2)$. Here ground state referring to the fact that the quantum number is the lowest and this is the least possible energy that can be associated with the Harmonic Oscillator if we accept that the Harmonic Oscillator is quantum mechanical, if we accept that the Schrödinger equation governs the motion of the Harmonic Oscillator both in space and in time we are only looking at the spatial solutions.

We accept that we come up with the requirement that the energies for the Harmonic Oscillator are non zero even when the quantum number is 0. A solution $\exp(-\alpha x^2/2)$, you remember that the limits of x where from $+\infty$ to $-\infty$. Therefore a plot of this function if we plot symmetrically on both side $x = 0$ we plot this $\exp(-\alpha x^2/2)$ as an even function meaning that $\psi_0(x) = \psi_0(-x)$. It is an even function and the maximum value of this plot is the constant associated with the ground state wave function, the normalization constant and the value of the function $\exp(-\alpha x^2/2)$ at $x = 0$ is 1. Therefore that is the maximum value of this plot. And the function per say does not any 0s anywhere except at both the extremes namely at $x = +\infty$ and $x = -\infty$. The function, $\exp(-\alpha x^2/2)$ is a very well known function in Mathematics, in Physics, in distributions, in the theory of distribution and it is known as the Gaussian function or Bell shaped function, in colloquial language we can call it as a Bell− shaped function.

The Gaussian function can be normalized. when you talk about this normalization what you mean is $\int\psi_0(x)\, \psi_0(x)dx$ since these functions are real we do not need to worry about complex conjugation the domain of the harmonic oscillation is $+\infty$ to $-\infty$, this is the normalization integral for the Harmonic Oscillator and this whole should be set to 1. The Gaussian function can be integrated quiet easily $\int\exp(-\alpha x^2)dx$ (with in $+\infty$ to $-\infty$) when you take the square of $\psi_0(x)$. This should to be set to 1 therefore the value that you get out for this integral which is $\sqrt{\pi/\alpha}$ this has to to be taken into account in the definition of $\psi_0(x)$ so that this integral is equal to 1. If we multiply this function $\psi_0(x)$ by $(\alpha/\pi)^{¼}$ then $\int\psi_0(x)\psi_0(x)dx$ (between $+\infty$ to $-\infty$) will be equals to 1 and therefore this is normalization constant for this problem for this particular wave function. Likewise you have to obtain the normalization constants for each one of these Harmonic Oscillator eigenfunctions.

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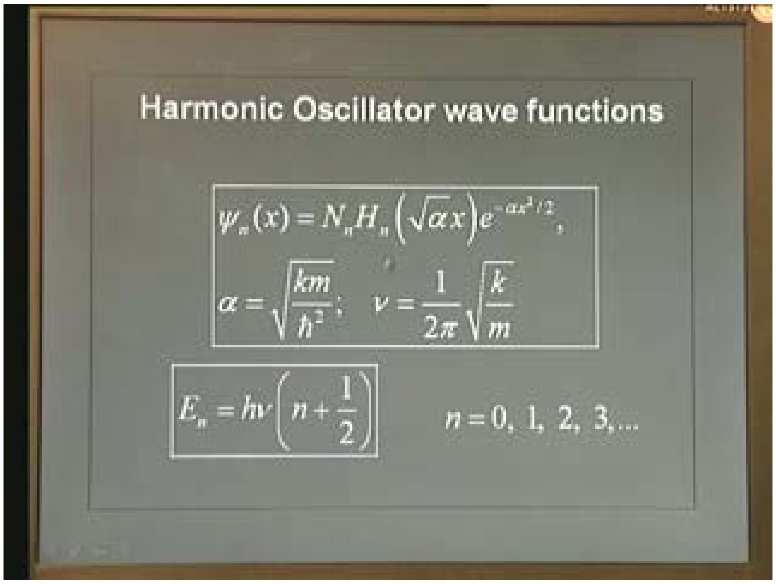

Harmonic Oscillator wave functions

$$\boxed{\begin{array}{l}\psi_n(x) = N_n H_n\left(\sqrt{\alpha}x\right)e^{-\alpha x^2/2}, \\ \alpha = \sqrt{\dfrac{km}{\hbar^2}}; \quad \nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}\end{array}}$$

$$\boxed{E_n = h\nu\left(n+\frac{1}{2}\right)} \qquad n = 0,\ 1,\ 2,\ 3, \ldots$$

The summary of the Harmonic Oscillator wave functions are given here for you to refresh. The wave function has the normalization constant $N_{n,}$ Hermite polynomial $H_n(\sqrt{\alpha}\ x)$, exponential $\exp(-\alpha x^2/2)$ and the energy is written as $E_n = h\upsilon(n + ½)$.

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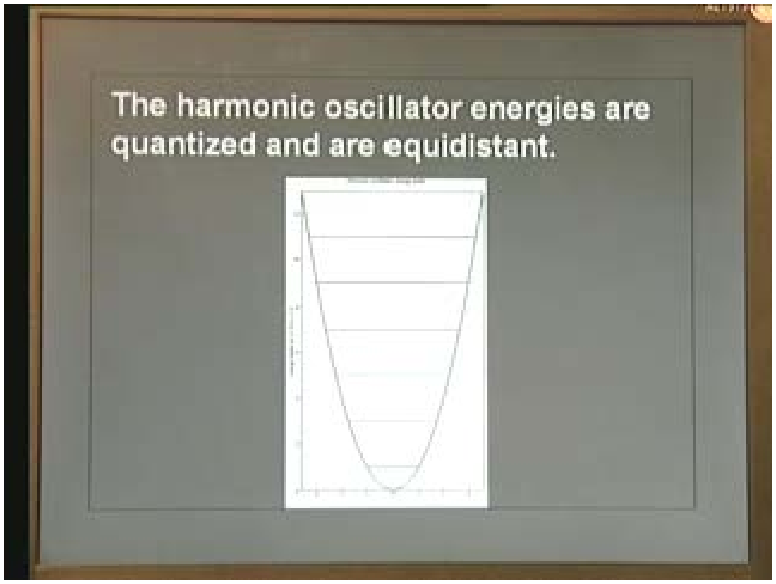

The harmonic oscillator energies are quantized and are equidistant.

The one other thing that was emphasized in the last lecture was that the Harmonic Oscillator energies as n increases from 0, 1, 2, 3, 4 etc are equally spaced for n = 0 it is ½$h\upsilon$, for n = 1 it is 3½$h\upsilon$, for n = 2 it is 5½$h\upsilon$ and so on. So, if you look at the particular picture the Harmonic Oscillator energies are plotted here and this is the classical potential energy curve in this picture it does not have any role y-axis is the energy axis and x-axis is only to mark the classical spread of the potential energy the x value and you see the lines here representing the Harmonic Oscillator energies $\frac{1}{2}h\upsilon$, $3\frac{1}{2}h\upsilon$, $5\frac{1}{2}h\upsilon$ and $7\frac{1}{2}h\upsilon$ and so on. So the distance between any pair of nearby energy levels is the same and that is equal to $h\upsilon$ that is $E_n - E_{n-1}$ is $h\upsilon$ for all n values, n – 1 should be 0 so the lowest level is E_0. If you go E_0, E_1, E_2 all of them are equidistant.

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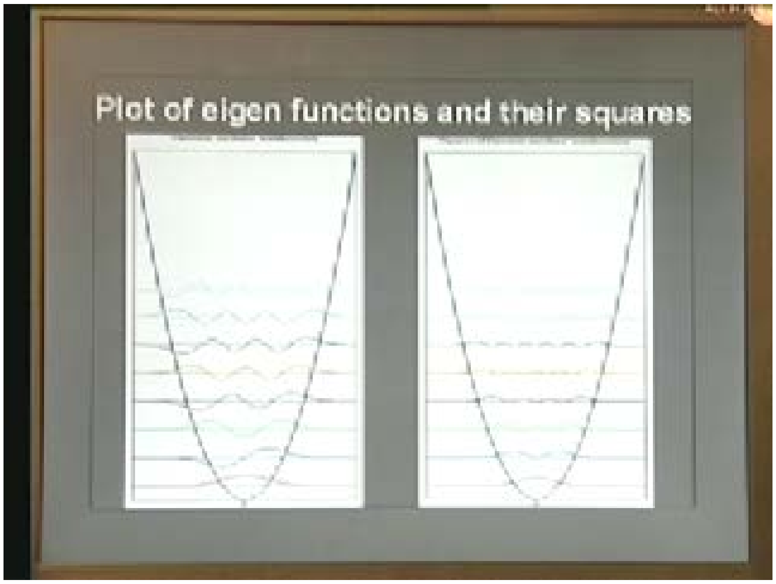

Plot of eigen functions and their squares

Now, let us give the graphical representations for these functions for higher that is the wave functions for n = 1, 2, 3 etc are what you call as the excited states of the Harmonic Oscillator. Let us look at the solution for H_1, $H_1(\sqrt{\alpha}\, x)$ is $2(\sqrt{\alpha}\, x)$. Therefore the wave function $\psi_1(x)$ is without the normalization constant is $2x \exp(-\alpha x^2/2)$. This is the first excited state wave function we call it excited state when the quantum number is not the lowest, is not the least value, when the quantum number is 1 or 2 or 3 etc are called first excited, second excited, third excited and so on of the Harmonic Oscillator.

