Basic Quantum Mechanics

Prof. Ajoy Ghatak

Department of Physics

Indian Institute of Technology, Delhi

Module No. # 06

Hydrogen Atom and other Two Body Problem

Lecture No. # 04

Two Body Problems: The Diatomic Molecule (Contd.) and the 3 Dimensional Oscillator

Our last lecture, we were discussing the spectrum from a diatomic molecule, and due to the vibrational motion and rotational motion. So, we will continue our analysis of the Diatomic Molecule and hopefully in this lecture, we will also discuss the 3 Dimensional Oscillator and after we finish that, that will be the end of simple solutions of the Schrodinger equation and we will go over to the bra and ket algebra, which is due to the Nobel prize winning physicist P.A.M. Dirac.

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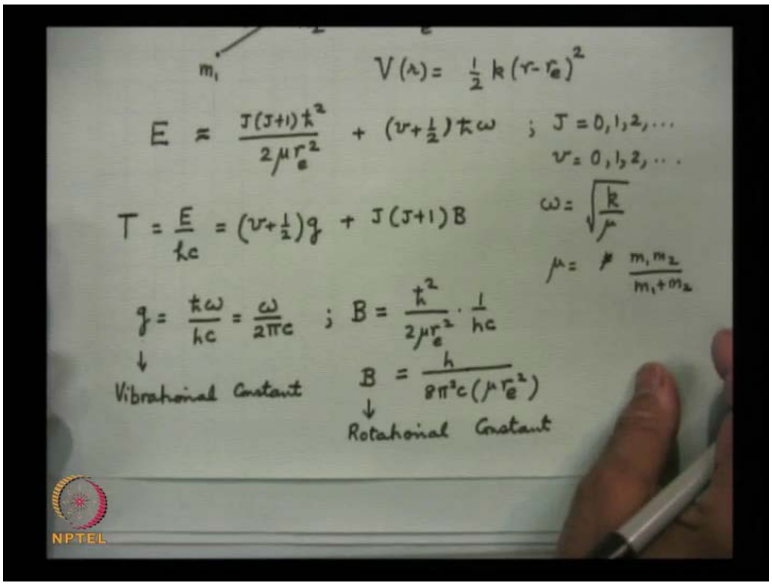

m_1

$$V(r) = \frac{1}{2}k(r-r_e)^2$$

$$E \approx \frac{J(J+1)\hbar^2}{2\mu r_e^2} + \left(v+\frac{1}{2}\right)\hbar\omega \quad ; \quad J = 0, 1, 2, \ldots \quad v = 0, 1, 2, \ldots$$

$$\omega = \sqrt{\frac{k}{\mu}}$$

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

$$T = \frac{E}{hc} = \left(v+\frac{1}{2}\right)g + J(J+1)B$$

$$g = \frac{\hbar\omega}{hc} = \frac{\omega}{2\pi c} \quad ; \quad B = \frac{\hbar^2}{2\mu r_e^2}\cdot\frac{1}{hc}$$

$g \downarrow$ Vibrational Constant

$$B = \frac{h}{8\pi^2 c(\mu r_e^2)}$$

$B \downarrow$ Rotational Constant

So, today we continue our discussions on the diatomic molecule, in our last lecture, we had said that we have two atoms of a molecule each one of mass m 1 and 1 of mass m 2 they are held together by a Hooke's law type force, and r e is the equilibrium distance.

And the potential energy describing, the interaction of the two atoms is assumed to be of the form of half k r minus r e square. Then we had the, solve the Schrodinger equation; corresponding to that, corresponding to this variation of the potential energy distribution; and we had found that for small vibrations with total energy consisted of two parts, J into J plus 1 h cross square by 2 mu r e square, this is the rotational energy of the diatomic molecule plus v plus half h cross omega, where these are due to the vibrational energy.

And the quantum number J is can take the values J equal to 0, 1, 2, 3 and the vibrational quantum number will also take values 0, 1, 2, 3 actually this is approximately equal to for small vibrations. But, this is a fairly good description of the energy levels of as we will see for for diatomic molecules. Now, here omega is the omega is the related to the force constant, Hooke's law type force constant k by this relation, when mu is the reduced mass of the two particles.

So, mu is equal to mu m 1 m 1 m 2 divided by m 1 plus m 2, as I had mentioned in my last lecture in spectroscopy, the energy levels are measured in wave number units and it is represented, the energy is represented by the symbol E, T and this is defined as E by h c. So, if I substitute this here, so we will get we will write a, so let me write down this first v plus half v plus half into g plus J into J plus 1 into B. So, here g as you would guess will be equal to h cross omega, this number divided by h c, so h cross is h over 2 pi, so this is equal to omega by 2 pi c.

And on the other hand the rotational constant, this is known as the vibrational constant this is known as the vibrational constant constant and the this is known as the rotational constant, and this will be equal to h cross square by h c, so h cross square by 2 mu r e square divided by h c. So, if you write this down, so this is h over 2 pi h square by 4 pi square, so this is a factor of 8, 1 h cancels out with here, so this will become h divided by 8 pi square c into mu r e square, so this is the rotational constant.

So, this is known as the, from the spectroscopic data, you will try to find both these rotational constant and the vibrational constant, and form there we will estimate the values of omega k and the inter atomic distance. So, this quantity capital B is known as the rotational rotational constant therefore, we rewrite this equation; we rewrite this expression for the energy levels for a diatomic molecule.

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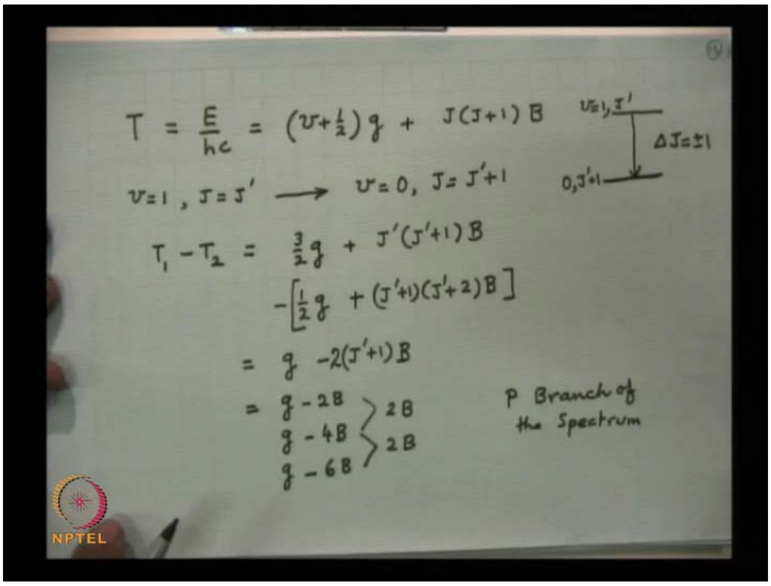

$$T = \frac{E}{hc} = \left(v+\tfrac{1}{2}\right) g + J(J+1) B$$

$v=1, J'$; $0, J'+1$; $\Delta J = \pm 1$

$$v=1,\ J=J' \longrightarrow v=0,\ J=J'+1$$

$$T_1 - T_2 = \tfrac{3}{2} g + J'(J'+1) B - \left[\tfrac{1}{2} g + (J'+1)(J'+2) B\right]$$

$$= g - 2(J'+1) B$$

$$= \left.\begin{matrix} g - 2B \\ g - 4B \\ g - 6B \end{matrix}\right\} \begin{matrix} 2B \\ 2B \end{matrix}$$

P Branch of the Spectrum

So, T is equal to E by h c v plus half into g plus J into J plus 1 into B, now let us suppose the transition is made from v is equal to 1 and J is equal to J prime and the transition is made to v is equal to 0 and J is equal to J prime plus 1. In fact, when a transition is made from one state to the other, the selection rule is that delta J would be either plus 1 or minus 1.

