Chemistry II: Introduction to Molecular Spectroscopy

Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

Lecture – 08
Born – Oppenheimer Approximation

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 Rob Maxborn and Robert Oppenheirmer, a physicist on the chemist, in 1927, right after the year when Schrödinger published his equation, the famous Schrödinger equation and applied this to the solution of the hydrogen atom.

Now, many of you have studied in the elementary chemistry, that molecule, molecular energies can be approximately expressed as sums of independent contributions, such as molecular translational motion, rotational motion, and energy due to molecular translational motion, the energy due molecular rotational motion, the energies of molecular vibration, and electronic energies. Where does this approximation come from? That is 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 difficult term to solve.

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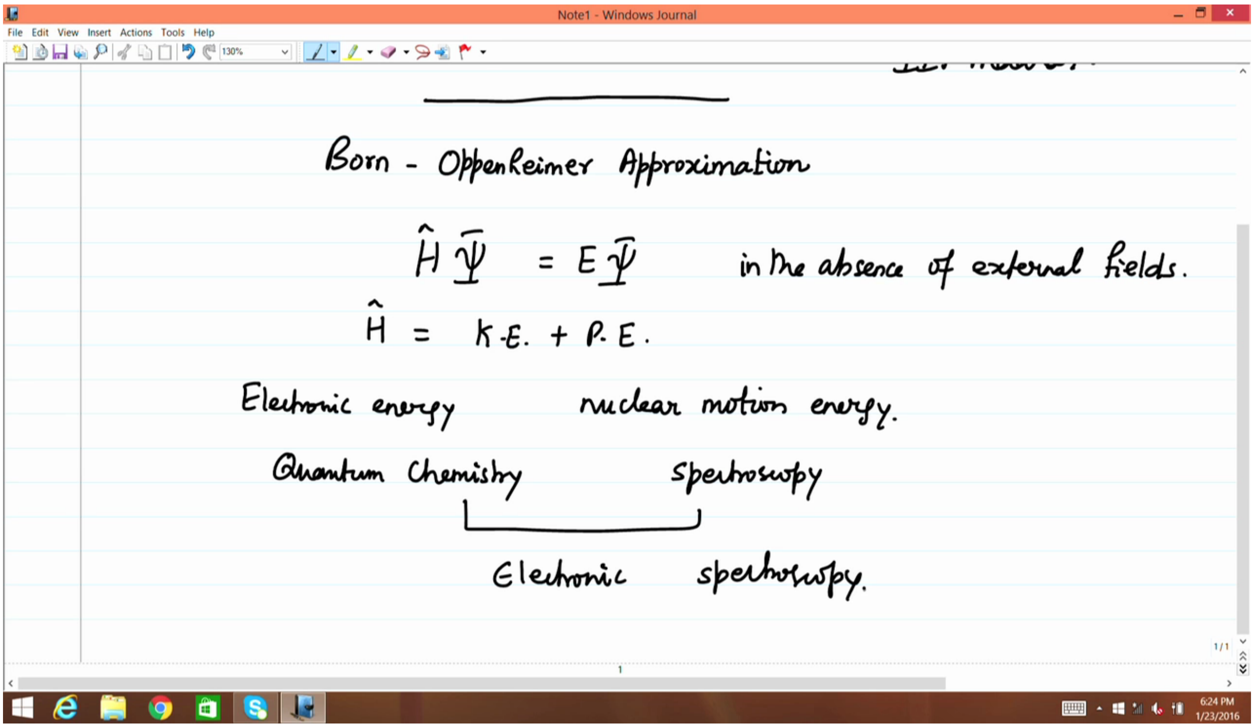

Born - Oppenheimer Approximation

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

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

Electronic energy nuclear motion energy.

Quantum Chemistry Spectroscopy

$\underbrace{\qquad\qquad\qquad}$

Electronic spectroscopy.

Let us look at, what is meant by this approximation therefore, let me write the Schrödinger equation time independent the 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 consists 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 the molecular systems in the absence of the electro magnetic 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 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, eh nuclei and then the nuclear motion energy which we 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. 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, 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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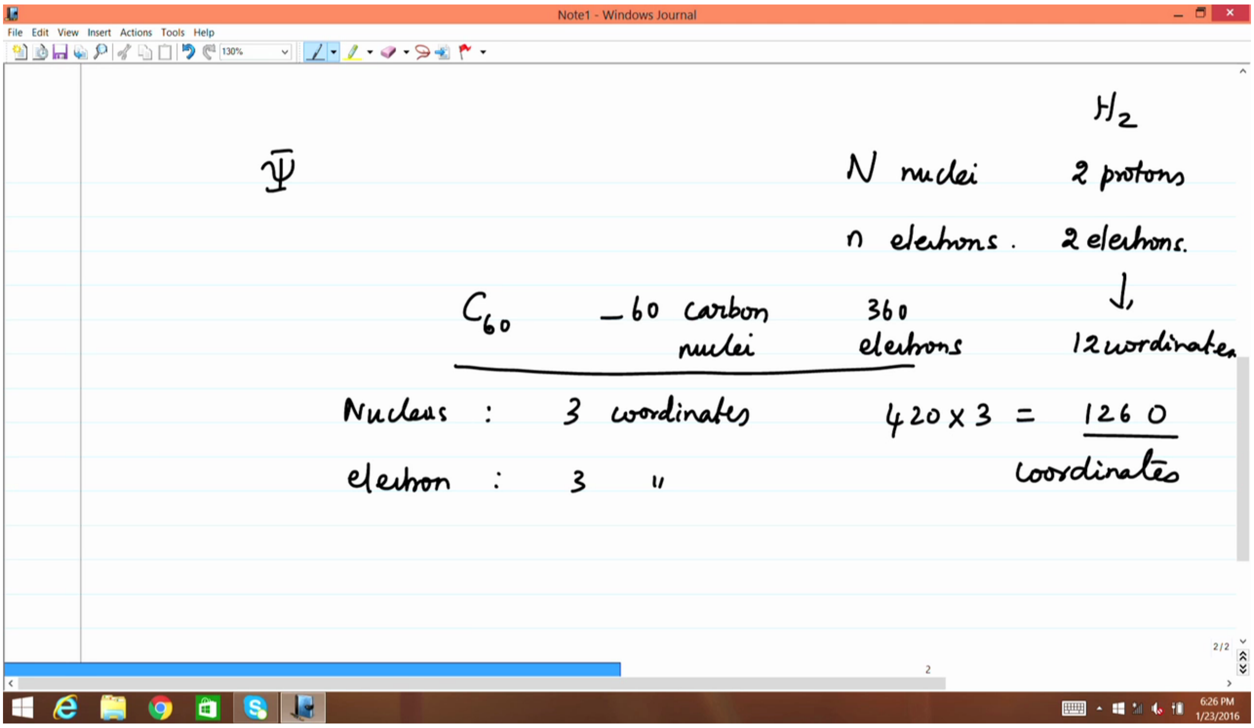

Ψ

H_2

N nuclei — 2 protons

n electrons. — 2 electrons.

$\downarrow$

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

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

electron : 3 "

So, let me write down the molecular wave function psi has say n nuclei and n electrons, some arbitrary number.

Let us do this parallel, for hydrogen molecule 2 new protons and 2 electrons. If you have to do this for something like carbon 60, you have 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 for 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 Schrödinger equation for the hydrogen atoms contains the 3 coordinates, the x y z, and it is solution using the polar coordinate 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 indeed, but you cannot solve such systems with such large number of coordinates, by any other means than approximation procedure.