The first state the wave function is given by $2x \exp(-\alpha x^2/2)$, if you were to plot this you see that $\psi_1(x)$ and $\psi_1(-x)$ are related to each other not by the above exponential factor this is the same because it is x square but there is x so that the relation is minus, so $\psi_1(x) =- \psi_1(-x)$, this is the odd function. Therefore with respect to x = 0 whatever is the way the graph is on the positive x will be the exact negative of that in the $x < 0$ domain. (Refer Slide Time: 13:33 min). So again with x = 0 if you plot this function because it is multiplied by x at x = 0 the function is 0 and the function is negative therefore it goes to 0 as x goes towards $-\infty$ from the negative side and it goes to 0 on the positive side from positive values. If you draw this carefully there is no inflection here. So this is a continuous function of x, $\psi_1(x) = 2x \exp(-\alpha x^2/2)$ appears like this.

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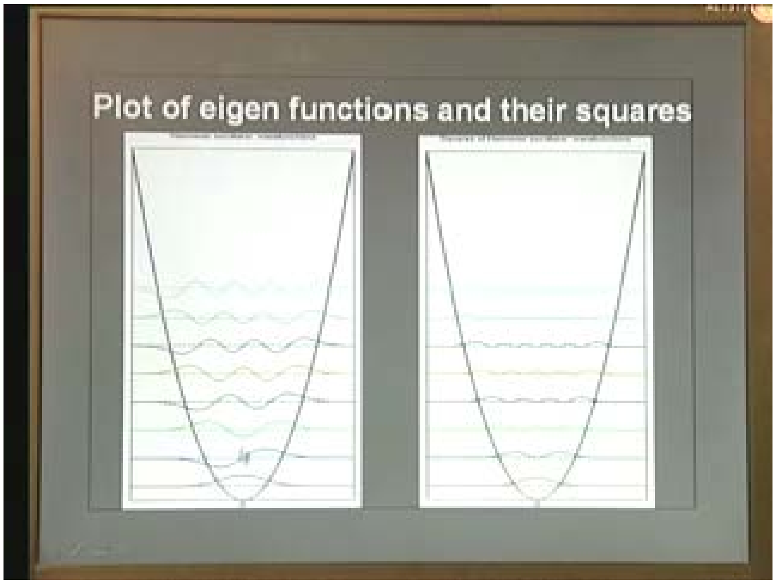

Plot of eigen functions and their squares

So let us see this particular graph where these functions are plotted. There is a node this point is called the node because this is where the function goes to 0 that happens at $x = 0$. The next function is the Harmonic Oscillator wave function $\psi_2(x)$ is not 2x but rather $(4x^2–2)\exp(-\alpha x^2/2)$ and this is by analogy with the previous wave functions and this is the same, $\psi_2(x) = \psi_2(-x)$ whether x is + or – so this is an even function.

Therefore it looks to be the same both ways $x < 0$ or $x > 0$. If you call this the $\psi(x)$ as x-axis so $(4x^2–2) \exp(-\alpha x^2/2)$ therefore at $x = 0$ the function is a negative function, a negative value this is 1 and it is symmetrical so the value of the function is normalization constant × **–2** it starts from somewhere there and then the function goes through a maximum before it goes to 0 on either side and these two peaks, maxima are the same.

So you can continue to plot these wave functions as you see here $n = 0$, $n = 1$, $n = 2$, $n = 3$, $n = 4$ and so on. And these functions alternate between odd and even characters, $n = 0$ is an even function and $n = 1$ is the odd and then the even and odd, even and odd and so on. Much as we plot the Eigenfunctions even more interesting is not the functions themselves but the square of the functions because the square of the functions calculated in a small region, multiplied by a small region give you the probability that the oscillator will be in that region.

So if you look at the square of the functions then that is given on the other side. These are all the various quantum numbers $n = 0$, $n = 1, 2, 3$ etc and what you have here is the $\psi_0^2(x)$, $\psi_1^2(x)$, $\psi_2^2(x)$ and so on. The number of nodes that is the number of places where the functions goes to 0 is the n value. If n is 1 there is one node and if n is 2 there are two nodes and when n is 3 there are three nodes and so on.

Now, this is a picture that we have to see a little bit more carefully with respect to what we understand as Harmonic Oscillator in the classical sense. Let me just draw the $\psi_0^2(x)$ plot at $x = 0$ and on the x-axis one side is the $-\infty$ limit and other side is the $+\infty$ limit and y-axis is the $\psi_0^2(x)$.

What you see here is that the probability of locating the Harmonic Oscillator in the region close to x = 0 is quiet high compared to the probability of locating the Harmonic Oscillator in either of these regions. The graph is symmetric so it does not matter which x you have + or –, the probability decreases the square of the function decreases. So, if you say $\psi_0^2(x)dx$, if you calculate this for a small range dx centered at about the value x you see that it is maximum at the center and it uniformly gets reduced as we go farther and farther away.

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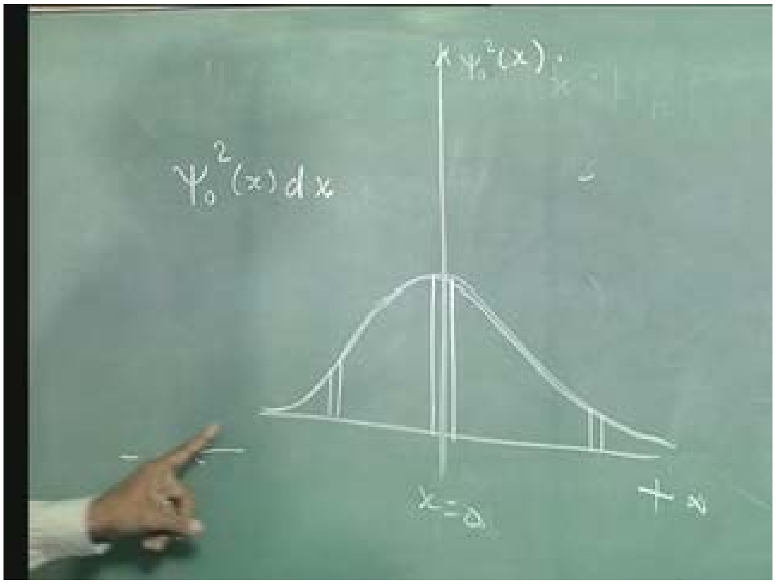

What it means is that the likelihood of finding the Harmonic Oscillator in the region centered at the equilibrium position is the maximum. Classically if you recall as the Harmonic Oscillator vibrates or oscillates between both extremes, classically you know that the velocity of the oscillator is 0 at the extreme and therefore this is the point where the oscillator seems to spend the maximum amount of time.

The probability of locating the oscillator on either extreme is higher than the probability of locating the oscillator right in the middle. It really runs fast right in the middle and at extremes you see that it is possible that it spends more time or the likelihood of locating the oscillators of either extremes of the classical domain is not what you see in Quantum Mechanics you see the contradiction by the way.

The probability of finding the oscillator right in the middle region is high. If this is controversial the next state of the Harmonic Oscillator is even worse because the next state when you plot the square of the probabilities for this is not the graph you get. The graph that you get for the $\psi_1^2(x)$ you see that the probability is practically 0, the function goes to 0 anyway, I should be careful in saying that the probabilities is not 0 but it is very small for $\psi_1^2(x)$ and this is positive x and this is the negative x. If the oscillator energy is slightly higher and it is in the first excited state the probability of locating the oscillator in the right at the middle region is much smaller than the probability of locating the oscillator in either of the regions of maxima or further down.

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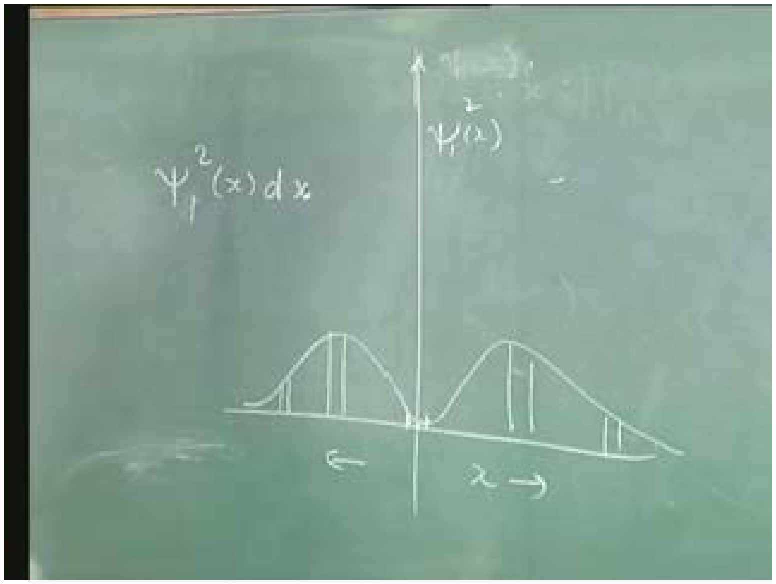

What is important in all of these is that the association of the classical ideas with the quantum mechanical ideas can get you in trouble very quickly. If we do not understand the solutions as they are but rather try to associate what the solutions mean and what classical results mean you will see that the classical results and quantum results are at their most variants when the energy of the system is low and when the particle mass is very low. That is, when the quantum effects are really important you cannot draw the same conclusions or you cannot draw analogies from classical results.

