Chemistry Atomic Structure and Chemical Bonding
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Lecture – 31
Born-Oppenheimer Approximation

Welcome back to the lectures, this lecture we 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 Rob 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 the applied this to the solution of the hydrogen atom.

Now, many of you have studied in the, The Elementary Chemistry that molecule, 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 is essentially what Born in Oppenheimer provided in the beginning.

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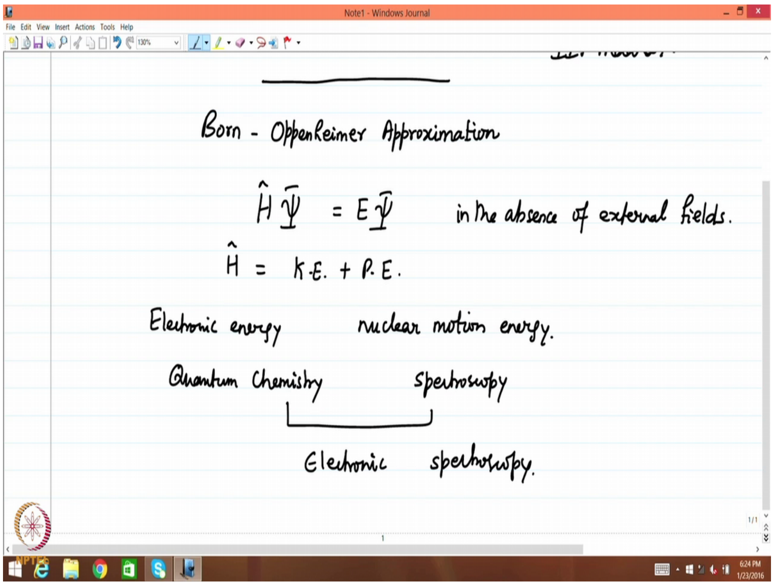

Born - Oppenheimer Approximation

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

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

Electronic energy nuclear motion energy.

Quantum Chemistry Spectroscopy

Electronic spectroscopy.

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. Let us look at what is meant by this approximation therefore, let me write the Schrodinger equation, time independent H psi is equal to E psi that is in the absence of external fields, and H is of course, the sum of the kinetic energy and the potential energy for the first time I am using the hat symbol, but it is not I am not consistent with that.

It is the kinetic energy of all the atoms and the electrons and the potential energy between the atoms the nuclei and the electrons. 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 neutral 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 is the Crux of the 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. You shall see that, in this lecture. This is a long lecture and I must tell you that, I do not know how to simplify this into 2 half an hour or 3 20 minutes or 4 15-minute lectures.

It is 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 is one beautifully important concept which I think everybody should understand reasonably, carefully.

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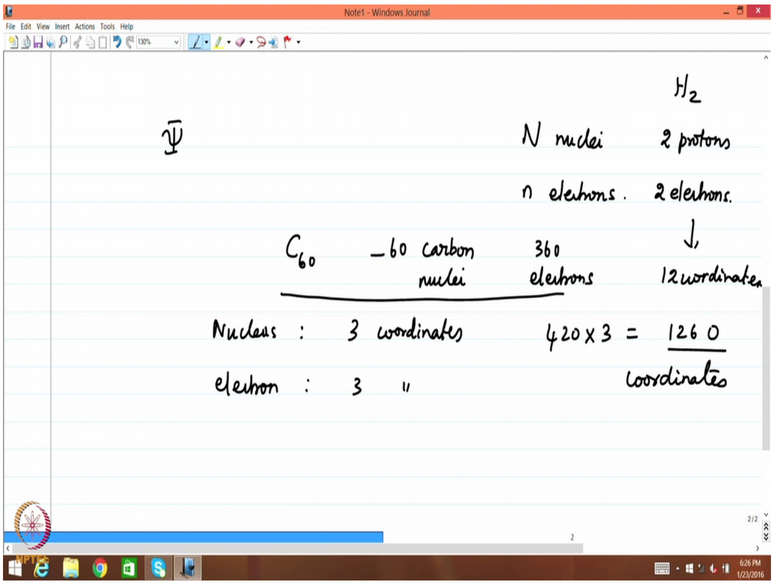

H_2

Ψ N nuclei 2 protons

n electrons. 2 electrons.

↓

C_{60} – 60 carbon nuclei 360 electrons 12 coordinates

Nucleus : 3 coordinates

electron : 3 "

$420 \times 3 = \underline{1260}$ coordinates

So, let me write down. The molecular wave function psi has say N nuclei and n electrons some arbitrary number. So, let us do this parallelly for Hydrogen molecule 2 new protons and 2 electrons, ok. If you have to do this for something like Carbon 60, you are 60 Carbon nuclei and 360 electrons each carbon having 6 electrons.

Now each nucleus, in a three-dimensional coordinate system has 3 coordinates and so, or 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 420 times 3, 1260 coordinates.

So, the Schrodinger equation for the Hydrogen atom contains 3 coordinates, the xyz and its solution using the polar coordinate system, which was given to you in a summary form in the last lecture, involves a fairly detailed the mathematical processes to understand and the solutions are very beautiful indeed, but you cannot solve such systems with such a large number of coordinates by any other means than approximation procedure.