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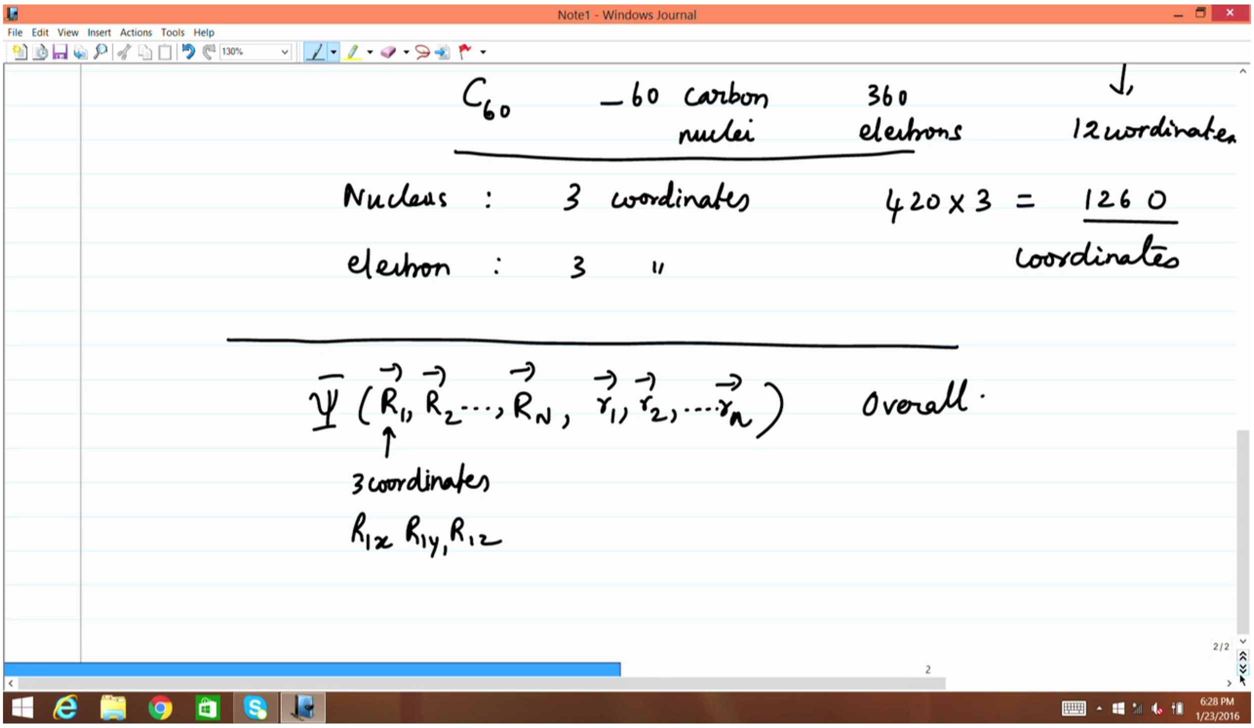

C_{60} – 60 carbon nuclei 360 electrons

↓

12 coordinates

Nucleus : 3 coordinates

electron : 3 "

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

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

↑

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 R’s from the m nuclei, and each one is 3, r 1 x, r 1 y, r 1 z, if you wish to, r 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, this is the overall molecular wave function.

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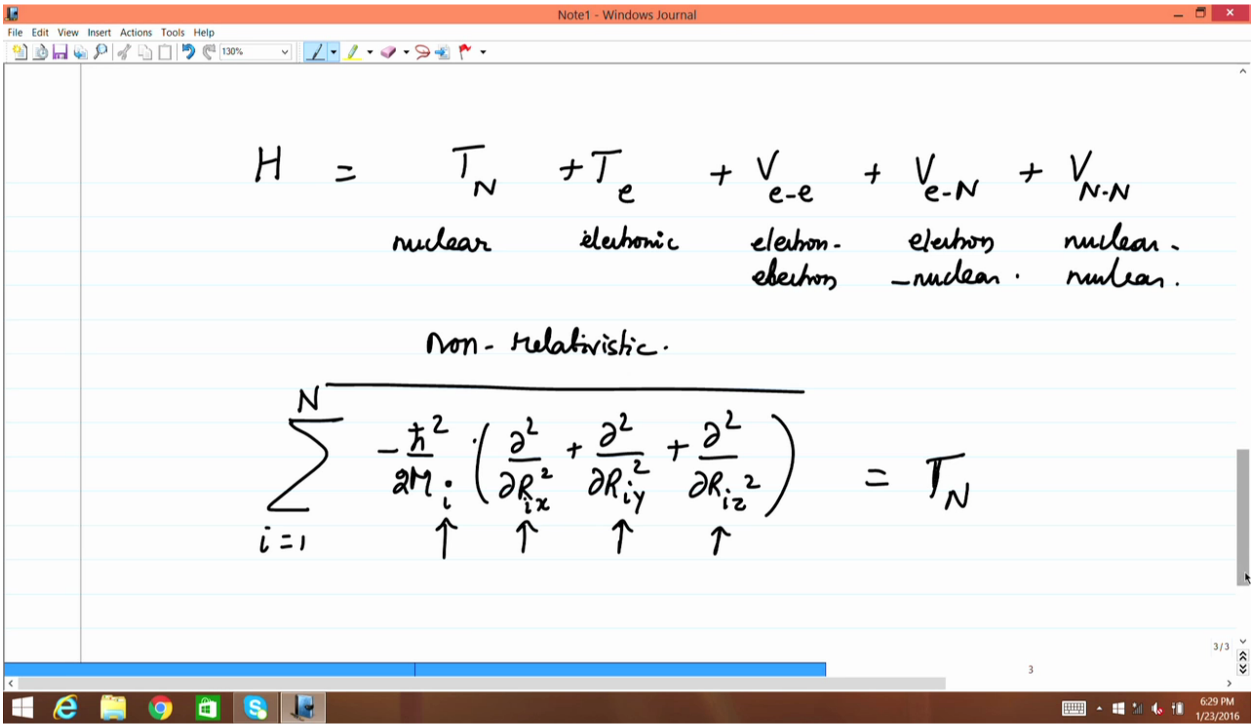

$$H = T_N + T_e + V_{e-e} + V_{e-N} + V_{N-N}$$

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

Non-relativistic.

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

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 contains, 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 x y z are the coordinates of that, and this is summed over all the atoms i is equal to 1 to n, all the nuclei. This is t n.

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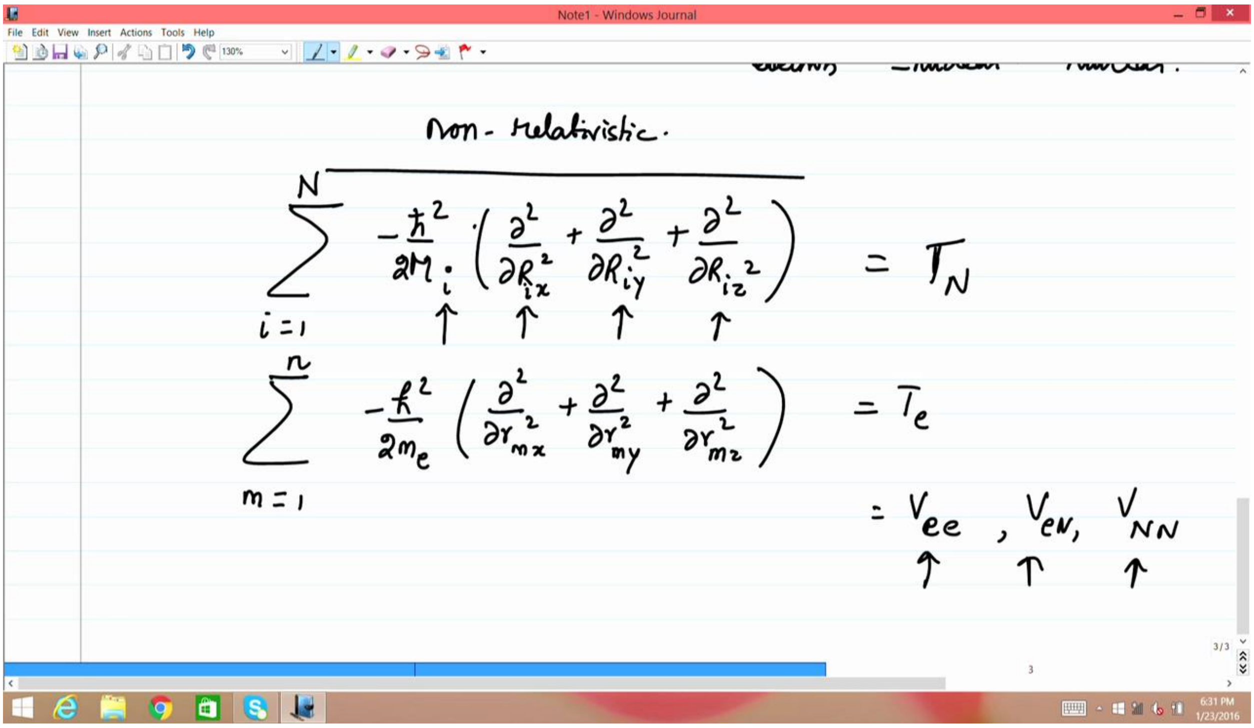