So, you have so you have from v equal to 1, so the so the energy that is that is emitted is T 1 minus T 2 and that will be equal to v equal to 1 will be 1 plus half is 3 by 2 g plus J prime into J prime plus 1 minus, if v is 0, so that is half g minus, so this is minus the term value of the second term that is from v equal to 1 and J is equal to J prime to v equal to 0 to J prime plus 1, so this is the transition that I am talking about.

So, this will be J prime plus 1 into J prime plus 1 plus 1, that is J prime plus 2, this will be here a B, here a B, so 3 by 2 minus half becomes g, so g so this will be minus if I take J prime plus 1 common, so this will be J prime plus 2 minus J prime. So, therefore, 2 will come out common, so 2 into B this is a very, these are the, so for this will become equal to from J prime equal to 0 becomes g minus 2 B for J prime equal to 1, this becomes g minus 4 B and g minus 6 B.

So, this leads to equally spaced lines and the spacing between the two, the spacing between the two lines in centimeter inverse will be 2 B, the spacing between the lines will be 2 B, these lines are referred to as the p branch of the spectrum p branch of the spectrum.

So, we will obtain equally spaced lines, now I will show you the experimental data in a moment, but before that let me consider the another transition. And the transition that we will be considering, that will be instead of J delta J equal to plus 1, we will consider delta J equal to minus 1.

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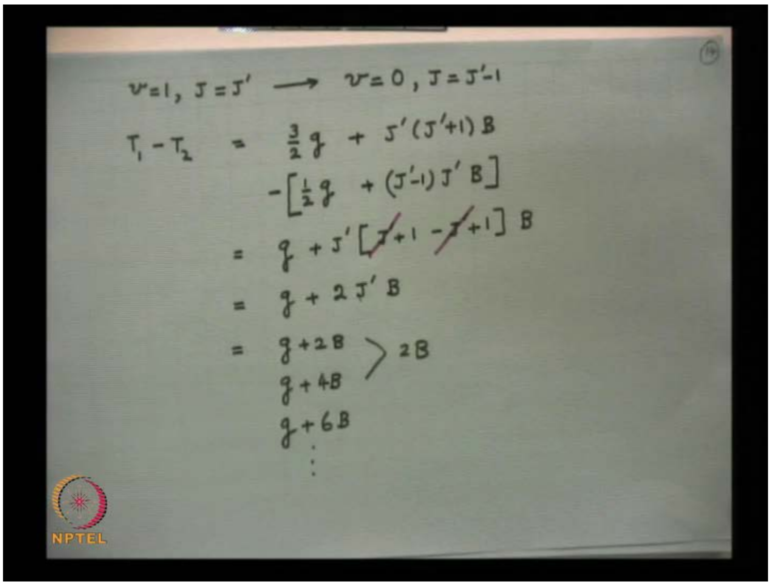

$$v=1,\ J=J' \longrightarrow v=0,\ J=J'-1$$

$$\begin{aligned} T_1 - T_2 &= \tfrac{3}{2}g + J'(J'+1)B \\ &\quad - \left[\tfrac{1}{2}g + (J'-1)J'B\right] \\ &= g + J'\left[\cancel{J'}+1 - \cancel{J'}+1\right]B \\ &= g + 2J'B \\ &= g+2B \\ &\quad\ g+4B \\ &\quad\ g+6B \\ &\quad\ \vdots \end{aligned}$$

$\Big\rangle\ 2B$

So that, let us consider a transition v equal to 1 J equal to J prime going over to v equal to 0, actually delta v is equal to plus 1, J is equal to J prime minus 1, so if I do that then it will be T 1 minus T 2 will be again 3 by 2 g plus J prime into J prime plus 1 B minus and then v is equal to 0, so half g half g and minus, so J prime minus 1 so it will be J prime minus 1 into J prime minus 1 plus 1, that is J prime.

So, if I calculate this 3 by 2 minus half 3 by 2 minus half will become g and minus minus, so this will be plus I am sorry so, this will be J prime, if I take outside, so you will get J prime and this will be J prime plus 1 minus J this is a very trivial (()), simple calculation into B. So, the J prime J prime cancels out, so this as earlier, so we will get 2 that is, this will be g plus 2 J prime B.

So, this will be for J prime equal to 1, so J prime equal to 1 to J prime J J equal to J prime to J equal to 0 transition, you will have g plus 2 B for J prime equal to 2, this will be g plus 4 B and g plus 6 B and so on. So, once again we will obtain equally spaced lines and on the either side of the value g, so the difference between these 2 will be 2 B.

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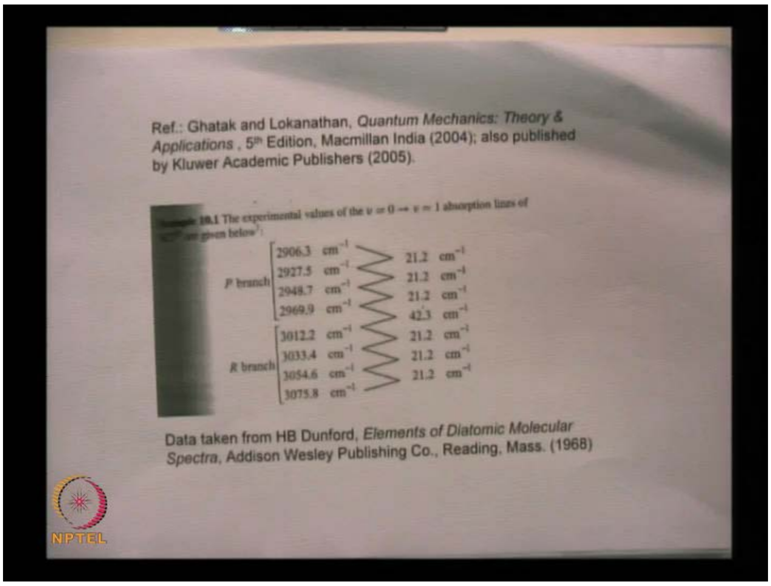

Ref.: Ghatak and Lokanathan, *Quantum Mechanics: Theory & Applications* , 5th Edition, Macmillan India (2004); also published by Kluwer Academic Publishers (2005).

[illegible] 10.1 The experimental values of the $v = 0 \rightarrow v = 1$ absorption lines of [illegible] given below:

	Line	Difference
P branch	2906.3 cm^{-1}	
		21.2 cm^{-1}
	2927.5 cm^{-1}	
		21.2 cm^{-1}
	2948.7 cm^{-1}	
		21.2 cm^{-1}
	2969.9 cm^{-1}	
		42.3 cm^{-1}
R branch	3012.2 cm^{-1}	
		21.2 cm^{-1}
	3033.4 cm^{-1}	
		21.2 cm^{-1}
	3054.6 cm^{-1}	
		21.2 cm^{-1}
	3075.8 cm^{-1}	

Data taken from HB Dunford, *Elements of Diatomic Molecular Spectra*, Addison Wesley Publishing Co., Reading, Mass. (1968)

So, if I I am now showing you the actual spectrum, the actual spectral lines in the P branch these are the observed lines and the difference between these two are always 21.2 centimeter inverse. And this is the R branch and as I had shown you earlier, that that in the R branch, we have g plus 2 B, g plus 4 B, g plus 6 B, so this is g plus 2 B, this is g plus 6 4 B and g plus 6 B, and the difference between these two is 2 B, so 21.2 centimeter inverse.

