Chemistry II: Introduction to Molecular Spectroscopy

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Lecture – 06
Introduction to quantum mechanics I

Welcome back to the lectures on chemistry and the course on Introductory Molecular Spectroscopy. The theory of spectroscopy is essentially developed using quantum mechanics. The quantum principles for molecular energy levels are understood by the solution of the Schrodinger equation. And in this lecture and probably the next one, I shall give you a brief summary of the elementary quantum results that we shall use for the whole course.

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Schrödinger equation. The time dependent:

$$i\hbar \frac{\partial \underline{\bar{\Psi}}}{\partial t} = \hat{H}\underline{\bar{\Psi}}$$

$\underline{\bar{\Psi}} = \underline{\bar{\Psi}}(\underset{\sim}{\vec{r}}, t)$ If $\hat{H}$ is independent of time,

In the previous course to this called chemistry 1, this is available from the NPTEL website ac dot in or NPTEL.AC.IN. I have introduced basic principles of quantum models that is, elementary models of quantum mechanics by about 10 to 15 hours; and therefore that may be you used as a reference every now and then, but here I shall give only this summary and the results that we shall be using for vibrational and rotational and also magnetic resonance spectroscopes.

So, let me start with the fundamental equation that be need to be concerned with the Schrodinger equation. The time dependent Schrodinger equation is given by this formula by this equation i h bar the partial derivative of psi with respect to time is equated to the operation of the Hamiltonian operator of the system under study acting on psi. And psi here which I shall use as a capital psi is a function of both the coordinates of the system and is a function of time, so that it is what is denoted as psi.

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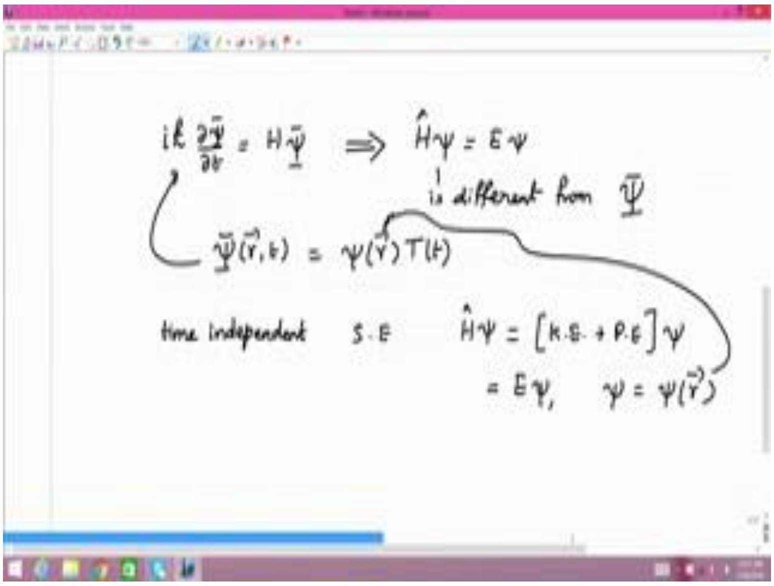

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \implies \hat{H}\psi = E\psi$$

is different from Ψ

$$\Psi(\vec{r}, t) = \psi(\vec{r})\,T(t)$$

time independent S.E $\quad \hat{H}\psi = [\text{K.E} + \text{P.E}]\psi$

$$= E\psi, \quad \psi = \psi(\vec{r})$$

However, if H is independent of time then the equation i h bar dou psi by dou t is equal to H psi can be reduced to a simpler time independent equation H psi is equal to E psi; this psi is different from capital psi which is used here. And the relation is the psi of r; t is factored into a function which depends only on the position coordinates of the system and a function which is only dependent. And as a result, if you substitute that into this equation, you will get the time independent for Schrodinger equation H psi which is given as the kinetic energy operator plus the potential energy operator acting on psi is equal to E psi, where the psi is the psi of the r that is the same the thing what you see here.

