

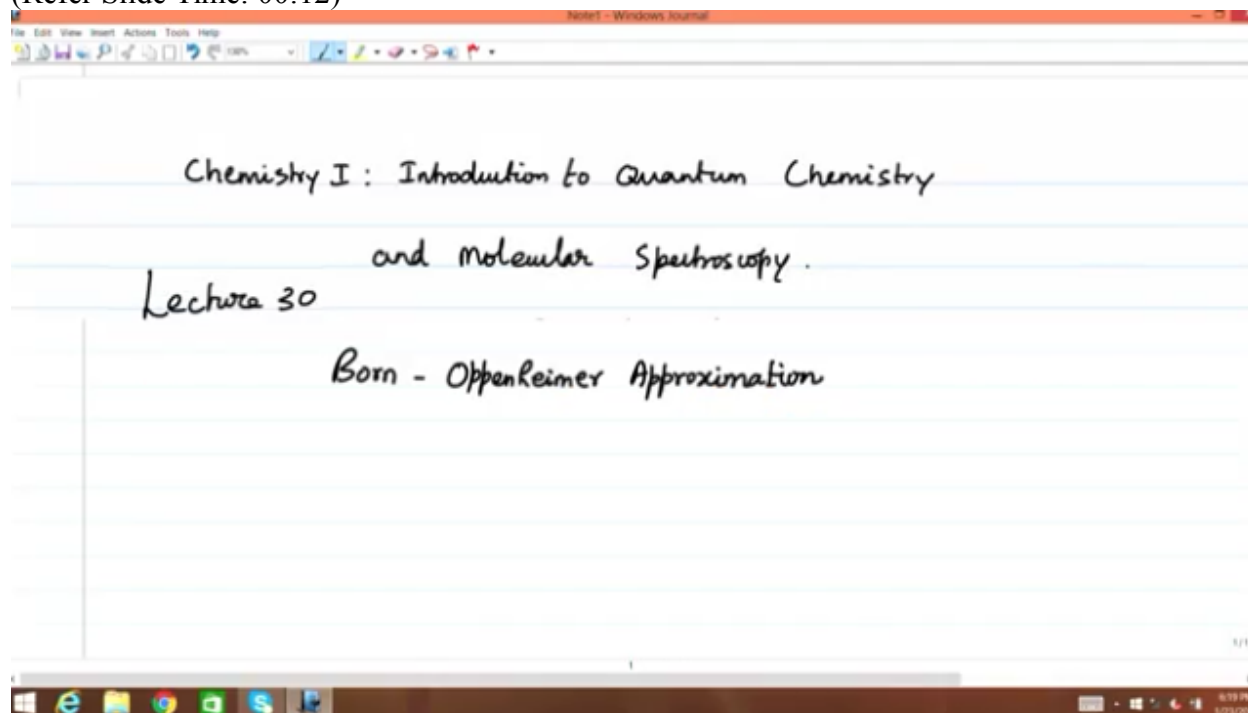
**NPTEL  
NPTEL ONLINE CERTIFICATION COURSE**

**Chemistry 1  
Introduction to Quantum Chemistry and  
Molecular Spectroscopy**

**Lecture 30  
Born-Oppenheimer Approximation**

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(Refer Slide Time: 00:12)



Welcome back to the lectures on chemistry and introduction to molecular spectroscopy. This lecture will have some introduction to the central approximation of molecular spectroscopy known as the Born Oppenheimer approximation.

Now this is a very important approximation in all of chemical physics. What you have here is a justification that was proposed by Max Born and Robert Oppenheimer a physicist and a chemist. In 1927 right after the year when Schrodinger published his equation the famous Schrodinger equation and applied this to the solution of hydrogen atom.

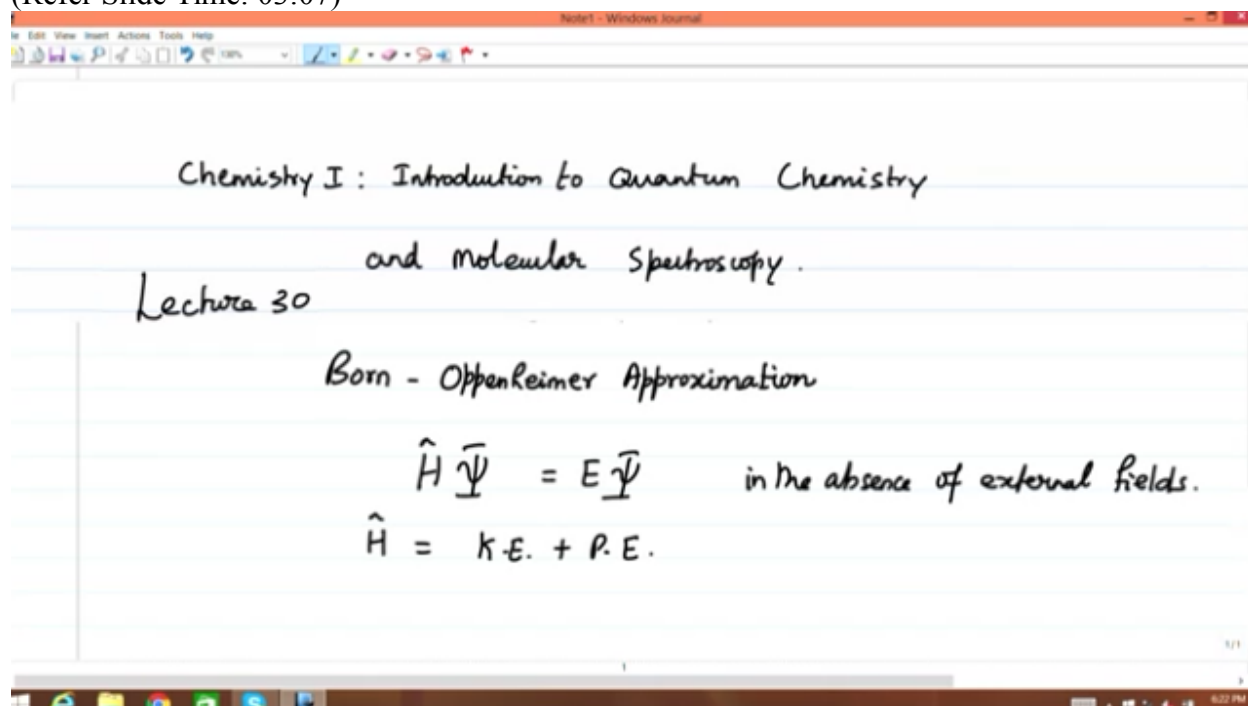
Now many of you have studied in the elementary chemistry that molecular energies can be approximately expressed as sums of independent contributions such as molecular translational

motion, rotational motion, the energy due to molecular translational motion, the energy due to molecular rotational motion, the energies of molecular vibration and electronic energies.