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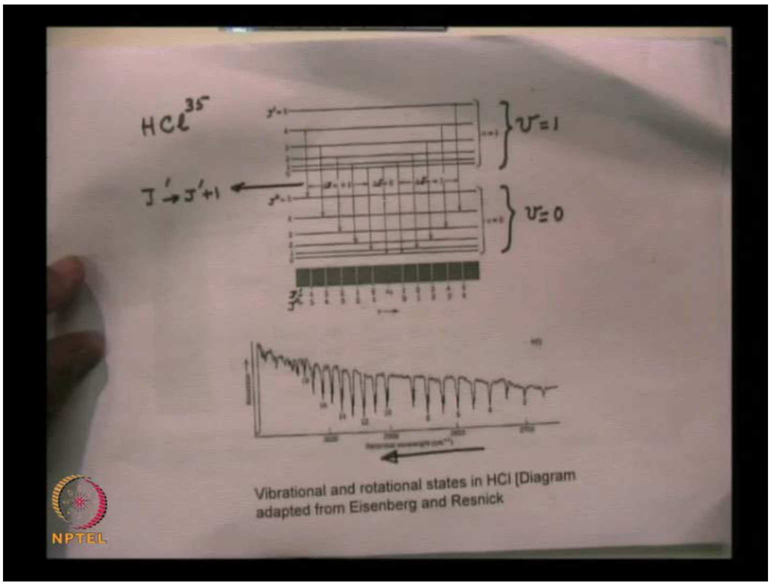

Vibrational and rotational states in HCl (Diagram adapted from Eisenberg and Resnick

Let me show you the actual spectrum let me show you the actual spectrum, this corresponds to the HCl actually, it is HCl 35 with the isotope which has an atomic mass of 35, so these are the energy levels. So, these corresponds the top diagram corresponds to v is equal to 1, the bottom diagram corresponds to v is equal to 0, this is v equal to 0 as I had tried to show.

Now, you can see here, that this line this is J prime to J prime plus 1, this is a 4 to 5 transition, this is 2 to 4, 3 to 4 transition, 2 to 3 transition and 1 to 2 transition, and 0 to 1. So, these transitions corresponds to J prime to J prime plus 1, and we have this is in centimeter inverse and the the reciprocal wavelength is increasing in this direction is increasing in this direction.

So, you will have and similarly, here also we will have v equal to 1 to 0, 1 to 0, so but, the lines the absorption spectra at equally spaced and that is what we have tried to show in the table, that this is the spectrum of the P branch and the R branch. And the difference between these two, difference in wave number units difference in the wave number units between these two absorption lines between these two absorption lines, these are all equally spaced in the reciprocal wavelength space.

And you will have you will have the difference is always 21.2 centimeter inverse, and so therefore, which validates the approximate theory that we have developed and we therefore, have we therefore have this the 2 B, we will find that 2 B is therefore, equal to

21.2 centimeter inverse, 2 B is the is the separation between two consecutive lines (Refer Slide Time: 16:12).

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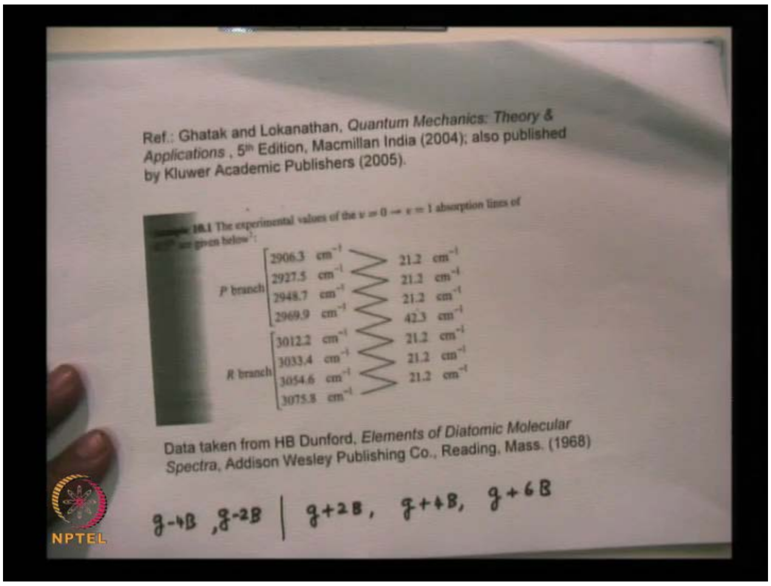

Ref.: Ghatak and Lokanathan, *Quantum Mechanics: Theory & Applications*, 5th Edition, Macmillan India (2004); also published by Kluwer Academic Publishers (2005).

10.1 The experimental values of the $v = 0 \rightarrow v = 1$ absorption lines of [illegible] are given below:

P branch	2906.3 cm^{-1}	21.2 cm^{-1}
	2927.5 cm^{-1}	21.2 cm^{-1}
	2948.7 cm^{-1}	21.2 cm^{-1}
	2969.9 cm^{-1}	42.3 cm^{-1}
R branch	3012.2 cm^{-1}	21.2 cm^{-1}
	3033.4 cm^{-1}	21.2 cm^{-1}
	3054.6 cm^{-1}	21.2 cm^{-1}
	3075.8 cm^{-1}	

Data taken from HB Dunford, *Elements of Diatomic Molecular Spectra*, Addison Wesley Publishing Co., Reading, Mass. (1968)

$$g-4B,\ g-2B \ \big|\ g+2B,\ g+4B,\ g+6B$$

And we can see that they are consistently 21. 2 centimeter, except the center J equal to J prime equal to 0 to J double prime equal to 0 that transition is forbidden. So, at the center you will have the spacing, because you will have g plus 2 B, g plus 4 B, g plus 6 B and on the other side g minus 2 B, g minus 4 B, etcetera. But, the g transition is not is not allowed, so from this you will obtain that 2 B is equal to 21.2 centimeter inverse.

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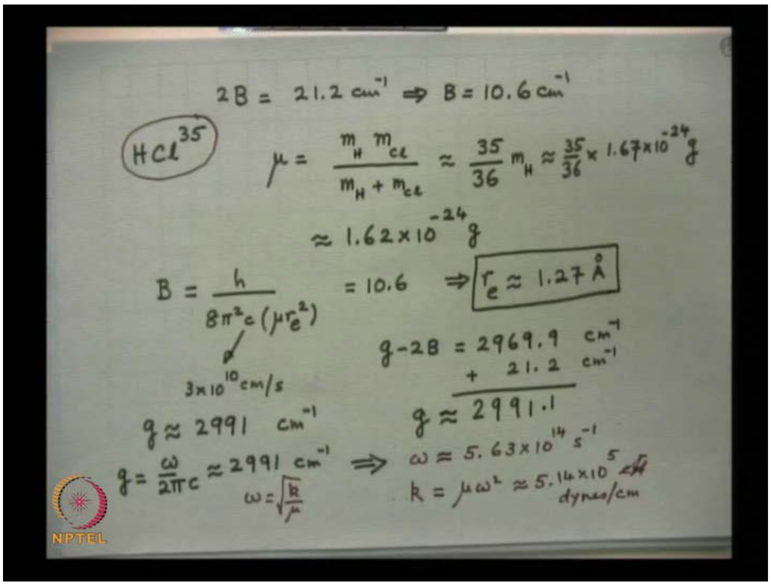

$$2B = 21.2\ cm^{-1} \Rightarrow B = 10.6\ cm^{-1}$$

HCl^{35}

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} \approx \frac{35}{36} m_H \approx \frac{35}{36} \times 1.67 \times 10^{-24}\ g$$

$$\approx 1.62 \times 10^{-24}\ g$$

$$B = \frac{h}{8\pi^2 c(\mu r_e^2)} = 10.6 \Rightarrow \boxed{r_e \approx 1.27\ \mathring{A}}$$

c: $3 \times 10^{10}\ cm/s$

$$g - 2B = 2969.9\ cm^{-1}$$
$$+\ 21.2\ cm^{-1}$$
$$g \approx 2991.1$$

$$g \approx 2991\ cm^{-1}$$

$$g = \frac{\omega}{2\pi c} \approx 2991\ cm^{-1} \Rightarrow \omega \approx 5.63 \times 10^{14}\ s^{-1}$$

$$\omega = \sqrt{\frac{k}{\mu}}$$

$$k = \mu\omega^2 \approx 5.14 \times 10^{5}\ \text{dynes/cm}$$

So, therefore, this implies that B is equal to 10.6 centimeter inverse and therefore, for the HCl 35 the reduced mass is given by the mass of the hydrogen atom multiplied by the mass of the chlorine atom with the (()) corresponding with 35 isotope divided by m H plus m c l. And this will be approximately equal to 35 m H square divided by 36 m h, and if you substitute the mass of the hydrogen atom, so this will be 35 by 36 into 1.67 into 10 to the power of minus 24 grams.