Quantum mechanics for spectroscopy uses both time dependent and time independent Hamiltonians. The molecular energy levels in the absence of the electromagnetic field are obtained by the solution of the Schrodinger equation, which is time independent. In the present of the radiation, the excitation of a molecule is often studied using a time dependent Hamiltonian for which one needs to use time dependent Schrodinger equation and use approximate procedure, approximation procedure such as perturbation theory to arrive at results for the intensity of radiation, the gets absorbed or emitted. So, spectroscopy uses both of these and in different domains, but for our problem, we need to have the knowledge of the energy levels of the molecular systems; some picture has to be some mental picture has to be there. And therefore, let me introduce the elementary mathematics and the model problem results right away in this lecture.

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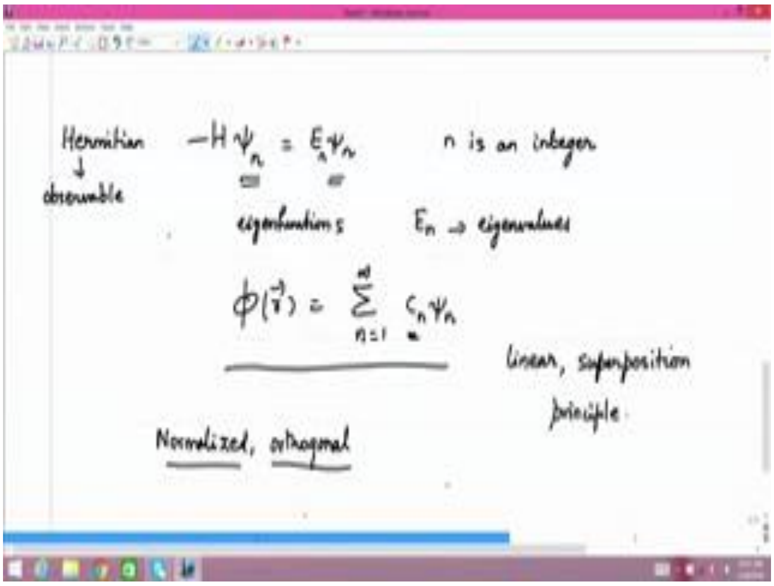

Hermitian
↓
observable

$-H\underline{\psi_n} = E_n\underline{\psi_n}$

n is an integer

eigenfunctions

$E_n \rightarrow$ eigenvalues

$$\underline{\phi(\vec{r}) = \sum_{n=1}^{\infty} c_n\psi_n}$$

linear, superposition principle

<u>Normalized</u>, <u>orthogonal</u>

First of all, when you say the time independent Schrodinger equation is H psi is equal to E psi it means your whole series of wave functions E n psi n. Where n can be an integer n is an integer and it can be finite or infinite for magnetic resonance systems that being function are finite for optical resonance using harmonic oscillators electronic wave function and so on the n can be infinite. Therefore, a whole group of wave functions these are called Eigen functions are used and E n’s are called Eigen values. These are what you will obtain if you measure the energy of the molecular system, one of these, what you will get with some probability.

Therefore, the wave function in general for a molecular system an arbitrary wave function of the system is expressed as a linear combination one to whatever number, let us write infinity here for optical resonance, what we have is a linear combination coefficient and the Eigen functions, this is called the a linear superposition principle. In this model, C n’s have very specific properties associated with them. And since I mention that the psi n’s are Eigen functions, they can be normalized and they are also orthogonal to each other being Eigen functions of the Hamiltonian operator and the Hamiltonian operator is a Hermitian operator. Hermitian operators are associated with observable properties, experimentally observable properties. So, the wave functions are normalized, the wave functions can be normalized wave functions are orthogonal.

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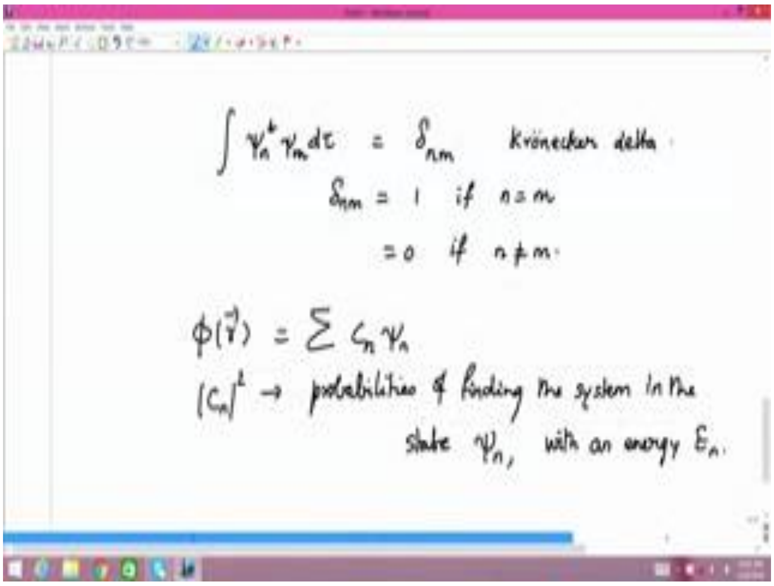