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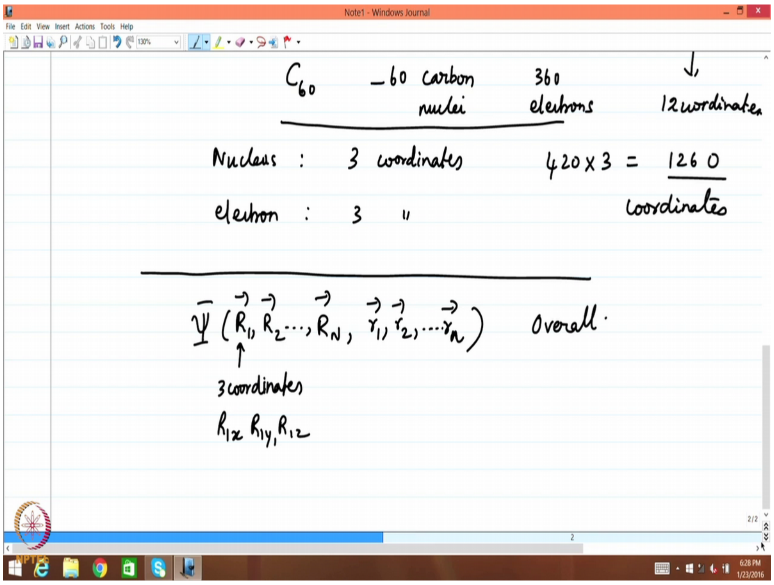

C_{60} – 60 carbon nuclei   360 electrons $\downarrow$ 12 coordinates

Nucleus : 3 coordinates $420 \times 3 = \underline{1260}$ coordinates

electron : 3 "

$$\bar{\Psi}(\vec{R}_1, \vec{R}_2 \ldots, \vec{R}_N, \vec{r}_1, \vec{r}_2, \ldots \vec{r}_n) \quad \text{Overall.}$$

$\uparrow$ 3 coordinates

$R_{1x}\ R_{1y}, R_{1z}$

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 Rs for the m nuclei and each one is 3 or 1 x or 1 y or 1 z if you wish to or 1 z, If you wish to and likewise for the others and let the electrons be r 1 r 2 small r s and r n.

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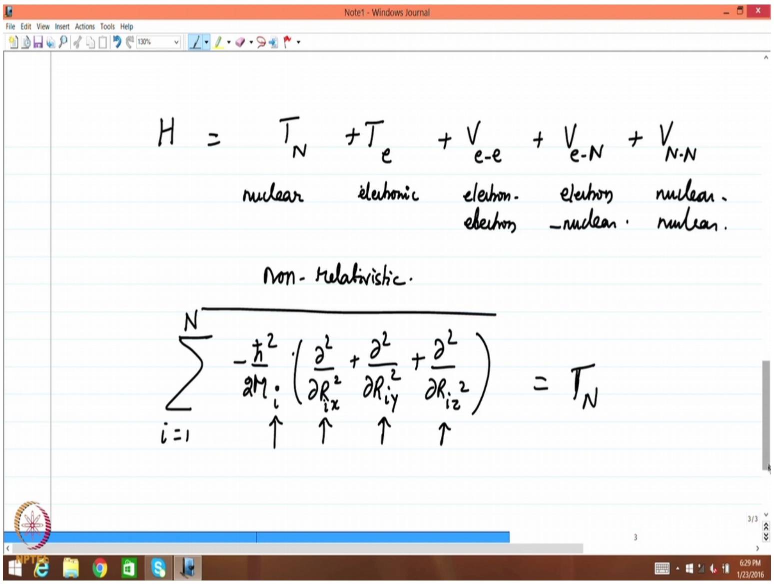

$$H = T_N + T_e + V_{e\text{-}e} + V_{e\text{-}N} + V_{N\text{-}N}$$

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

Non-relativistic.

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

This is the overall molecular wave function and this wave function is Solved for the Hamiltonian which contains the nuclear kinetic energy T capital N the electronic kinetic energy. The electron, electron repulsion terms, this is the potential energy term, the electron nuclear attraction terms. This is also part of the potential energy and the nuclear, nuclear repulsion terms and I use non-relativistic form to make things simpler.

Therefore, the kinetic energy terms contain minus h bar square by 2 M capital M which is the mass of each nucleus say, M i. Let me write dou square by dou R x i x square plus dou square by dou R i y square plus dou square by dou R i z square, where i is the atom index or the nuclear index, and the xyz are the coordinates of that and this is summed over all the atoms i is equal to 1 two and all the nuclei.

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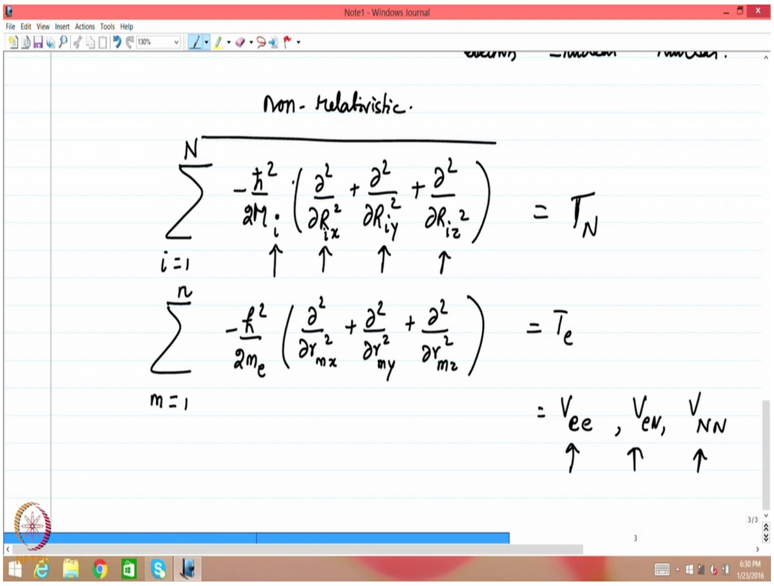

Non-relativistic.