Non-relativistic.

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

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

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

The t electron, likewise, is given by minus h bar square by 2 m e all the electrons have the same mass, therefore, you write dou square by dou little r say, m I, 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. Likewise you can write v e e, v e n, v n n, I do not want write that in detail, because there are all going to be multiplying the wave functions therefore, they do not have the special significance or the Born Oppenheimer approximation that we have with derivative operators, 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.

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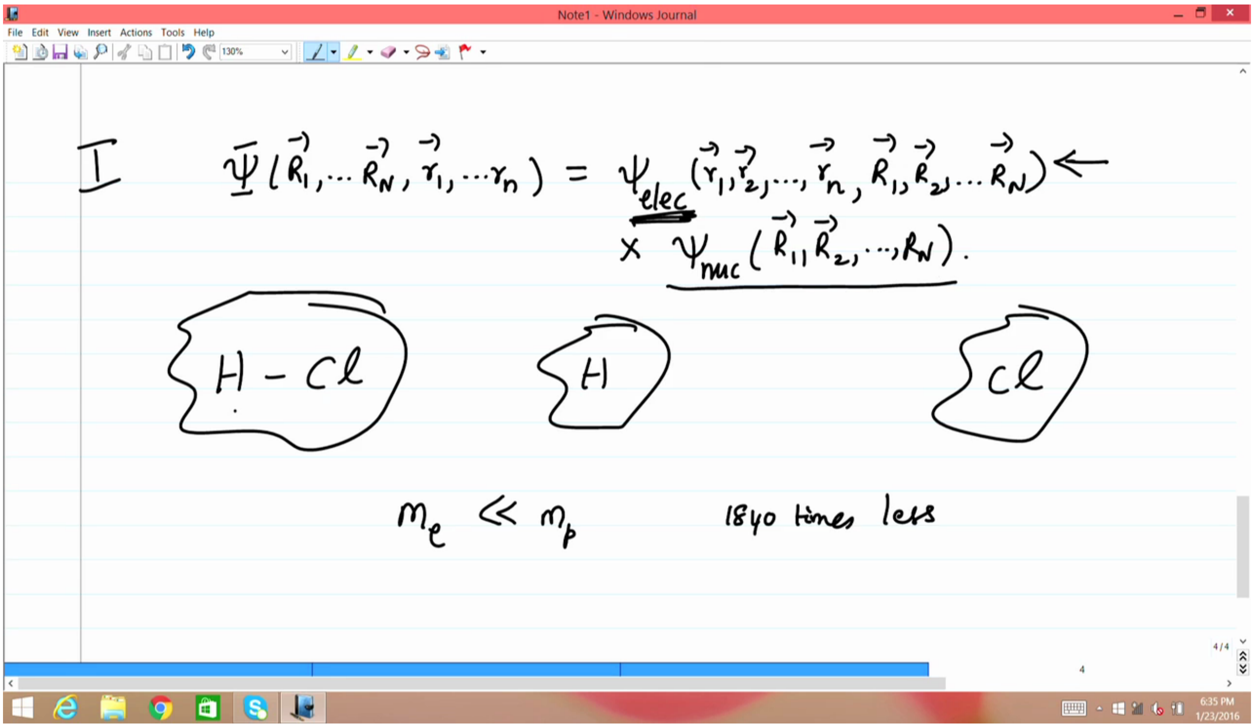

I $$\Psi(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots\vec{r}_n) = \underline{\psi_{elec}}(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_n,\vec{R}_1,\vec{R}_2\dots\vec{R}_N) \leftarrow$$
$$\times\ \underline{\psi_{nuc}(\vec{R}_1,\vec{R}_2,\dots,\vec{R}_N)}.$$

$m_e \ll m_p$ 1840 times less

And the approximation 1 psi, which is a function of all the nuclear coordinates and all the electron coordinates, the Born Oppenheimer proposes this to be a product of 2 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 are r 1, r 2, r capital N times, a psi nuclear which is only a function of the nuclear coordinate's r n. This is the first of the 2 steps that the born Oppenheimer provides in order to reasonably separate the molecular Hamiltonian into two independent, nearly independent domains of problems to be solved. Electronic wave function is a function of all the coordinates. So, 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, have been may not be a molecule, this may be 2 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, the part of the electron density of the hydrogen atom, go towards chlorine and so on, you know electron negativity principles 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 a nuclei come together.

Therefore, the electronic wave function, being the function of nuclear coordinates is a natural thing for a chemists 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 rearrangement of the electron rearrangement of the electron density, therefore, the electronic wave function being a function of both nuclear and electronic coordinates make 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 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 b square m b square, if you think about it, half m b square v is much larger for the electron than for the nuclei in a classical sense. What it means is that, nuclear motion is almost instantly, adjusted by the electronic positions and therefore, the nuclear coordinates, that is a nuclei, do not have to worry about the electron density, in a sense, that the electro, the nuclear wave functions are nearly independent of the electronic coordinates, the electrons all most instantly readjust themselves to the nuclear positions.

And therefore, the 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 it is immediate dependence of the electron. The other dependencies far more crucial for chemical bond and therefore, keep the electronic wave function as dependent on nuclear and electronic coordinate.