All these are important with respect to molecular vibrations because when you talk about the molecular vibrations we do see what the region is of high probability or low probability etc and this is particularly useful when one studies electronic spectroscopy later on. So please remember that, from the squares of the wave functions and from the plot of the squares of these wave functions and from the analogy for the probabilities we have some interesting conclusions that need to be kept in mind.

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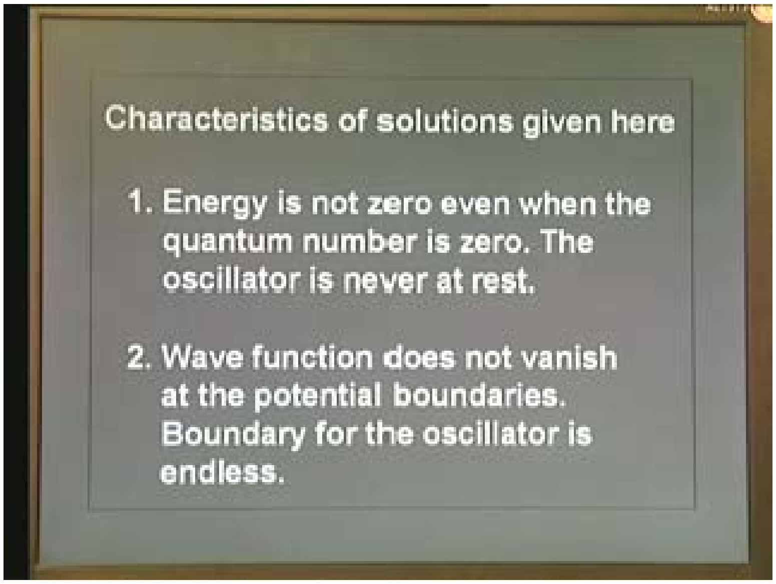

Characteristics of solutions given here

1. Energy is not zero even when the quantum number is zero. The oscillator is never at rest.
2. Wave function does not vanish at the potential boundaries. Boundary for the oscillator is endless.

Let me summarize this solution today and then we will move on the hydrogen atom. So, first one that comes as a surprise is that the energy is not 0 even when the quantum number is 0, the oscillator is never at rest and this was explained in the last lecture. And this is consistent with the Heisenberg's uncertainty principle.

The second is that the wave function does not vanish as you see in pictures like whether it is a square of the wave function or it is the wave function you see that the wave functions vanish at certain points which are the roots of the Hermite polynomial but they do not vanish otherwise and the wave functions are finite even when x is very large. What it means is that even when the classical potential boundary has been exceeded the probability of finding the oscillator in classically forbidden regions exists in Quantum Mechanics. This leads to an interesting phenomenon called tunneling but we will not worry much about it. The boundary for the oscillator is endless that is important to remember.

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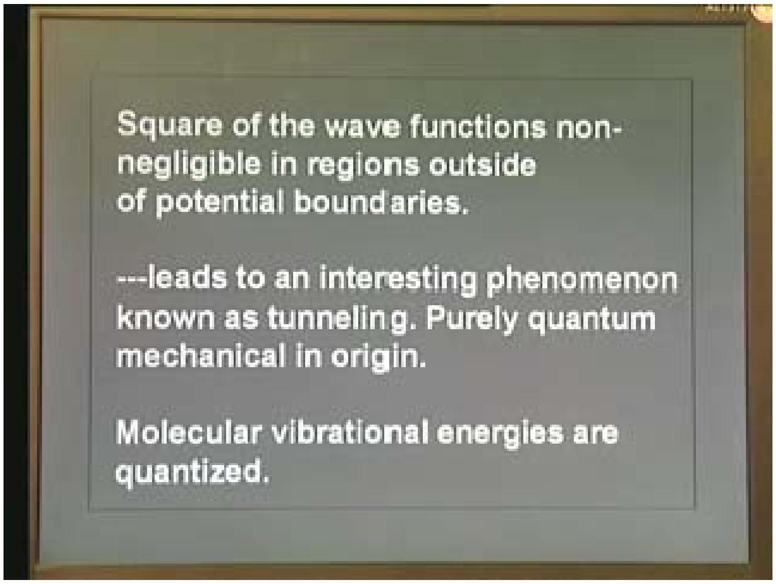

Square of the wave functions non-negligible in regions outside of potential boundaries.

---leads to an interesting phenomenon known as tunneling. Purely quantum mechanical in origin.

Molecular vibrational energies are quantized.

And since the wave functions do not vanish the squares of the wave functions are also non negligible and that essentially means the likelihood of locating the oscillator outside the classical potential boundary regions. All of these are related to molecules when we study molecular vibrations and we will see that the molecular vibrational energies are quantized and this will be used to understand vibrational spectroscopy at an elementary level.

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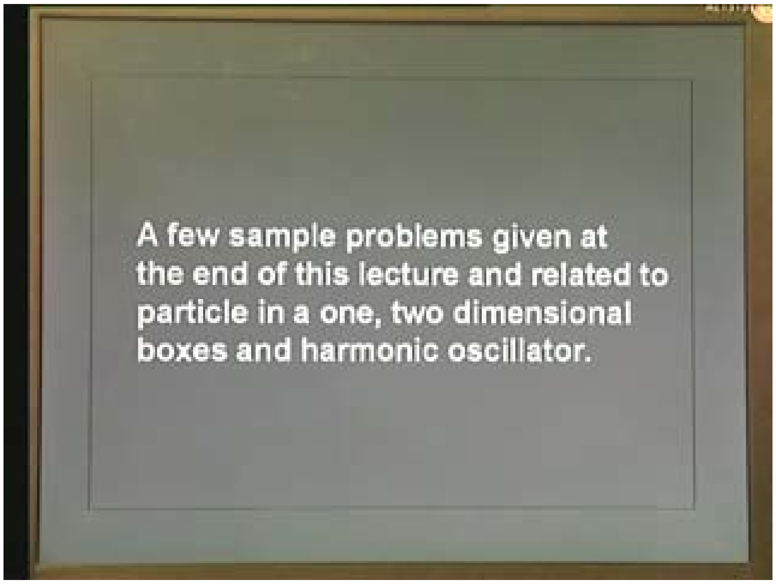

A few sample problems given at the end of this lecture and related to particle in a one, two dimensional boxes and harmonic oscillator.

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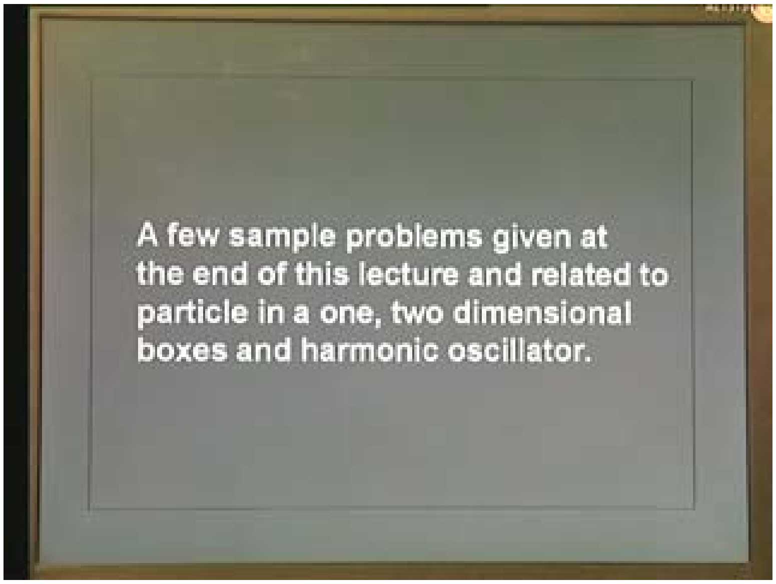

A few sample problems given at the end of this lecture and related to particle in a one, two dimensional boxes and harmonic oscillator.

Now we will move on to the most important topic that a chemist always has to worry about when studying the Quantum Mechanics namely the hydrogen atom. Obviously it is the most important problem for chemist who wants to understand Quantum Mechanics because the hydrogen atom solutions or the fundamental solutions based on which the other atomic energy level solutions and molecular energy levels are constructed.

All the atomic orbitals which are concepts of hydrogen atom Schrödinger equation are used throughout in Chemistry or in everywhere organic Chemistry, inorganic Chemistry everywhere in understanding why reactions take place the way they do, why bonding takes place the way it does. So the modern concepts of chemical bonding basically originated from the solution of the hydrogen atom. Also, from the point of view of history in Quantum Mechanics the hydrogen atom is the probably the only realistic system that could be solved analytically using the Schrödinger equations.

The one dimensional and two dimensional particles are models, the hydrogen atom with electron and proton stuck together due to columbic interactions is the only real problem three dimensional problem where you can get exact analytical solutions. Therefore this was extremely important and its solutions were studied at great details.