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

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

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

This is T N the T electron likewise, is given by minus h bar square by 2 m e. All the electrons are the same mass therefore, you write dou square by dou little or say mi m x let us write that m th electron m x square plus dou square by dou r m y square plus dou square by dou r m z square and you sum over all the electrons m is equal to 1 to the little n. This is the potential energy. And likewise, we can write V e e, V e n, V n n.

I do not want like that in detail, because they 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 the derivative operators. Therefore, I have written the derivatives, more explicitly and write the others as simply symbolic.

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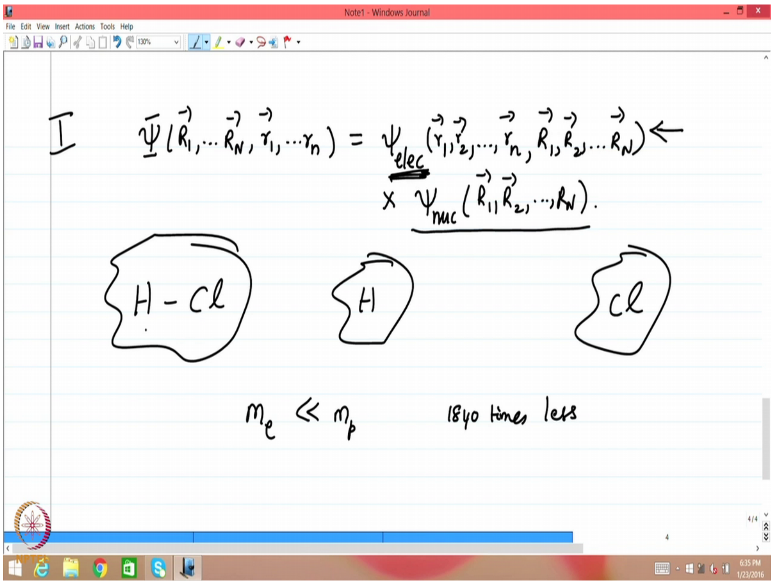

$$\text{I} \quad \Psi(\vec{R}_1,\ldots\vec{R}_N,\vec{r}_1,\ldots\vec{r}_n) = \underline{\psi_{elec}}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n,\vec{R}_1,\vec{R}_2\ldots\vec{R}_N) \leftarrow$$
$$\times\ \underline{\psi_{nuc}(\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N)}.$$

$m_e \ll m_p$ 1840 times less

For the Hydrogen molecule we can see what they are later. And the approximation 1 psi which is a function of all the nuclear coordinates and all the electron coordinates. Born on the Oppenheimer proposed, this to be a product of two terms one which depends on electronic coordinates and the nuclear coordinates.

So, let us write that as r 1 r 2 r n the n electrons and all the nuclear coordinates R 1 R 2, R capital n times 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 reasonably separate to the molecular Hamiltonian into 2 independent, nearly independent domains of problems to be solved.

Electronic Wave function is a function of all the coordinates. A nuclear wave function is a function of only the nuclear coordinates. What does 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, I mean mid, may not be a molecule, this may be 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 density seems to have spread out in such a way that part of the electron density of the Hydrogen atom goes towards fluorine and so on.

You know electro negativity a, a principle and you know this bond is partially co it is partly covalent, but partly ionic and so on. But the point is the 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 there seems to be a change in the electron density as the 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 the possibility a forming a bond, there is a possibility of rearrangement of the 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 proton. It is about 1840 times less. Therefore, for a given kinetic energy, the electrons are much faster moving v square mv square if you think about it half mv 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 electron the nuclear wave functions are 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 are slow moving. Therefore, we are not too worried about the nuclear motion unless we come to molecular spectroscopy. And we will not worry about its immediate dependence of the electron.

The other dependencies for more crucial for chemical bond and therefore, keep the electronic wave function as dependent on nuclear and electronic coordinate. I mean in a, in a sense this is, this makes a chemical sense and with this approximation Born-Oppenheimer suggests to the separation of the overall Hamiltonian as follows.