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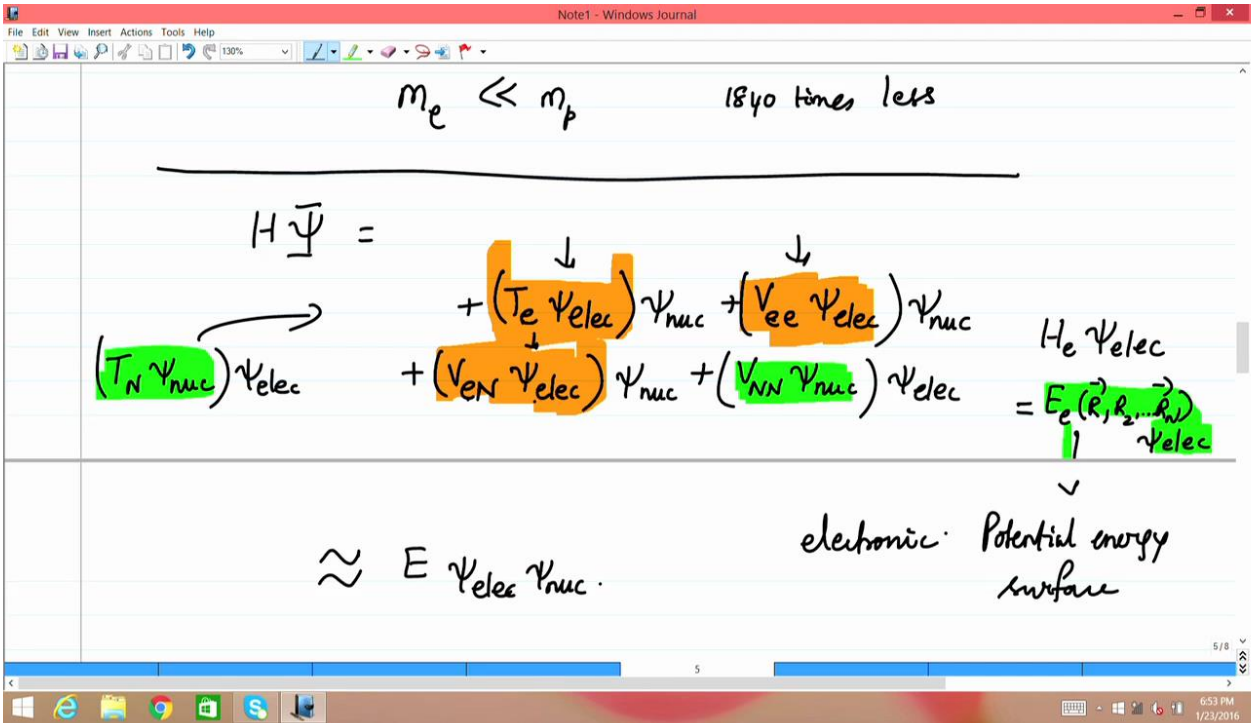

$m_e \ll m_p$ 1840 times less

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

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

electronic · Potential energy surface

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

I mean in a in a sense, this is, this makes a chemical sense and with this approximation, the Born Oppenheimer suggest the separation of the overall Hamiltonian as follows. h psi is now, let me write them individually, t n psi electronic psi nuclear plus t e psi electronic, and psi nuclear plus 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 discus, t n psi electronic psi nuclear, we will see what it needs to be changed to, but the other brackets are quiet 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 nuclei for the electron 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 brackets 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 the psi nuclear, because it is possible with this to separate the Hamiltonian. What about to the t n psi electronic psi nuclear?

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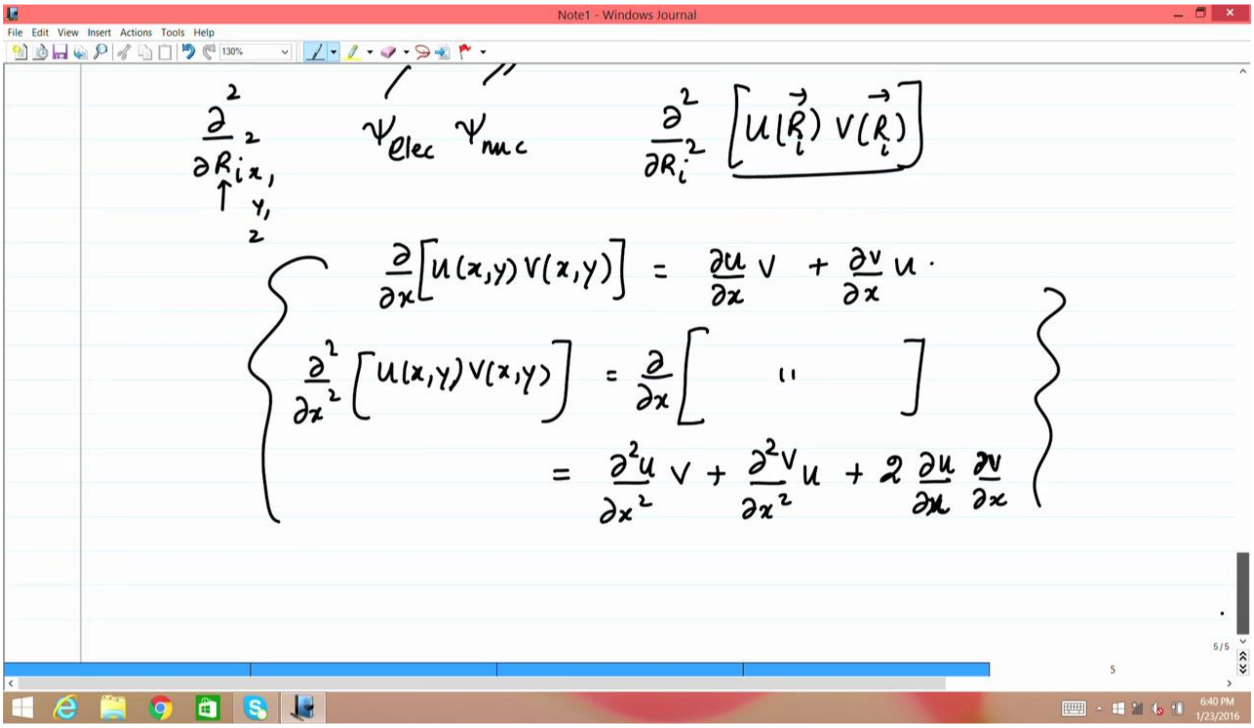

$$\frac{\partial^2}{\partial R_{i x,}^2} \quad \overset{/}{\Psi_{elec}} \quad \overset{//}{\Psi_{nuc}} \qquad \frac{\partial^2}{\partial R_i^2}\left[U(\vec{R}_i)\, V(\vec{R}_i)\right]$$

$\uparrow$ y, z

$$\left\{ \begin{aligned} \frac{\partial}{\partial x}\left[u(x,y)\,v(x,y)\right] &= \frac{\partial u}{\partial x} v + \frac{\partial v}{\partial x} u \\ \frac{\partial^2}{\partial x^2}\left[u(x,y)\,v(x,y)\right] &= \frac{\partial}{\partial x}\left[\quad '' \quad \right] \\ &= \frac{\partial^2 u}{\partial x^2} v + \frac{\partial^2 v}{\partial x^2} u + 2\frac{\partial u}{\partial x}\frac{\partial v}{\partial x} \end{aligned} \right\}$$