$$\int \psi_n^* \psi_m d\tau = \delta_{nm} \quad \text{Krönecker delta}$$

$$\delta_{nm} = 1 \text{ if } n = m$$

$$= 0 \text{ if } n \neq m$$

$$\phi(\vec{r}) = \sum C_n \psi_n$$

$|C_n|^2 \rightarrow$ probabilities of finding the system in the state ψ_n, with an energy E_n.

And they have the specific property namely the integral psi n star psi n over all the coordinate system a space available to the system psi m is delta n m which is the Kronecker delta. Delta n m is 1, if n is equal to m; and it is equal to 0, if n is not equal to m. With this property, you can see that the wave function phi which is written as linear combination of all the Eigen functions, the coefficient C n square or probabilities of finding the system in the state psi n with an energy E n. What it means is that if you have identical copy of the system many, many copies, and you repeat the experiment of measuring the energy of the system, the energy would be one of the possible Eigen values, the outcome would be one of the Eigen values. And the state at which the system will remain would be the Eigen state of that Eigen value. Therefore, psi n would be one of the measurable state of the system, and E n is the energy associated with it. What is the probability that you look at the system that you get 1 psi n or another or another that probability is given by the linear combination square C n square.

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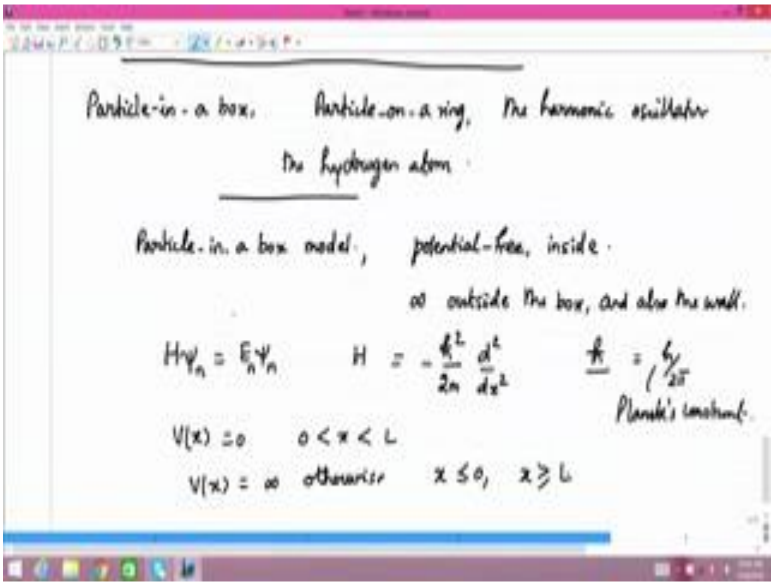

Particle-in-a box, Particle-on-a ring, The harmonic oscillator

The hydrogen atom

Particle-in-a box model, potential-free, inside

∞ outside the box, and also the wall.

$H\psi_n = E_n\psi_n \qquad H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad \hbar = h/2\pi$

Planck's constant

$V(x) = 0 \qquad 0 < x < L$

$V(x) = \infty$ otherwise $\quad x \leq 0, \quad x \geq L$

And therefore, since it is a probability statement, what it means is that all such probabilities should to give you unity that is the safe system will in one of the Eigen states that when it is measured. So, this is a fundamental principle and there are simple model problems to illustrate this. So, let me just give you the three model problem results. The particle in a box - one model; the particle on a ring - the harmonic oscillator which is very important for vibrational spectroscopy; and then the hydrogen atom which is used as the basis for understanding molecular states of all the molecules all the atoms on molecules with more than one electron. Hydrogen atom is the simplest one electron model that could be solved and exactly and all these models particles in the box on a ring, harmonic oscillator, they all have exact solutions.