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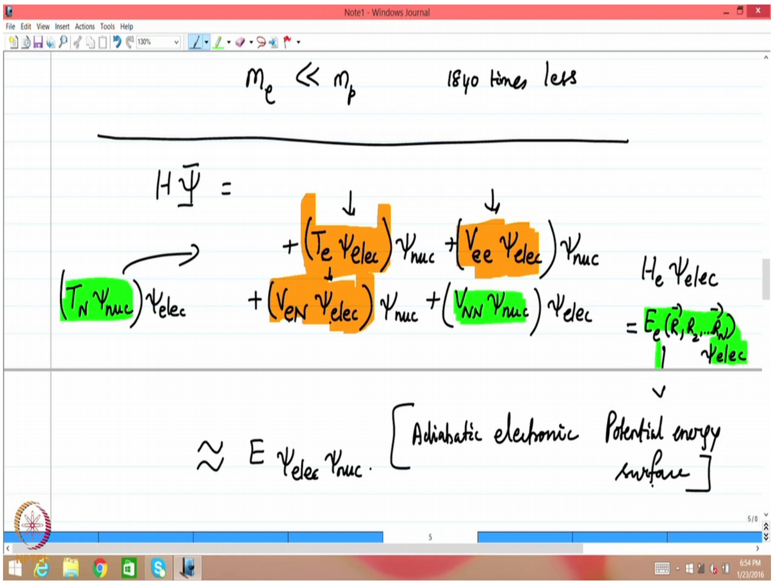

$m_e \ll m_p$ 1840 times less

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

$H_e \psi_{elec} = E_e(\vec{R}_1, \vec{R}_2, \ldots \vec{R}_N)\, \psi_{elec}$

$\approx E\, \psi_{elec}\, \psi_{nuc}$.

[Adiabatic electronic Potential energy surface]

H psi, is now let me write down individualizing, T N psi electronic psi nuclear plus T e psi electronic and psi nuclear plus the V e e psi electronic psi nuclear plus V e n psi electronic times psi nuclear plus V N N psi nuclear times psi electronic, and this is equal to E psi electronic psi nuclear.

Now the brackets have some special meaning. There is no bracket here, because this is the term we are going to discuss. T N psi electronic psi nuclear we will see what it needs to be changed to, but the other brackets are quite clear T e contains only derivatives of the electron coordinates. We see that, contains only the derivatives of the electron coordinates that you see here. Therefore, in the overall wave function if you look at it the electron coordinate dependence happens only for the nuclear for the electronic wave function.

Therefore, the derivative operators do not change, the derivative operator does not change the psi nuclear. So, what it does, is it only acts on the psi electronic therefore, I have put that in bracket. The rest is a multiple this multiplied by psi 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 psi electronic together. The electron-nuclear attraction the psi electronic together and the nuclear-nuclear with to the psi nuclear, because it is possible with this to separate the Hamiltonian.

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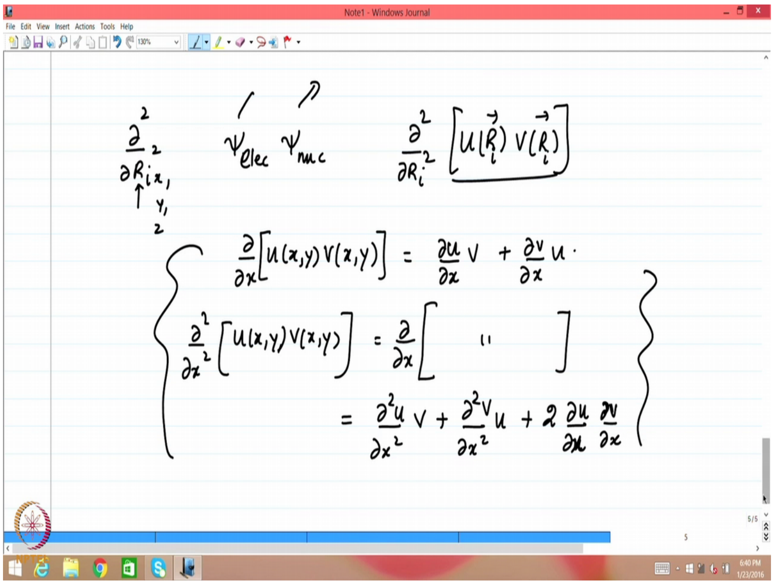

$$\frac{\partial^2}{\partial R_{i x,y,z}^2} \qquad \psi_{elec}\,\psi_{nuc} \qquad \frac{\partial^2}{\partial R_i^2}\left[u(\vec{R}_i)\,v(\vec{R}_i)\right]$$

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

$$\frac{\partial^2}{\partial x^2}\left[u(x,y)\,v(x,y)\right] = \frac{\partial}{\partial x}\left[\quad " \quad\right]$$

$$= \frac{\partial^2 u}{\partial x^2}v + \frac{\partial^2 v}{\partial x^2}u + 2\frac{\partial u}{\partial x}\frac{\partial v}{\partial x}$$

What about to the T N psi electronic psi nuclear; the crux of the approximation is there only T N please remember contains the derivative operator dou square dou Ri square x y z, if you wish to. Therefore, when it acts on psi electronic and psi nuclear, remember, both of these are dependent on the nuclear coordinates.

So, the derivative acts on something like a function u of R, v of R if you want to write this specifically R i R i. So, dou square by dou R i square. Now, remember that, the derivative rule is that if you have a function say d by, d dx or a function dou by dou x u of x comma y some other variable and v of x comma y.

Then, you know that, this derivative is expressed as dou u dou x times v plus dou v by dou x times u and the second derivative dou square by dou x square on u of x comma y v of x comma y, is the derivative dou by dou x, acting on this term, this the sum of these two terms and therefore, what you get is dou square u by dou x square times v plus dou square v by dou x square times u plus you will get the cross term also 2 dou u by dou x dou v by dou v by dou x.

