

Engineering Chemistry - 1
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Module 1: Atoms and Molecules
Lecture - 10
Model Problems in Quantum Chemistry
Born-Oppenheimer Approximation and Superposition

Welcome to the lectures on the National Programme on Technology Enhanced Learning sponsored by the Ministry of Human Resource Development. The lecture series I have been giving is on Chemistry, the first year introductory Chemistry to science and engineering students. The lectures have so far has been on the Quantum Chemistry or what I would call as the atomic description of matter as is relevant for the chemist. In the last few lectures we have been looking at hydrogen atom and we arrived at the description of the hydrogen atom orbitals.

The purpose of doing all these quantum chemical calculations like particle in [one dimensional](#) box, particle in a two dimensional box, the harmonic oscillator, the hydrogen atom etc is to understand the procedures by which we can actually study the chemistry of molecules.

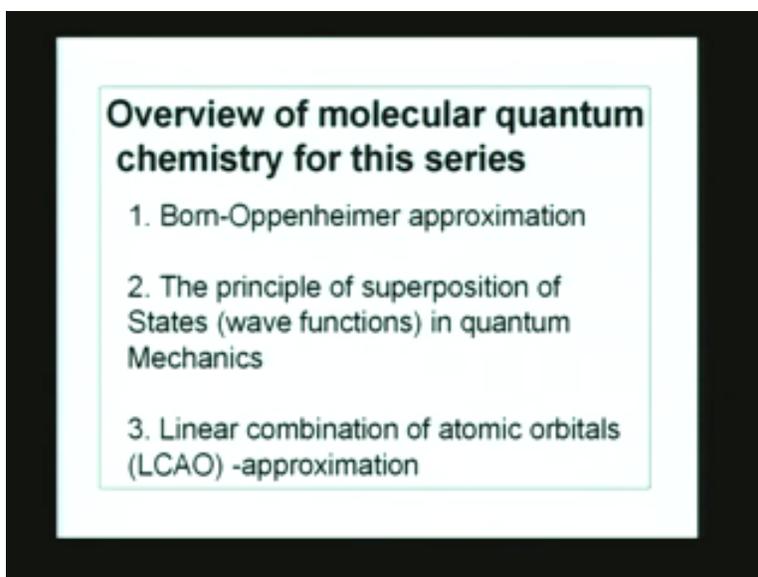
As a chemist what is of interest from the fundamental theory point of view is how we understand the transformation of molecules, how we understand the formation of molecules, and what is meant by chemical bonding? There are classical or what you call as qualitative pictures given as early as almost 100 years ago by G N Lewis and then many of his scientific colleagues. But how do we understand them rigorously from the developments of quantum mechanics which was important development in the last century? If we are able to understand from atomistic point of view then we will be in a position to predict when molecules form, what kind of stability that we can attach to them, what kind of reaction dynamics that we can expect from them and these are not stories any more mean the computational techniques and the Quantum Chemistry have developed so much that today computers are used on a routine basis to do the things that you would not want to do in the laboratory all the time, to do the kind of experiments that are not possible in the laboratory and to study the structure of matter from the chemical transformation point of view. All of this is possible if you understand a bit about the molecular structure for which the Quantum Chemistry basis is an extremely important one.

The lectures so far have given you the background of the quantum mechanical tools that one has to have and the most important tool namely the orbitals of the hydrogen atom.

The orbitals of the hydrogen atom are fundamental in [one's](#) ability to visualize molecular orbitals, be it organic chemistry or inorganic chemistry or physical chemistry no matter what discipline of chemistry you go. The orbital description is extremely important to understand the reaction mechanisms as well as the properties of molecules. Therefore we spent several lectures about 4 or 5 lectures on hydrogen atom trying to understand them not necessarily fully mathematical but from how to understand the mathematical description, we may not able to derive them.

In the same spirit in the next few lectures we will look at how the molecules form, what kind of stability that we are attaching to the molecules and how do we understand from the chemistry point of view. This series of lectures is from the National Programme on Technology Enhanced Learning a project funded by the Ministry of Human Resource Development. And my name is Mangala Sunder, I **have been** giving you the last 10 or 9 lectures on the Chemistry the preliminary Chemistry that all of us engineers or scientists must have.

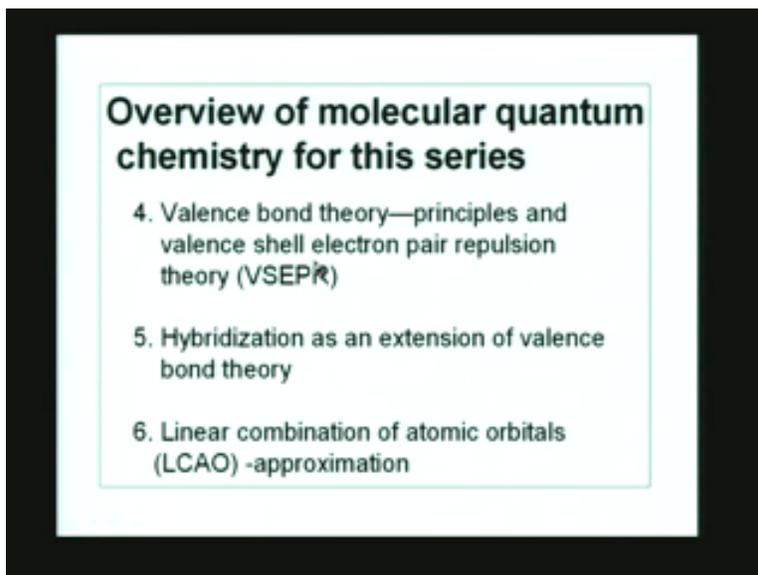
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The overview of this and the next few lectures we will concentrate on what is called the Quantum Chemistry for the molecules. These are the following things we will look at. One of the most important methods by which we understand molecules is the method proposed by Max Born and Robert Oppenheimer almost immediately after **the** Schrödinger derived the famous equation the Schrödinger equation. The Born and Robert Oppenheimer approximation allows us to study molecules as against the approach proposed by Schrödinger and Heisenberg which was a study of atoms and the atomic spectrum. The approximation extends their approach to that of molecules such as the formation, the stability etc.

The second most important principle which is again a principle in quantum mechanics is that of the superposition of wave functions or states. This is a fundamental principle, in fact the principle of superposition of states forms the basis of introduction of quantum mechanics in the **celebrated** lecture series by Richard Feynman the most known American physicist in the last century. The same method when it is applied to chemistry in the study of atoms and molecules takes the name the **L**inear combination of atomic orbitals or the LCAO approximation **where** L for linear, C for combination, A **for** atomic and O **for** orbital **is** the LCAO approximation. This is the basis for the molecular orbital theory.

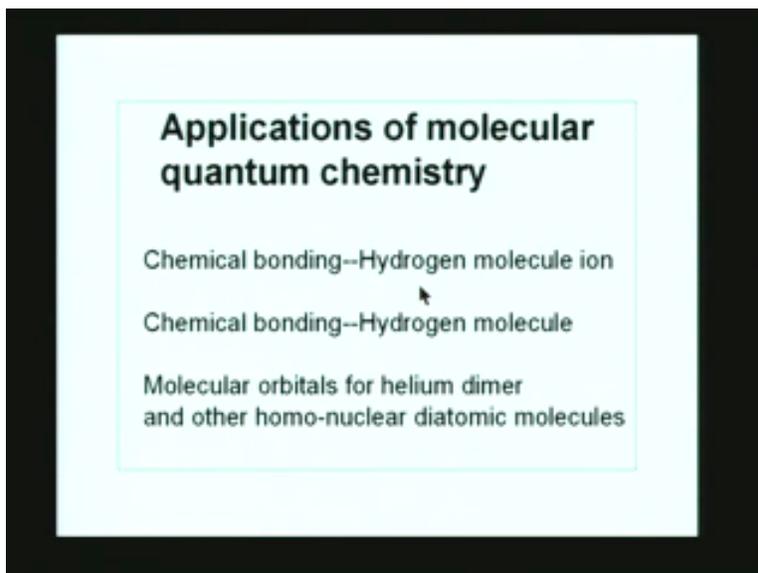
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There is a parallel development in understanding Chemistry through Valence bond theory and the Valence bond theory is of course a nice mathematical description of a more qualitative picture developed earlier known as the Valence Shell Electron Pair Repulsion theory VSEPR which many of you studied in your high school on the basis of the electron dots.