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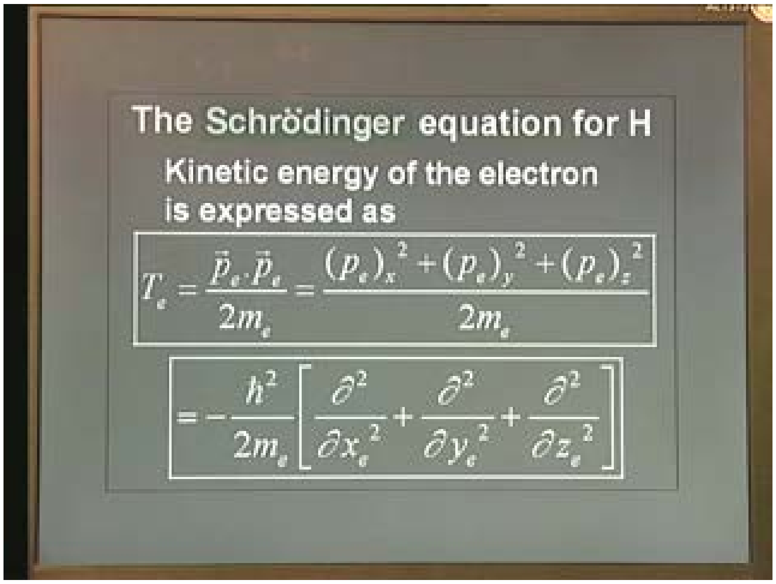

The Schrödinger equation for H

Kinetic energy of the electron is expressed as

$$T_e = \frac{\vec{p}_e\cdot\vec{p}_e}{2m_e} = \frac{(p_e)_x^2+(p_e)_y^2+(p_e)_z^2}{2m_e}$$

$$= -\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right]$$

We will do mechanically what we have to do for at least the first part of the lecture. Mechanically meaning let us set up the Schrödinger equation let us try and see how we can solve it. A detailed study of the methods of the solutions of the hydrogen atom is not possible now because that will involve understanding differential equations in a different level. We will again study only the final solutions but not the method of solving them.

The hydrogen atom, the simplest classical picture you recall from Neils Bohr is that the negatively charged electron keeps moving around the positively charged proton. The particulate the particle nature of the hydrogen atom was emphasized in Neils Bohr's treatment rather a very ADHOC treatment but it was a first one which looked at the solution from the stand point of quantizing some of its energies.

Classically if you represent the hydrogen atom with the electron and proton with a separation r, the interaction energy between the electron and the proton depends only on the distance. Therefore if you imagine a spherical atom of hydrogen with the electron moving on top of the sphere so the interaction energy between the nucleus at the center and the electron anywhere on the sphere of radius r is the same.

The kinetic energy of the electron as it moves around in certain orbits classically. Again from the classical perspective the kinetic energy is again given by $p^2/2m$ where p is the linear momentum associated with it even though the hydrogen atoms moves in a bounded region you can still associate a linear momentum with it and you can express the classical kinetic energy of the hydrogen atom as simply $[(p_e)_x^2 + (p_e)_y^2 + (p_e)_z^2]/2m_e$, m is mass of the electron because the nucleus is very heavy almost 2000 times heavier than that of the electron.

Let us deal with this problem with the assumption that the nucleus is stationary. If the nucleus is not stationary it is moving then you have to include its kinetic energy also in the process. We will not have to worry about this but we will treat hydrogen atom as the stationary atom in the sense that the nucleus is heavy it does not move. Therefore when you talk about the kinetic energy of the system you are only writing the kinetic energy of the electron, one electron.

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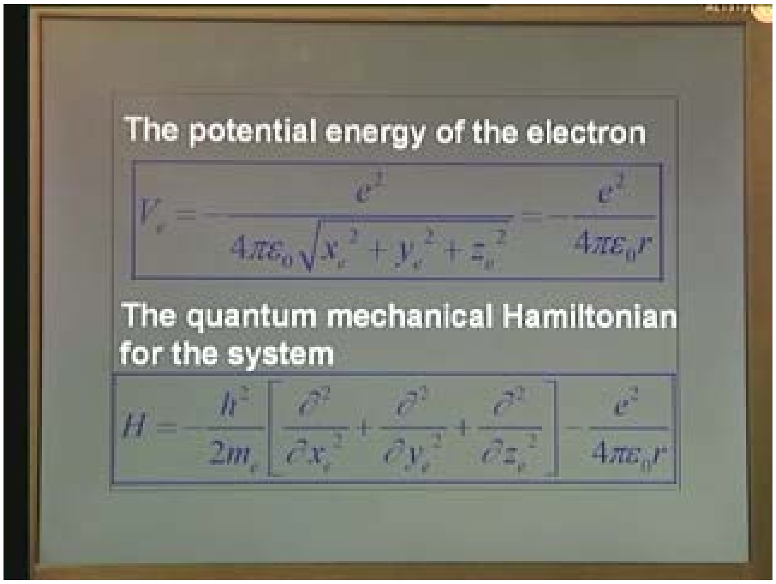

The potential energy of the electron

$$V_e = -\frac{e^2}{4\pi\varepsilon_0\sqrt{x_e^2+y_e^2+z_e^2}} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

The quantum mechanical Hamiltonian for the system

$$H = -\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}$$

And the potential energy that the electron has in its interactions with the positively charged nucleus is of course the columbic interaction $-e^2/r$ because this is a nuclear charge with e with one positive and I would rather write ze as a nuclear charge, z is the atomic number the number protons here and e^- and the electron nucleus interaction energy is attractive with a minus sign this $4\pi\varepsilon_0$ is for taking into account the SI units. ε_0 is the permittivity but we will concentrate on these $\sqrt{(x_e^2+y_e^2+z_e^2)}$ what is under the square root that is the distance r. If you imagine the electron to move anywhere on a sphere and if you associate the origin of this coordinate system with the nucleus, the origin is right here (0, 0, 0) with respect to that the electron coordinates are x, y and z. Then the potential energy of the hydrogen atom the electron nucleus interaction is $-e^2/4\pi\varepsilon_0 r$ because the kinetic energy is $p^2/2m$ and it is now in three dimensions.

We can write the quantum mechanical equation by changing the p into $-i\hbar$ d/dx partial derivative now and you are familiar with that from a particle in a two dimensional box this has been mentioned already therefore p^2 now replaced by the three partial derivatives, $p^2/2m$ is now written as $-\hbar^2/2m\ [\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2]$, the e referring to the electronic coordinate. This is the kinetic energy, then the potential energy is already written as $-e^2/4\pi\varepsilon_0\sqrt{(x_e^2+y_e^2+z_e^2)}$ which is in spherical coordinate system and it is $-e^2/4\pi\varepsilon_0 r$. Therefore one can write the Hamiltonian of the hydrogen atom the electron in the hydrogen atom with the stationary nucleus immediately as the kinetic energy plus the potential energy. The kinetic energy plus the potential energy is $-e^2/4\pi\varepsilon_0 r$.

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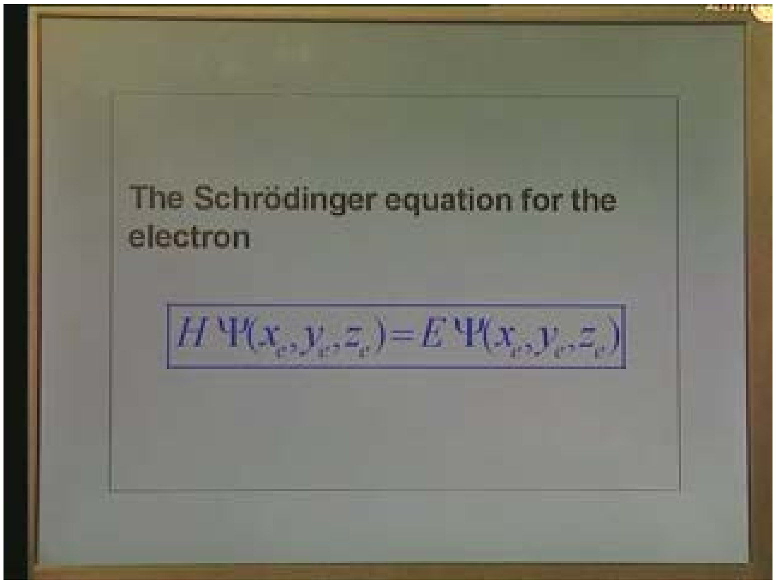

The Schrödinger equation for the electron

$$\boxed{H\Psi(x_e,y_e,z_e)=E\Psi(x_e,y_e,z_e)}$$

Then the Schrödinger equation is obviously the equation that we want to solve H si which is now a function of the electron position (x_e, y_e, z_e) = E, the constant energy times $\Psi((x_e, y_e, z_e)$. That is, $H\Psi(x_e, y_e, z_e) = E\Psi(x_e, y_e, z_e)$.

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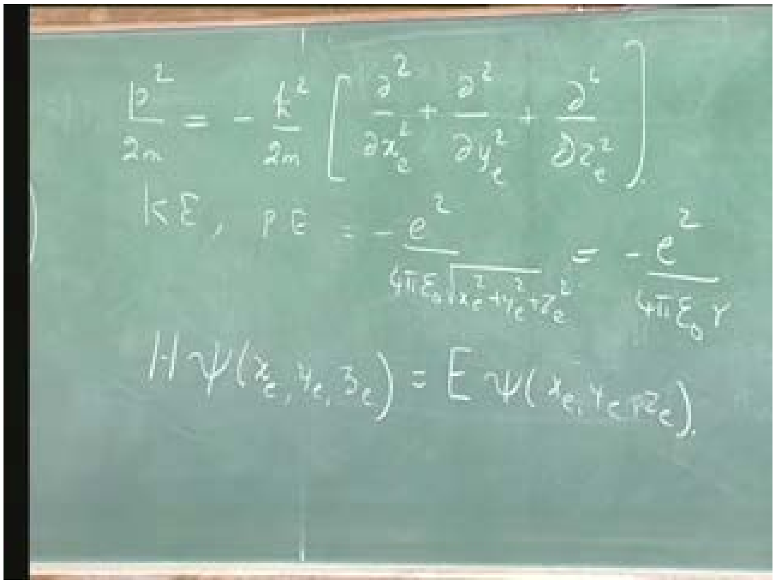

$$\frac{p^2}{2m} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right]$$

KE, PE $= -\frac{e^2}{4\pi\varepsilon_0\sqrt{x_e^2+y_e^2+z_e^2}} = -\frac{e^2}{4\pi\varepsilon_0 r}$

$$H\psi(x_e, y_e, z_e) = E\psi(x_e, y_e, z_e)$$

The solution now is the differential equation containing $p^2/2m$ acting on Ψ plus the potential energy $-e^2/4\pi\varepsilon_0\sqrt{(x_e^2+y_e^2+z_e^2)}$ acting on Ψ giving you the E Ψ.

