Engineering Chemistry - 1

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Lecture - 1

Physical and Theoretical Chemistry

Hello, welcome to the National Programme on Technology Enhanced Learning. This is a programme funded by the Ministry of Human Resource Development for the benefit of the engineering students in the country. What we proposed to do here in this programme is to provide you a series of lectures on various topics and I am here to give you a series of lectures on the basic Chemistry.

The first year deals with core Chemistry curriculum that most engineering students should be familiar with in order to appreciate the fundamentals as well as the role of such fundamental ideas in engineering applications. So the purpose here is to introduce you to basic principles of Chemistry. Let me introduce myself, I am Mangala Sunder, I teach in the department of Chemistry Indian Institute of Technology Madras in Chennai. The address for electronic mail communication to me is mangal@iitm.ac.in.

Now, the core Chemistry curriculum that we are interested in giving you in the form of lectures concerns with the principles of Chemistry and not necessarily the applications of Chemistry in engineering. It is our sincere opinion that the applications of Chemistry in Engineering are best taught by the respective specialized engineers. The basic ideas in Chemistry as the Chemist understand, as the fundamental Scientist understand, as are relevant for the engineering principles and applications etc. they are of interest to us. Therefore this series of lectures let me give you the sequence of lecture in Chemistry.

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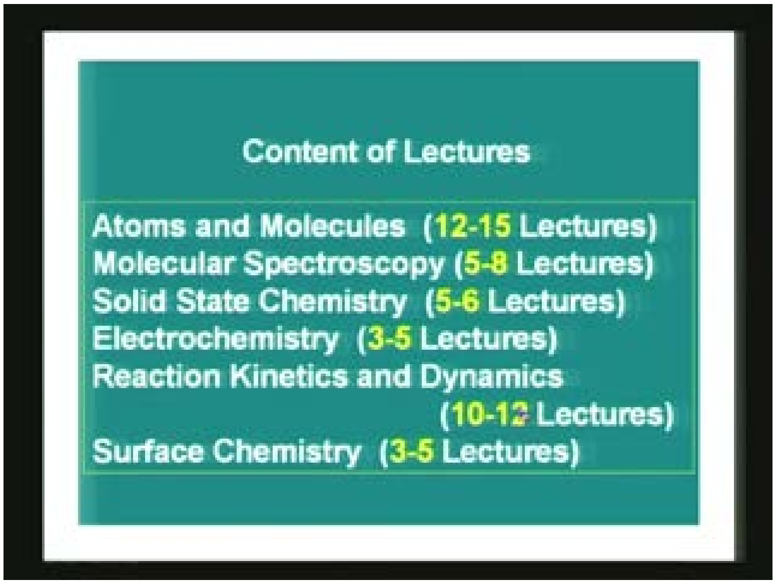

Content of Lectures

Atoms and Molecules (12-15 Lectures)
Molecular Spectroscopy (5-8 Lectures)
Solid State Chemistry (5-6 Lectures)
Electrochemistry (3-5 Lectures)
Reaction Kinetics and Dynamics (10-12 Lectures)
Surface Chemistry (3-5 Lectures)

The first 12 to 15 lectures will be on Atoms and Molecules. This is essentially the basic Quantum Chemistry that we should be familiar with. This will be followed by a series of lectures on Molecular Spectroscopy. These are fundamentally important subjects for all of Chemistry, Physics, Engineering, Biological Sciences, what not? The applications of spectroscopy, the applications of detection techniques everything is described in detail in Molecular Spectroscopy. Of course, I would not do all of that but introduce you to the basic principles of Spectroscopy.

There will be a few lectures on Solid State Chemistry, Electrochemistry approximately 3 to 5 lectures and Elementary Chemical Reaction Kinetics and Dynamics. Again some 10 to 12 lectures followed by Surface Chemistry approximately 3 to 5 lectures. This is the organization of the series of lectures that I proposed to give on the Engineering Chemistry course of the NPTEL project.