And if I evaluate this, this will come out to be about you may know write down 6 2 into 10 to the power of minus 24 grams, we are consistently working in the cgs system of units. So, as I had mentioned earlier that B the rotational constant is given by h over 8 pi square c mu r e square, and I know the value of h which is about 6.6 into 10 to the power of minus 27 (()).

c is about the velocity of light in free space, this is about 3 into 10 to the power of 10 centimeter per second, mu we know and the rotational constant we know, that is equal to 10.6. So, the only unknown is the inter atomic distance and that will if you substitute this it is a very simple algebra, this will come out to be 1.27 angstrom.

Now, so this allows me that the inter atomic spacing between the hydrogen atom and the chlorine atom in HCl 35 is about 1.27 angstrom, secondly we had shown that the spectral lines will correspond to g minus 2 B, g minus 4 B etcetera. So, g minus 2 B comes out to be 2969.9 centimeter inverse, you can I had shown this, that this corresponds to g plus 2 B, this corresponds to g minus 2 B in order to find the value of g, I can add these two and divide by 2, that is also possible or I can just add 2 B here (Refer Slide Time 19:57).

So, this corresponds to g minus 2 B, this corresponds to g minus 4 B these are equally spaced spectral lines, this is g minus 6 B, this is g minus 8 B and similarly, here this is g plus 2 B. So, I can add these two and divide by 2 I will get g or I I can add 2 B here, and I will get the value of, g let me add 2 B there does not matter it is it is the same thing. So, 2 B is 21.2 and so this is 21.2 centimeter inverse and if I add this 9 9 9, so this is the value of g.

So, we assume that g is equal to 2991 centimeter inverse and this was equal to omega by 2 pi c is equal to then 2991, so this is g is equal to so much, we know the value of pi, we know the value of c. And from this we can easily calculate the value of omega and the value of omega will be omega will be simple exercise 5.63 into 10 to the power of 14 second inverse. And I have I already know the value of k, so k the force constant is equal to mu omega square you may recall that omega was equal to under root of k by mu, so k is equal to mu omega square, I know the value of omega, I know the value of mu and this comes out to be 5.14 into 10 to the power of 5 centimeter inverse, I am sorry dynes per centimeter, dynes in the cgs system of unit this is the force constant, the force constant.

So, there are before I proceed further, I must give the appropriate reference, this diagram is actual spectrum is adapted from a book on quantum physics by Eisberg sorry Eisberg, not Eisenberg, Eisberg and Resnick. And these data that I have taken; this is analyzed in our book on quantum mechanics by myself and professor Lokanathan and published by Macmillan and also Kluwer (Refer Slide Time: 22:39). But, the actual data was taken from a very beautiful book by HB Dunford, elements of diatomic molecular spectra, published by Addison Wesley publishing company, so the data is actually taken from HB Dunford’s book.

Now, the very fact that you have equally spaced lines proves, the validity of our theory that the diatomic molecular spectra can be explained by assuming a simple Hooke’s law type of force between the two atoms. And that the vibrational distance rho you remember, we defined the symbol rho for r minus r e is the vibrational distance is small compare to r e. So, the very fact that we have been our experiment, the experiment shows equally spaced lines for the diatomic molecular spectrum, validates the theory that we have developed.

I will give you one more example, and that is the, so we have considered in this example, the hydrogen chloride this is the example, that we have considered we will consider one more example, and that is the carbon 12 O 16 that is carbon monoxide carbon monoxide. This is a molecule which consist of carbon which corresponding to the isotope 12, mass number and oxygen and here also you obtain equally spaced lines.

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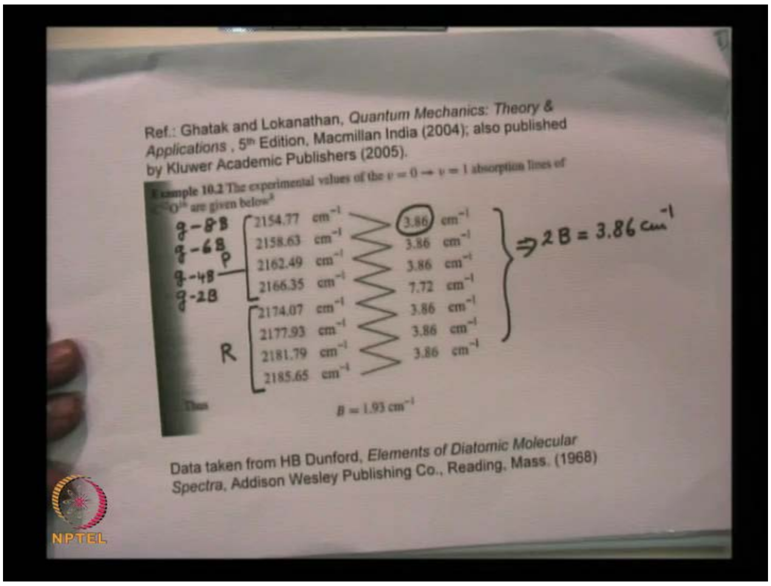

Ref.: Ghatak and Lokanathan, *Quantum Mechanics: Theory & Applications*, 5th Edition, Macmillan India (2004); also published by Kluwer Academic Publishers (2005).

Example 10.2 The experimental values of the $v = 0 \rightarrow v = 1$ absorption lines of O^{16} are given below[3]

P
$g - 8B$ 2154.77 cm^{-1}
$g - 6B$ 2158.63 cm^{-1}
$g - 4B$ 2162.49 cm^{-1}
$g - 2B$ 2166.35 cm^{-1}

R
2174.07 cm^{-1}
2177.93 cm^{-1}
2181.79 cm^{-1}
2185.65 cm^{-1}

$\boxed{3.86}$ cm^{-1}
3.86 cm^{-1}
3.86 cm^{-1}
7.72 cm^{-1}
3.86 cm^{-1}
3.86 cm^{-1}
3.86 cm^{-1}

$\Rightarrow 2B = 3.86\ cm^{-1}$

Thus

$B = 1.93\ cm^{-1}$

Data taken from HB Dunford, *Elements of Diatomic Molecular Spectra*, Addison Wesley Publishing Co., Reading, Mass. (1968)

Here, also as I will show this is also discussed in an example in our book by myself and professor Lokanathan and but, the experimental data is actually of HB Dunford from elements of diatomic molecular spectrum published by Addison Wesley publishing.

So, here also as we will see, you will obtain equally spaced lines equally spaced lines this is the P branch this is the P branch of the spectrum and this is the R branch, and the energy difference is equal is equal which once again validates our theory, so this difference. So, this is this is equal to g minus 2 B, this is g minus 4 B and g minus 6 B and g minus 8 B, I hope you understand what I am trying to say, so each line is separated from the adjacent line by 2 B; so this quantity is equal to 2 B. So, form here we from this data we get that since, their equally spaced lines that 2 B is equal to 3.86 centimeter inverse.

So, once again the very fact that you obtain equally spaced spectral lines, validates the model that we have developed and from this now, we can find out once again the inter atomic spacing.