So, let me recall in the rest of this lecture, and also the next lecture, the primary results that we need to know the Eigen values the model the Eigen vectors etcetera. As I mentioned in the beginning, a more detail a more elaborate process of how we get these things is there in another course chemistry-1, which is proceeded in this course therefore, you may see the videos at your convenience on those specific topics if you need more information. Otherwise, you can also write them on the discussion board.

Now, let us start with the simplest model namely the particle in a box model. This is essentially a potential free model inside the box; and the potentials are infinity outside the box and also the wall. So, what it means is that you study the Hamiltonian, you study the solutions of the Hamiltonian H psi is equal to E psi or H psi n is equal to E n psi n using the Hamiltonian which contains only the kinetic energy of the particle which in quantum mechanics is given in one dimension by h bar square by 2 m d square by d x square h bar is obviously, h by 2 pi Planck’s constant. Please remember these things all the time Planck’s constant. And therefore, you solve these equation for the potential model namely V of x is 0 for x in a certain region, may be length of the box being L and V of x is infinity otherwise, meaning x less than or equal to 0, x greater than or equal to L. So, this is the box model and what are the solutions.

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$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad n = 1, 2, 3, \ldots$$

$$E_n = \frac{h^2 n^2}{8mL^2} \qquad \frac{h^2}{8mL^2} \rightarrow \text{energy}$$

$$\int_0^L \psi_n(x) \psi_m(x) \, dx = \delta_{mn}$$

$$\psi(x) = \sum_{n=1}^{\infty} C_n \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad \langle E \rangle = \sum_{n=1}^{\infty} |C_n|^2 \frac{h^2 n^2}{8mL^2}$$

The solutions are the wave function of psi n of x is normalized using the box length root 2 by L sin n pi x by L, and the n can take the values 1, 2, 3etcetera all the way to infinity. And the energies E n are given by the formula h square n square by 8 m L square. So, the model of the mass of the particle and the length of the box which are the parameters for this particle in a box model determine the spread of the energies on the discreetness in the energy, because H Square by 8 m L square has the energy unit or energy dimension. And n square is the quantum number which tells you the energies are 1, 4, 69, 16, 25 36 times this base unit. And the base unit of energy for that model depends on the length of the box that you chosen, also the mass of the particle that is being studied or the mass of the molecule that is being studied the mass of the electron whatever that you do this is the solution. This is the simple one process that you can immediately recall.

And of course, you have the same relations as I mentioned in the earlier namely the psi n star which being a real function is the same as the psi n of x and psi m of x and d x the range for the particle is 0 to L the motion within the box and this is the d tau that you talked about, this is delta m n meaning that the wave functions are normalized when n is equal to m. The probability of finding the particle inside the box is unity for all states of the system and second is that the wave functions are orthogonal to each other. So, this is the summary result.

And therefore, any particle wave function in principle any arbitrary wave function or any arbitrary state of the system inside the box can be written as the sum n is equal to 1 to infinity C n root 2 by L sin n pi x by L. And for this state, the average value of the energy turns out to be sum over n equal 1 to infinity C n square the absolute square times h square N Square by 8 m L square. This is the average value for the energy, but the average is obtained only when you do many, many measurements and take the average of all of this. Otherwise, every individual measurement will give you one of the energies and it will also fix the state into that Eigen state. So, this is a particle in a box model.

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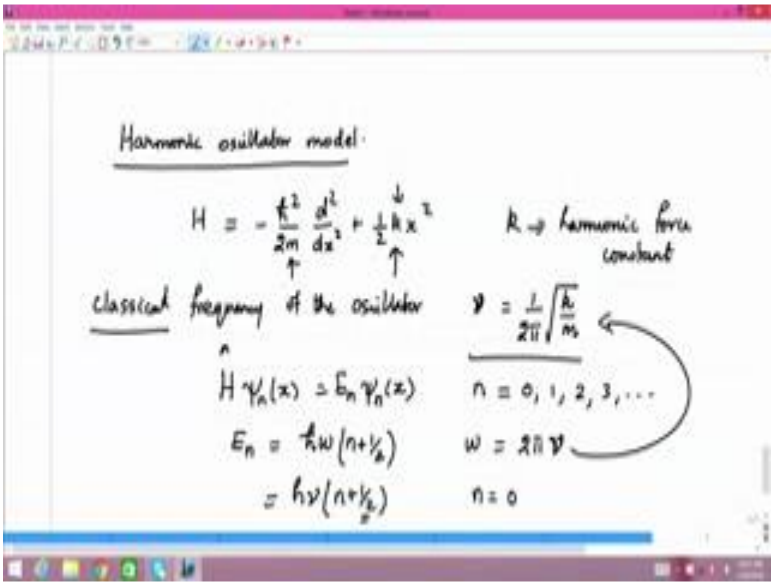