We will start with the first and a most important aspect of Chemistry namely the constituents of chemical systems the atoms. There are obliviously 114 types of atoms that we have and the mechanics of the atoms when they are together the interactions between the atoms to form molecules etc, are fundamental to what one calls as chemical transformations. So the first module is on the Atoms and Molecules.

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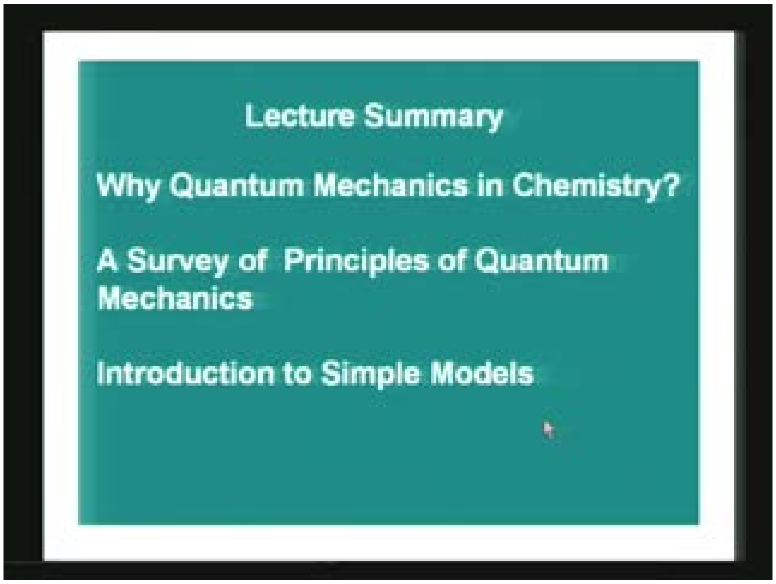

Lecture Summary

Why Quantum Mechanics in Chemistry?

A Survey of Principles of Quantum Mechanics

Introduction to Simple Models

What do we propose to do in this Atoms and Molecules lecture is we will basically look at the elementary Quantum Mechanics as applied to chemical systems or as is done in Chemistry courses, an elementary survey of the principles of Quantum Mechanics as well as some introduction to simple models. These are of interest to us in understanding the atomic structure and consequently from the atomic structure how the atoms form molecules and therefore the molecular structure.

Quantum Mechanics is of course fundamentally an important subject. This series of lectures will only give you what are called the prescriptions of Quantum Mechanics. This is not a place nor do

I have the expertise to tell you that at the end of this you will understand Quantum Mechanics, in fact nobody does. Therefore, when we talk about the importance of Quantum Mechanics or the importance of Quantum Chemistry I would focus my attention on the methods by which we apply the rules of Quantum Mechanics.

This course is to understand the rules as they are and manipulate the rules to follow how molecules form in some elementary manner. The principles of Quantum Mechanics I will only list to them as principles without any discussion on how they were arrived at.

The only way to become familiar with Quantum Mechanics is not by asking the question by how I understand Quantum Mechanics but by asking and trying to answer the question how do I use the methods of Quantum Mechanics as prescribed in the text books or as prescribed by the founding fathers of the subject. What are the methods, what are the principles that I should apply? Let me not question the principle, how do I apply, how do I become familiar and later on in a process of continuous education let me try and understand why these principle arose the way they are now. So it is not about understanding Quantum Mechanics but it is about becoming operational in using the algebraic procedure in Quantum Mechanics.

Why is quantum Chemistry extremely important in Chemistry? Quantum Mechanics is important in Chemistry? It is the basis of the understanding chemical bonding at the molecular level.