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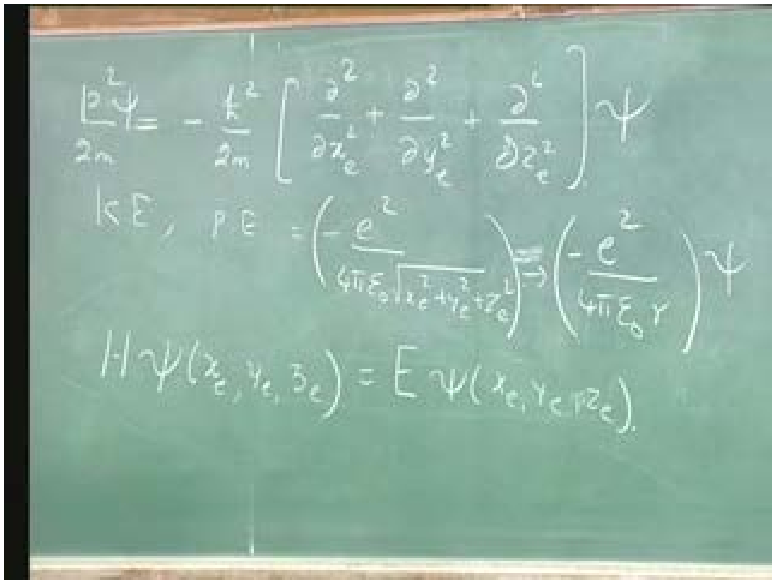

$$\frac{p^2}{2m}\psi = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right]\psi$$

$$KE,\quad PE = \left(-\frac{e^2}{4\pi\varepsilon_0\sqrt{x_e^2+y_e^2+z_e^2}}\right) \Rightarrow \left(-\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi$$

$$H\psi(x_e, y_e, z_e) = E\psi(x_e, y_e, z_e).$$

The differential equation is rather complex so we will not be able to go through the process of solving it.

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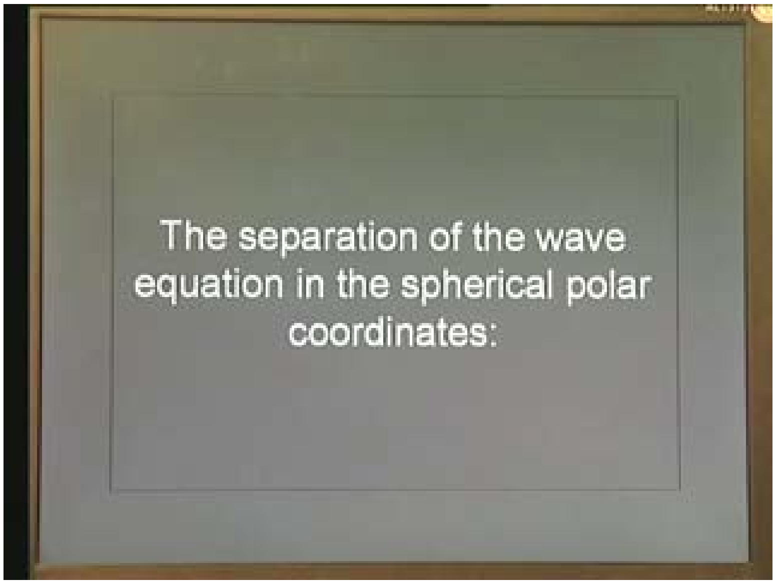

The separation of the wave equation in the spherical polar coordinates:

The thing that one can find in dealing with such types of equations is where the derivatives are all additive, no cross derivative $\partial^2/\partial x_e^2$ but there is no derivative like $\partial/\partial x_e$ or $\partial/\partial y_e$ when the derivatives are all additives. And the rest of the terms contain separable quantities. If you use spherical polar coordinate system you would see that it contains only r the radial distance in spherical polar coordinate systems. Therefore the solution of this problem is probably more easily accomplished in spherical polar coordinate system than it is in Cartesian coordinate system because in Cartesian coordinate system you have a square root involving all the three coordinates.

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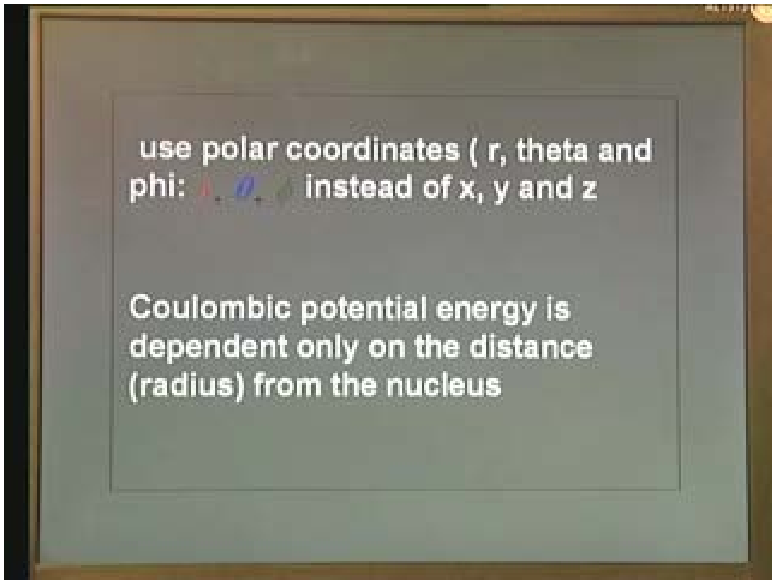

use polar coordinates (r, theta and phi: r, θ, φ instead of x, y and z

Coulombic potential energy is dependent only on the distance (radius) from the nucleus

The spherical coordinate system is the spherical polar coordinate system. You need to know θ and ø and r, θ, ø, how they are defined and how the equation can be transformed into the r, θ, ø representation. This kind of separation is possible because the Coulombic potential energy is dependent only on the distance from the nucleus i.e. radius.

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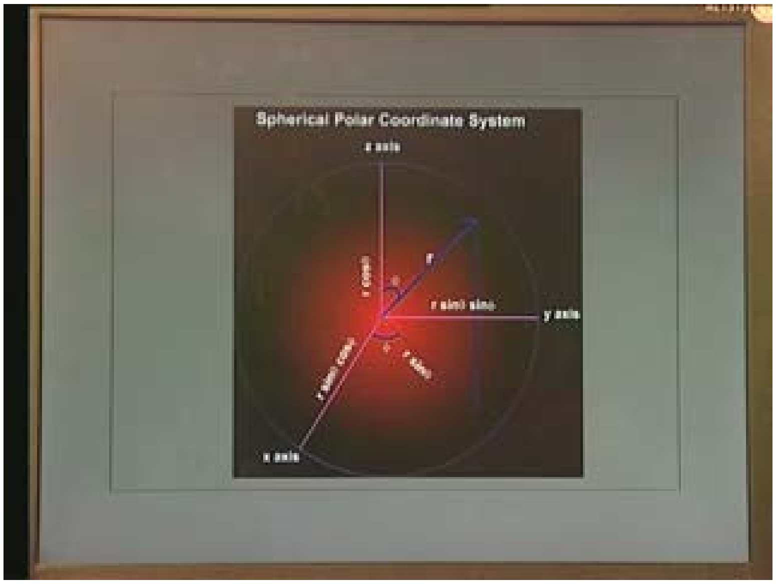

Spherical Polar Coordinate System

This is not a sphere but anyway you will see the actual sphere in the animation.

The construction of the spherical polar coordinate system let me explain with that animation. If the z axis or the polar axis is represented like this and the x and y axis this is the right handed coordinate system any point r represented by the radius vector r can be decomposed along the x-axis, y-axis and the x-axis, y-axis and the z-axis through the θ and ø. The θ represents the polar angle which is from the polar axis; θ is 0 to π to the negative axis from North Pole to South Pole if you recall the association with earth. The ø represents the axis which rotates which is basically a circle. When you section this sphere perpendicular to the polar axis the ø represents the 360° rotation that is the other coordinate. Let us see it clearly in one of these animations.