The crux of the approximation is there only, t m please remember, contains the derivative operator dou square dou r i 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, d x, are a function by 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 by dou x times b 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 2 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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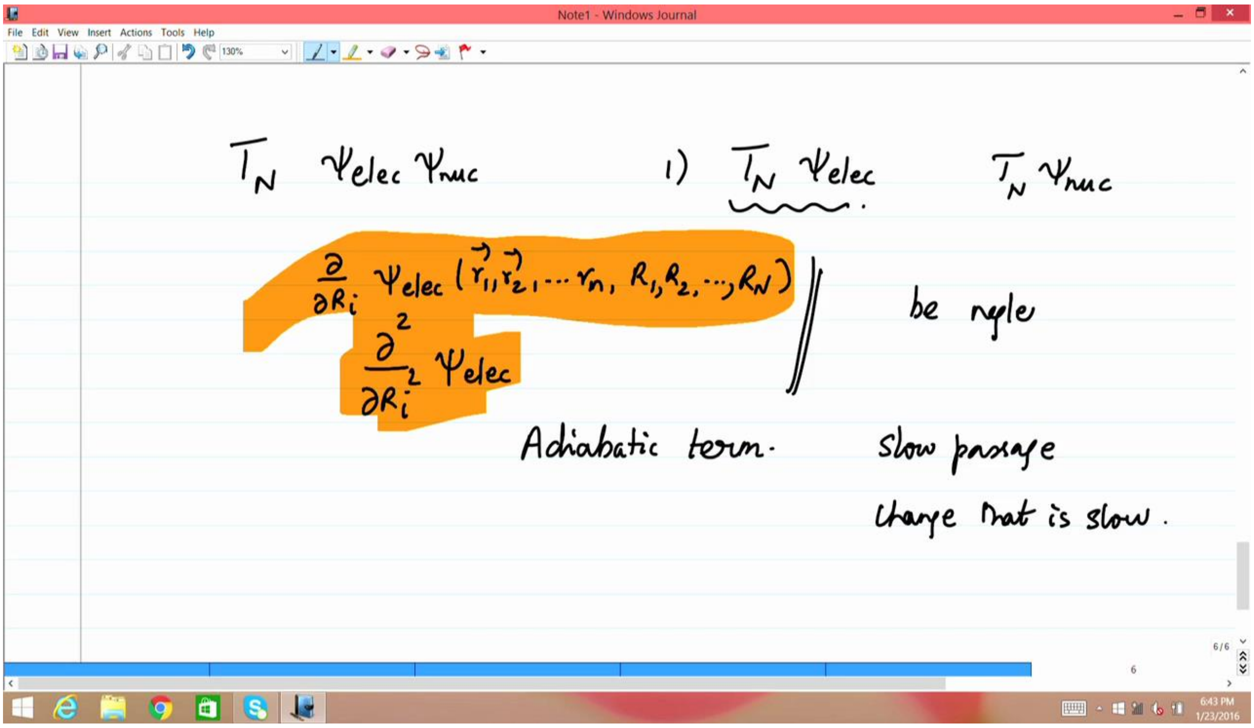

$T_N \quad \Psi_{elec} \Psi_{nuc}$ 1) $\underset{\sim\sim\sim}{T_N \Psi_{elec}}$ $T_N \Psi_{nuc}$

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

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

be negle

Adiabatic term.

Slow passage

change that is slow.

Therefore, with this sort of elementary mathematics in mind, it is easy to see that the nuclear kinetic energy operator, acting on this psi electronic and the psi nuclear, will have 1, the t n operators in psi electronic, and the other t n 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 openheimers suggest to be, an adiabatic change, an adiabatic term. In physics and in thermal dynamics 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 that derivative of the electronic coordinates this whole thing is sufficiently small the change of electronic with respect to the nuclear coordinate, that rate of changes sufficiently small, that is a reason why it is called adiabatic, it is sufficiently small that we can throw away, we can neglect that, you can also, if that change is small the rate of rate of change is also going to be small or even smaller and therefore, let us not consider these 2 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 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 nuclear coordinates the electronic wave function is, but it is rate of change and the rate of rate of change with respect to nuclear coordinates we dropped off, and that is approximation 2.

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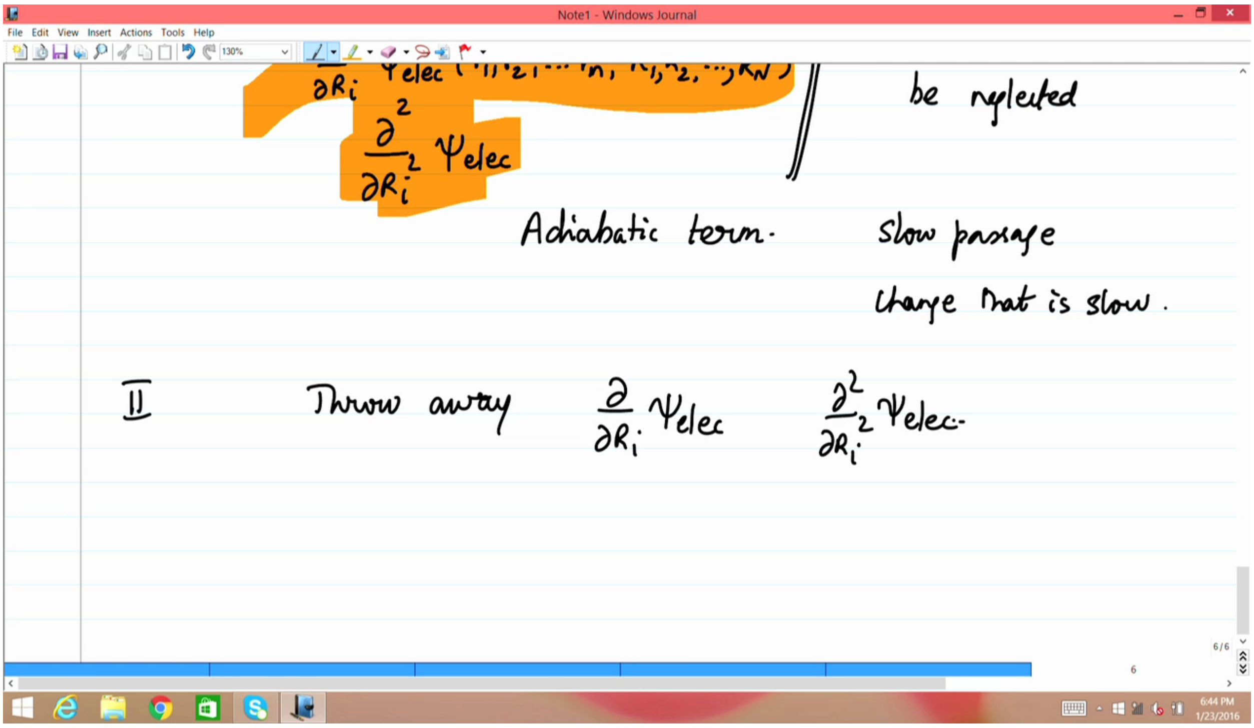

$\partial R_i \; \Psi_{elec}(r_1, r_2, \ldots r_n, R_1, R_2, \ldots, R_N)$

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

be neglected

Adiabatic term.

Slow passage

change that is slow.

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

Throw away dou by dou r I psi electronic dou square by dou r i square psi electronic, what does this do? This does something beautiful.

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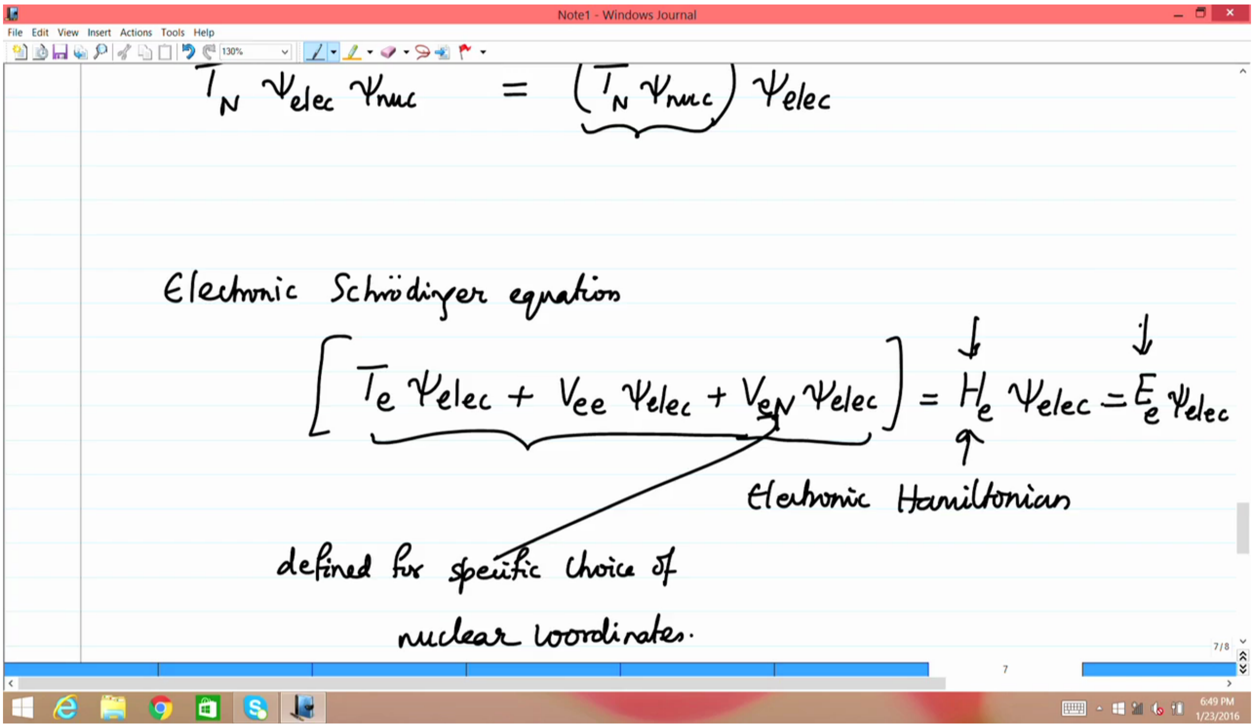