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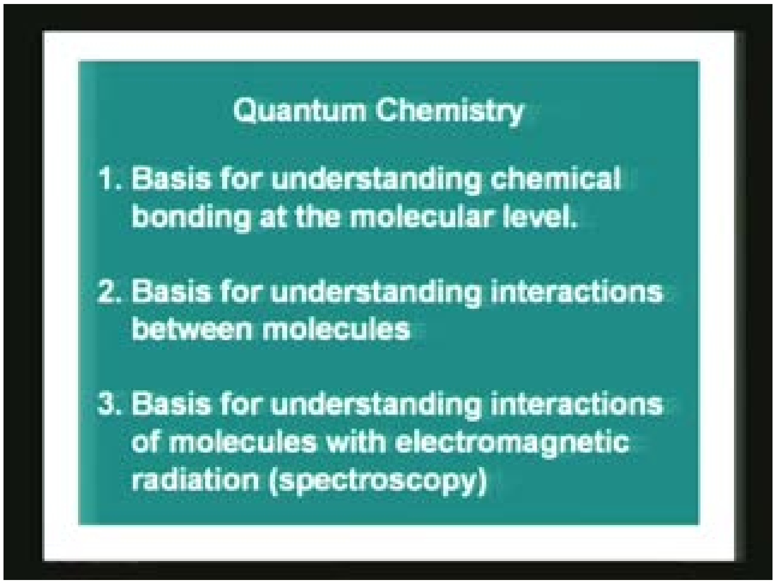

Quantum Chemistry

1. Basis for understanding chemical bonding at the molecular level.
2. Basis for understanding interactions between molecules
3. Basis for understanding interactions of molecules with electromagnetic radiation (spectroscopy)

As you see here it is the basis for understanding the molecular interactions. Quantum Chemistry provides the basis for understanding chemical bonding. Why molecules form? Why molecules disintegrate? Why molecules dissociate? Rearrange? The basic ideas of formation, rearrangement, dissociation of molecules and the basis of understanding are of course in Quantum Chemistry. Also, the interactions between molecules which are responsible for chemical reactions, which are responsible for physical transformations are also from the principles of Quantum Chemistry. And most importantly for a practical chemist the quantum

Chemistry provides the basis for understanding the interactions of molecules with electromagnetic radiation; this is the branch of spectroscopy.

Spectroscopy is how we detect, we determine, quantitatively access various chemical species intermediates in a chemical reaction and many other things. So, an important aspect of Molecular Spectroscopy is that the basic theory is provided by the methods of Quantum Mechanics and the methods of Quantum Chemistry. Now, let me summarize how we got to where we are today, that is, we are summarizing the effects of a little more than 106 years to be exact.

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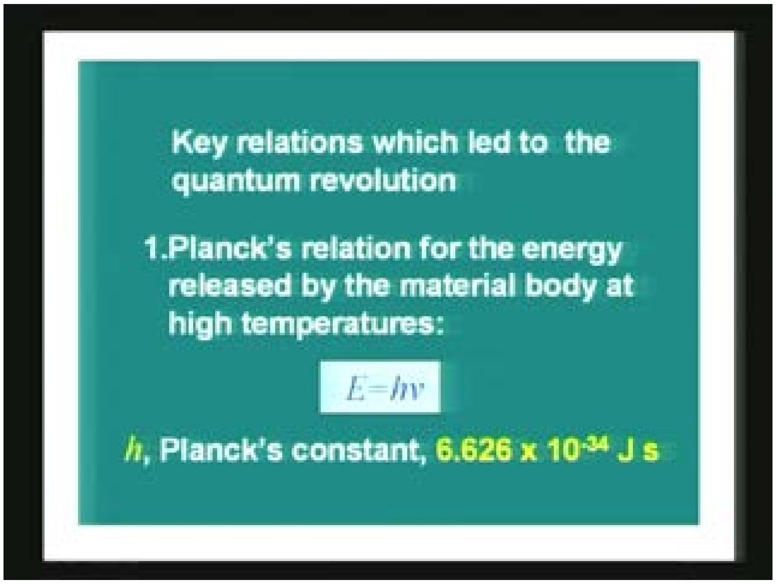

Key relations which led to the quantum revolution

1. Planck's relation for the energy released by the material body at high temperatures:

$$E = h\nu$$

h, Planck's constant, 6.626×10^{-34} J s

In 1900 Max Plank proposed a relation for the energy released by the material body at high temperatures. Max Plank was studying a certain phenomenon called black body radiation. The phenomenon could not be understood in complete form by the methods of classical mechanics, the Newtonian mechanics, and classical electro magnetism.