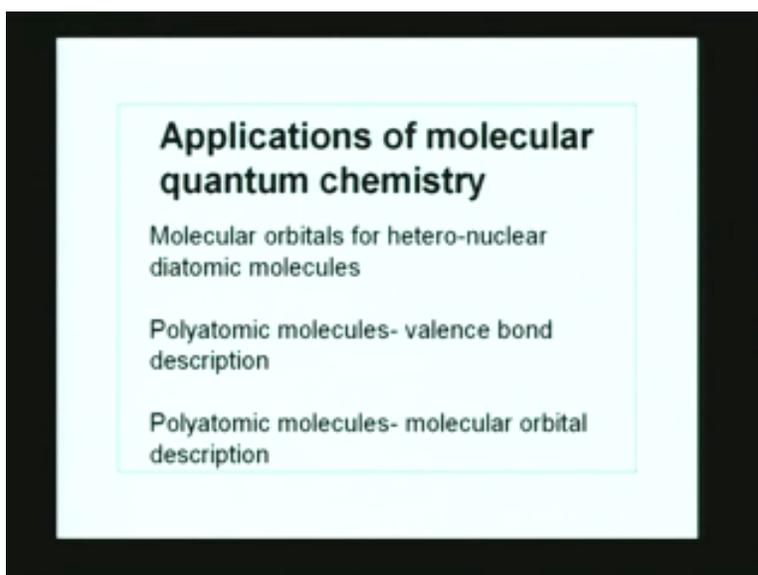
The Valence bond theory also leads as an extension of some of the ideas to the idea of hybridization or how the atomic orbitals or the molecular orbitals are oriented in space. And of course today been the most familiar method to the chemist is the Linear combination of atomic orbitals which is the basis of molecular orbital theory. These are all described in some detail and application of those methods the methods I just described to chemical bonding.

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We will study some of the simplest molecular species the hydrogen molecule ion it is two hydrogen atoms with one electron it is a H_2^+ ion probably the simplest molecule that one can form that is a molecule with **only** one electron. And you would be surprised that there is **a** sufficient amount of mathematical details which you will go into the understanding of molecule ion. This can also be extended to the study of one of the most well known molecular species also the simplest one the hydrogen molecule, H_2 . The concept of molecular orbitals has developed from these two will be applied further to the study of other homo-nuclear diatomic molecules that is diatomic molecules in which both the atoms are the same helium dimer, lithium dimer, beryllium **dimer** and so on to understand little bit about the progression of these ideas.

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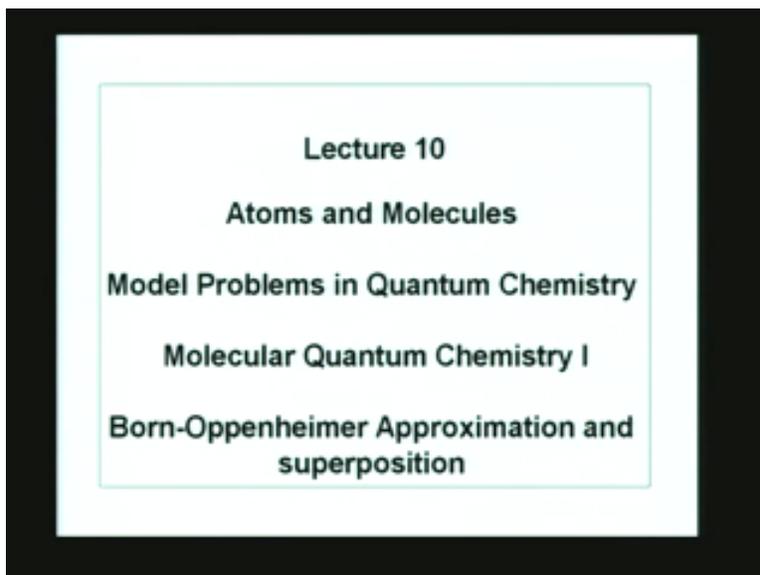


We will also study a little bit about the molecular orbital for the hetero-nuclear diatomic molecules, *i.e.* molecules in which the two atoms are different. For example carbon monoxide, hydrogen chloride things like that in which the atoms are not the same, hetero-nuclear. This cannot be carried out in detail to the study of polyatomic molecules without mathematical background. Therefore what we will try to do in the case of polyatomic molecules is to reiterate the Valence bond description that you are familiar with and look into how the Quantum Physics describes the corresponding principles here. The same thing will be done with the molecular orbital description.

Let us also look at the programme for calculating the molecular orbitals in Chemistry, the programme for the molecular structure in Chemistry. For the stability in Chemistry the programme is known as the Gaussian. John Purple was formerly Professor of Chemistry in Carnegie Mellon University and John Purple came up with the procedure for studying the chemistry of molecules through the computer and the method he proposed known as Gaussian was eventually recognized by the Nobel committee and he won the Nobel prize and he shared it with another physicist Walter Con a few years ago for his discovery of the computational methods in chemistry.

We will also introduce little bit of the Gaussian program. There are similar programs available in the literature. The study of molecular structure is a fairly serious business. A little about the introduction of computational chemistry and its applications will be described and description will be given on how we follow through the computational chemistry web portals the websites which contains more information about the computational Chemistry.

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Now let us get to the lecture on the Born-Oppenheimer approximation let me call that as molecular Quantum Chemistry 1 in the module on Quantum Chemistry. The Born-Oppenheimer Approximation and the principle of superposition is what we will look at today. First of all when we talk about approximations just recall from your elementary background what you mean by an

approximate solution to a mathematical problem. I will give you two simple examples so that you can recall that there are procedures for doing this systematically.

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What do we mean by an approximate solution?

Consider the series

$$f(x) = 1 + \frac{1}{x} + \frac{1}{x^2} + \frac{1}{x^3} + \dots \infty$$

Its closed form solution is

$$\frac{1}{1 - \frac{1}{x}}$$

x # 1

Let me start with a simple series a function of $f(x) = 1 + 1/x + 1/x^2 + 1/x^3 + \dots \infty$. This is an infinite series. if for certain values of x of course this infinite series converges to a finite value and for $x = 1$ for example there is a problem here, we will not worry about this but wherever this series exist the closed form solution for this series you understand from high school algebra is given by $1/(1 - 1/x)$ it is easy to see that it is a closed form analytic solution and obviously it is not valid for $x = 1$. But in this case we know the final solution but we will see what is meant by an approximate solution to the series.

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The value of $f(x)$ truncated to various terms for $x=2$ is given in the Table below. They are all approximate values.

$1 + \frac{1}{x}$	1.5
$1 + \frac{1}{x} + \frac{1}{x^2}$	1.75
$1 + \frac{1}{x} + \frac{1}{x^2} + \frac{1}{x^3}$	1.875
$1 + \frac{1}{x} + \frac{1}{x^2} + \frac{1}{x^3} + \frac{1}{x^4}$	1.9375

Exact value of $\frac{1}{1 - \frac{1}{x}}$ is 2 for $x=2$

If you truncate the series to several terms for a certain value of x an example, if you truncate the series by the first two terms you will get a value, truncate this to the third term you will get another value and so on and that is what is given in [the table](#).

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What do we mean by an approximate solution?