Harmonic oscillator model.

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

k → harmonic force constant

classical frequency of the oscillator $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \qquad n = 0, 1, 2, 3, \ldots$$

$$E_n = \hbar\omega(n+½) \qquad \omega = 2\pi\nu$$

$$= h\nu(n+½) \qquad n = 0$$

The next important model that you have to remember for vibration spectroscopy is the harmonic oscillator. Now, harmonic oscillator Hamiltonian is the potential energy is given by the potential energy which is parabolic or which is quadratic. And the kinetic energy is of course, p square by 2 m which is written as minus h square by 2 m d square by d x square plus half k x square. And k is the harmonic force constant expressing the stiffness of the harmonic emotion whether the motion is very rigid or the motion is very flexible; and the value of k will determine the harmonic the extent to which the system can be harmonic. So, k is system dependent.

And every harmonic oscillator has a fundamental frequency. The classical frequency of the oscillator is known from elementary physics and that frequency nu is given by 1 by 2 pi square root of k by m. Again you see that parameters which determine the system or m and k and the frequency is expressed in terms of k by m. The ratio k by m, the square root this is of course, classical. What happens when you solve the Schrodinger equation for this system with H psi n of x is equal to E n psi n of x, you get again infinitely many energies, but one thing one should remember is that n can be 0, 1, 2, 3 etcetera, the integer n is equal to 0 is also allowed.

The solutions turn out to be for E n given by this formula namely h bar omega times n plus half. And omega is 2 pi times nu, the same nu that you have here. Therefore, you see that the harmonic oscillator energy is given in terms of h nu, if you want to write that because there is a 2 pi in the denominator that cancels this, h nu into n plus half and the half ensures that n equal to 0 is also an allowed value. Which means even if the harmonic oscillator is in the lowest possible energy state with no quantum number input to that it is still has an energy called energy equivalent to half of the h bar omega and h is the Planck’s constant, omega it is natural angular frequency.

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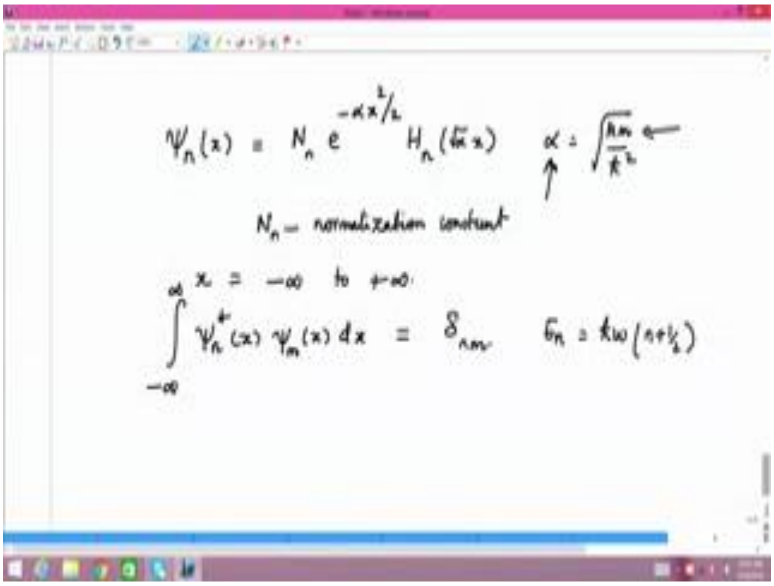

$$\psi_n(x) = N_n e^{-\alpha x^2/2} H_n(\sqrt{\alpha}\, x) \qquad \alpha = \sqrt{\frac{km}{\hbar^2}}$$