$$T_N \Psi_{elec} \Psi_{nuc} = \underbrace{\left(T_N \Psi_{nuc}\right)} \Psi_{elec}$$

Electronic Schrödinger equation

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

Electronic Hamiltonian

defined for specific choice of nuclear coordinates.

Let us see 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 where they are. Therefore, let me write this terms here itself, as t n psi nuclear, psi electronic, it is an approximation, therefore, I would not write this as e psi, but rather I would write this as approximate e psi.

So, what you have here is, therefore, this term goes away, and this replaced by this term, t n, psi nuclear, and then you have t e psi electronic, the v e e psi electronic, v e n psi electronic, remember all these things depends on the electronic coordinates. This is solved as the electronic Schrödinger 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.

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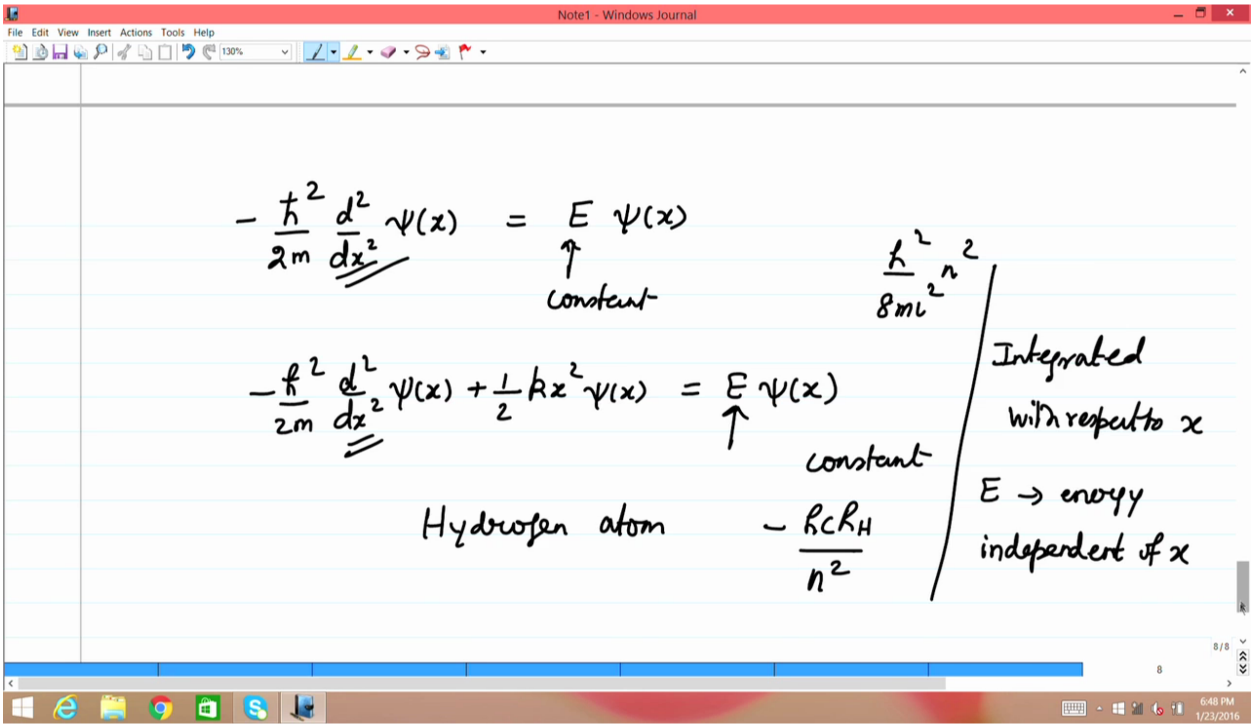

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \underset{\substack{\uparrow \\ \text{constant}}}{E}\,\psi(x)$$

$$\frac{h^2}{8ml^2}n^2$$

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

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

Integrated with respect to x

$E \rightarrow$ energy

independent of x

Keep this in mind. Now let me take you off to a slightly different discussion, the particle in the 1 dimensional box, when you solved this equation, bar square by 2 m d square by d x square psi of x when you solve 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, then 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 this is equal to e psi of x, this is a constant, and so for the hydrogen atom, the energy is simply minus h c r h, by n 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 just go back and look at this one, when you solved the Schrödinger equation for the electronic Hamiltonian as written here, the solution of this, if it is to be written as e epsi electronic, if that is Schrödinger 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, you do not touch the nuclear coordinates, you leave them they are as they are. You solved this problem for each set of nuclear coordinates and when you solve, you will get many many energies, like the particle in a box or like the harmonic oscillator, or the hydrogen atom, you get a whole lot of energies and you get a whole lot of a wave functions, all of which are for 1 configuration of the nuclear coordinates m, because the v e n depends on both the electron coordinates, as well as the nuclear position coordinates, therefore, you do not change the nuclear coordinates, keep them to a fixed value, clamp them.

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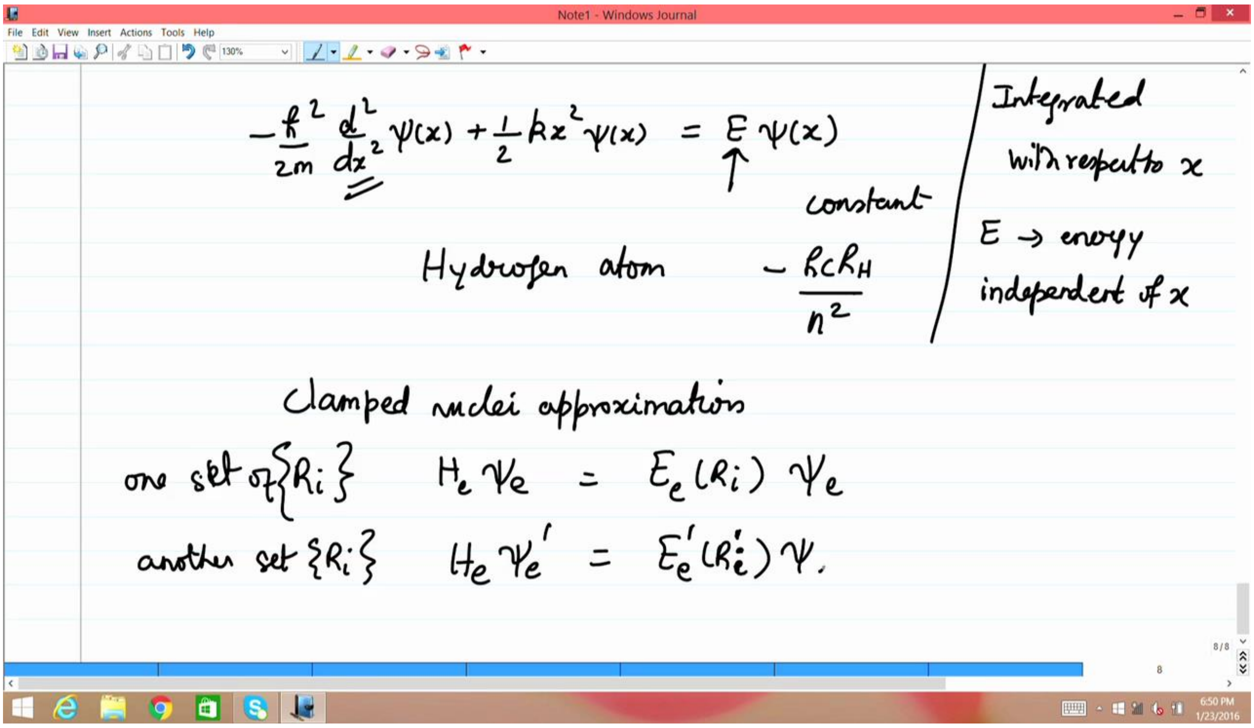