Where does this approximation come from? That's essentially what Born Oppenheimer provided in the beginning. The overall molecular energy represented by the operator, the total energy Hamiltonian which contains the kinetic energy and the potential energy is a very difficult term to solve, okay.

Let's look at what is meant by this approximation therefore, let me write the Schrodinger equation time independent, the  $\hat{H} \psi = E \psi$  that's in the absence of external fields, and  $\hat{H}$  is of course is sum of the kinetic energy and the potential energy, for the first time I'm using the hat symbol but it's not consistent with that, it's the kinetic energy of all the atoms and the electrons and the potential energy between the atoms, the nuclei and the electrons.

(Refer Slide Time: 03:07)



Chemistry I: Introduction to Quantum Chemistry  
and molecular Spectroscopy.  
Lecture 30  
Born - Oppenheimer Approximation  
 $\hat{H} \bar{\psi} = E \bar{\psi}$  in the absence of external fields.  
 $\hat{H} = K.E. + P.E.$

Even a simple molecule like hydrogen molecule has a very large number of terms the kinetic energy terms and the potential energy terms and therefore the simplest molecule neutron molecule that you can think of is not exactly solvable in quantum mechanics. In spectroscopy of course we need to know the energy levels of molecular systems in the absence of the electromagnetic radiation or in the absence of the perturbation, the field perturbation therefore it is important for us to have even approximately the picture of molecular energies and molecular quantum mechanical solutions.

Born Oppenheimer approximation plays a crucial role in separating the molecular Hamiltonian problem into two independent nearly independent problems, electronic energy and nuclear motion energy, they are nearly independent they are not exactly independent of each other, that's the cracks of whole approximation, the electronic energy essentially leads to what we know today as quantum chemistry, the study of electronic energy, potential energy surfaces for fixed

configurations of nuclear, nuclei, and then the nuclear motion energy which is essentially what we call as molecular spectroscopy. And the link between the two will turn out to be electronic spectroscopy, we shall see that in this lecture,  
 (Refer Slide Time: 05:03)

Born - Oppenheimer Approximation

$$\hat{H} \bar{\Psi} = E \bar{\Psi} \quad \text{in the absence of external fields.}$$

$$\hat{H} = \text{K.E.} + \text{P.E.}$$

Electronic energy                      nuclear motion energy.  
 Quantum Chemistry                      Spectroscopy  
 └──────────────────────────────────┘  
 Electronic spectroscopy.

this is a long lecture and I must tell you that I do not know how to simplify this into two half an hour or 3:20 minutes or 4:15 minute lectures, it's an important concept and I would rather take the time to explain to you, you can break this lecture at any point of time, and start listening to the rest of it from where you left off when you have the time, but I would rather have this as one long lecture, because it's one beautifully important concept which I think everybody should understand, reasonably carefully, okay.

So let me write down the molecular wave function  $\Psi$  has say  $N$  nuclei and  $N$  electrons, some arbitrary number, so let's do this parallelly for hydrogen molecule 2 nuclei protons and 2 electrons, okay, if you have to do this for something like carbon 60, they are 60 carbon nuclei and 360 electrons each carbon having 6 electrons.

Now each nucleus in a 3 dimensional coordinate system has 3 coordinates and so are the electrons, each electron has 3 coordinates therefore in the case of hydrogen molecule you are looking at 12 coordinates, and in the case of carbon 60 you are looking at  $60 \times 3 = 180$  coordinates,  
 (Refer Slide Time: 07:18)

$\Psi$

|            |          |                   |                    |
|------------|----------|-------------------|--------------------|
|            |          | $N$ nuclei        | $H_2$<br>2 protons |
|            |          | $n$ electrons     | 2 electrons        |
|            |          |                   | ↓                  |
|            | $C_{60}$ | -60 carbon nuclei | 360 electrons      |
|            |          |                   | 12 coordinates     |
| Nucleus :  | 3        | coordinates       |                    |
| electron : | 3        | "                 |                    |
|            |          | $420 \times 3 =$  | <u>1260</u>        |
|            |          |                   | coordinates        |

so the Schrodinger equation for the hydrogen atom contains 3 coordinates the X, Y, Z and its solution using the polar coordinates system which was given to you in a summary form in the last lecture, involves a fairly detailed mathematical processes to understand and the solutions are very beautiful indeed, but you cannot solve such systems with such larger number of coordinates by any other means that approximation procedure, so what is the Born Oppenheimer procedure for this?

First the wave function is a function of all the nuclear coordinates which let me write as the capital R's for the N nuclei and each one is 3 or 1X or 1Y or 1Z if you wish too, or 1Z if you wish too and likewise for the others, and let the electrons be  $r_1, r_2$  small r's and  $m$ , okay, this is the overall molecular wave function,  
(Refer Slide Time: 08:32)



$$H = T_N + T_e + V_{e-e} + V_{e-N} + V_{N-N}$$

nuclear
electronic
electron-  
electron
electron-  
-nuclear
nuclear-  
nuclear

non-relativistic.

$$\sum_{i=1}^N \frac{-\hbar^2}{2M_i} \left( \frac{\partial^2}{\partial R_{ix}^2} + \frac{\partial^2}{\partial R_{iy}^2} + \frac{\partial^2}{\partial R_{iz}^2} \right) = T_N$$

the T electron likewise is given by  $-\hbar^2/2m_e$  all the electrons of the same mass therefore you write  $\nabla^2/\nabla^2 r$  say  $M_i$ ,  $M_i$  let's write that,  $M_i$  electron,  $M_i$  square +  $\nabla^2/\nabla^2 R$   $M_i$  square +  $\nabla^2/\nabla^2 R$   $M_i$  square and you sum over all the electrons  $M_i = m_e$  to the little  $m$ , this is the potential energy.