N_n – normalization constant

$x = -\infty$ to $+\infty$

$$\int_{-\infty}^{\infty} \psi_n^*(x)\, \psi_m(x)\, dx = \delta_{nm} \qquad E_n = \hbar\omega\left(n+\tfrac{1}{2}\right)$$

What are the Eigen functions for the system? The Eigen functions are given by a combination of the Gaussian e to the minus alpha x square by 2, and the harmonic polynomials H n root of alpha x. What is alpha, alpha is square root of k m by h bar square. Again alpha is the physical constant associated with the system, the mass of the harmonic oscillator and the force constant that the oscillator has. So, if the oscillator is very strong, it is force constant is very high, then alpha is very large square root of that of course, k m, and if the oscillator is very heavy, so is alpha.

So, the parameters of the system the model that you study are used to define the wave functions and the energies. The N n is the normalization constant. And in the case of harmonic oscillator, x is taken all the way from minus infinity to plus infinity, therefore, the wave functions when you talk about the orthogonality, it is from minus infinity to plus infinity psi n star of x psi m of x d x is delta n m. Which tells you that the wave functions also satisfy the same orthogonality and normalization relation for the harmonic oscillator? What is important with the harmonic oscillator is something unique namely the energies are h bar omega n plus half meaning that the energies are all equidistant.

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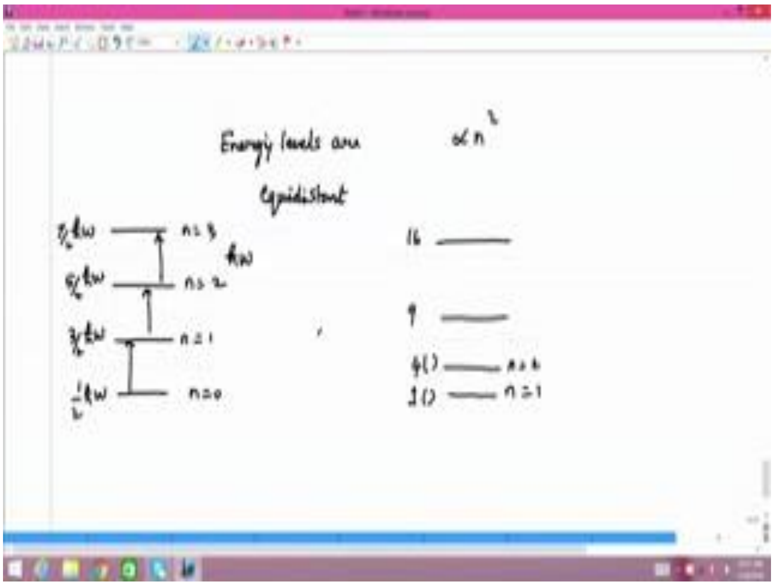

So, if you write half h bar omega here for n equal to 0, and if you write for n equal to 1, it is 3 half h bar omega; and for n equal to 2, it is 5 h bar omega and so on; 3 - 7 half h bar omega and so on. So, energies are equidistant, energy levels are equidistant. For a particle in a one-dimensional box, of course, you remember is proportional to n square whatever the unit that you have is. Therefore, if you put n equal to 1 here and then if you put in equal to 2, it is 4; n equal to 2, this is 4 times that fundamental unit, this is 1 times that fundamental unit. The next one would be 9 times 1, 4. So, I believe the differences the 3, 3, 3, so it should be somewhere here. Next one is 9 times and the third one is 16 times and so on. So, the energies are not separated from each other by the same distance in the case of particle in a box.

In the case of harmonic oscillators, they are all separated by this same gap. The difference between any pair of successive energy levels is h bar omega, which would be needed later when we study vibration spectroscopy of a harmonic oscillator diatomic molecule. In the harmonic oscillator model, you would see that the spectrum for a simple diatomic molecule contains only one line and that one line corresponds to the difference between the two nearby energy levels. It is not possible for a harmonic oscillator to be excited to levels for away from the starting point, there are starting rules for that, but the quantum mechanics of harmonic oscillator gives you all these results later when we need them for a spectroscopy of a diatomic molecule.