$$-\frac{\hbar^2}{2m}\underline{\underline{\frac{d^2}{dx^2}}}\psi(x) + \frac{1}{2}kx^2\psi(x) = \underset{\uparrow}{E}\,\psi(x)$$

constant

Integrated with respect to x

$E \rightarrow$ energy independent of x

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

Clamped nuclei approximation

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

another set $\{R_i'\}$ $\quad H_e\psi_e' = E_e'(R_i')\,\psi'$

And that is called Clamped Nuclei Approximation. Solving h e, psi e, for 1 set of r i, gives you e e, which is a function of that r i, times psi e change to another set of r i, you will get again another solution psi prime, which will give you e e prime, some other value, r 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 the 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 left over part in the equation that we have here. So, what we have done is to consider t e psi is a electronic, which is part of the electronic Hamiltonian, v e psi electronic, which 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 position r 1, r 2, r n times psi electronic, therefore, we substitute that, and solve the rest of the problem, rest, rest of the problem contains the nuclear. Let us use a different color, yeah, there is the problem contains the nuclear kinetic energy, the nuclear, 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 are in green, are known as the Schrödinger 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 the 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 surfaces provided by the electronic Schrödinger equation, and this with the approximation that the nuclear kinetic energy operator, does not change, the electronic wave function drastically, therefore, the d by d r i, the derivative or 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 diabetic process, and it is called the non Born openheimers, or it is also known as the failure or the break down of the born Oppenheimer Approximation.

That is then in a slightly more advanced course of chemical physics and of course, 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 mass due to the nuclei, translational motion of the nuclei.

The rotational motion of the atoms, and the vibrational motion of the relative replacements 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, and this is the molecular spectroscopy problem; obviously, the electron provides the link here, and therefore, when you see electronic spectroscopy, these 2 things really get together, and that is much more complicated.

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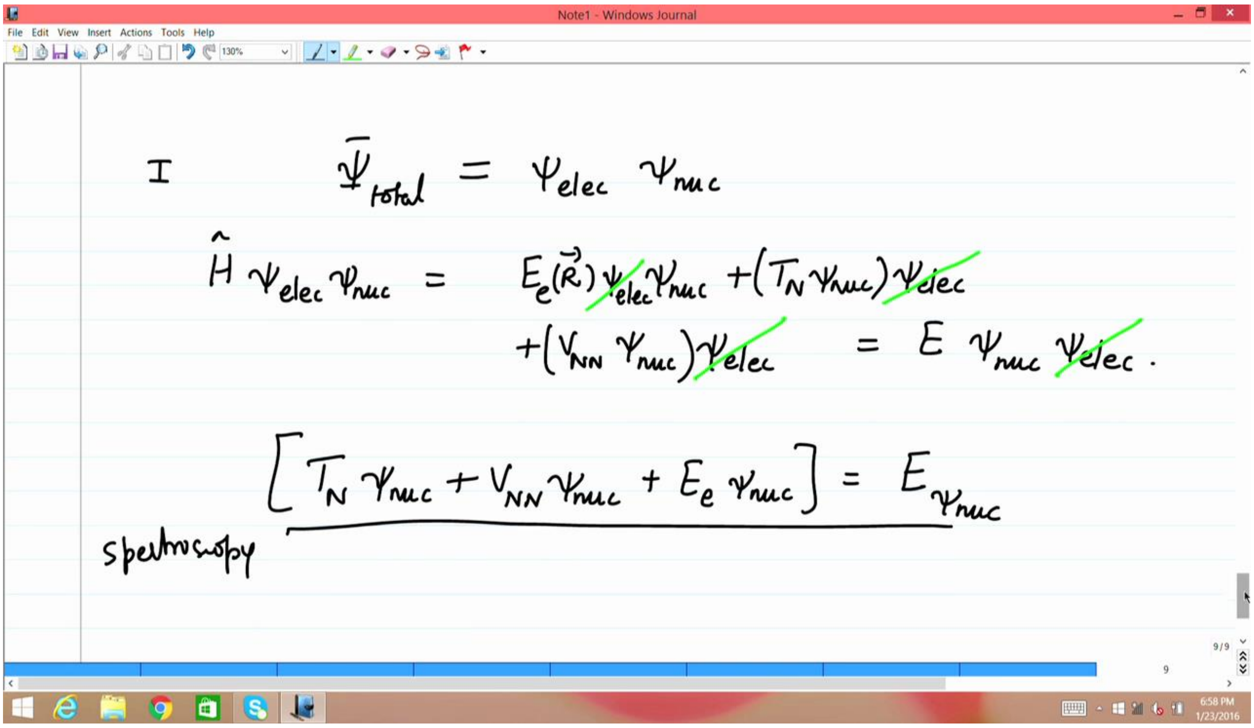

I $$\bar{\Psi}_{total} = \Psi_{elec}\,\Psi_{nuc}$$

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

$$+(V_{NN}\,\Psi_{nuc})\,\cancel{\Psi_{elec}} = E\,\Psi_{nuc}\,\cancel{\Psi_{elec}}\,.$$

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

spectroscopy

So, let me summarize this part of the lecture, namely the Born Oppenheimer Approximation 1, 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 n n, sorry, v n n psi nuclear, psi electronic, and that is equal to e, psi nuclear, psi electronic, and what shall we do is; obviously, replace this y, e, e which is the function of the nuclear coordinates, all of them, psi electronic.

So, now with this form, you see that the psi electronic is a multiple to the entire function. So, you can get rid off that, you can get rid off that, that, that, and what you get is of course, the nuclear Hamiltonian, t n psi nuclear, plus v n n 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 the fixed configurations of the nuclei, and of course, you can keep changing them and then put that potential energy.