Consider the series

$$f(x) = 1 + \frac{1}{x} + \frac{1}{x^2} + \frac{1}{x^3} + \dots \infty$$

Its closed form solution is $\frac{1}{1 - \frac{1}{x}}$

x # 1

So, when you truncate it to the 1st term $1 + 1/x$ the value here for $x = 2$ is 1.5, the next term 1.75 and after 1.875, 1.9375 it keeps on closing towards or convergent towards the exact value when you put $x = 2$ in this expression you know $1 / (1 - 1/x) = 2$ so the exact value is 2 but the approximate method of truncating this series if you did not know this formula converges slowly towards the value $x = 2$. This is what you mean by approximation in this case.

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This is a relatively easy exercise.

Another slightly more complicated example is:

The value of the following integral:

$$\int_0^a e^{-cx^2} dx, \quad a < \infty$$

There is no analytic solution. We only know that it is less than $\frac{1}{2}\sqrt{\frac{\pi}{c}}$

Another example, the previous one is a relatively easy exercise but slightly more complicated example. Let us calculate the value of the $\int \exp(-c x^2) dx$ where c is a constant and the integral is calculated between $x = 0$ and $x = a$, finite value. It is not possible to derive a closed form analytic solution for this integral when 'a' is finite. In fact this is known as the error function integral in mathematics. But if x is infinity you will be surprised that there is an analytic solution to that when x is infinity the analytic solution is $\frac{1}{2}\sqrt{\pi/c}$ whatever is the constant here. Now let us try and find out how closely this integral approximates as 'a' increases to very large values and eventually to infinity.

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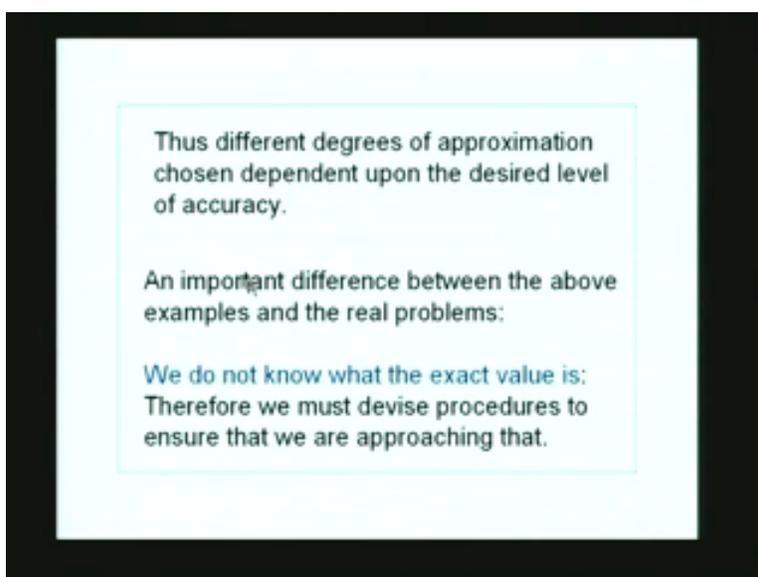
The value of the integral is obtained through approximate numerical procedures.

The table below gives approximate values to various levels of accuracy.

Function	a=	value
$\int_0^a e^{-cx^2} dx$	2	0.882081
	3	0.886207
	10	0.886227
	∞	$\sqrt{\pi}/2 = 0.886227$

Here is the table which gives you the numerical value for the same integral with $c = 1$, $\exp(-x^2)$ dx . So when the upper limit $a = 2$ the value of this integral from numerical procedures is 0.882081, when $a = 3$ closer to the infinity. Now between 2 and 3 it is not much but you will be surprised that as far as this function is concerned when $a = 3$ it is almost close to the exact value 0.886207. Now you put $a = 10$ it looks like the integral does not change by much you see it is 0.886227 the change after fourth decimal point. So the approximate value for this integral numerically that can be obtained for $a = 10$ is to this level of truncation in decimal points is same as when $a = \infty$ for which we know the analytic solution is $\sqrt{\pi}/2$ is 0.886227. So, what we mean by approximation is that we try to truncate or we try to take certain simple limits to evaluate the function as accurately as we can.

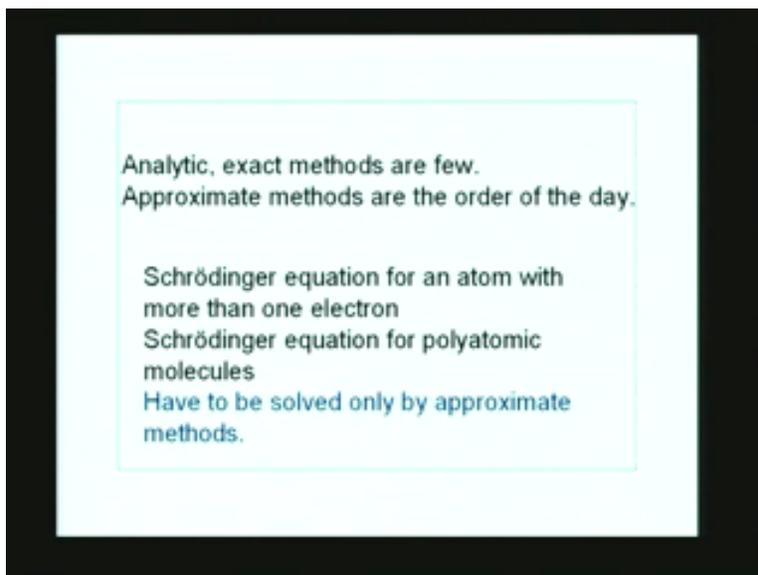
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So different degrees of approximations are chosen and that depends upon the desired level of accuracy. The one nice thing about this particular example is that in both cases we know the exact value and therefore we see how quickly our approximate values reach the exact value.

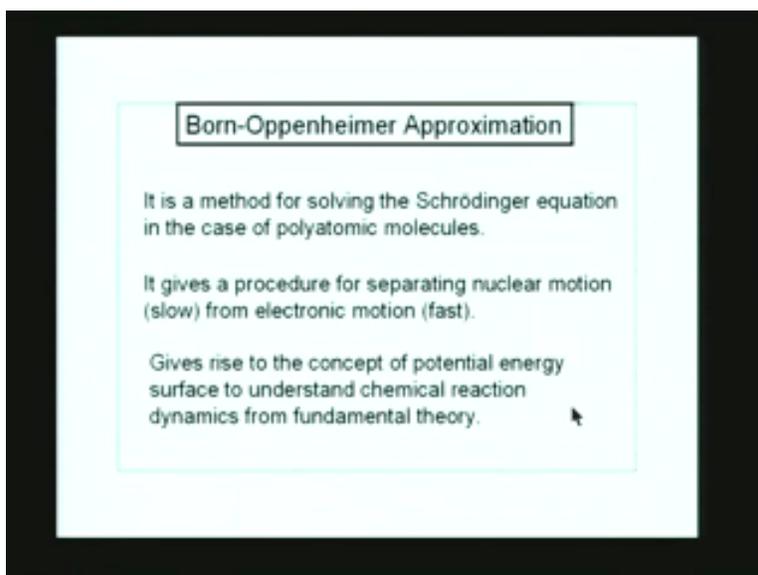
In real life, in quantum mechanical problems, in Quantum Chemistry problems we do not what the exact value is because we just cannot calculate them analytically. The hydrogen atoms, atomic orbitals could be calculated analytically with all those functions I described and hydrogen atom is probably the last in quantum mechanics for which the exact solution could be given. For all the others we do not know what the exact solution is or what the exact value for the functions is at various points. Therefore we have to have procedures which ensure that we are approaching the exact value somehow mathematically correct procedures. Analytic exact methods are very few.

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Approximate methods for solving Quantum Chemistry problems are the order of the day. That is those are the only ways by which we know how to study the system. The example of the Schrödinger equation for an atom with more than one electron it is not possible to solve by analytic means but one has to solve this by approximate methods. Perhaps the approximation is very good but it is not analytic. There is no chance that one can study the Schrödinger equation for polyatomic molecules by analytical methods. One has to devise procedures by which the algebra could be carried up to a certain point and beyond which one has to study the algebra through its implementation in a computer using a numerical program and so on. So they have to be solved by approximate methods.