And likewise we can write  $V_{ee}$ ,  $V_{eN}$ ,  $V_{NN}$ , I don't want to write that in detail because there are all going to be multiplying the wave functions therefore they do not have the special significance for the Born Oppenheimer approximation that we have with a derivative operators, (Refer Slide Time: 11:20)

non-relativistic.

$$\sum_{i=1}^N \frac{-\hbar^2}{2M_i} \left( \frac{\partial^2}{\partial R_{ix}^2} + \frac{\partial^2}{\partial R_{iy}^2} + \frac{\partial^2}{\partial R_{iz}^2} \right) = T_N$$

$$\sum_{m=1}^n \frac{-\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial r_{mx}^2} + \frac{\partial^2}{\partial r_{my}^2} + \frac{\partial^2}{\partial r_{mz}^2} \right) = T_e$$

$$= V_{ee}, V_{eN}, V_{NN}$$

therefore I have written the derivatives more explicitly and write the others as simply symbolic for the hydrogen molecule we can see what they are later, and the approximation one sai which is a function of all the nuclear coordinates and all the electron coordinates, Born Oppenheimer propose this to be a product of two terms one which depends on electronic coordinates and the nuclear coordinates, so let's write that as  $R_1, R_2, R_N, R_N$  electrons and all the nuclear coordinates  $R_1, R_2, R$  capital  $N$  times a  $\psi$  nuclear which is only a function of the nuclear coordinates, this is the first of the two steps that Born Oppenheimer provide in order to (Refer Slide Time: 12:31)

$$\underline{I} \quad \Psi(\vec{R}_1, \dots, \vec{R}_N, \vec{r}_1, \dots, \vec{r}_n) = \psi_{elec}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \times \psi_{nuc}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N).$$

reasonably separate to the molecular Hamiltonian into two independent, nearly independent domains of problems to be solved, okay.

Electronic wave function is a function of all the coordinates, nuclear wave function is a function of only the nuclear coordinates, what is that mean? For example, let us take the hydrogen chloride molecule very near to each other and also the hydrogen chloride, the so called molecule may not be a molecule, it's maybe two independent atoms, hydrogen and chlorine which are so far away from each other that the electron density remains more or less localized to the individual atoms, whereas in this case the electron densities seems to have spread out in such a way that part of the electron density of the hydrogen atom goes toward chlorine and so on, (Refer Slide Time: 13:22)

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$$\Psi(\vec{R}_1, \dots, \vec{R}_N, \vec{r}_1, \dots, \vec{r}_n) = \Psi_{elec}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \times \Psi_{nuc}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N).$$

H-cl      H      cl

and you know electro negativity, your principals and you know this bond is partially, it's partly covalent but partly and so on, but the point is to following that the electron density which is the square of the electronic wave function is dependent on how far the nuclei are from each other and that seems to be a change in the electron density as a nuclei come together, therefore the electronic wave function being a function of the nuclear coordinates is a natural thing for a chemist to consider because atoms which are far away from each other when they come close to each other, there is a possibility of forming a bond, there is a possibility of rearranging probably electron, rearrangement of the electron density, therefore the electronic wave function being a function of both nuclear and electronic coordinates makes sense.

What about the nuclear wave function, why are they not functions of the electron coordinates? The argument that you find often in textbooks is that the mass of the electron is a very, very small quantity compared to the mass of the propel, so what 1840 times less, therefore for a given kinetic energy, the electrons are much faster moving  $V$  square, (Refer Slide Time: 14:46)



I

$$\Psi(\vec{R}_1, \dots, \vec{R}_N, \vec{r}_1, \dots, \vec{r}_n) = \psi_{\text{elec}}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \leftarrow$$

$$\times \psi_{\text{nuc}}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N).$$

$m_e \ll m_p$       1840 times less

MB square if you think about it half MB square,  $V$  is much larger for the electron than for the nuclei in a classical sense, what it means is that the nuclear motion is almost instantly adjusted by the electronic positions and therefore the nuclear coordinates, the nuclei do not have to worry about the electron density in a sense that the nuclear wave functions or nearly independent of the electronic coordinates, the electrons almost instantly readjust themselves to the nuclear position, and therefore as a first approximation let us not consider the nuclear wave function also being dependent on the electron coordinates, leave that out, nuclei or slow moving, therefore we are not too worried about the nuclear motion unless we come to molecular spectroscopy, okay.

And we will not worry about it's immediate dependents of the electron, the other dependences for more crucial for chemical bond and therefore keep the electronic wave function as dependent on nuclear and electronic coordinate, I mean in a sense this is, this makes a chemical sense and with this approximation Born and Oppenheimer suggest to the separation of the overall Hamiltonian as follows,  $H$  is now let me write them individually  $T_N$  sai electronic sai nuclear +  $T_E$  sai electronic and sai nuclear +  $V_{EE}$  sai electronic sai nuclear +  $V_{EN}$  sai electronic times sai nuclear +  $V_{NN}$  sai nuclear times sai electronic and this is equal to  $E$  sai electronic sai nuclear, okay, now the brackets have some special meaning,  
(Refer Slide Time: 17:14)

$$H\bar{\Psi} = T_N \psi_{elec} \psi_{nuc} + (T_e \psi_{elec}) \psi_{nuc} + (V_{ee} \psi_{elec}) \psi_{nuc} + (V_{eN} \psi_{elec}) \psi_{nuc} + (V_{NN} \psi_{nuc}) \psi_{elec}$$

$$= E \psi_{elec} \psi_{nuc}$$

there is no bracket here because this is the term we are going to discuss TN sai electronic sai nuclear, we'll see what it needs to be changed too, but the other brackets are quite clear, TE contains only derivatives of the electron coordinates, you see that contains only the derivatives of the electron coordinates that you see here, (Refer Slide Time: 17:36)

$$\sum_{i=1}^n -\frac{\hbar^2}{2m_i} \left( \frac{\partial^2}{\partial R_{ix}^2} + \frac{\partial^2}{\partial R_{iy}^2} + \frac{\partial^2}{\partial R_{iz}^2} \right) = T_N$$

$$\sum_{m=1}^n -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial r_{mx}^2} + \frac{\partial^2}{\partial r_{my}^2} + \frac{\partial^2}{\partial r_{mz}^2} \right) = T_e$$

$$= V_{ee}, V_{eN}, V_{NN}$$

$$I \quad \bar{\Psi}(\vec{R}_1, \dots, \vec{R}_N, \vec{r}_1, \dots, \vec{r}_n) = \psi_{elec}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) \leftarrow$$

therefore in the overall wave function if you look at it the electron coordinate dependence happens only for the electronic wave function, okay. (Refer Slide Time: 17:53)

$m = 1$

$= V_{ee}, V_{eN}, V_{NN}$   
 $\uparrow \quad \uparrow \quad \uparrow$

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$\hat{I} \quad \bar{\Psi}(\vec{R}_1, \dots, \vec{R}_N, \vec{r}_1, \dots, \vec{r}_n) = \underbrace{\Psi_{elec}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)}_{\leftarrow} \times \underbrace{\Psi_{nuc}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)}_{\leftarrow}$

H-cl

H

cl

Therefore the derivative operators do not change, the derivative operator does not change the sai nuclear, so what it does is it only acts on the sai electronic therefore I have put that in bracket, the rest is the multiple, this multiplied by sai nuclear and potential energies are even though they are operators they multiply the wave functions therefore I have put for the electron, electron repulsion, the sai electronic together, the electron nuclear attraction the sai electronic together and the nuclei, nuclear with the sai nuclear because it's possible with this to separate the Hamiltonian.