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Hydrogen atom

two-particle two body system

$\cdot e^{-}$

$\cdot e^{+}$ proton $\quad r$

$$-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

permittivity of the medium

$$\mu = \frac{m_p m_e}{m_p + m_e} \qquad m_p \gg m_e$$

reduced mass $\mu \sim \underline{\underline{m_e}}$

The next important model the real physical model in addition to harmonic oscillator is the hydrogen atom. The hydrogen atom with the proton and then the electron separated by a distance or has they have the proton electron system has a potential energy given by minus z e square by 4 pi epsilon naught r where epsilon the permittivity of the medium. And the hydrogen atom is a two body system, two particles or a two body system; and it can be separated into a center of mass coordinate that is a system in which all the masses concentrated on the central mass. And also a relative particle system in which the relative particle has the mass mu and that is given by the proton m p times the electron m e by m p plus m e. And you know that m p is much, much greater than m e, therefore mu is the reduced mass is approximately the same as m e, because this will be m p and that cancels m p. So, it is about m e.

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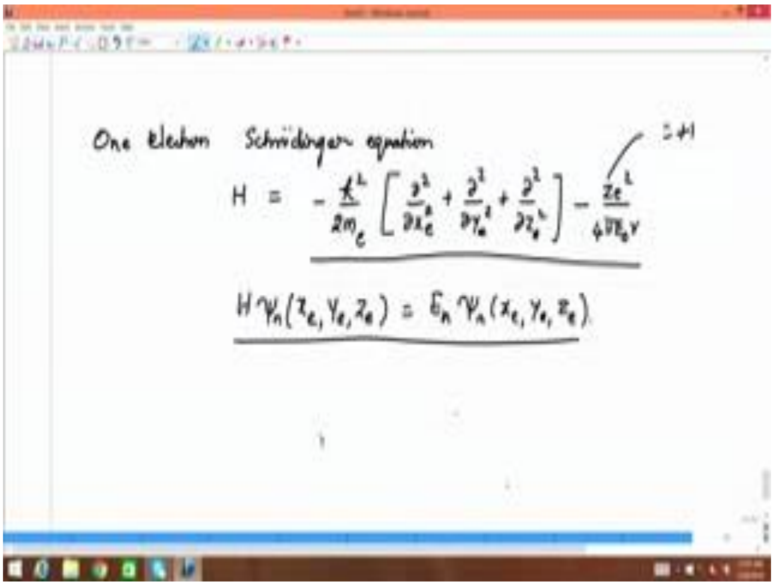

One electron Schrödinger equation

$$H = -\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right] - \frac{\overset{=+1}{Z}e^2}{4\pi\varepsilon_0 r}$$

$$H\psi_n(x_e, y_e, z_e) = E_n \psi_n(x_e, y_e, z_e)$$

And this is what we normally use in writing down the one electron Schrodinger equation for the hydrogen atom. You do not worry about the center of mass, the nucleus is too heavy, we do not consider the kinetic energy of the nucleus or kinetic energy of the whole atom system, but only the one electron system that we need to study. And the Hamiltonian for the one electron system is given by minus h bar square by 2 m e - the mass of the electron. So, three-dimensional system therefore, the kinetic energy contains three components, the derivative with respect to the three coordinates x e square plus dou square by dou y e square plus dou square by dou z e square and the potential energy minus z e square by 4 pi epsilon naught r z is the charge on the nucleus of course, that is equal to plus 1.

And so what you have is the ze square by 4 pi epsilon naught r and these are the coordinates of the electron with respect to the central mass, where it is approximately on the nucleus and so on. Therefore, this the Schrodinger equation that we need to solve and obtain the solution H psi n which is now a function of the three coordinates x e, y e and z e is equal to E n times psi n of x e, y e, z e. So, these solutions the psi n's and the E n's in the case of hydrogen atoms are slightly more complex and what you see in the particle in the one-dimensional box or the harmonic oscillator.

Now, it is almost like thirty minutes since we started this lecture. So, let me stop here. And in the second part of this lecture, which is continuing to the quantum mechanics, let me complete to the exercise of writing down the energy levels and the wave functions for the hydrogen atom. And also the most important aspect of the hydrogen atom that relevant to spectroscopy namely the concept of angular momentum would be introduced in the second lecture. The next lecture and this would be a quick summary, and a review of the basic quantum mechanics that you need for understanding the rest of the course.

Until then, thank you very much.