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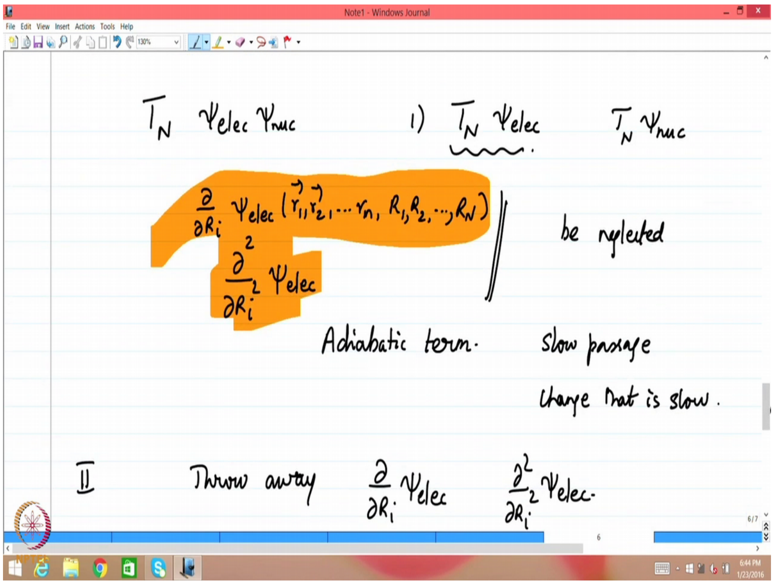

$T_N \; \psi_{elec} \psi_{nuc}$ 1) $T_N \; \psi_{elec}$ $T_N \; \psi_{nuc}$

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

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

Adiabatic term. slow passage

change that is slow.

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

Therefore, with this sort of elementary mathematics in mind it is easy to see that the nuclear kinetic energy operator acting on the psi electronic and the psi nuclear, will have one the T N operating on psi electronic and the other TN operating on psi nuclear.

Now, this contains dou by dou R i psi electronic, the electronic coordinates and the nuclear coordinates R n. It also contains the second derivative dou square by dou R i square of psi electronic. Born and Oppenheimers suggest, this to be an Adiabatic change an Adiabatic term.

In Physics and in Thermodynamics and in chemistry, adiabatic means, slow passage or change that happens slowly 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 the change of this psi electronic with respect to the nuclear coordinate that rate of change is sufficiently small, that is the reason why it is called adiabatic.

It is sufficiently small that, we can throw away, we can neglect that, we can also if that change is small the 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 that the coordinate, but we have assumed 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 its rate of change and the rate of, rate of change with respect to nuclear coordinates be dropped off and that is approximation II throw away dou by dou Ri psi electronic and dou square by dour Ri square psi electronic. What does this do; this does something beautiful.

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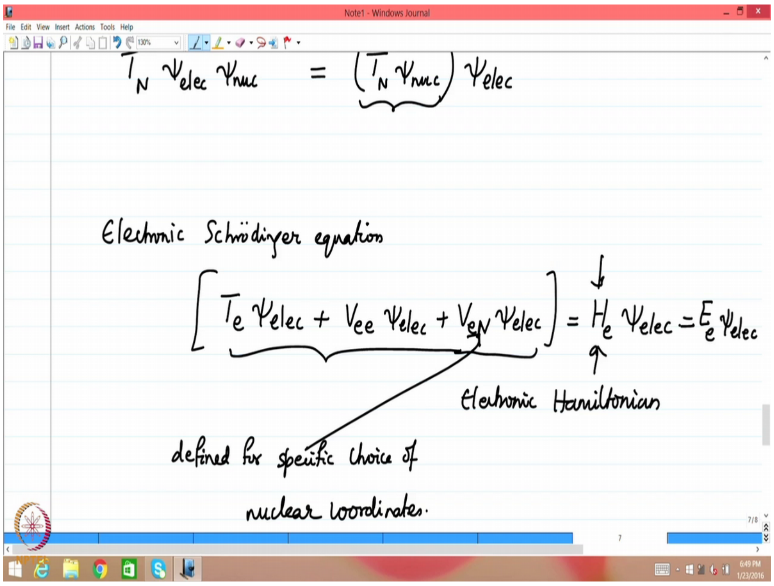

$$T_N \psi_{elec} \psi_{nuc} = \underbrace{(T_N \psi_{nuc})} \psi_{elec}$$

Electronic Schrödinger equation

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

Electronic Hamiltonian

defined for specific choice of nuclear coordinates.

Let us say what that is, therefore, when you write T N psi electronic psi nuclear, essentially what you have done is to write this as T N psi nuclear, because you have dropped off the dependence of the electronic coordinates. Therefore, this is the only thing.

Now, you go back and see why these brackets are wave they are. Therefore, let me write to this term, here itself as T N psi nuclear psi electronic it is an approximation. Therefore, I would not write this as E psi, but rather to write this as approximate E psi.

So, what you have here is therefore, this term goes away and is replaced by this term T N psi nuclear and then you have T psi electronic V e e psi electronic V e N psi electronic. Remember, all these things depend on the electronic coordinates.