What about the TN sai electronic sai nuclear? The cuts of the approximation is there only, TN please remember contains a derivative operator dou square dou RI square X, Y, Z if you wish to, therefore when it acts on sai electronic and sai nuclear remember both of these are dependent on the nuclear coordinates, so the derivative acts on something like a function U(R) V(R) if you want to write this, specifically RI, RI, so dou square/dou RI square, okay.

Now remember that the derivative rule is that if you have a function say D/DX or a function dou/dou X U(X, Y) some other variable and V(X, Y), then you know that this derivative is expressed as dou U/dou X times V + dou V/dou X times U, and the second derivative dou square/dou X square on U(X, Y) V(X, Y) is the derivative dou/dou X acting on this term, the sum of these two terms and therefore what you get is dou square U/dou X square times V + dou square V/dou X square times U + you will get the cost term also 2 dou U/dou X dou V/dou X, therefore with this sort of elementary mathematics in mind, it's easy to see that to the nuclear (Refer Slide Time: 20:39)

$\frac{\partial^2}{\partial R_i^2} \psi_{elec} \psi_{nuc}$ 
 $\frac{\partial^2}{\partial R_i^2} [U(\vec{R}_i) V(\vec{R}_i)]$

$$\frac{\partial}{\partial x} [u(x,y)v(x,y)] = \frac{\partial u}{\partial x} v + \frac{\partial v}{\partial x} u$$

$$\frac{\partial^2}{\partial x^2} [u(x,y)v(x,y)] = \frac{\partial^2 u}{\partial x^2} v + \frac{\partial^2 v}{\partial x^2} u + 2 \frac{\partial u}{\partial x} \frac{\partial v}{\partial x}$$

kinetic energy operator acting on the sai electronic and the sai nuclear will have 1, the TN operating on sai electronic and the other TN operating on sai nuclear, okay, now this contains dou/dou RI sai electronic, the electronic coordinates and the nuclear coordinates RN. It also contains a second derivative dou square/dou RI square of sai electronic, okay.

Born Oppenheimer suggest this to be an adiabatic change, and adiabatic term in physics and in thermal dynamics and in chemistry adiabatic means slow passage or change that happens slowly, (Refer Slide Time: 21:40)

$T_N \psi_{elec} \psi_{nuc}$ 
 $1) \underbrace{T_N}_{\text{Adiabatic term}} \psi_{elec} \psi_{nuc}$

$$\frac{\partial}{\partial R_i} \psi_{elec} (\vec{r}_1, \vec{r}_2, \dots, r_n, R_1, R_2, \dots, R_N)$$

$$\frac{\partial^2}{\partial R_i^2} \psi_{elec}$$

Adiabatic term.

change that is slow, so what is the slow here? The slow is that we refer to here is that the electronic wave function that you see here is actually a function of the nuclear coordinates, but the derivative of the electronic coordinates this whole thing is sufficiently small, (Refer Slide Time: 22:20)

The image shows handwritten notes on a whiteboard. At the top, the total wave function is written as  $T_N \Psi_{elec} \Psi_{nuc}$ . Below this, the electronic wave function is defined as  $\Psi_{elec}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, R_1, R_2, \dots, R_N)$ , where the nuclear coordinates  $R_i$  are treated as parameters. The notes then show the derivative terms  $\frac{\partial}{\partial R_i} \Psi_{elec}$  and  $\frac{\partial^2}{\partial R_i^2} \Psi_{elec}$ , which are labeled as "Adiabatic term" and "slow passage change that is slow".

the change of the  $\Psi_{elec}$  with respect to the nuclear coordinate that rate of changes sufficiently small, that's a reason why it's called adiabatic, it's sufficiently small that we can throw away, we can neglect to that, we can also, if that change a small the rate of rate of change is also going to be small or even, smaller and therefore let us not consider these two terms as important, this was the suggestion which today is known as the Born Oppenheimer approximation that the rate of change of the electronic wave function with respect to the nuclear coordinates and the rate of rate of change of the electronic wave function with respect to the nuclear coordinate terms be neglected, not equal to 0 be neglected, please understand if the derivative is 0 then that function is independent of the coordinate, but we have assume that the wave function to be dependent on the nuclear coordinates because we argued that the electron densities keep changing when the nuclei come together.

Therefore the wave function is dependent on the nuclear coordinates, the electronic wave function is, but it's rate of change and the rate of rate of change with respect to nuclear coordinates be dropped off and that's approximation 2, throw away  $\frac{\partial}{\partial R_i} \Psi_{elec}$  and  $\frac{\partial^2}{\partial R_i^2} \Psi_{elec}$ . What is this  $\frac{\partial}{\partial R_i}$ , does this something beautiful, (Refer Slide Time: 24:06)

$\frac{\partial^2}{\partial R_i^2} \Psi_{elec}(\dots, R_i, \dots, R_N)$  be neglected  
 Adiabatic term. slow passage charge that is slow.

II Throw away  $\frac{\partial}{\partial R_i} \Psi_{elec}$   $\frac{\partial^2}{\partial R_i^2} \Psi_{elec}$

let's see what that is? Therefore when you write TN sai electronic sai nuclear essentially what you have done is to write this as TN sai nuclear because you have dropped off the dependence of the electronic coordinates, so this is the only thing, now you go back and see why this brackets are where there are, okay.