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And the most important approximation in all of Quantum Chemistry I would even say in understanding the molecular structure came by Robert Oppenheimer and Max Born. Max Born you already were introduced to who gave the interpretation for the wave functions in terms of the probabilities, the absolute square of the wave functions being related to the probabilities.

Robert Oppenheimer an American Physicist was associated with Max Born in the early days of quantum mechanics development and both of them devised a procedure by which the Schrödinger equation could be approximately solved for the molecular problems. If you do not know Robert Oppenheimer also was the leader of the Manhattan project in the United States during the Second World War which eventually led to the development of the atomic bomb and which brought an end to the Second World War. Robert Oppenheimer was the head of the team which consisted of physicist, chemist and many engineers and he was very well known for his contribution for bringing the Second World War to an end. Of course the atom bomb came out of that as a result.

The Born-Oppenheimer is a method for solving the Schrödinger equation in the case of polyatomic molecules. Here are the mathematical procedures. The procedure gives a method for separating nuclear motion from the electronic motion. We never discussed this in the case of hydrogen atom. In the case of hydrogen atom we looked at the motion of the electron we never considered the motion of the proton, the nuclear motion.

It was implicit that the origin was fixed at the proton and the proton did not move. It was an approximation we already used even though it is not necessary to use that approximation. The proton electron problem in the case of hydrogen atom is a two body problem. In Physics two body problems can be separated into a center of mass and a relative coordinate problem and it is possible to solve the hydrogen atom problem exactly by taking into account the hydrogen nuclear motion. He did not do that but if he had did that all our masses we used to calculate for the electronic motion should be replaced by the reduced mass of the electron proton system and the only thing that was needed.

Now, in the case of molecules it is important to recognize that there are many nuclei, there are many electrons and the nuclei move with a certain amount of kinetic energy and the electron also moves with a certain amount of kinetic energy and the nuclear electron system involves too many terms such as the nuclear kinetic energies, The electron kinetic energies, the nuclear electron interaction energies, [electron](#) interaction energies and many of them. Therefore in the mess how do we separate the Schrödinger equation to a problem that is solvable was first proposed by Born and Oppenheimer and it is a procedure for separating nuclear motion from the electronic motion.

The nuclear motion is assumed to be slow and the electronic motion is fast and as a result of their method we also get the new concept the concept of potential energy surfaces for molecular motion and this is fundamental to the understanding of chemical reaction dynamics from Quantum Chemistry. So there are certain advantages to using the Born-Oppenheimer procedure and thereby can develop the potential energy surfaces for molecules.

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$m_e = 9.10939 \times 10^{-31} \text{ kg}$ (electron)

$m_p = 1.67262 \times 10^{-27} \text{ kg}$ (proton)

$\frac{m_p}{m_e} = 1836 !$

In classical mechanics limit, particle's kinetic energy (thermal) is approximately $\frac{3}{2} k_B T$

Now, why is this possible? Please recall that the mass of the electron is of the order of about 2000 times less. The mass of the electron is 9.10939 times 10^{-31} kg. The mass of the proton in a typical nucleus is 1.67262×10^{-27} kg. The mass of the proton you know in any nucleus containing x number of protons you simply multiply this, the mass of the neutron is pretty close to that but what is important is the proton to the electron mass ratio is about to 1836. Now, if you assume that the molecules have approximately the kinetic energy of $3/2 k_B T$ and this energy were to be equally distributed between the nuclei and the electrons so one can make a simple estimation namely that the kinetic energy of the individual species is $1/2 mV^2$, and for the electron also it is $1/2 mV^2$.

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Momentum for the heavier nucleus $\frac{m_N V_N^2}{2} = E_{kin}$

Momentum for the lighter electron $\frac{m_e V_e^2}{2} = E_{kin}$

Electrons move generally much faster than the nuclei

If we look at that you see that the masses of the proton and the masses of the electron are such that for the same kinetic energy for both you see the nucleus moves much more slowly than the electron because of the very large mass. This is the first important issue in deciding how we set up the molecular wave function. The electrons move generally much faster than the nuclei and therefore it is possible to separate the electronic motion from that of the nuclear motion. First let me introduce Max Born through the pictures here.

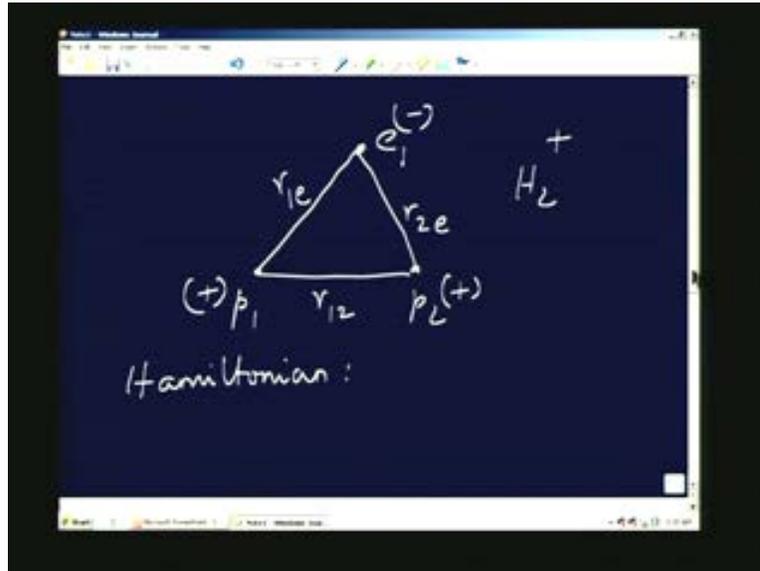
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And Robert Oppenheimer the proposal was given in 1927 through one of their most celebrated papers in Quantum Chemistry. The approximation is as follows. Here is a simple case of two nuclei and one electron a fictitious case but we will see what is meant by the approximation. So this is proton one p_1 and proton two p_2 and this is electron e_1 .

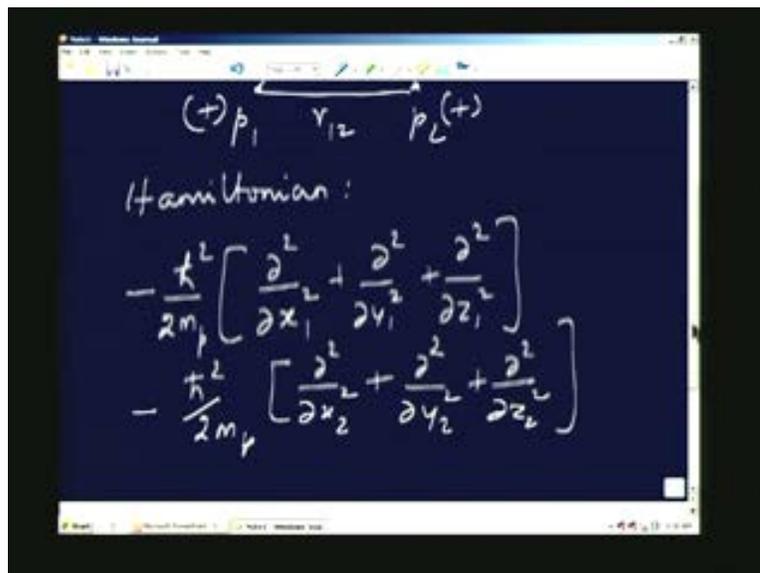
Now, if you look at the Hamiltonian for this system the Hamiltonian contains kinetic energy of the two nuclei proton p_1 and proton p_2 like two hydrogen atoms with one electron so it is like H_2^+ you want to think about it to give a physical representation to the model like the hydrogen molecule ion. So you have got two protons and the electrons and if you mark the distance between them are r_{1e} and r_{2e} and let us call the distance between p_1 and p_2 is r_{12} so that you have the appropriate distances and these are all charges these protons are positively charged this electron is negatively charged. Therefore the potential energy of this system is the columbic attraction as well as the repulsion terms and the kinetic energy is the kinetic energy of the individual species this proton and this electron.