This is solved as the electronic Schrodinger equation T e psi electronic plus V e e psi electronic plus V e N psi electronic. Let us call this as a Hamiltonian for the electronic motion, acting on psi electronic. This is called the electronic Hamiltonian, defined for very specific positions of the nuclear coordinates, defined for specific choice of nuclear coordinates.

Keep this in mind now let me take you off to a slightly different discussion, the particle in a one-dimensional box, when you solve this equation h bar square by 2 m d square by d x square psi of x when you solved that you got the energy which is independent of x. It is a constant and this was h square by 8 m l square n square no x here. When you solve the harmonic oscillator problem, h bar square by 2 m d square by d x square psi of x plus half k x square psi of x is equal to E psi of x, this is a constant.

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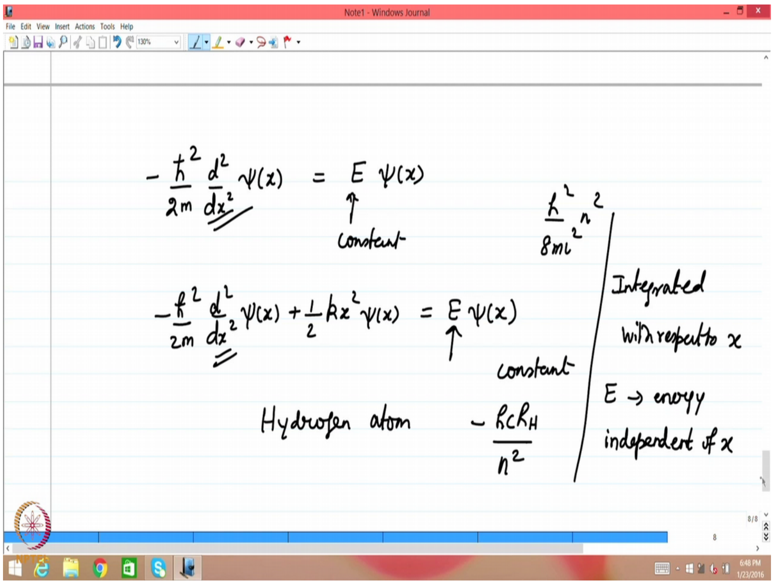

$$-\frac{\hbar^2}{2m}\underline{\underline{\frac{d^2}{dx^2}}}\psi(x) = \underset{\substack{\uparrow \\ \text{constant}}}{E}\,\psi(x) \qquad \frac{h^2}{8ml^2}n^2$$

$$-\frac{\hbar^2}{2m}\underline{\underline{\frac{d^2}{dx^2}}}\psi(x) + \frac{1}{2}kx^2\psi(x) = \underset{\substack{\uparrow \\ \text{constant}}}{E}\,\psi(x)$$

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

Integrated with respect to x

$E \rightarrow$ energy independent of x

And. So, for the Hydrogen atom, the energy is simply minus h c R H by m square. There is no x dependence or R dependence or theta dependence or phi dependence in it, 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.

Now, with this let us go back and look at this one, when you solve the Schrodinger equation for the electronic Hamiltonian as written here, the solution of this if it is to be written as E e psi electronic, if that is a Schrodinger equation for the electronic motion the E e is a constant with respect to all the electron coordinates of this Hamiltonian, all of them.

However, the E e is a function of the nuclear coordinates because in the process of solving it you do not touch the nuclear coordinates, you leave them they are as they are. You solve this problem for each set of nuclear coordinates and when you solve you will get many-many energies, like the particle 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 the V e N depends on both the electron coordinates, as well as the nuclear position coordinates.

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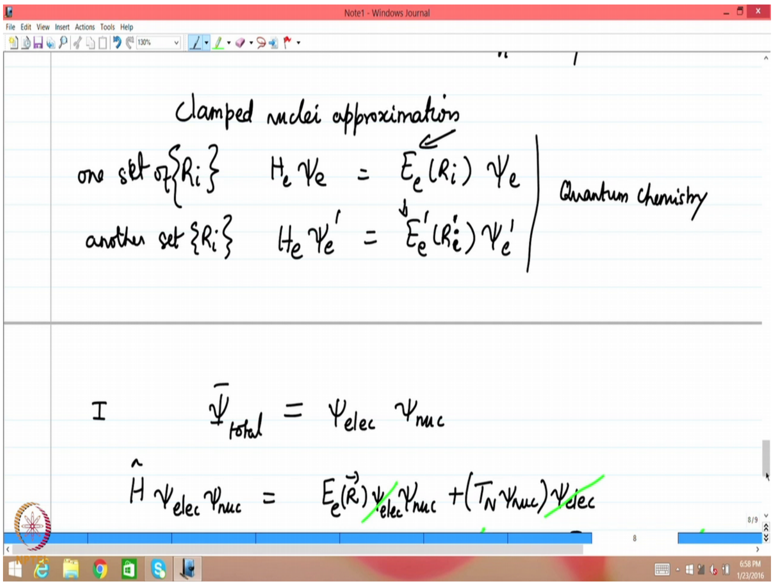

Clamped nuclei approximation

one set of $\{R_i\}$ $H_e \Psi_e = E_e(R_i)\, \Psi_e$

another set $\{R_i\}$ $H_e \Psi_e' = E_e'(R_i')\, \Psi_e'$

Quantum chemistry

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

$$\hat{H}\, \Psi_{elec}\, \Psi_{nuc} = E_e(\vec{R})\, \cancel{\Psi_{elec}}\, \Psi_{nuc} + (T_N \Psi_{nuc})\, \cancel{\Psi_{elec}}$$

Therefore, you do not change the nuclear coordinates keep them to a fixed value clamp them and that is called Clamped nuclei approximation. Solving H e psi e for one set of Ri, gives you E, e which is a function of that Ri times psi e change to another set of Ri. You will get again, another solution psi e prime which will give you E e prime some other value or i this is a different set of coordinates and psi e prime.