Therefore let me write to this term,  
 (Refer Slide Time: 24:43)

$$\begin{aligned}
 H \bar{\Psi} &= \\
 & T_N \Psi_{elec} \Psi_{nuc} + (T_e \Psi_{elec}) \Psi_{nuc} + (V_{ee} \Psi_{elec}) \Psi_{nuc} \\
 & \quad + (V_{eN} \Psi_{elec}) \Psi_{nuc} + (V_{NN} \Psi_{nuc}) \Psi_{elec} \\
 & = E \Psi_{elec} \Psi_{nuc}.
 \end{aligned}$$

$\frac{\partial^2}{\partial R_i^2} \Psi_{elec} \Psi_{nuc} \rightarrow \frac{\partial^2}{\partial R_i^2} [U(\vec{R}) V(\vec{R})]$

here itself as TN sai nuclear sai electronic, it's an approximation, therefore I would not write this as E sai, but rather I would write this as proximate E sai, so what you have here is therefore this term TN sai nuclear and then you have T sai electronic VEE sai electronic,

(Refer Slide Time: 25:23)

$$H \Psi = (T_N \Psi_{nuc}) \Psi_{elec} + (T_e \Psi_{elec}) \Psi_{nuc} + (V_{ee} \Psi_{elec}) \Psi_{nuc} + (V_{eN} \Psi_{elec}) \Psi_{nuc} + (V_{NN} \Psi_{nuc}) \Psi_{elec}$$

$$\approx E \Psi_{elec} \Psi_{nuc}$$

$$\frac{\partial^2}{\partial \mathbf{r}_n^2} \Psi_{nuc} \Psi_{elec} \quad \frac{\partial^2}{\partial \mathbf{r}_e^2} [U(\vec{R}) V(\vec{R})]$$

VEN sai electronic, remember all these things depend on the electronic coordinates, okay.

This is solved as the electronic Schrodinger equation TE sai electronic + VEE sai electronic + VEN sai electronic, let us call this as a Hamiltonian for the electronic motion acting on sai electronic, this is called the electronic Hamiltonian. Defined for very specific positions of the nuclear coordinates, defined for specific choice of nuclear coordinates, okay, keep this in mind.

Now let me take you off to your slightly different discussion,  
(Refer Slide Time: 26:33)

Electronic Schrödinger equation

$$\left[ T_e \psi_{elec} + V_{ee} \psi_{elec} + V_{eN} \psi_{elec} \right] = H_e \psi_{elec}.$$

↑  
Electronic Hamiltonian

defined for specific choice of nuclear coordinates.

the particular the one dimensional box when you solved to this equation  $\hbar^2/2m D^2 \psi(X)$ , when you solve that you got the energy which is independent of X, it's a constant, okay, and this was  $\hbar^2/8mL^2 N^2$ , no X here, when you solve the harmonic oscillator problem  $\hbar^2/2m D^2 \psi(X) + 1/2 KX^2 \psi(X) = E \psi(X)$  this is a constant, and so for the hydrogen atom, the energy is simply  $-H^2 R^2/N^2$ , there is no X dependence or R dependence or theta dependence or phi dependence in it, okay, simply a function of N square.

What you did was essentially you integrated over the coordinates which are the ones with respect to which you have written the derivatives integrated with respect to X. And therefore the energy is independent of X.

(Refer Slide Time: 28:09)



Notes - Windows Journal

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x)$$

↑  
constant

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + \frac{1}{2} kx^2 \psi(x) = E \psi(x)$$

↑  
constant

Hydrogen atom

$-\frac{hcR_H}{n^2}$

$\frac{\hbar^2}{8m^2 n^2}$   
Integrated with respect to x  
E → energy independent of x

Now with this let's go back and look at this one, when you solve the Schrodinger equation for the electronic Hamiltonian as written here, (Refer Slide Time: 28:20)

Notes - Windows Journal

$$T_N \psi_{elec} \psi_{nuc} = \underbrace{(T_N \psi_{nuc})}_{\psi_{elec}} \psi_{elec}$$

Electronic Schrödinger equation

$$\left[ T_e \psi_{elec} + V_{ee} \psi_{elec} + V_{eN} \psi_{elec} \right] = \underbrace{H_e}_{\text{Electronic Hamiltonian}} \psi_{elec}$$

defined for specific choice of nuclear coordinates.

the solution of this if it is to be written as  $E_{elec}$  electronic, if that's Schrodinger equation for the electronic motion, the  $E_{elec}$  is a constant with respect to all the electron coordinates of this Hamiltonian, all of them, however the  $E_{elec}$  is a function of the nuclear coordinates because in the process of solving in your own touch the nuclear coordinates you leave they are as they are, you solve those problem for each set of nuclear coordinates and when you solve you will get many

many energies like the particular in the box, or like the harmonic oscillator or like the hydrogen atom you get a whole lot of energies, and you get a whole lot of wave functions, all of which are for one configuration of the nuclear coordinates  $N$ , because that  $V_{EN}$  depends on both the electron coordinates as well as the nuclear position coordinates, therefore you don't change the nuclear coordinates, keep them to a fixed value, clamp them and that is called clamped nuclei approximation, solving  $H_{E \text{ sai } E}$  for one set of  $R_i$  gives you  $E_{EE}$  which is a function of that  $R_i$  times  $\text{sai } E$ .

Change to another set of  $R_i$ , you will get again another solution  $\text{sai } E \text{ prime}$  which will give you  $E_{EE \text{ prime}}$ , some other value  $R_i$ , this is a different set of coordinates and  $\text{sai } E \text{ prime}$ ,  
(Refer Slide Time: 30:17)

The image shows a whiteboard with handwritten mathematical equations and text. At the top, the Schrödinger equation for a hydrogen atom is written:  $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + \frac{1}{2} kx^2 \psi(x) = E \psi(x)$ . Below this, it says "Hydrogen atom" and "constant" with an arrow pointing to the energy  $E$ , and the formula  $-\frac{\hbar^2 k_H}{n^2}$ . To the right, a vertical line separates the equation from the text "Integrated with respect to x" and "E → energy independent of x". Below this, the text "Clamped nuclei approximation" is written, followed by two equations: "one set of  $\{R_i\}$   $H_e \psi_e = E_e(R_i) \psi_e$ " and "another set  $\{R_i\}$   $H_e \psi_e' = E_e'(R_i') \psi_e'$ ".

therefore what you do is that you solve the electronic equation for each and every possible set of coordinates of all the nuclei, and in that process you generate electronic energies  $E_{EE}$  which are functions of the position of the nuclei. What does this do? This goes back to the left over part in the equation that we have here.