Max Plank came up with a radical suggestion that the energy released by the material body as it is raised to very high temperatures, the energy is released in the form of light, in the form of radiation, the energy is released in packets from the material body. And he defined the size of this packet by the relation the energy associated with the material bodies the energy packets which appear is a constant times the frequency of the radiation, $E = h\nu$ the first relation proposed by Max Plank where h subsequently was called Plank's constant and if you look at the value of Plank's constant it is an extremely small quantity 6.626 times 10 raise to – 34 joules second. Plank's constant has the dimensions of energy into time, frequency has a dimension of one by time therefore this is energy and the discreteness in the energy that is being released. The discreteness is so small as you see it, the number h is so small that we probably did not know until then that energy is coming from the hot body in packets but we thought that it was a continuous radiation. Max Plank proposed to this as a hypothesis and was able to explain the phenomenon of black body radiation completely. It was a proposal it was a hypothesis but most importantly he introduced a constant which bears to his name. This is the first phenomenon in which the idea of a quantum of energy was introduced.

Five years later Albert Einstein who was very young at that time came up with a brilliant explanation of one of the unsolved problems in Physics at that time for a phenomenon known as the photoelectric effect. It was in the year 1905 and now we celebrate the 101st year since Albert Einstein published three most important papers in all of physics and in all of science. In one of the papers describing the effect known as the photoelectric effect Einstein came up with an explanation and in summary what he said was that light or the electromagnetic radiation itself consists of packets of energy. there is no other Scientist in the world that I know of whose work was never questioned for the award of Nobel prizes everybody thought Albert Einstein would win the prize the Nobel committee had no doubts that it should give a prize to Einstein. The only question was which of the three papers that he published in 1905 should be given recognition for Nobel Prize. One was photoelectric effect, the other was his radical revolutionary idea that is the theory of special relativity for which he drew substantial guidance from other Physicist most importantly Lawrence and the third paper that Einstein published in that year was on Brownian Motion. Einstein was probably the greatest Physicist ever to have lived in the last century. His idea was that light itself consists of packets of energy we call them us photons today. Einstein did not call them as photons but I believe it was a chemist Gilbert Newton Lewis who probably coined the name photons for the light packets almost some 10 or 15 years later.

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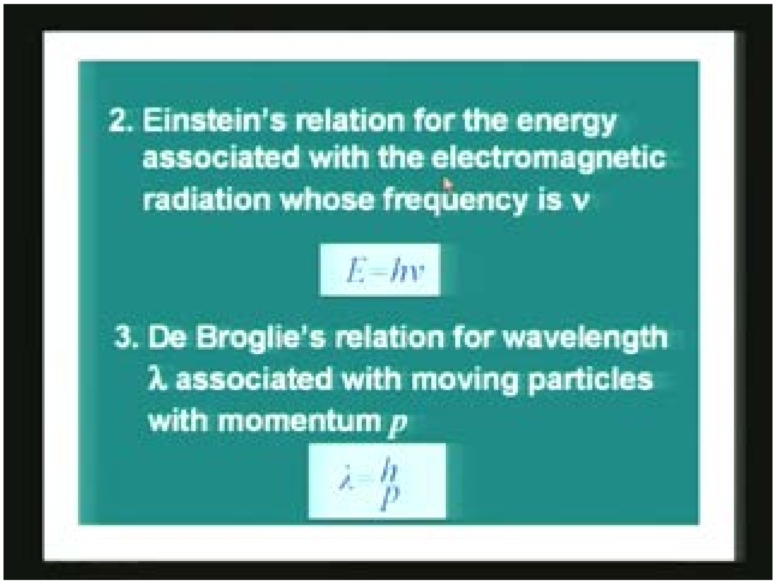