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 e, which are functions of the position of the nuclei. What does this do; this goes back to the leftover part in the equation, that we have here.

So, what we have done is to consider Te psi electronic which is part of the electronic Hamiltonian V e psi electronic which is also part of the potential energy and then V e N psi electronic and call all these things together by H e psi electronic. And what does it give? It gives you E e a function of the nuclear positions or 1 or 2 or n times psi electronic.

Therefore, we substitute that and then solve the rest of the problem. Rest of the problem contains the nuclear, let us use a different color. Yeah, the rest of the problem contains the nuclear kinetic energy, the nuclear, nuclear repulsion energy and of course, then 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 are in green, are known as the nuclear Schrodinger equation and that is what you solve in Molecular Spectroscopy and what do you get in the nuclear equation, not just the nuclear kinetic energy not just the nuclear-nuclear repulsion energy. But an energy term which comes from the electronic Schrodinger equation which is a function of the nuclear positions and therefore, that is 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 operator does not change the Electronic Wave function drastically. Therefore, the d by d Ri the derivative of the Electronic Wave function with respect to nuclear coordinates they are 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 is called a non-Born-Oppenheimer or it is also known as the failure or the breakdown of the Born-Oppenheimer Approximation.

That is done in a slightly more advanced course of chemical physics and therefore, let us not do that here for all our purposes, we will stick to the simple Born-Oppenheimer Approximation, the adiabatic potential energy surface. This is called adiabatic electronic potential energy surface, 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 bus is due to the nuclei, translational 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 is a Quantum Chemistry problem, 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 is much more complicated.

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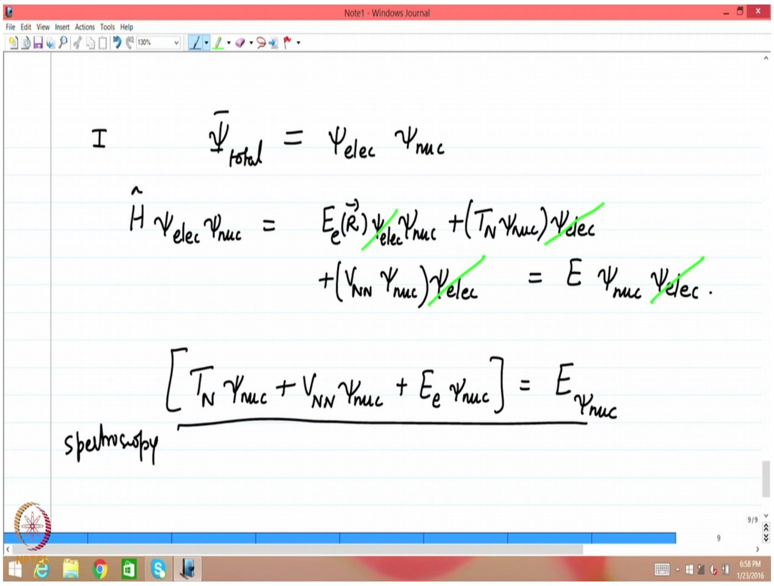

I $\bar{\Psi}_{total} = \psi_{elec}\,\psi_{nuc}$

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

$$\underbrace{\left[T_N\,\psi_{nuc} + V_{NN}\,\psi_{nuc} + E_e\,\psi_{nuc}\right] = E_{\psi_{nuc}}}$$

spectroscopy

So, let me summarize this part of the lecture, namely the Born-Oppenheimer Approximation I is psi total is expressed as, the psi total is expressed as, psi electronic psi nuclear. And then the H on psi electronic psi nuclear is expressed as H electronic psi electronic times psi nuclear plus the T nuclear psi nuclear, psi nuclear times psi electronic plus V e N V NN sorry, V NN psi nuclear psi electronic and that is equal to E psi nuclear psi electronic and what we shall do is; obviously, replace this by E e, which is a function of the nuclear coordinates, all of them psi electronic.

So, now, with this form you see that, the psi electronic is the multiple to the entire function. So, you can get rid of that; you can get rid of that, in that and what you get is of course, the nuclear Hamiltonian T N psi nuclear plus V NN psi nuclear plus E e psi nuclear is equal to the total energy E times psi nuclear. This is Spectroscopy; 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.