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So if you write down the Hamiltonian for this system it is you recall from the hydrogen atom that we were writing as $-\hbar^2/2m_p[\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2]$ let us call it p_1 this 1 corresponds to the proton 1 and all of this is the kinetic energy term in the quantum mechanical form for proton 1. And likewise for the second proton also you have got the kinetic energy $-\hbar^2/2m_p[\partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2]$. These are the two kinetic energies of the two protons.

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It is not enough it is not complete then we have got the electron kinetic energy that you are familiar with this from the hydrogen atom. And let me write this as $-\hbar^2/2m_e[\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2]$ where subscript e is to indicate that this is the electron energy term. Basically here this

$-\hbar^2/2m_e \partial^2/\partial x_e^2$ is the momentum along the x coordinate of the electron momentum square $p^2/2m$. You recall the quantum that. So we have got for this three particle system you have got 9 coordinates x_1, y_1, z_1 for particle one proton p_1 and x_2, y_2, z_2 for proton p_2 and the x_e, y_e, z_e for the electron. All of this is only kinetic energy but what about the potential energy?

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$$-\frac{\hbar^2}{2m_p} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right]$$

$$-\frac{\hbar^2}{2m_p} \left[\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right]$$

$$-\frac{\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right]$$

Potential energy is obviously $-e^2/4\pi\epsilon_0$. Remember that the model we have is proton p_1 , proton p_2 and the distances are r_{12}, r_{1e}, r_{2e} . So what you have is for the proton-electron attraction here you have got $-e^2/4\pi\epsilon_0 r_{1e}$ and this proton-electron attraction you have got the other term $-e^2/4\pi\epsilon_0 r_{2e}$ and the proton-proton repulsion as $+e^2/4\pi\epsilon_0 r_{12}$. So you have got how many terms? You have 9 terms in a kinetic energy 3 dimensional coordinate system and 3 terms all of which involved. This r_{1e} involves the square root of the difference between these two x coordinates, y coordinates, z coordinates etc so it is a fairly complicated expression and therefore solving this if you call all of these things as the H as the sum of the potential energy plus the kinetic energy.

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$$-\frac{e^2}{4\pi\epsilon_0 r_{1e}} - \frac{e^2}{4\pi\epsilon_0 r_{2e}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$
$$H = P.E + K.E$$

The solution you have to worry about is $H\psi = E\psi$, what is ψ a function of massive, it is a function of x_1, y_1, z_1 the coordinates of the proton one, x_2, y_2, z_2 the coordinates of the proton two and x_e, y_e, z_e the coordinates of the electron. So ψ is the function of these nine coordinates and Hamiltonian contains derivatives of all these nine coordinates with respect to these as well as the interaction energy. Therefore you see that the problem is intractable meaning cannot be solved analytically.

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$$4\pi\epsilon_0 r_{12}$$
$$H = P.E + K.E$$
$$H\psi = E\psi$$
$$\psi[x_1, y_1, z_1, x_2, y_2, z_2, x_e, y_e, z_e]$$

Intractable - cannot be solved analytically

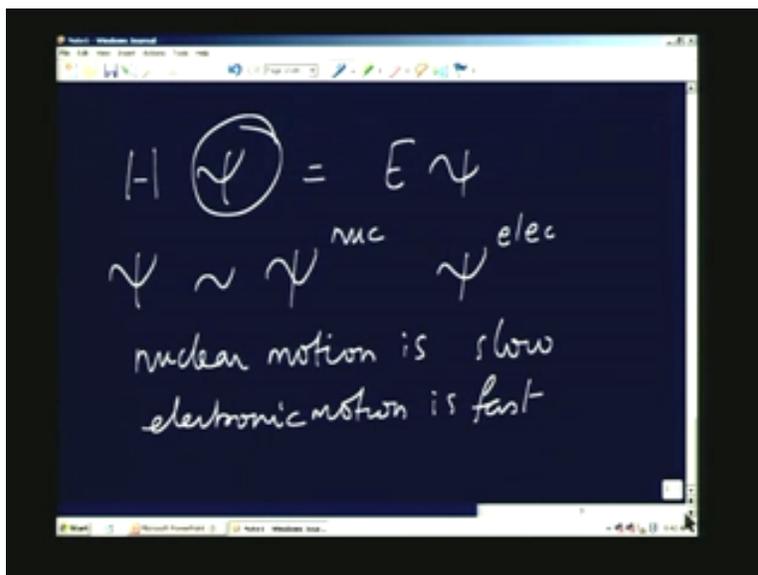
This is for hydrogen molecule ion. What is the case of hydrogen molecule? Typically for a hydrogen molecule if you want to solve the quantum problem you have got two protons and two

electrons namely proton p_1 , proton p_2 , electron e_1 , electron e_2 and if you compute the number of terms for this proton p_1 there is a kinetic energy term has three coordinates and other three also have of them each so there are twelve coordinates which are part of this and the interaction energies are now the repulsion energies between the two protons, the repulsion energies between the two electrons, the attraction between this proton p_1 and this electron e_1 , and between this proton p_1 and this electron e_2 , and between this proton p_2 and this electron e_1 , and between this proton p_2 and this electron e_2 . It is interplay of all these interactions which one has to understand as determining the stability or the formation of the hydrogen molecule.

Therefore the problem becomes more and more computationally difficult and therefore some approximate methods are needed right away the moment you write the solutions for the hydrogen atom you know that it cannot be taken over directly to that of the hydrogen molecule or even the hydrogen molecule ion in the simplest case. So the first approximation that Born and Oppenheimer made was the following with respect to the solution $H\psi = E\psi$ one has to separate the ψ in terms of a ψ_{nuc} and ψ_{elec} .

You recall that we are very fond of separating the wave functions in terms of various coordinates involved. Hydrogen atom you have separated the (x, y, z) problem by writing in the spherical polar coordinates and the last four lectures were summarizing that radial coordinate and angular coordinate and so on. So the separability of wave function is important in solving the differential equation as simply as possible. Therefore the separability of wave function here one starts with the ψ as ψ_{nuc} and ψ_{elec} but with the following in mind namely nuclear motion is slow and the electronic motion is fast.

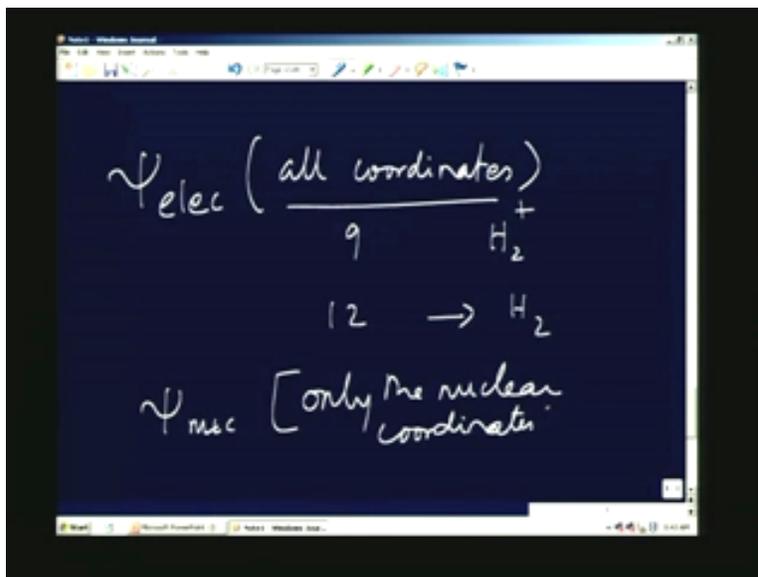
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Therefore what one assumes is that the ψ -electronic wave function is a function of all the nine coordinates in the case of H_2^+ and all the 12 coordinates for H_2 . And if you think about C_{60} fullerene you want to understand the stability from solving the Schrödinger equation you have got 60 carbon atoms and 360 electrons. So you have got 420 species \times 3 coordinates. One should

be mad but people have solved such problems anyway. So the ψ_{elec} the electronic wave function is a function of all these coordinates but the nuclear wave function is a function of only the nuclear coordinate.