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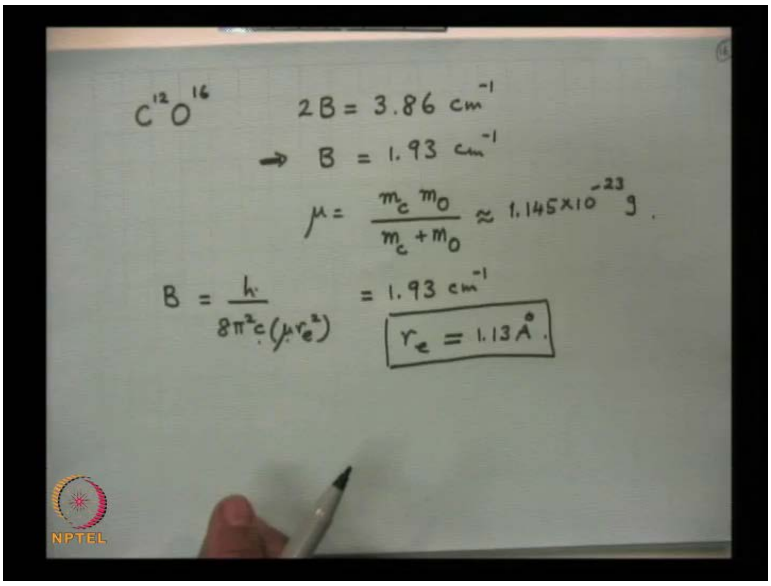

$C^{12}O^{16}$ $\quad 2B = 3.86\ \text{cm}^{-1}$

$\rightarrow B = 1.93\ \text{cm}^{-1}$

$$\mu = \frac{m_c\, m_O}{m_c + m_O} \approx 1.145 \times 10^{-23}\ \text{g}.$$

$$B = \frac{h}{8\pi^2 c(\mu r_e^2)} = 1.93\ \text{cm}^{-1}$$

$$\boxed{r_e = 1.13\ \text{Å}.}$$

So, 2 B is equal to 3.86 centimeter inverse and therefore, this implies that B is equal to 1.93 centimeter inverse and you have the reduced mass is mass of the carbon atom, mass of the oxygen atom, it is not 0, it is O and then mass of the carbon atom plus mass of the oxygen atom. If you substitute these masses, then this comes out to be about 1.145 into 10 to the power of minus 23 grams.

So, the rotational constant comes out to be is equal to h by 8 pi square c mu r e square and you will obtain this as equal to 1.93 centimeter inverse and I know here h, I know c, I know mu, from which I will get r e is equal to 1.13 angstrom and similarly, since 2 B is 2 B is 3.16, so this is this is 2166.35.

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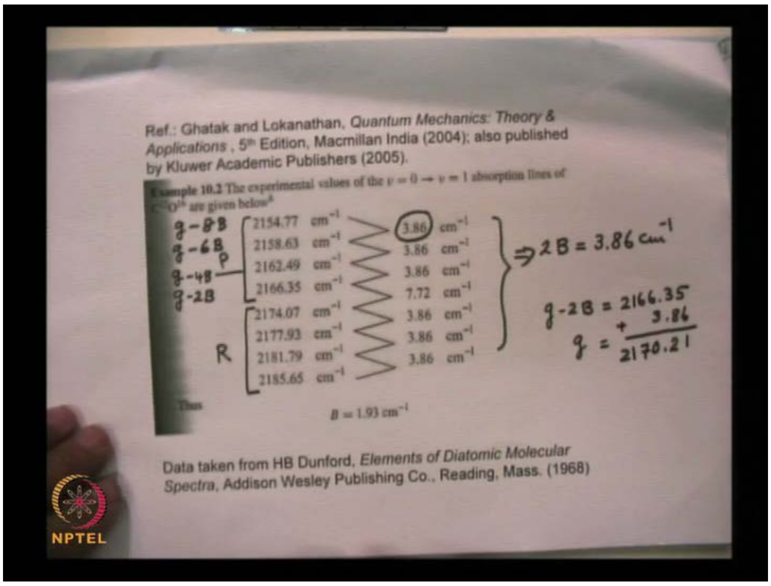

Ref.: Ghatak and Lokanathan, *Quantum Mechanics: Theory & Applications*, 5th Edition, Macmillan India (2004); also published by Kluwer Academic Publishers (2005).

Example 10.2 The experimental values of the $v = 0 \to v = 1$ absorption lines of $C^{12}O^{16}$ are given below

$g-8B$	P	2154.77 cm^{-1}	3.86 cm^{-1}
$g-6B$		2158.63 cm^{-1}	3.86 cm^{-1}
$g-4B$		2162.49 cm^{-1}	3.86 cm^{-1}
$g-2B$		2166.35 cm^{-1}	7.72 cm^{-1}
	R	2174.07 cm^{-1}	3.86 cm^{-1}
		2177.93 cm^{-1}	3.86 cm^{-1}
		2181.79 cm^{-1}	3.86 cm^{-1}
		2185.65 cm^{-1}	

$\Rightarrow 2B = 3.86\ \text{cm}^{-1}$

$$g - 2B = 2166.35$$
$$+\ 3.86$$
$$g = 2170.21$$

Thus

$B = 1.93\ \text{cm}^{-1}$

Data taken from HB Dunford, *Elements of Diatomic Molecular Spectra*, Addison Wesley Publishing Co., Reading, Mass. (1968)

So, g minus 2 B is equal to 2166.35, so 2 B is 3.86, so therefore, g will be equal to plus 3.86, so if you add this 20721, so g will be equal to.

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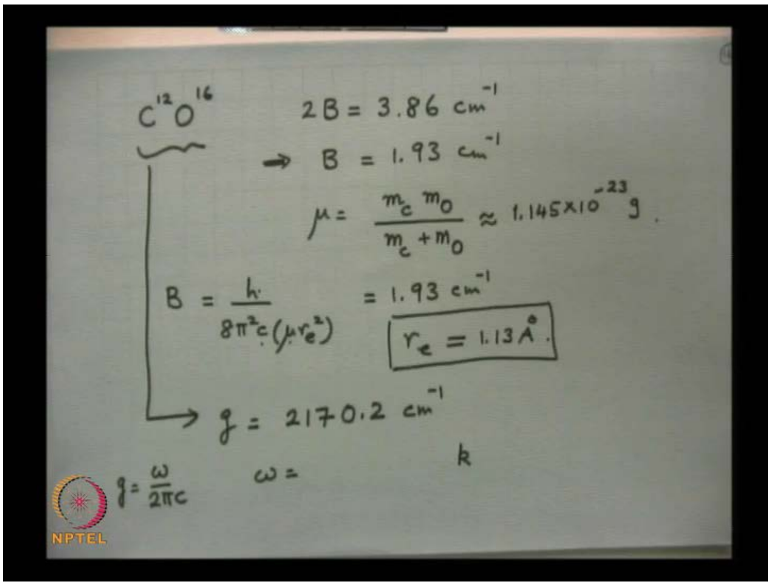

$C^{12}O^{16}$

$2B = 3.86\ \text{cm}^{-1}$

$\rightarrow B = 1.93\ \text{cm}^{-1}$

$\mu = \dfrac{m_c m_o}{m_c + m_o} \approx 1.145 \times 10^{-23}\ \text{g}.$

$B = \dfrac{h}{8\pi^2 c(\mu r_e^2)} = 1.93\ \text{cm}^{-1}$

$\boxed{r_e = 1.13\ \text{Å}.}$

$\rightarrow g = 2170.2\ \text{cm}^{-1}$

k

$g = \dfrac{\omega}{2\pi c}$ $\quad \omega =$

So, for the this molecule for the this molecule the quantity g will be equal to 2170.2 centimeter inverse and we know the reduced mass I leave it as an exercise for you to calculate omega from this is g is equal to omega by 2 pi c. So, I can calculate what is omega and then I can also calculate what is the force constant which are holding the two atoms together.

So, that completes I have given you two examples, one corresponding to hydrogen chloride and actually the hydrogen hydrogen chloride spectrum consist of two very closely spaced lines. If you look at this carefully, one one line if you can see this on the screen one line corresponds to HCl 35 the other is of HCl 37. So, these are two isotopes of chlorine which are present in hydrogen chloride which gives to two lines, two very closely spaced lines in the in the molecular spectrum.

So, that completes the application of the solution of the Schrodinger equation to the atomic molecular spectrum.