So what we have done is to consider  $T_{E \text{ sai } e}$  electronic which is part of the electronic Hamiltonian,  $V_{E \text{ sai } e}$  electronic which is also part of the potential energy and then  $V_{EN \text{ sai } e}$  electronic and call all these things together by  $H_{E \text{ sai } e}$  electronic.  
(Refer Slide Time: 31:17)

$m_e \ll m_p$       1840 times less

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$$H\bar{\Psi} =$$

$$\begin{aligned} & \xrightarrow{(T_N \Psi_{nuc}) \Psi_{elec}} \quad + (T_e \Psi_{elec}) \Psi_{nuc} + (V_{ee} \Psi_{elec}) \Psi_{nuc} \quad H_e \Psi_{elec} \\ & \quad + (V_{eN} \Psi_{elec}) \Psi_{nuc} + (V_{NN} \Psi_{nuc}) \Psi_{elec} \end{aligned}$$

$$\approx E \Psi_{elec} \Psi_{nuc}$$

And what does it give? It gives you EE a function of the nuclear positions  $R_1, R_2, R_N$  times  $\psi_{elec}$ , therefore we substitute that and then solve the rest of the problem, rest of the problem contains the nuclear. Let's use a different color, yeah the rest of the problem contains the nuclear kinetic energy, the nuclear repulsion energy and of course when you solve this or when you substitute this by  $H_e$  you have to put this back into that equation therefore all the things which (Refer Slide Time: 32:03)

$m_e \ll m_p$       1840 times less

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$$H\bar{\Psi} =$$

$$\begin{aligned} & \xrightarrow{(T_N \Psi_{nuc}) \Psi_{elec}} \quad + (T_e \Psi_{elec}) \Psi_{nuc} + (V_{ee} \Psi_{elec}) \Psi_{nuc} \quad H_e \Psi_{elec} \\ & \quad + (V_{eN} \Psi_{elec}) \Psi_{nuc} + (V_{NN} \Psi_{nuc}) \Psi_{elec} \quad = E_e(\vec{R}_1, \vec{R}_2, \vec{R}_N) \Psi_{elec} \end{aligned}$$

$$\approx E \Psi_{elec} \Psi_{nuc}$$

are in green are known as the nuclear Schrodinger equation and that's what you solve in molecular spectroscopy and what you get in the nuclear equation, not just the nuclear, kinetic

energy, not just the nuclear, nuclear repulsion and energy, but an energy term which comes from the electronic Schrodinger equation which is a function of the nuclear positions and of course that's called the electronic potential energy surface, this term, potential energy surface.

Electronic potential energy surface, therefore the nuclear motion is studied in a surface provided by the electronic Schrodinger equation and this is with the approximation that the nuclear kinetic energy operated does not change the electronic wave function drastically, therefore the D/DRI, the derivative of the electronic wave function with respect to nuclear coordinates they're all not there, if they are there this simplification will not happen, and such a case when they are there is actually called the adiabatic process and it's called the non-Born Oppenheimer or its also known as the failure or the breakdown of the Born Oppenheimer approximation, that's done in the slightly more advanced course of chemical physics, anyhow let's not do that here, for our purposes we will stick to the simple Born Oppenheimer approximation, the adiabatic potential energy surface, this is called adiabatic electronic potential energy surface, okay.

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$m_e \ll m_p$       1840 times less

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$$H \Psi = (T_N \Psi_{nuc}) \Psi_{elec} + (T_e \Psi_{elec}) \Psi_{nuc} + (V_{ee} \Psi_{elec}) \Psi_{nuc} + (V_{eN} \Psi_{elec}) \Psi_{nuc} + (V_{NN} \Psi_{nuc}) \Psi_{elec} = H_e \Psi_{elec} = E_e(R_1, R_2, \dots, R_N) \Psi_{elec}$$

$$\approx E \Psi_{elec} \Psi_{nuc} \quad \left[ \text{Adiabatic electronic Potential energy surface} \right]$$

Which provides the potential energy surface for the nuclei to dance for the nuclei to move around and therefore the nuclear motion Hamiltonian which is largely considered to be the motion of the nuclei being translational motion of the whole molecule, electrons are very light, therefore you can replace that much of the motion, the masses due to the nuclei, translation motion of the nuclei, the rotational motion of the atoms and the vibrational motion of the relative displacements of the nuclei between with respect to each other, all these things are called nuclear motion Hamiltonian, and the nuclear motion Hamiltonian is the fundamental the Hamiltonian that we study in spectroscopy with the understanding that all of this happens due to the potential energy surface that was generated by the solution of the electronic equation, so that's the quantum chemistry problem and this is the molecular spectroscopy problem, obviously the electron provides the link here and therefore when you see electronic spectroscopy these two things really get together and that's much more complicated.

So let me summarize this part of the lecture namely the Born Oppenheimer approximation 1 is sai total is expressed as, the sai total is expressed as sai electronic sai nuclear and then the H on sai electronic sai nuclear is expressed as H electronic sai electronic times sai nuclear + the T nuclear sai nuclear times sai electronic + VNN sai nuclear sai electronic and that's equal to E sai nuclear sai electronic. And what we shall do is obviously replace this by EE which is a function of the nuclear coordinates, all of them sai electronic.  
 (Refer Slide Time: 36:48)

The image shows a screenshot of a Windows Journal window with handwritten mathematical equations. The equations are:

$$\Psi_{\text{total}} = \Psi_{\text{elec}} \Psi_{\text{nuc}}$$

$$\hat{H} \Psi_{\text{elec}} \Psi_{\text{nuc}} = E_e(\vec{R}) \Psi_{\text{elec}} \Psi_{\text{nuc}} + (T_N \Psi_{\text{nuc}}) \Psi_{\text{elec}} + (V_{NN} \Psi_{\text{nuc}}) \Psi_{\text{elec}} = E \Psi_{\text{nuc}} \Psi_{\text{elec}}$$

So now with this form you see that the sai electronic is a multiple to the entire function so you can get rid of that, you can get rid of that, that, and what you get is of course the nuclear Hamiltonian  $T_N$  sai nuclear +  $V_{NN}$  sai nuclear +  $E_e$  sai nuclear is equal to the total energy  $E$  times sai nuclear, okay, this is spectroscopy,  
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I

$$\bar{\Psi}_{total} = \Psi_{elec} \Psi_{nuc}$$

$$\hat{H} \Psi_{elec} \Psi_{nuc} = E_e(\vec{R}) \Psi_{elec} \Psi_{nuc} + (T_N \Psi_{nuc}) \Psi_{elec} + (V_{NN} \Psi_{nuc}) \Psi_{elec} = E \Psi_{nuc} \Psi_{elec}.$$

spectroscopy 
$$\left[ T_N \Psi_{nuc} + V_{NN} \Psi_{nuc} + E_e \Psi_{nuc} \right] = E_{nuc} \Psi_{nuc}$$