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What is the basis for this? The basis for this is the fact that the proton to the electron mass ratio is so large that the proton or the nuclei which in this case of number of proton plus number of neutrons multiplying approximately by this number and you see that the separation tells you the following. Physically one has to visualize this way. As the nuclei move as they undergo vibrations they undergo rotation. The molecule in any finite temperature has many possible motion translational motion, rotational motion and relatively to each other they undergo vibrations. As the nuclei moves the electron motion associated with the nuclei is much faster than that of the nuclei that the electrons instantly readjust themselves to their new nuclear positions.

The electronic wave function does depend on where the nuclei are? Whether they are **too** far away or they are **too** close because if they are this far away there may be no interaction there may be no molecule there may be local atoms. (Refer Slide Time: 35:15 min) But when they come together the molecule is formed there is some stability attached therefore the electron wave function does depend on the nuclear positions the nuclear coordinates. On the other hand the nuclei do not necessarily feel the electron because the electrons instantly readjust themselves therefore the nuclear wave functions is not dependent on the electronic coordinate as assumption one.

Therefore, if we denote all the nuclear coordinates as R_1 let me write down the coordinates in our case the hydrogen molecule ion, the ψ_{nuc} is a function only of the nuclear coordinates namely x_1, y_1, z_1 and x_2, y_2, z_2 and it is independent of the electronic coordinates the molecule ion the third particle. Whereas the ψ_{elec} is a function of all of these x_1, y_1, z_1 and x_2, y_2, z_2 and x_e, y_e, z_e so the overall ψ is a function of ψ_{nuc} times ψ_{elec} which is step one.

(Refer Slide Time: 36:45 min)

The image shows a chalkboard with the following handwritten equations:

$$\Psi_{\text{nuc}}(x_1, y_1, z_1, x_2, y_2, z_2)$$
$$\Psi_{\text{elec}}(x_1, y_1, z_1, x_2, y_2, z_2, x_e, y_e, z_e)$$

$$\Psi = \Psi_{\text{nuc}} \Psi_{\text{elec}} \quad \text{①}$$

What is the next step? When you apply this to the Hamiltonian, this is a proposal **and** the proposal is Ψ is $\Psi_{\text{nuc}} \Psi_{\text{elec}}$. Now with this proposal we solve the Schrödinger equation $H \Psi = E \Psi$ which means $H \Psi_{\text{nuc}} \Psi_{\text{elec}}$ is $E \Psi_{\text{nuc}} \Psi_{\text{elec}}$ where E a constant independent of all these coordinates.

(Refer Slide Time: 37:24 min)

The image shows a chalkboard with the following handwritten equations:

Proposal: $\Psi \approx \Psi_{\text{elec}} \Psi_{\text{nuc}}$

$$H \Psi = E \Psi$$
$$\text{① } H \Psi_{\text{elec}} \Psi_{\text{nuc}} = E \Psi_{\text{elec}} \Psi_{\text{nuc}}$$

Now, if you look at the form of H it has $-\hbar^2/2m_p [(\text{del})_1^2 + (\text{del})_2^2]$ let me write the overall derivative for the nucleus one as $(\text{del})_1^2$. The $(\text{del})_1^2$ is $[\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2]$ this is the nuclear motion for the first nucleus and $(\text{del})_2^2$ is the corresponding one. You can simply replace **subscript 1 by 2** so you will get $(\text{del})_2^2 = [\partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2]$ here you see that the two Laplacians as they are called corresponding to the kinetic of the two nuclei and **then** $-\hbar^2/2m_e$

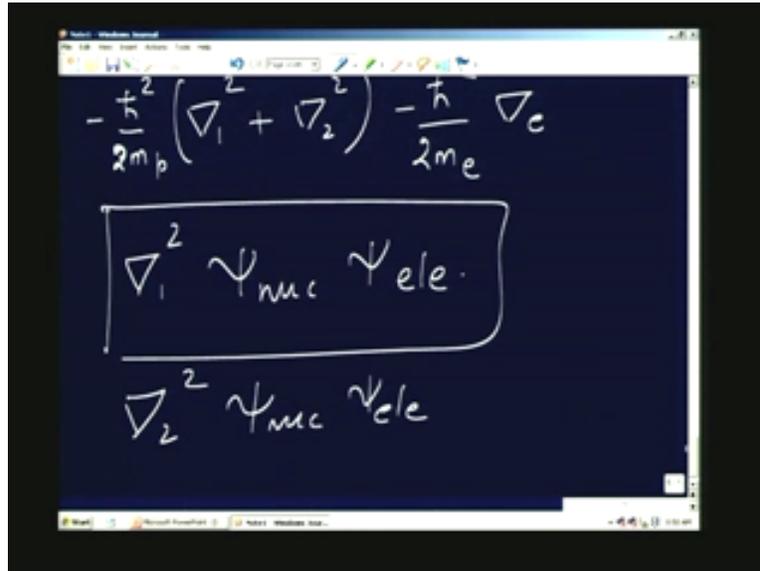
$(\text{del})_e^2$ which is the corresponding kinetic energy term for the electronic motion what is $(\text{del})_e^2$ you can easily write to this $(\text{del})_e^2$ as $[\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2]$.

(Refer Slide Time: 38:55 min)

$$\begin{aligned}
 & \textcircled{H} \Psi_{\text{elec}} \Psi_{\text{nuc}} = E \Psi_{\text{elec}} \Psi_{\text{nuc}} \\
 & -\frac{\hbar^2}{2m_p} (\nabla_1^2 + \nabla_2^2) - \frac{\hbar^2}{2m_e} \nabla_e^2 \\
 & \nabla_e^2 = \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}
 \end{aligned}$$

And if I use this notation it is sort of clear you see that this is a derivative containing only the nuclear coordinate 1, this is the derivative containing only the nuclear coordinates 2 and this is a derivative set containing only the electronic coordinates that is extremely important in the next approximation that they used. Now, if you apply $(\text{del})_1^2 \Psi_{\text{nuc}} \Psi_{\text{elec}}$ you have to solve this equation because after all $H\Psi = E\Psi$ is what we want to solve. Therefore when you operate $H\Psi$ you are going to get one term like this, you are going to get another term corresponding to $(\text{del})_2^2 \Psi_{\text{nuc}} \Psi_{\text{elec}}$.

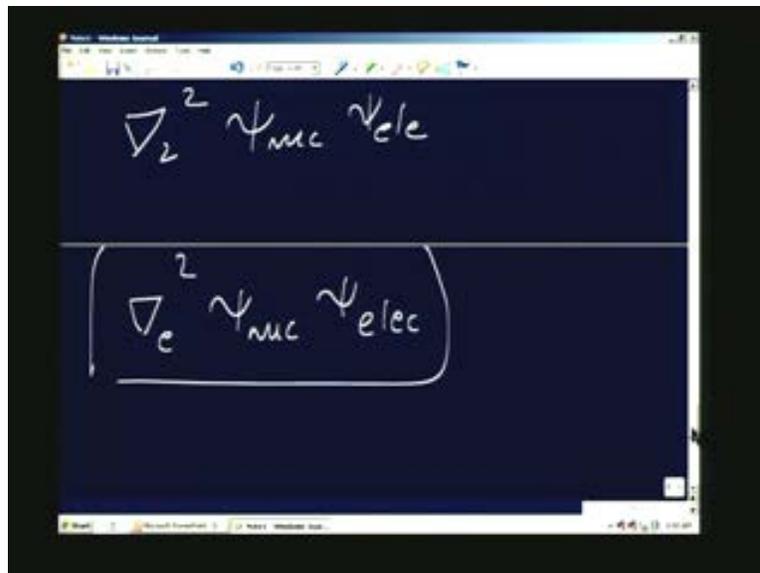
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The image shows a digital chalkboard with handwritten mathematical expressions. At the top, there are two terms: $-\frac{\hbar^2}{2m_p} (\nabla_1^2 + \nabla_2^2)$ and $-\frac{\hbar^2}{2m_e} \nabla_e^2$. Below these, there are two boxed expressions: $\nabla_1^2 \psi_{nuc} \psi_{ele}$ and $\nabla_2^2 \psi_{nuc} \psi_{ele}$.