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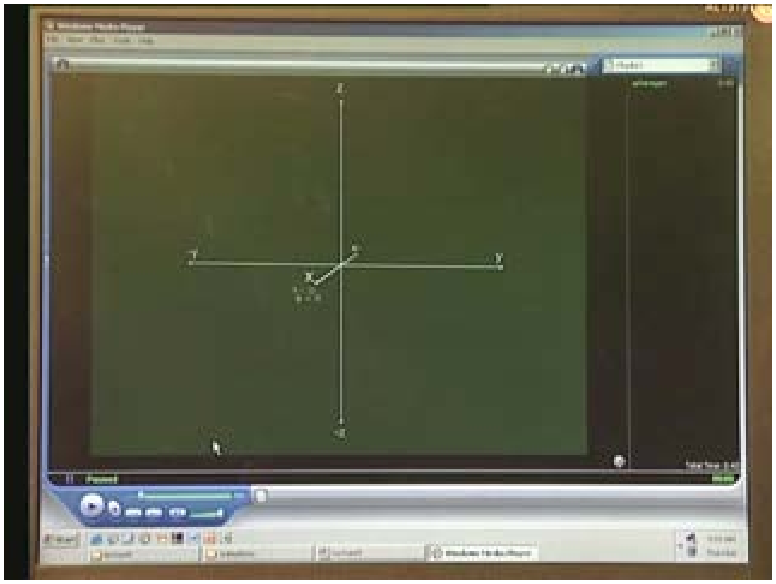

In this animation that you will see now let me represent to the polar angle θ and ø. The angle ø is with respect to the x-axis that is an axis perpendicular to the polar axis, the angle ø is defined as 0 to 360° so ø = 30°, 60°, 90° and so on and is the ø axis. The ø axis represents an axis that is a plane which is perpendicular to the polar axis and represents all the 360° rotations about that.

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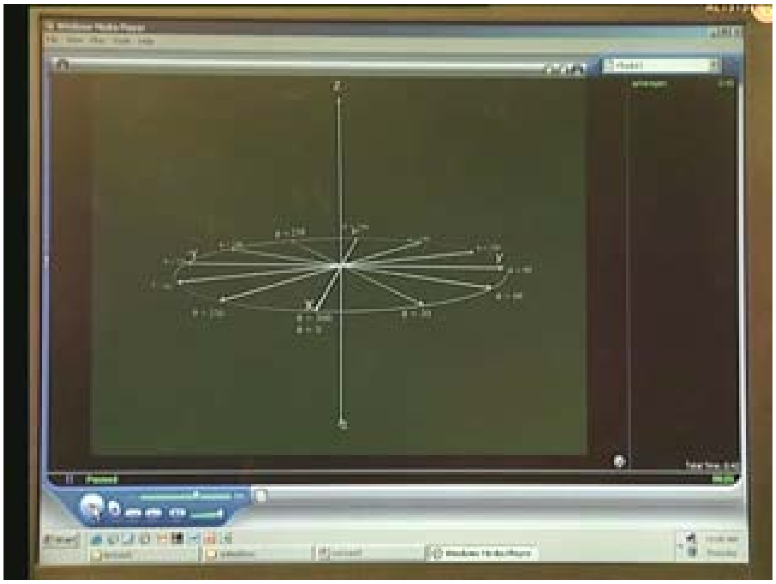

Now the θ axis, the value for θ is with respect to the polar axis that is the θ representation. You see that θ is 0 to 180° and ø can be any one of these from 0 to 360°. And if you travel through both of these coordinates you generate the entire surface area of the sphere. You generate entire surface area of the sphere when you go through this. So the values of the coordinates are for spherical system is the radius of the sphere r.

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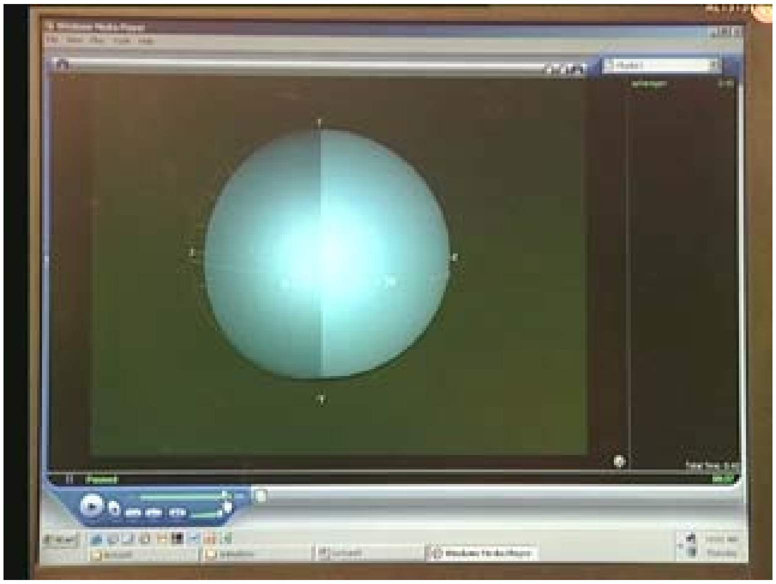

Here we have assumed one particular radius and therefore we have drawn a sphere of that radius. For that any radius the value for θ the variation are from 0 to π and ø the values are from 0 to 2π and the radius of this sphere of course can be from 0 to ∞ so this generates the entire three dimensional Universes. These are the accessible regions for the electron in the hydrogen atom in exactly the same way that you had accessibility for a particle in a one dimensional box from $x = 0$ to $x = L$ or in the Harmonic Oscillator $x = -\infty$ to $+\infty$. Now, the three dimensional region in spherical polar coordinate system these are the variables that you have to remember.

Let us now look at the other animations on the coordinates. How we get this $r \sin\theta \sin\text{ø}$, $r \sin\theta$, $r \cos\theta$ etc. let us write them by looking at the movie carefully. What you have there is an arbitrary position or a radius vector r anywhere on the sphere making an angle θ with respect to the polar axis z.

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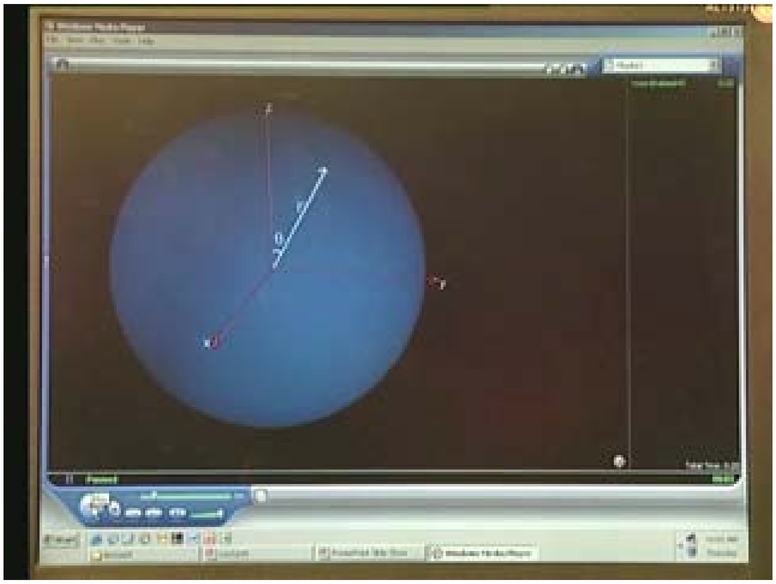

Therefore its projection along the z-axis is going to be $r\cos\theta$ and its projection perpendicular to the plane, this is an arbitrary position it can be anywhere and this is going to be $r\sin\theta$. But now the ø value is an arbitrary value ø from the x-axis therefore $r\sin\theta$ will have a projection along the x-axis as $r\sin\theta \cos\text{ø}$. That is, the x-axis projection and the y-axis projection is of course $(90 - \text{ø})$ is this angle so that is $r\sin\theta \cos(90 - \text{ø})$ or $r\sin\theta \sin\text{ø}$. So this is what you have in the final frame that the spherical coordinates are $x = r\sin\theta \cos\text{ø}$, $y = r\sin\theta \sin\text{ø}$ and $z = r\cos\theta$.

These are the coordinate transformations one has to remember in switching from the usage of (x, y, z) coordinates to the coordinates r, θ and ø. Of course you can easily invert them, this procedure of inverting them, that is if you want to express r in terms of x and y and z you know that if you take $(x^2 + y^2 + z^{2)}$ you are going to get $r^2\sin^2\theta \cos^2\text{ø} + r^2\sin^2\theta \sin^2\text{ø} + r^2\cos^2\theta$ which gives you r^2 therefore r is $\sqrt{}(x^2+y^2+z^2)$. Not a surprise you have already used this result in writing down the potential energy $1/\sqrt{}(x^2+y^2+z^2)$ as $1/r$ it is obvious. What about θ? If you take the ratio of y/x you get tanø, y/x is tanø or ø is Arc tan(y/x) or $\tan^{-1}(y/x)$. So now you can express r in terms of (x, y, z) and ø in terms of (x, y, z) and the last one of course is θ and $\sqrt{}(x^2+y^2)$ will give $\sqrt{}[r^2\sin^2\theta(\cos^2\text{ø} + \sin^2\text{ø})]$.