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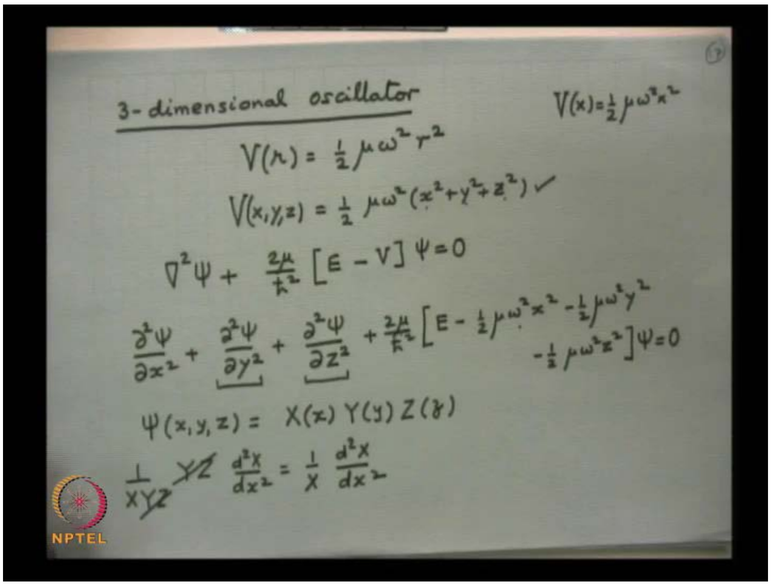


3-dimensional oscillator

$V(x)=\frac{1}{2}\mu\omega^2x^2$

$$V(r)=\frac{1}{2}\mu\omega^2r^2$$

$$V(x,y,z)=\frac{1}{2}\mu\omega^2(x^2+y^2+z^2)\ \checkmark$$

$$\nabla^2\psi+\frac{2\mu}{\hbar^2}[E-V]\psi=0$$

$$\frac{\partial^2\psi}{\partial x^2}+\underbrace{\frac{\partial^2\psi}{\partial y^2}}+\underbrace{\frac{\partial^2\psi}{\partial z^2}}+\frac{2\mu}{\hbar^2}\Big[E-\frac{1}{2}\mu\omega^2x^2-\frac{1}{2}\mu\omega^2y^2-\frac{1}{2}\mu\omega^2z^2\Big]\psi=0$$

$$\psi(x,y,z)=X(x)\,Y(y)\,Z(z)$$

$$\frac{1}{X\cancel{YZ}}\cancel{YZ}\frac{d^2X}{dx^2}=\frac{1}{X}\frac{d^2X}{dx^2}$$

Now, this was one application and the last application in the solution of the Schrodinger equation that we will be discussing is the 3 dimensional 3 dimensional harmonic oscillator ocsilator just oscillators. So, the after, this after we finish this then we will start with the bra ket algebra due to Dirac. So, in this we consider a two body interaction in which the potential energy distribution is given by half mu omega square; mu is the reduced mass, omega is the natural frequency of the oscillator time r square.

So, you would like to solve this 3 dimensional oscillator problem you may recall that we had, we had solved V of X is equal to half mu omega square x square, this we had solved. Now, there are two methods of solving this problem and we will briefly discussed both of them actually (()) I will leave them as problems and first I can convert this into Cartesian coordinates and solve by the method of separation of variables. And the second method will be, since it is a spherically symmetric potential, it depend only on the distance between these two particles, we can use the, we can solve the Schrodinger equation, as we have done for the hydrogen atom problem, we will briefly discuss both of them.

So, let me first do the by writing it in Cartesian coordinate, so in Cartesian coordinates m omega square this becomes x square plus y square plus z square, whenever the potential energy distribution is such, that it can be written as sum function of x plus function of y plus function of z, then you can use the method of separation of variables.

Now, we will write V (()) as a function of r but, V as a function of x, y, z, so del so the Schrodinger equation is del square psi plus 2 mu by h cross square E minus B E minus B, so that is E minus V of x, y, z into psi is equal to 0.

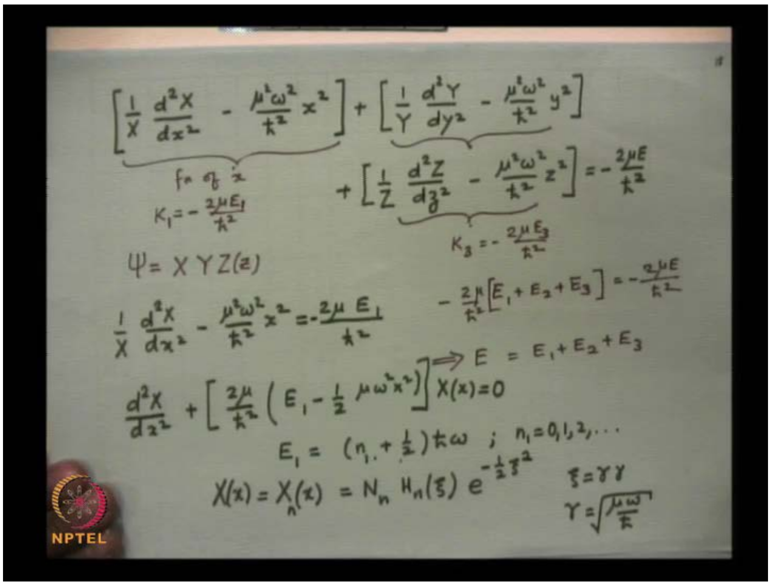
So, we will use first this representation and therefore, we will use the Cartesian system of coordinates that is delta 2 psi by delta x square plus delta 2 psi by delta y square plus delta 2 psi by delta z square plus 2 mu by h cross square E minus half mu omega square x square minus half mu omega square y square minus half mu omega square z square psi is equal to 0.

Now, what we will do is, this is the standard method for separation of variables by now, you should be all familiar with this, that psi of x, y, z let us do this carefully, this I write down as a function of X times, function of y times a function of Z, I substitute this and divide by psi.

So, I will get one side the, first term let me write it down, so I have 1 over capital X, Y, Z when I differentiate with respect to x, this can be taken outside, so Y, Z can be taken outside, so this will become d 2 x by dx square. So, y, z y, z will cancel out, so this will be 1 over X d 2 X by dx square similarly, when you substitute this will give you 1 by y d 2 y by dy square similarly, this term will give me 1 by z (()) 2 z by d z square.

And then, I have divided by psi, so this term will cancel out I will obtain a term depending only on x, depending on y, and depending on z. And if you if you multiply this to this, you get mu square omega square by h cross square mu square omega square by h cross square, so we have here we have here, if you let me do this carefully.

(Refer Slide Time: 35:38)



$$\underbrace{\left[\frac{1}{X}\frac{d^2X}{dx^2} - \frac{\mu^2\omega^2}{\hbar^2}x^2\right]}_{\substack{\text{fn of } x \\ K_1 = -\frac{2\mu E_1}{\hbar^2}}} + \underbrace{\left[\frac{1}{Y}\frac{d^2Y}{dy^2} - \frac{\mu^2\omega^2}{\hbar^2}y^2\right]}$$

$$+ \underbrace{\left[\frac{1}{Z}\frac{d^2Z}{dz^2} - \frac{\mu^2\omega^2}{\hbar^2}z^2\right]}_{K_3 = -\frac{2\mu E_3}{\hbar^2}} = -\frac{2\mu E}{\hbar^2}$$

$$\psi = XYZ(z)$$

$$-\frac{2\mu}{\hbar^2}\left[E_1 + E_2 + E_3\right] = -\frac{2\mu E}{\hbar^2}$$

$$\frac{1}{X}\frac{d^2X}{dx^2} - \frac{\mu^2\omega^2}{\hbar^2}x^2 = -\frac{2\mu E_1}{\hbar^2}$$

$$\Rightarrow E = E_1 + E_2 + E_3$$

$$\frac{d^2X}{dx^2} + \left[\frac{2\mu}{\hbar^2}\left(E_1 - \frac{1}{2}\mu\omega^2x^2\right)\right]X(x) = 0$$

$$E_1 = \left(n_1 + \frac{1}{2}\right)\hbar\omega \; ; \; n_1 = 0, 1, 2, \ldots$$

$$X(x) = X_n(x) = N_n H_n(\xi)\, e^{-\frac{1}{2}\xi^2} \qquad \xi = \gamma x \qquad \gamma = \sqrt{\frac{\mu\omega}{\hbar}}$$

So, you will have 1 over X d 2 X by dx square that is the first term and if I multiply this to this you will get mu square omega square by h cross square times x square plus a similar term for y, 1 over Y d 2 Y by dy square minus mu square omega square by h cross square y square plus another term for z, that is 1 over Z d 2 Z by d z square minus mu square omega square by h cross square z square. This must be equal to minus 2 mu E by h cross square, this I have taken to the right hand side, 2 mu E by h cross square.