And also the third term involving the derivative you get $(\text{del})_e^2$ corresponding to $\psi_{nuc} \psi_{elec}$. Now these are individual terms as you have them here.

(Refer Slide Time: 40:40 min)



The image shows a digital chalkboard with handwritten mathematical expressions. At the top, there is the expression $\nabla_2^2 \psi_{nuc} \psi_{ele}$. Below it, there is a boxed expression $\nabla_e^2 \psi_{nuc} \psi_{elec}$.

Now, if you go back and look at the approximation about the wave function namely ψ_{nuc} depends only on the nuclear coordinate, ψ_{elec} depends on all of them electronic and the nuclear coordinates. Let us see what the derivatives do without evaluating the derivatives? $(\text{del})_e^2$ on ψ_{nuc} will contain, now you have to remember the uv formula you recall $\partial^2/\partial x^2$ on a function $u(x) v(x)$, a product of two functions what is the derivative? Let us not even do $\partial^2/\partial x^2$ but let us just do

$\partial/\partial x$. What is $\partial/\partial x$ on $u(x) v(x)$? It is going to be $[u \partial v/\partial x + v \partial u/\partial x]$. Two terms are there from elementary calculus you know this for partial derivatives.

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$$\nabla_c^2 [\Psi_{nuc} \Psi_{elec}]$$

$$\frac{\partial}{\partial x} [U(x)V(x)] = U \frac{\partial V}{\partial x} + V \frac{\partial U}{\partial x}$$

And if you have to do this for $\partial^2/\partial x^2$ on uv you are going to get $u \partial^2 v/\partial x^2 + 2 \partial u/\partial x \partial v/\partial x + v \partial^2 u/\partial x^2$. So you are going to get the terms which are the derivatives of both these functions. Here you have got $\Psi_{nuc} \Psi_{elec}$ and this $(\text{del})_e^2$ is the electronic derivative and Ψ_{nuc} does not contain any electronic coordinates. Therefore this derivative does not act on this but it only acts on Ψ_{elec} .

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$$\nabla_c^2 [\Psi_{nuc} \Psi_{elec}]$$

$$\frac{\partial}{\partial x} [U(x)V(x)] = U \frac{\partial V}{\partial x} + V \frac{\partial U}{\partial x}$$

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

So this is extremely simple that $(\text{del})_e^2 [\Psi_{nuc} \Psi_{elec}]$ is $\Psi_{nuc} [(\text{del})_e^2 \Psi_{elec}]$.

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

$$\nabla_e^2 [\Psi_{nuc} \Psi_{elec}] = \Psi_{nuc} \nabla_e^2 \Psi_{elec}$$

So this is simple enough but the next term is the order one, $(\text{del})_1^2 [\Psi_{nuc} \Psi_{elec}]$. You are going to get these derivatives, now this is a function of the nuclear coordinates as well, this is a function of nuclear coordinates only therefore what Max Born and Robert Oppenheimer chose to write was basically this as $\Psi_{elec} [(\text{del})_1^2 \Psi_{nuc}]$. What are the terms which are being dropped off when you write like this?

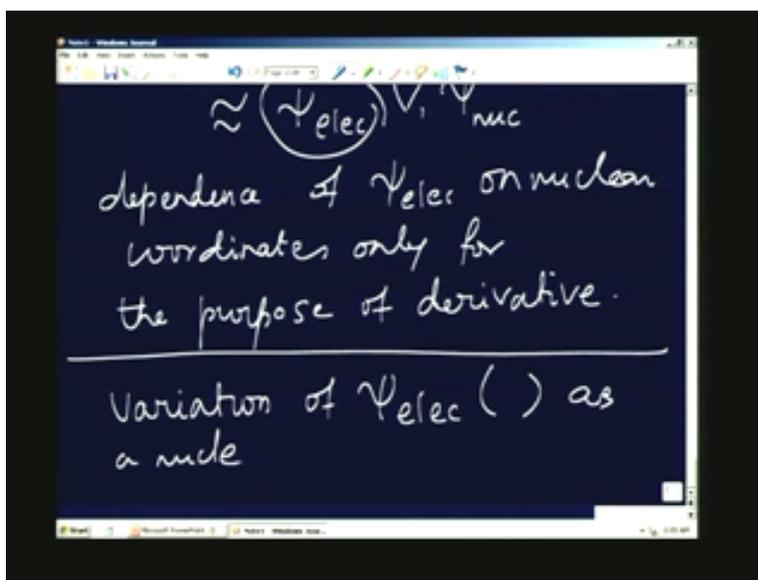
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$$\nabla_1^2 \Psi_{nuc} \Psi_{elec} \approx \Psi_{elec} \nabla_1^2 \Psi_{nuc}$$

Go back and look at the product rule. If there is a derivative of x with respect to two function of here with respect to x when you take the derivative of a product you see that there are $u \frac{\partial^2 v}{\partial x^2} + 2 \frac{\partial u}{\partial x} \frac{\partial v}{\partial x} + v \frac{\partial^2 u}{\partial x^2}$ square and so on.

Now, what you have assumed is this to be independent of x for the purpose of taking the derivatives not as a function. When you say that v is independent of x obviously this derivative $\partial v/\partial x$ you are going to throw away and you are going to throw away this derivative $\partial^2 v/\partial x^2$ and therefore you approximately write this as $v \partial^2 u/\partial x^2$ (Refer Slide Time: 43:55 min). Please remember, when you write $(\text{del})_1^2 [\Psi_{\text{nuc}} \Psi_{\text{elec}}]$ as roughly $\Psi_{\text{elec}} [(\text{del})_1^2 \Psi_{\text{nuc}}]$ what are you doing? You are throwing away the dependence of Ψ_{elec} on nuclear coordinates only for the purpose of the derivative calculations. That is the variation to be very precise **and** the variation of Ψ_{elec} as a function of the nuclear coordinates.

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You are not throwing away or you are not making the approximation that Ψ_{elec} is independent of nuclear coordinates. You are only saying that the electronic wave function is a function of nuclear coordinates but its rate of change with respect to nuclear coordinates is negligible compared to the rate of change with respect to the electronic coordinates.

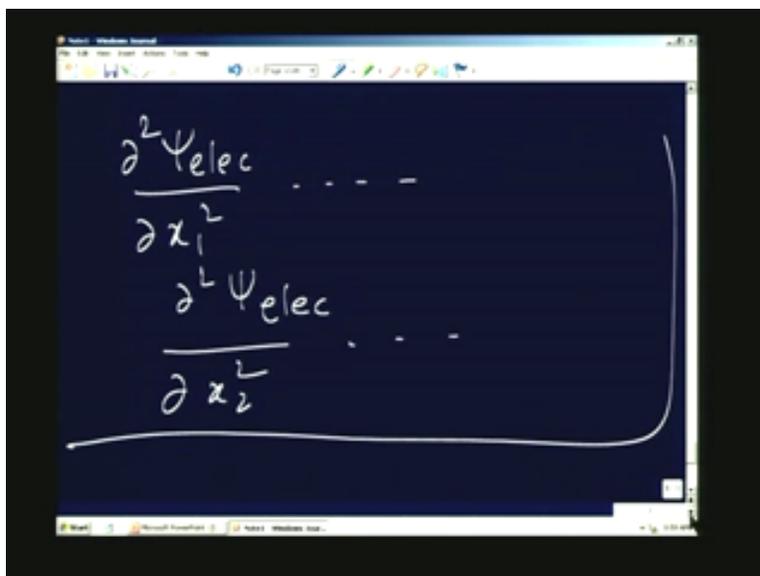
The rate of change of the electronic wave function with respect to the nuclear coordinates is negligible, the function itself is a function of nuclear coordinates but its rate of change with respect to the nuclear coordinates it is not 0 but it is negligible compared to all other rates of change. It is not only the rate of change but also the second derivative what is called the $\partial \Psi_{\text{elec}}$ with respect to $\partial \Psi_{\text{nuc}}$ coordinates and $\partial^2 \Psi_{\text{elec}}$ with respect to $\partial \Psi_{\text{nuc}}$ coordinates. You are throwing these terms away as approximately small compared to the other derivative terms compared to the other potential energy terms. This is the sum and substance of the Born-Oppenheimer approximation of the entire molecular chemistry program. (Refer Slide Time: 46:45 min)