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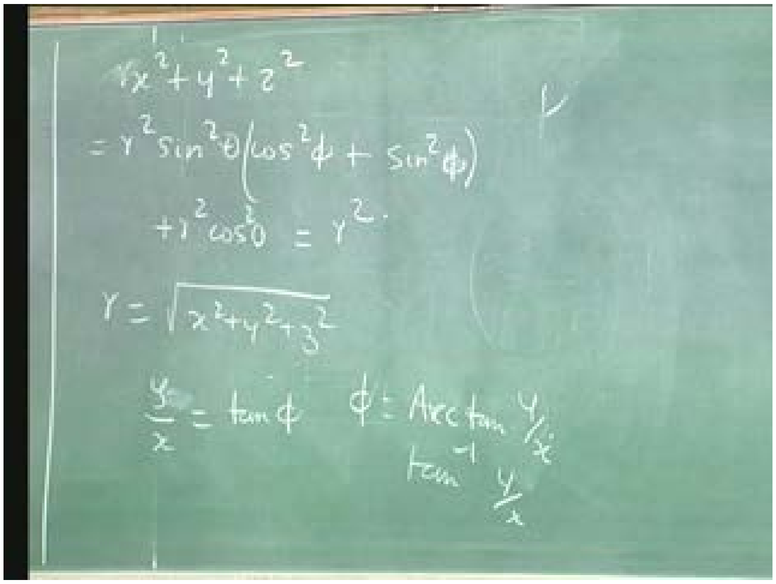

$$\sqrt{x^2+y^2+z^2}$$

$$= r^2\sin^2\theta(\cos^2\phi+\sin^2\phi)$$

$$+r^2\cos^2\theta = r^2.$$

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

$$\frac{y}{x} = \tan\phi \quad \phi = \text{Arc tan } y/x$$

$$\tan^{-1} y/x$$

So what you get is rsinθ and you know z is rcosθ. Therefore the ratio of these two gives you tanθ which is $\sqrt{(x^2+y^2)}/z$. Therefore θ is Arc tan $\sqrt{(x^2+y^2)}/z$ here instead of Arc tan you can write $\tan^{-1}$. So these coordinate transformations are important because when we write the Schrödinger equation in Cartesian coordinates and when we want to change the Schrödinger equation into spherical polar coordinates because the potential energy depends only on r so we must remember these transformations. You must be able to switch between these two.

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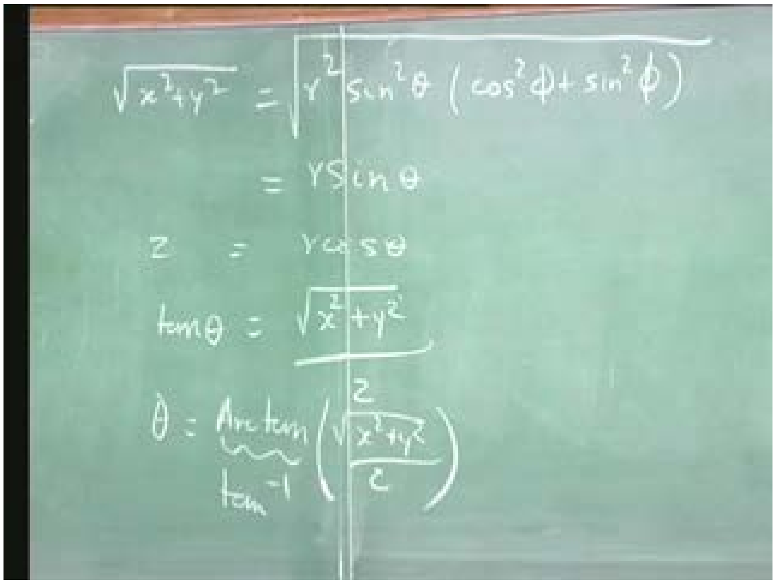

$$\sqrt{x^2+y^2} = \sqrt{r^2\sin^2\theta\,(\cos^2\phi+\sin^2\phi)}$$

$$= r\sin\theta$$

$$z = r\cos\theta$$

$$\tan\theta = \frac{\sqrt{x^2+y^2}}{z}$$

$$\theta = \underbrace{\text{Arc tan}}_{\tan^{-1}}\left(\frac{\sqrt{x^2+y^2}}{z}\right)$$

It takes nearly about 5 to 6 hours to go through the process of deriving the Schrödinger equation in spherical polar coordinate system from that of the Cartesian coordinate system only if even a single mistake is not made. So let us just get the result of what the equation looks like in spherical polar system here.

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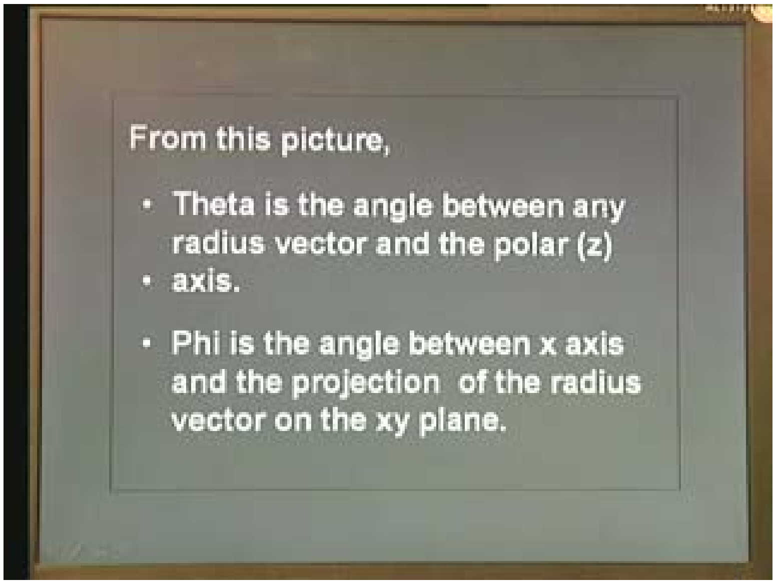

From this picture,

- Theta is the angle between any radius vector and the polar (z)
- axis.
- Phi is the angle between x axis and the projection of the radius vector on the xy plane.

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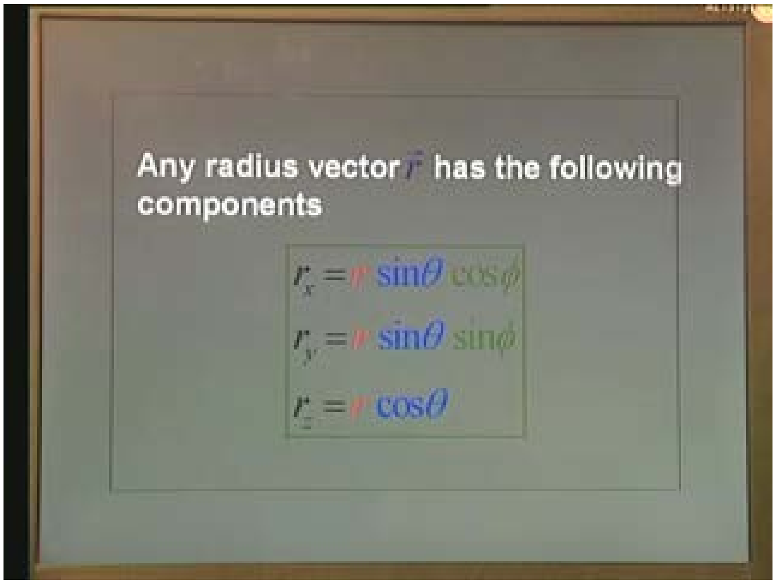

Any radius vector $\vec{r}$ has the following components

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

$$r_y = r\sin\theta\sin\phi$$

$$r_z = r\cos\theta$$

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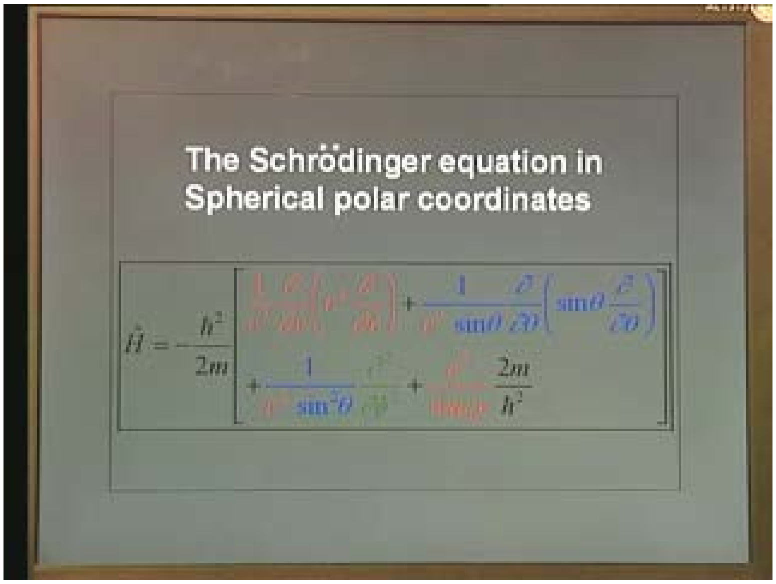

The Schrödinger equation in Spherical polar coordinates

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{e^2}{4\pi\varepsilon_0 r}\frac{2m}{\hbar^2}\right]$$

So what you have here is of course both the kinetic energy and the potential energy of the hydrogen atom electron represented now using spherical polar coordinate system. The derivation of this is not important for these lectures but you should be able to do it when you understand partial differential equations and when you understand how to transform between coordinate systems using Jacobians etc. This is basically partial derivatives you should be able to transform from one set of coordinates to another set of coordinate using the chain rule of partial differential equation. We will not worry about that as Chemistry student. We will believe that the Physicists and the Mathematicians have done it right and therefore we will take this equation as God given or as the Physicist given. We will believe that this is right and let us work on this equation.