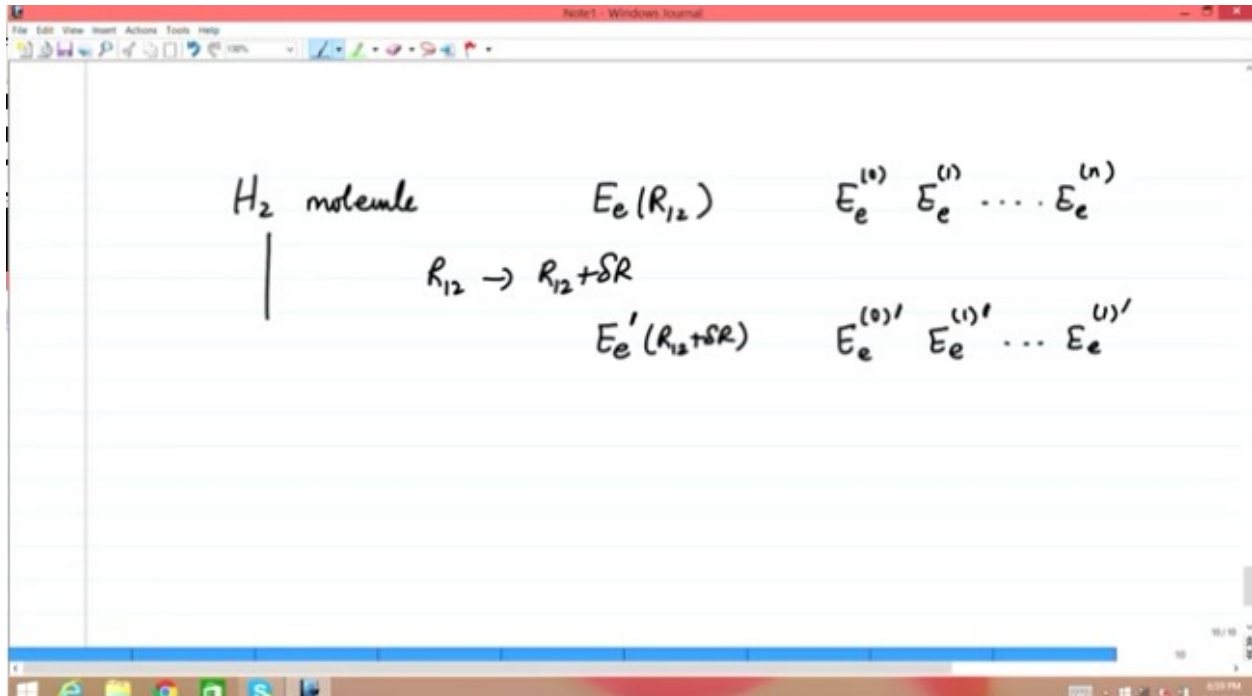
this is quantum chemistry, quantum chemistry solution of the electronic equation for fixed configurations of the nuclei and of course you can keep changing them and then put that potential energy, okay.

So in a simple case like a hydrogen molecule what does this do? So case of hydrogen molecule we don't need to worry about all the 6 coordinates of the two nuclei, but let's just concern ourselves with the inter nuclear distance between the two hydrogen atoms, therefore when you solve for the EE you get many energies for a given value of the inter nuclear separation  $R_{12}$  which is  $R_1 - R_2$  vector, okay.

For one value you get many energies, you get EE, ground state, then you get the EE the higher energy states like the Schrodinger equation for the electron you get many many energies.

And then of course change  $R_{12}$  to the next value  $R_{12} + \Delta R$ , solve this again you will get EE prime,  $R_{12} + \Delta R$ , okay, again a whole set of energies  $EE_0$ , EE prime, some other value  $EE_1$  and so on,