The wave function Ψ_{elec} is a function of nuclear coordinates and electronic coordinates. You are not saying that it is not, it was the first step. But what is being thrown away is the $\partial \Psi_{\text{elec}}/\partial x_1$ and $\partial \Psi_{\text{elec}}/\partial y_1$ and $\partial \Psi_{\text{elec}}/\partial z_1$ all of these are nuclear coordinates of nucleus one and $\partial \Psi_{\text{elec}}/\partial x_2$ likewise the other two terms. You throw away these as unimportant not significant you do not make them as 0. If you make them as 0 automatically the interpretation is that the wave function

itself is independent of the coordinates which is not true. The electronic wave function does depend on the nuclear coordinates otherwise the molecular formulation cannot be explained and the electron density keeps changing as the two nuclei come together.

The electronic densities are described by their positions at whatever the space is. Therefore they are dependent on where the nuclei are, how close they are, how far away they are, how far apart they are, all these things are important. You are not neglecting the dependence of the electronic wave functions as a function of nuclear coordinates. What you are doing is you are neglecting the variation the derivative of the electronic wave function with respect to the nuclear coordinates the first derivatives and the second derivatives both of them. So $\partial^2 \psi_{elec} / \partial x_1^2$ all the two other terms and $\partial^2 \psi_{elec} / \partial x_2^2$ and the corresponding two terms and these are the terms you neglect.

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What is the outcome of this? Now let us write the algebra very quickly. Therefore H now contains an operator T_{nuc} for the nuclear kinetic energy containing the derivatives, an operator T_{elec} for the electron kinetic energy a sum of various terms and it also contains the electron nuclear attraction potential energy the V_{e-N} plus the V_{nuc} in this case. Since there is only one electron we do not worry about any further term. These are the only terms which are present. Now, when you write $H[\psi_{elec} \psi_{nuc}]$ as $E[\psi_{elec} \psi_{nuc}]$

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$$H = \hat{T}_{nuc} + \hat{T}_{elec} + \hat{V}_{e-N} + \hat{V}_{NN}$$

$$H(\psi_{elec} \psi_{nuc}) = E \psi_{elec} \psi_{nuc}$$

What do the kinetic energy terms do? You have $[\hat{T}_{nuc} + \hat{T}_{elec} + \hat{V}_{e-N} + \hat{V}_{NN}] \psi_{elec} \psi_{nuc} = E [\psi_{elec} \psi_{nuc}]$. Now \hat{T}_{nuc} on ψ_{elec} we have made this several times. The \hat{T}_{nuc} does not change ψ_{elec} but only changes the ψ_{nuc} . Therefore what you have is $\psi_{elec} [\hat{T}_{nuc} \psi_{nuc}]$. And the electron term of course the kinetic energy has only derivatives of this, this is independent of the electron coordinate therefore the second very easy namely the $\psi_{nuc} [\hat{T}_{elec} \psi_{elec}]$ kinetic energy term.

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$$(\hat{T}_N + \hat{T}_e + \hat{V}_{e-N} + \hat{V}_{NN}) \psi_{elec} \psi_{nuc}$$

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

$$\psi_{elec} [\hat{T}_{nuc} \psi_{nuc}] + \psi_{nuc} [\hat{T}_e \psi_{elec}]$$

We keep this in focus plus we have talked about the kinetic energy plus the two kinetic energies plus $\hat{V}_{e-N} \psi_{elec} \psi_{nuc}$ plus $\hat{V}_{NN} [\psi_{elec} \psi_{nuc}] = [\psi_{elec} \psi_{nuc}]$.

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$$\Psi_{elec} [T_{nuc} \Psi_{nuc}] + \Psi_{nuc} [T_e \Psi_{elec}]$$

$$+ V_{eN} \Psi_{elec} \Psi_{nuc} + V_{NN} \Psi_{elec} \Psi_{nuc} = E \Psi_{nuc} \Psi_{elec}$$

When you do this what happens is it separates the Hamiltonian equation that we have here the differential equation into two sets. One set corresponding to the electronic motion only and another set corresponding to the nuclear motion only and the electronic motion problem when it is solved for a given set of nuclear coordinates it is called the electronic energy solution or the Quantum Chemistry problem.

When you solve these set of equations for nuclear motion you are studying this as the dynamics of the nuclear motion and this is what constitutes the branch of spectroscopy.

Let me summarize this, so what you have is a $\Psi_{nuc} [T_{elec} \Psi_{elec} + V_{e-N} \Psi_{elec}]$ plus you have got a $\Psi_{elec} [T_{nuc} \Psi_{nuc} + V_{NN} \Psi_{nuc}]$. These are the terms when you rearrange them **then it is equal to the** $E [\Psi_{elec} \Psi_{nuc}]$. Now, if you look at this particular form here is the wave equation corresponding to the electronic kinetic energy operator the electron nuclear potential energy both of which depend on the electron coordinates there is a wave function which depends on the electron coordinates. The solution of this becomes the solution of the electron problem for a particular set of nuclear coordinates.

Now, if you vary this nuclear coordinates to some other values you will have another equation to solve. You solve this electronic problem for every set of possible nuclear coordinates. And once you have solved them the solution of this problem will be the energies for each set of nuclear coordinates.

Therefore this equation becomes Ψ_{nuc} times an energy which is a function of nuclear coordinates times Ψ_{elec} . This is the Schrödinger equation for the electron problem this particular $[T_{elec} \Psi_{elec} + V_{e-N} \Psi_{elec}]$ is the Schrödinger equation for the electron problem and it gives you for every value of the nuclear coordinates which determines this potential energy $E(nuc) \Psi_{elec}$ and this has to be added to this term the $\Psi_{elec} [T_{nuc} \Psi_{nuc} + V_{NN} \Psi_{nuc}]$.

When you add this particular term ψ_{nuc} to the remaining term in this it gives you the nuclear solution to the Born-Oppenheimer problem. (Refer Slide Time: 56:15 min) Therefore what you have in summary is that the overall Hamiltonian for the electron nuclear problem involving many atoms and many electrons which is separated into two equations of motion one for the electronic motion alone but the energies that come out of the electronic motion are dependent on a set of nuclear positions because $V_{\text{e-N}}$ is there the nuclear coordinates are there. Now if you vary the nuclear coordinates to another set you will solve the same equation you will get other energy.

Therefore you get many as such energies and then you solve for all these energy the final you get is the electron energy as a function of the nuclear positions, use that to solve the remaining nuclear coordinates problem and that is the spectroscopy problem because spectroscopy deals with nuclear motion, rotational motion, vibrational motion. To solve for the nuclear spectroscopy problem you need to solve the electronic motion problem and this is what you call as the Quantum Chemistry.

Therefore the Born-Oppenheimer approximation allows you to separate the overall chemical problem into a static stationary energy solution problem that of the electronic motion and a dynamical problem that of the motion of the nuclei in the presence of an overall potential generated by this electronic motion and that leads to the concept of the potential energy surface.