The form of the equation is something that we should write down just to familiarize ourselves with notation. The Hamiltonian $H\psi$, now ψ is expressed in terms of r, θ and ø. Then $H\psi(r, \theta, \text{ø}) = E\psi(r, \theta, \text{ø})$ is to be written now, the Hamiltonian operator is the expression given $-\hbar^2/2m\{[{}^{1}/r^2\ \partial/\partial r(r^2\ \partial/\partial r)]+[{}^{1}/(r^2\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial/\partial\theta)]+[{}^{1}/(r^2\sin^2\theta)\ \partial^2/\partial\text{ø}^2]+[e^2/4\pi\varepsilon_0 r \text{ x } 2m/\hbar^2]\}$. Only gives you time to write these equations and try and understand this is the operator h containing a derivative expression in r, a derivative expression in θ and a derivative expression in ø and the potential energy term involving r.

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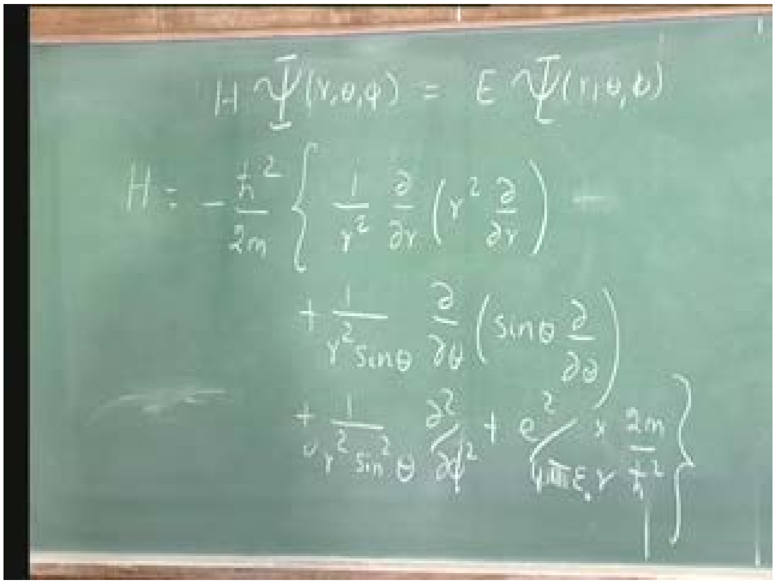

$$H\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

$$H = -\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{e^2}{4\pi\epsilon_0 r}\times\frac{2m}{\hbar^2}\right\}$$

The painful process of going through this transformation is to ensure that the wave functions we are trying to obtain can be separated into functions depending only on r, functions depending only on θ and functions depending only on ø. So what one tries to do is to simplify the wave functions by separating them into independent coordinate dependent functions only and this is the process you are familiar with from particle in a two dimensional box where you represented the wave function for this solution of this equation $-\hbar^2/2m(\partial^2/\partial x^2 + \partial^2/\partial y^2)\psi(x, y) = E\psi(x, y)$.

You represented ψ(x, y) as a function X depends only on x and a function Y depends only on y and the product of these. And this enabled you to write a two one dimensional Schrödinger equations and then study the solutions rather straight forward. So in the same way we tried to use the right coordinate system in which the wave functions can be expressed rather simply and then study the solutions in that coordinate system. All the atomic orbital pictorial representations that I will give are given in spherical polar coordinate systems and the underlying Mathematics is given here. Now, there is a notation here, so when you write H si = E si what it means is that this operator H acting on ψ.

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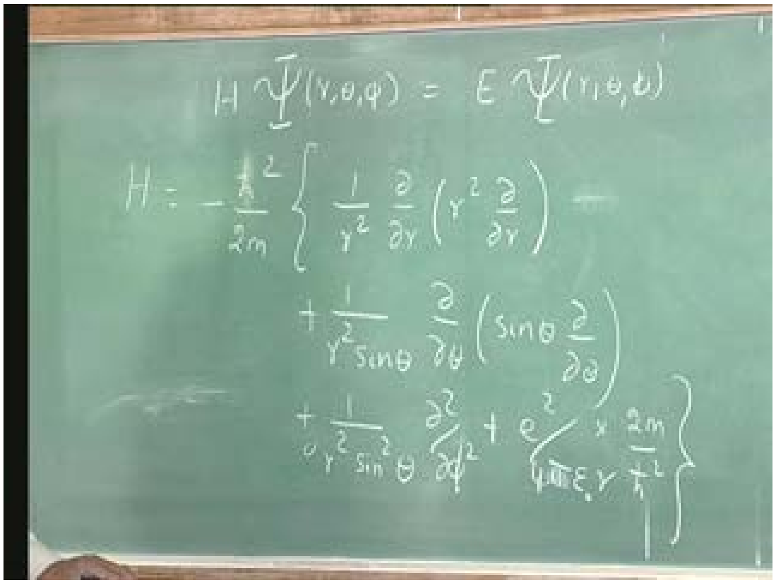

$$H\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

$$H = -\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{e^2}{4\pi\epsilon_0 r}\times\frac{2m}{\hbar^2}\right\}$$

So, if you write this as HΨ this whole thing is operating on Ψ to give EΨ, $[{}^{1}/r^{2]}\partial/\partial r(r^{2}\ \partial/\partial r)]\Psi$ what does this mean? It means the following: ${}^{1}/r^{2}\ \partial/\partial r(r^{2}\ {}^{\partial}/_{\partial r}\Psi)$ that is the first term. And this of course is a compact notation and you can expand this in solving the equation you have to anyway do this. The differential now will act on uv kind of a product. Then the product is ${}^{1}/r^{2}(\partial^{2}/\partial r^{2})\Psi$ multiplied by r^2 and in addition to this you have one more term ${}^{1}/\ r^{2}\ (2r\ \partial\Psi/\partial r)$. Now if the differential acts on r^2 what you have is $2r\ \partial\Psi/\partial r$, which is $\partial^{2}\Psi/\partial r^{2}+2/r\ \partial\Psi/\partial r$. This is the expression which is represented by a compact form like that. So that is what is given here when you write $-\hbar^{2}/2m\ {}^{1}/r^{2}\ \partial/\partial r(r^{2}\ \partial\Psi/\partial r)$, what it means is the derivative expression $-\hbar^{2}/2m[{}^{2}/r\ \partial\Psi/\partial r + \partial^{2}\Psi/\partial r^{2}]$. Likewise when you write $-\hbar^{2}/2m[{}^{1}/(r^{2}\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial\Psi/\partial\theta)]$, what it means is the derivative expression which has to be expanded exactly like what you have done here and it gives you $-\hbar^{2}/2m[(\cos\theta/r^{2}\sin\theta)\ \partial\Psi/\partial\theta + {}^{1}/r^{2}\ \partial^{2}\Psi/\partial\theta^{2}]$.

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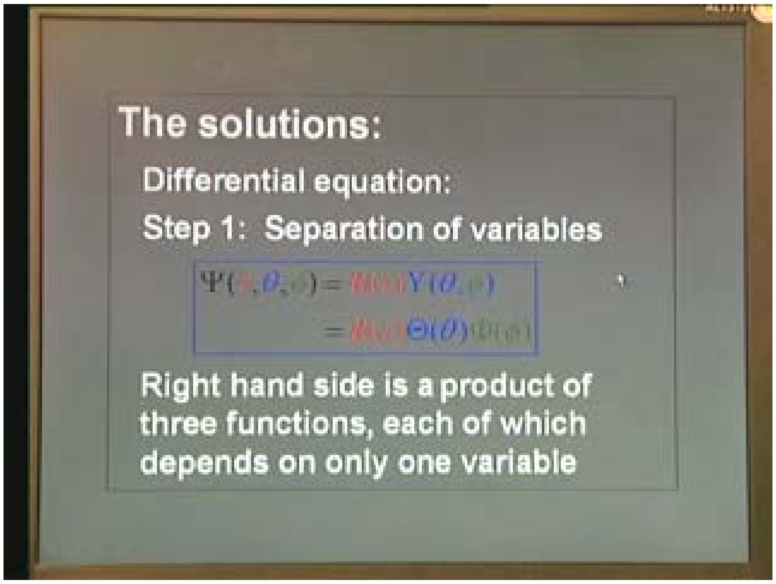

The solutions:

Differential equation:

Step 1: Separation of variables

$$\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$
$$= R(r)\Theta(\theta)\Phi(\phi)$$

Right hand side is a product of three functions, each of which depends on only one variable

We will not solve the equation today and we will not solve the equation in this course but we will rather give the solutions of this equation in the next couple of lectures with corresponding pictorial illustrations. And I will also tell you a little bit about the method of solving the differential equation, how we separate the wave functions into products of three different functions and how we obtain the final result, what is the final result and then we will try to picture the final results in this whole process.

So we have discussed about the Harmonic Oscillator continued from the previous lecture by way of pictorially representing the Harmonic Oscillator wave functions and the squares of the wave functions and we noticed that the squares of the wave functions have certain properties which are not what would you except when you associate them with the corresponding classical solutions using Newton's laws.

So the Harmonic Oscillator in Quantum Mechanics presents some things which are difficult to digest for a Physicist or a Chemist who is well versed with classical Harmonic Oscillator. This was then followed by focusing on the problem of the hydrogen atom, what is it that is going to be important for us as a Chemist is that the stationary nucleus with the electron moving around in the classical sense being now replaced by a quantum mechanical wave function and the Hamiltonian the Schrödinger equation that one needs to solve being the H si = E si.