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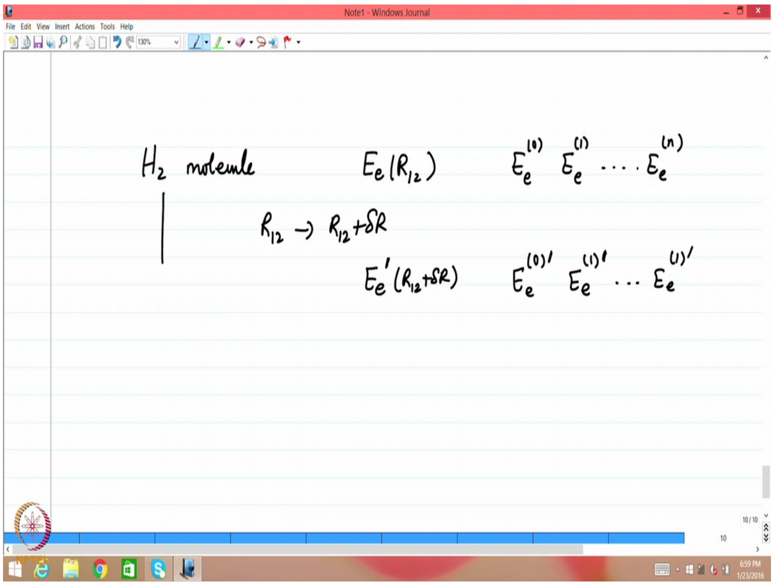

H_2 molecule $E_e(R_{12})$ $E_e^{(0)}\ E_e^{(1)} \cdots E_e^{(n)}$

$R_{12} \rightarrow R_{12}+\delta R$

$E_e'(R_{12}+\delta R)$ $E_e^{(0)'}\ E_e^{(1)'} \cdots E_e^{(1)'}$

So, in a simple case like a hydrogen molecule what does this do? So, a case of hydrogen molecule we do not need to worry about all the 6 coordinates of the 2 nuclei, but let us 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 minus R 2 vector. 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 plus a delta R solve this again, you will get E e prime R 12 plus delta R.

Again, a whole set of energies E e 0, E e prime some other value E e 1 and so what 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 is shown in this animation. That is shown in this animation.

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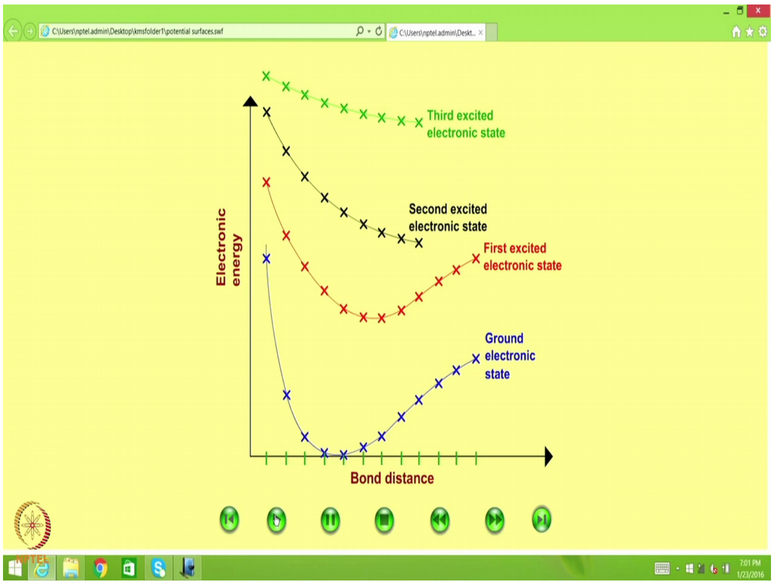

So, what I have here is the inter nuclear distance R 12 is along the x axis and then the electronic energy solution, that you get multiple solutions that you get for solving the electronic equation. So, for that R 12 you get different values, like you get in the case of Hydrogen atom you get the n equal to 1 n equal to 2 n equal to 3, there the quantum numbers are well known.

Here, some quantum numbers come out, fine, when the point is you get multiple energies then you slightly change the R you get another set energy eigenvalue, 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 is connected to give you, what is called the ground state potential energy surface the next higher.

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.

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. That is the essence of Born and 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 and 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 in taking the rotational motion also away from them you have 3 vibrational, what are called coordinates nuclear inter nuclear coordinates and the potential energy for the electron is a function of these 3 nuclear coordinates. Therefore, the potential energy is not a graph. It is a function of three variables therefore, it is a surface actually a three-dimensional surface; four-dimensional surface because you need three coordinates to represent and the fourth dimension is the actual point.

Therefore, even a triatomic molecule, you need a four-dimensional system to actually plot people use color as the fourth-dimension to indicate such a potential energy surfaces, but if you have an n atom molecule. In general, there are 3 n minus 6 such vibrational coordinates for a non-linear molecule what are called independent coordinates leaving the translation and rotation out 3, 3 each you have 3 n minus 6 independent coordinates and these are called normal coordinates and these normal coordinates determine the electronic energy surface.

The electronic energy surface is 3n minus five-dimensional, because the n minus 6 coordinates and the dimension for plotting that. So, it is impossible to plot potential energy surfaces in for an any real molecule in a 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 is the contour maps are used and there is a lot of information, which has been generated in the last 70 years, on many small molecular systems on these potential energy surfaces ground state, the excited state and the higher energy excited states and so on.

Therefore, that is 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 minute, in the next lecture I will 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 a microwave spectroscopy. And then what is known as the infrared spectroscopy and then the coupling between these microwave and infrared spectroscopy has so, rotational vibrational spectroscopy and so on.

Therefore, applying this Born-Oppenheimer Approximation in the sequential form it is possible for us to express the Hamiltonian, as approximate sums, but the procedure is approximate.

Thank you.