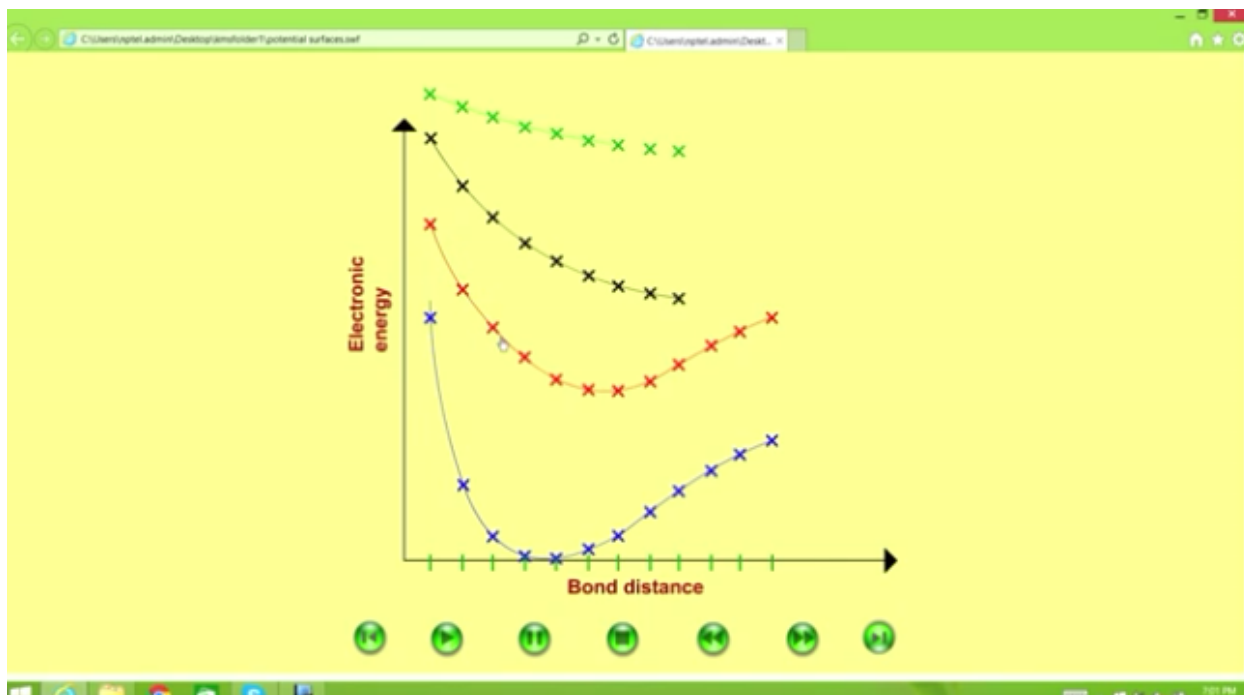
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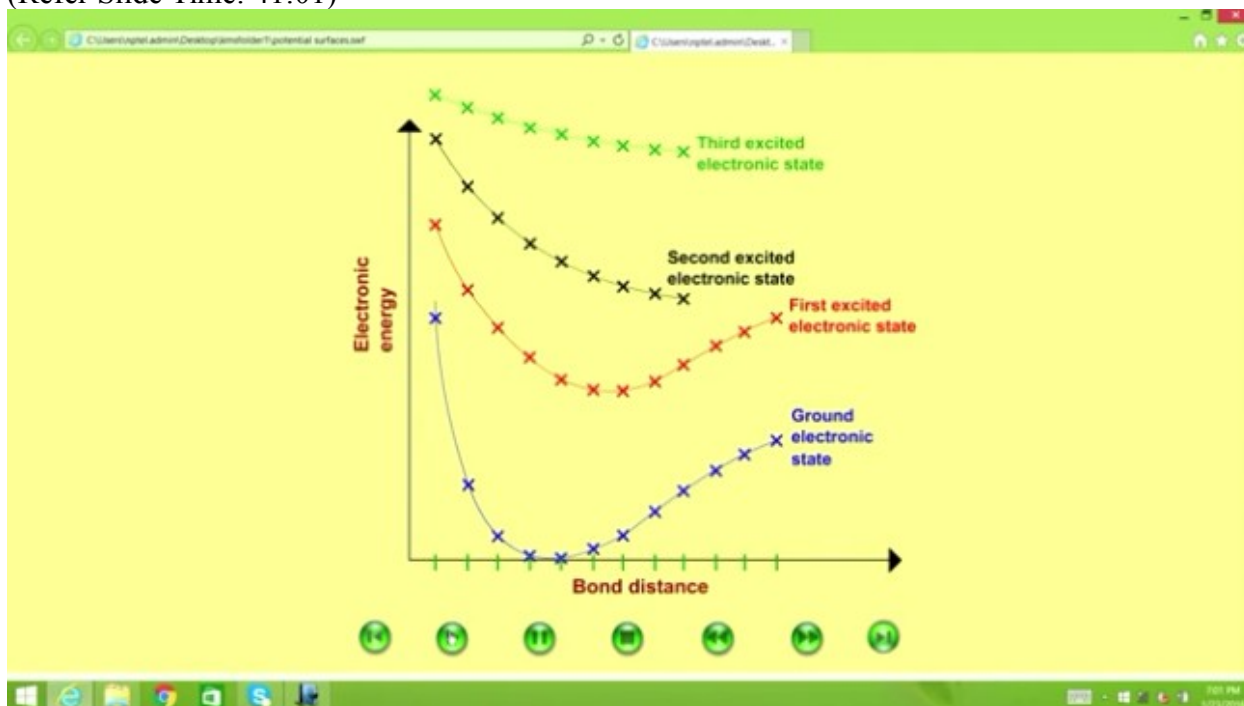
therefore for the hydrogen molecule you actually get a whole series of energies for each and every value of the inter nuclear distance and that's shown in this animation, okay, that's shown in this animation.

So what I have here is the inter nuclear distance  $R_{12}$  is along the X axis and then the electronic energy solution that you get, multiple solutions that you get for solving the electronic equation, so for that  $R_{12}$  you get different values, like you get in the case of hydrogen atom you get the  $N = 1, N = 2, N = 3$ , there the quantum numbers are well known, here some quantum numbers come out, fine, but the point is you get multiple energies, then you slightly change the  $R$ , you get another set of energy Eigenvalues, continue this process, you get many many such things and of course you can draw using these points which are created from the solutions of the hydrogen, of the hydrogen molecule here, of course what you can do is I have colored them to show that the lowest energy solution for each value of the nuclear configuration is all in blue that's connected to give you what is called the ground state potential energy surface, then next higher, (Refer Slide Time: 40:43)





the next higher energy, the second energy for each and every such configuration that you get which I have connected using a red line is called the first excited electronic state energy and then you have the second excited state electronic energy, the third excited state electronic energy and so on, okay,  
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therefore you see how the electronic energy surfaces which you are normally drawn in your elementary spectroscopy classes, how they come from a deeper understanding of the molecular Hamiltonian and the approximations provided by which we are able to reproduce these electronic energy states, thus this is the essence of Born Oppenheimer approximation, and I would want



you to go back and think about the same thing using some other molecular system instead of hydrogen molecule if you have a slightly more complex, complex molecule even a triatomic molecule you will see that the coordinates, the nuclear coordinates for a triatomic molecule there are 9 coordinates.

Taking the translational motion away from this picture which takes three coordinates out of them and taking the rotational motion also away from them you have three vibrational what are called coordinates, nuclear, inter nuclear coordinates and the potential energy for the electron is a function of these three nuclear coordinates, therefore the potential energy is not a graph, it's a function of 3 variables therefore it's a surface, it's actually a 3 dimensional surface, 4 dimensional surface because you need 3 coordinates to represent and the fourth dimension is the actual point, therefore even a triatomic molecule you need a 4 dimensional system to actually plot, people use color as the fourth dimension to indicate such potential energy surfaces, but if you have a N atom molecule in general there are  $3N - 6$  such vibrational coordinates for a nonlinear molecule, what are called independent coordinates leaving the translation and rotation out 3 3 each, you have  $3N - 6$  independent coordinates and these are called the normal coordinates, and these normal coordinates determine the electronic energy surface, the electronic energy surfaces  $3N - 5$  dimensional, because  $3N - 6$  coordinates and to the dimension for plotting that, so it's impossible to plot potential energy surfaces in for any real molecule in a visual form and what you do is to use what are called the constant energy surfaces or constant coordinate surfaces you do them, this contour maps are used and there is a lot of information which has been generated over the last 70 years or many small molecular systems on these potential energy surfaces, ground state, the excited state and the higher energy excited state and so on.

Therefore that's a whole field of quantum chemistry which provides such surfaces for us to understand molecular motion through spectroscopic means, in that sense Born Oppenheimer approximation separates nuclear to electronic.

In the next part to this another 15, 20 minutes, in the next lecture I'll tell you how such a model, when it is applied to rotations and vibrations, it also gives you another separation at a lower level to give you what is called the microwave spectroscopy and then what is known as the infrared spectroscopy and then the coupling between these microwave and infrared spectroscopy as a rotational vibrational spectroscopy and so on, therefore applying this Born Oppenheimer approximation in the sequential is possible for us to express the Hamiltonian as approximates also, but the procedure is approximate. Thank you.

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