Now, you see as we have done in the past, the variables have indeed separated out, we have used the method of separation of variables and the variables have been indeed separated out, this the first term is a function of x only, this is a function of x, this is a function of y, and this is a function of z.

And this added together gives me a constant, this can only happen, if this is a constant this is a constant and this is a constant, this is how the method of separation of variable works (Refer Slide Time: 37:45). So, let me write this down as, that this is equal to minus 2 mu E 1 8 by h cross square just some constant, that mu is known, h cross is known E 1 is another (()) and this is minus 2 mu E 2 by h cross square, this is minus 2 mu E 2 E 3 by h cross square.

So, once again I use the method of separation of variables that is I wrote the wave function function of X, function of Y and function of Z, I substituted in the Schrodinger equation and manipulated it. And I find there are three terms, the first term depends only on the X coordinate, the second term depends only on the Y coordinate and the third term depends only on the Z coordinate. Now, these three added together must be equal to a constant, a function of X when multiplied by function added to a function of Y and added to another function of Z, can now will be equal to a constant, unless each one of them is a constant.

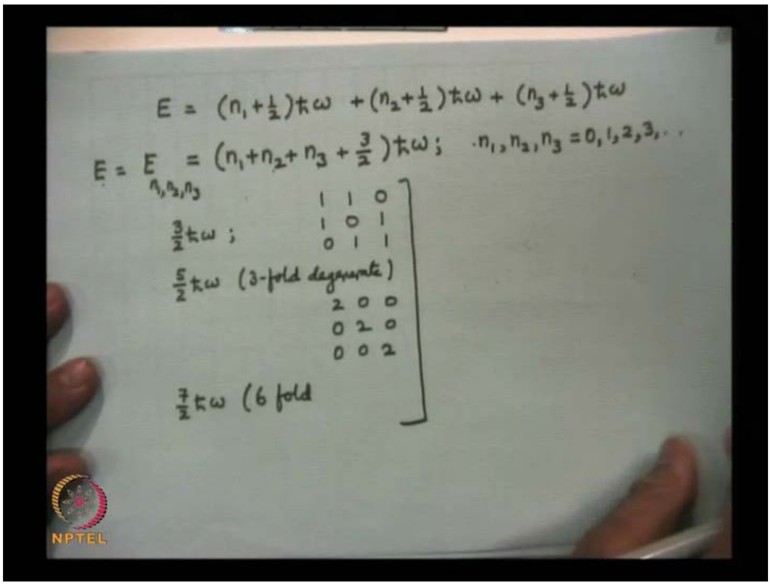
So, we set this equal to minus 2 mu, we can set this equal to k 1 and that I write as minus 2 mu E 1 by h cross square, this I write as minus 2 mu E 2 by h cross square and this I write as K 3 which is equal to minus 2 mu E 3 by h cross square. So, you will have E 2 mu by h cross square E 1 plus E 2 plus E 3 that is the left hand side will be equal to, with a negative sign will be equal to minus 2 mu E by h cross square; so this will give me E will be equal to E 1 plus E 2 plus E 3.

Now, let me write down the equation determining equation involving X, so I will have 1 by capital X please see this carefully, d 2 X by dx square minus mu square omega square by h cross square x square is equal to 2 mu E 1 by h cross square with a minus sign, so I rearrange this, so I will get d 2 X by dx square plus, if I take 2 mu by h cross square outside, then you will have E 1 minus half mu omega square x square X of x this is the 1 dimensional harmonic oscillator problem.

And we had solved that in great detail, and we had found that E 1 was equal to n plus half h cross omega actually, I will put a subscript n 1 and n 1 will be equal to 0, 1, 2, 3 etcetera. And X of x will be equal to X of x corresponds to each value we have found that out is equal to N n of n H n of xi e 2 the power of minus half xi square, where xi is equal to gamma x and gamma was equal to mu omega by h cross (No audio from 42:05 to 42:14).

So, now I have solved the problem E 1 is equal to so much, E 2 will be a similar expression and E 3 will be a similar expression, so the total energy we have got will be the sum of individual energies and the total wave function will be product of the hermite gauss function. So, we have solved the problem corresponding to the 3 dimensional oscillators, so for this problem we had started out with V of x is equal to so much, the solution of this equation that is what we have been wanting to find out.

(Refer Slide Time: 43:07)



$$E = (n_1+\tfrac{1}{2})\hbar\omega + (n_2+\tfrac{1}{2})\hbar\omega + (n_3+\tfrac{1}{2})\hbar\omega$$

$$E = E_{n_1,n_2,n_3} = (n_1+n_2+n_3+\tfrac{3}{2})\hbar\omega ; \quad n_1, n_2, n_3 = 0, 1, 2, 3, \ldots$$

$\frac{3}{2}\hbar\omega$;

$\frac{5}{2}\hbar\omega$ (3-fold degenerate)

1 1 0
1 0 1
0 1 1
2 0 0
0 2 0
0 0 2

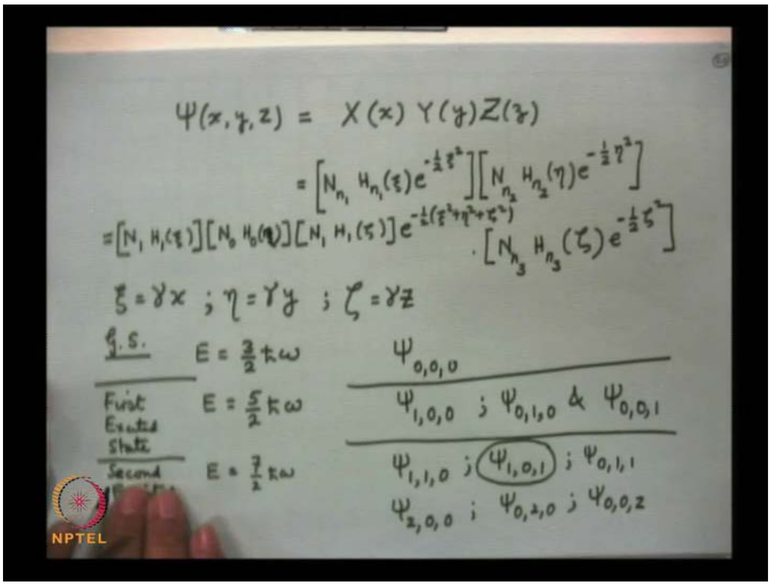
$\frac{7}{2}\hbar\omega$ (6 fold

We will find that the total energy will be n 1 plus half h cross omega plus n 2 plus half h cross omega plus n 3 plus half h cross omega. So I can write this down as n 1 plus n 2 plus n 3 plus 3 by 2 h cross omega, where n 1, n 2 and n 3 each one of them can independently take values 0, 1, 2, 3 etcetera.

So, this is the Eigen values of the problem, so I write E which dependent on 3 quantum numbers n 1, n 2, n 3 and one can, now see that the ground state energy Eigen value the ground state energy Eigen value will be 0, 0, 0, so 3 by 2 h cross omega. The first excited state will be either 1, 0, 0 or 0, 1, 0 or 0, 0, 1, so 1 plus 3 by 2 is 5 by 2 h cross omega and this will be 3-fold degenerate, it will be 3 independent Eigen functions corresponding to this.