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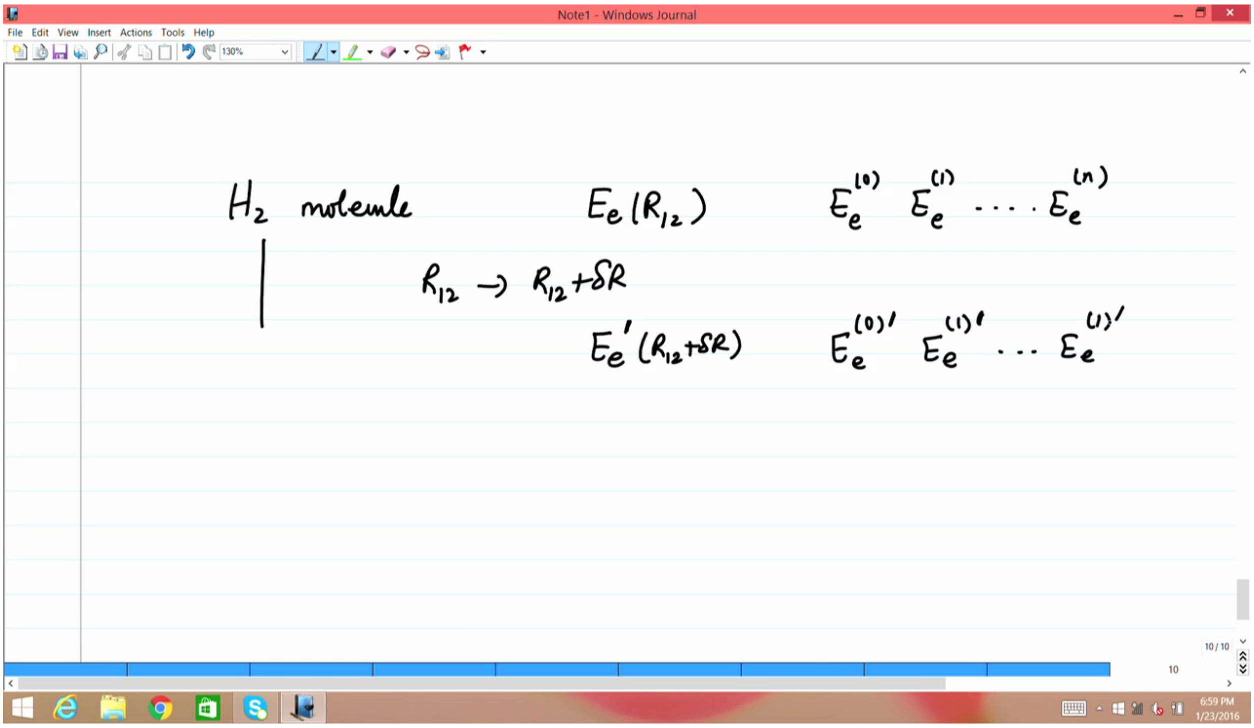

H_2 molecule $E_e(R_{12})$ $E_e^{(0)}$ $E_e^{(1)}$ .... $E_e^{(n)}$

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

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

So, in a simple case like a hydrogen molecule what does this do? So, in a case of hydrogen molecule, we need to worry about all the 6 coordinates of the 2 nuclei, but let us just concern ourselves with inter nuclear distance between the 2 hydrogen atoms. Therefore, when solve for the e e, you get many energies for a given value of the inter nuclear separation, r 1 2, which is r 1 minus r 2 vector, for 1 value, you get many energies, you get e e ground state, then you get the e e the higher energies states, like the Schrödinger equation for the electron, you get many, many energies, and then of course, change r 1 2 to the next value, r 1 2 plus a delta r, solve this again you will get e e prime, r 1 2 plus delta r.

Again a whole set of energies, e 0, e e prime, some other value, e e 1 and. So, on therefore, for the hydrogen molecule, you actually get a whole series of energies, for each and every value of inter nuclear distance, and that is shown in this animation.

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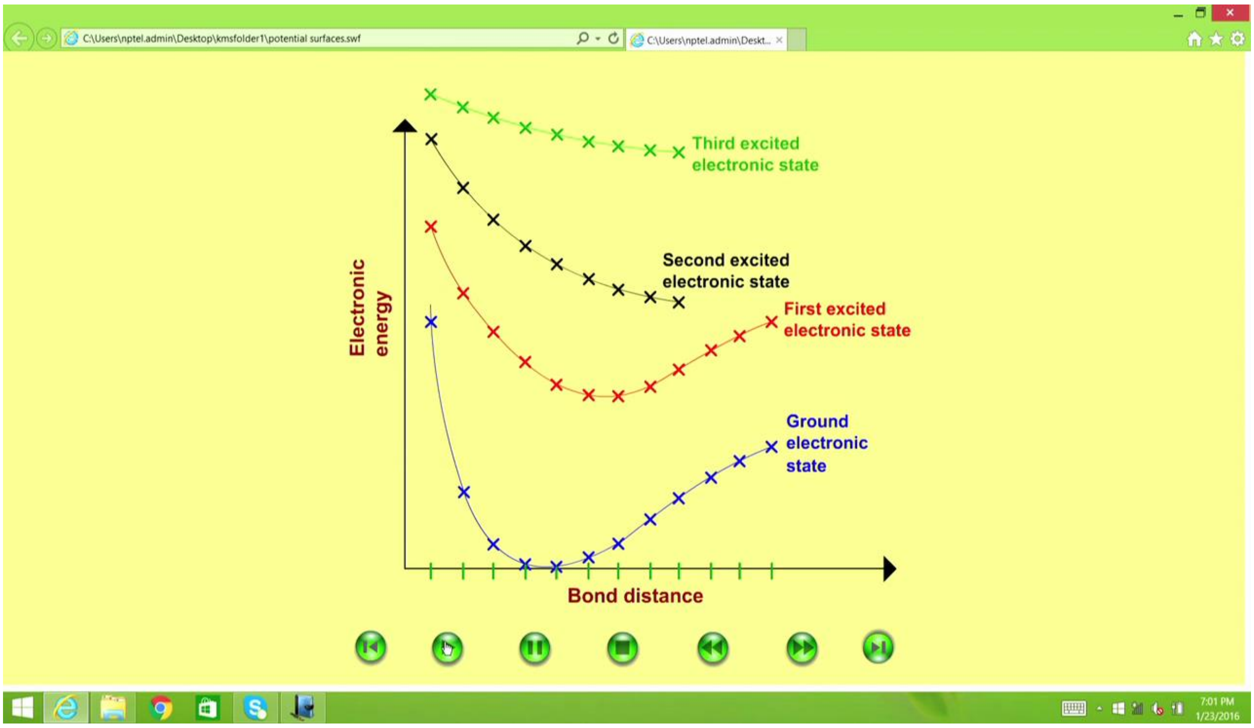

That’s shown in this animation. So, what I have here is inter nuclear distance, r 1 2 is along the x axis, and then the electronic energy solution that you get, multiple solutions that you get for solving the electronic equation. So, for that r 1 2, you get different values, like you get in the case of hydrogen atom, you get the n equal to 1, n equal to 2, n equal to 3, there are the quantum numbers well known, here some quantum numbers come out fine. Now the point is you get multiple energies, then you slightly change the r, you get another set energy igon values, 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 is.

I have colored them, to show that the lowest energy solution for each value of the nuclear configuration is all in blue, thats 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 we are normally drawn on 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, this is the a sense of Born Oppenheimer Approximation, and I would want you to go back and think about this same thing, using some other molecular system, instead of hydrogen molecule, if you have a slightly more 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 3 coordinates out of them, and 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 3 variables therefore, it is a surface, it is 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 the triatomic molecule, you need a 4 dimensional system to actually plot. People use colors as the fourth dimension to indicate such 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 a normal coordinates, and these normal coordinates determine the electronic energy surface.

The electronic energy surface is 3n minus 5 dimensional, because 3n minus 6 coordinates, and the dimension for plotting that. So, it is impossible to plot potential energy surfaces, in for any real molecule, in a in a visual form, and what do you do is to use, what are called constant energy surfaces, or constant coordinate surfaces, you do them, this the contour maps are used and there is a lot of information which has been generated in last 70 years, on 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 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 minutes, 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 lower level to give you ones called a microwave spectroscopy, and then what is known as the infrared spectroscopy, and then the coupling between this microwave and infrared spectroscopy, as 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 (Refer Time: 44:37), but the procedure is approximate.

Thank you.