Then you have please see, 1 1 0, 1 0 1, 0 1 1 and then 2 0 0, 0 2 0, 0 0 2 all of them will have the Eigen value 1 plus 1 is 2 2 plus 3 by 2 is 7 by 2 h cross omega. So, that is will be a 6-fold degenerate state, because there are 6 sets of quantum numbers which will give rise to the same Eigen value E and what will be my Eigen function.

(Refer Slide Time: 46:00)



$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

$$= \left[N_{n_1} H_{n_1}(\xi) e^{-\frac{1}{2}\xi^2}\right]\left[N_{n_2} H_{n_2}(\eta) e^{-\frac{1}{2}\eta^2}\right] \cdot \left[N_{n_3} H_{n_3}(\zeta) e^{-\frac{1}{2}\zeta^2}\right]$$

$$= [N_1 H_1(\xi)][N_0 H_0(\eta)][N_1 H_1(\zeta)] e^{-\frac{1}{2}(\xi^2+\eta^2+\zeta^2)}$$

$\xi = \gamma x$; $\eta = \gamma y$; $\zeta = \gamma z$

g.S. $E = \frac{3}{2}\hbar\omega$ $\psi_{0,0,0}$

First Excited State $E = \frac{5}{2}\hbar\omega$ $\psi_{1,0,0}$; $\psi_{0,1,0}$ & $\psi_{0,0,1}$

Second $E = \frac{7}{2}\hbar\omega$ $\psi_{1,1,0}$; $\boxed{\psi_{1,0,1}}$; $\psi_{0,1,1}$

$\psi_{2,0,0}$; $\psi_{0,2,0}$; $\psi_{0,0,2}$

NPTEL

So, let me write it down the Eigen functions as you, as I had told you that psi of x, y, z the Eigen value is add up, and the Eigen functions will be product, X of x Y of y and Z of z and so therefore, this will be this will be N of n 1 H n 1 xi e 2 the power of minus half xi square. And then this will be N of n 2 H n 2 of eta E to the power of minus half eta square multiplied by N of n 3 H n 3 zeta e to the power of minus half zeta square, where xi is equal to gamma x, eta is equal to gamma y and zeta is equal to gamma z.

So, these are the rigorously correct, normalized Eigen functions, ortho normal Eigen functions for the 3 dimensional oscillator problems that is for V of x given by this, these are the Eigen values. So, here this, so let me write it down once again, so we will have for for the ground state for the ground state n 1 is 0, n 2 is 0, n 3 is 0, so the total energy is 3 by 2 h cross omega and you have the equation psi 0, 0, 0. Then you have the first excited state, so you will have state, you will have E is equal to 1, 0, 0 that is 5 by 2 h cross omega and there will be three wave functions 1, 0, 0, 0, 1, 0 and 0, 0, 1.

The second excited state will have 6 Eigen functions and this will be 2 plus 0 plus 0, that is 7 by 2 h cross omega, and so this will be psi 1, 1, 0 psi 1, 0, 1 psi 0, 1, 1 and then you will have psi 2, 0, 0 psi 0, 2, 0 psi 0, 0, 2. There will be 6 wave functions, there will be 3 wave functions here and one wave function here, so these are the values of n 1, n 2 and n 3.

So, let me write just any one, so let me write down for this, so what will be psi 1, 0, 1, so that will be that will be is equal to, so let me write it down, so N of 1 H 1 of xi H 1 of xi and I can take the exponential outside N of 2, N 2 is 0, so N 0 H 0 of xi and then N 1 sorry eta I am sorry eta and N 1 H 1 of zeta multiplied by e to the power of minus half xi square plus eta square plus zeta square.

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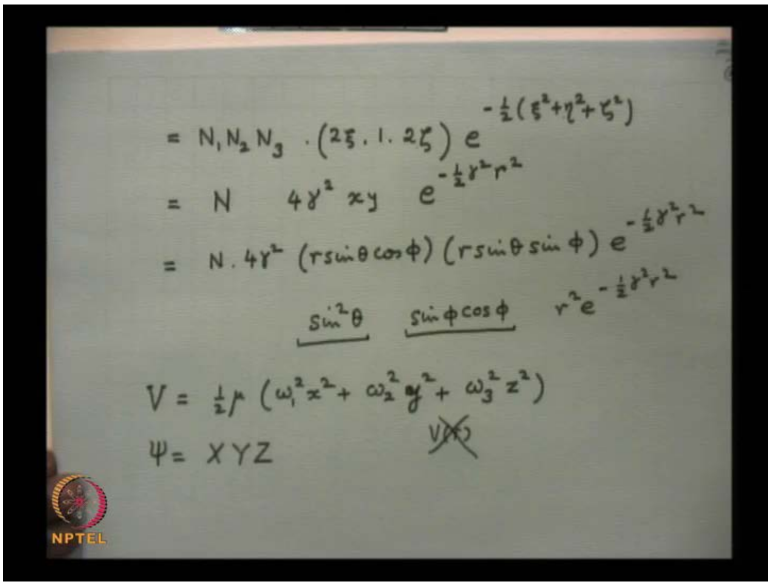

$$= N_1 N_2 N_3 \cdot (2\xi \cdot 1 \cdot 2\zeta)\, e^{-\frac{1}{2}(\xi^2+\eta^2+\zeta^2)}$$

$$= N \quad 4\gamma^2\, xy \quad e^{-\frac{1}{2}\gamma^2 r^2}$$

$$= N \cdot 4\gamma^2 (r\sin\theta\cos\phi)(r\sin\theta\sin\phi)\, e^{-\frac{1}{2}\gamma^2 r^2}$$

$$\underline{\sin^2\theta} \quad \underline{\sin\phi\cos\phi} \quad r^2 e^{-\frac{1}{2}\gamma^2 r^2}$$

$$V = \frac{1}{2}\mu\,(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2)$$

$$\psi = XYZ \qquad \cancel{V(r)}$$

Let me write it down in expansion, so this will be equal to N 1 N 2 these are just normalization constant, h 1 of xi is 2 xi, h 0 of eta is 1 and h 1 of zeta is equal to 2 zeta; so this will be e to the power of minus half xi square plus eta square plus zeta square. So, if you write down in terms of x, y, z, so this will be 4 gamma square, so N 1 N 2 N 3 I write it as N, so 4 gamma square x y times e to the power of minus half gamma square, x square plus y square plus z square, so r square.

So, you can write this in terms of because, it is a spherically symmetric potential, you will have N into 4 gamma square x as you all know is r sin theta cos phi and y is r sin theta sin phi multiplied by e to the power of minus half gamma square r square. So, I have written this also, if I rearrange this, so I will get sin square theta sin phi cos phi and then r square e to the power of minus half gamma square r square.

So, it is a function of r theta and phi also, as we should have expected, we will after all it is a spherically symmetric potential, you can write it, write the solution as a function of r times y l m theta phi and this is what we will indeed do in my next lecture.

So, you can do it either with the spherical polar coordinates or with the Cartesian coordinates, it so happens that the Cartesian coordinates is is little easier in this particular case, and in fact you can you can generalize I leave as an exercise for you, to work out the solutions for not the isotropic oscillator, like this half mu omega 1 square x square plus omega 2 square y square plus omega 3 square z square.

So, it is not an isotropic oscillator, so in this case also I can write the solution as capital X, capital Y, capita Z and separate the variables, once the variables have separated out I can write the solutions as a product of functions which depend on X, Y and Z.

Since, I cannot write this function as V of r, I cannot write this, so we cannot then use the spherical polar, we cannot solve the Schrodinger equation in spherical polar coordinate; in the beginning of the next lecture, we will solve this Schrodinger equation for the 3 dimensional oscillator, we will work out the solutions for an isotropic oscillator using spherical polar coordinates, thank you.