2. Einstein's relation for the energy associated with the electromagnetic radiation whose frequency is ν

$$E = h\nu$$

3. De Broglie's relation for wavelength λ associated with moving particles with momentum p

$$\lambda = \frac{h}{p}$$

The expression that Einstein came up with for the discrete packets of energy for the electromagnetic radiation whose frequency is ν is also the same relation that Einstein gave E = hυ. And Einstein was the first to recognize that this h is exactly the same as h of the Max Plank. This was the second revolution that the energy emitted by the material bodies or the energy of the electromagnetic radiation itself consists of discrete packets or quanta of energy and the quanta or the quantum is given by hv. Then came another important discovery, this was by Louis de Broglie a French Physicist, a French History student turned Physicist. Louis de Broglie graduated in B. A. History but in a few years he became a first rate Physicist.

And de Broglie proposed the idea that light if it has to be particulate or it has to behave like particles or if it has to behave like waves it is not just light, de Broglie proposed that all material particles moving can be treated as matter with a certain wavelength. He introduced the idea matter waves. What he suggested was that the wavelength **λ** is associated with the moving particles, particles with a mass m and therefore a momentum p which is mass times the velocity if the velocity is not very large. Then de Broglie proposed a relation for the wavelength **λ by, λ** = h/p where this h is again the same constant the Planck's constant. So, by this time people realized that there is something fundamental about h the Planck's constant which is the action constant. It is that it has a certain importance in Physics and of course it has a fundamental importance in Chemistry through the Schrödinger equation. These are the three most important phenomena that I would like to highlight before moving onto the basic formulation of Quantum Mechanics as we know today.

In a typical Physics course you will probably learn the details of how black body radiation phenomenon has been studied by Max Planck through all the derivations. You might also go through the derivations of photoelectric effect. In fact, if I recall the textbook for High Schools the Central Board of Secondary Education class 12 textbook describes the photoelectric effect in detail so you must have studied them already. The matter wave is a new idea. That is, all material particles which are moving in a certain speeds have in them an associated wavelength. That is, we are all like waves, when I start moving like this there is a wavelength associated with me. These are all ideas which eventually culminated in the formulation that we know today the formulation by the Austrian Physicist Erwin Schrödinger.

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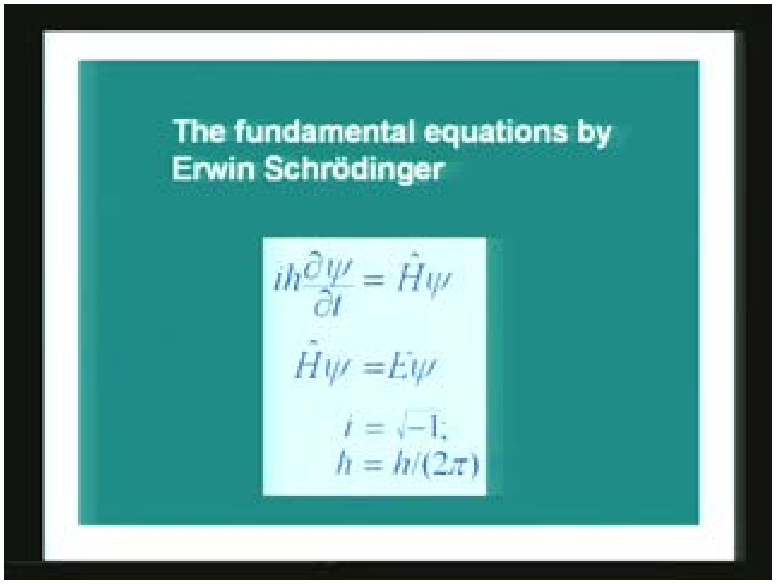

The fundamental equations by Erwin Schrödinger

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

$$\hat{H}\psi = E\psi$$

$$i = \sqrt{-1};$$

$$\hbar = h/(2\pi)$$

I am going to give you a prescription, what is a prescription? You go to a doctor with the idea that you want to cure something, the doctor gives you a medicine. Very few of you will probably ask why should I take this medicine and why not something else? Or why should I take this medicine two pills four times a day and why not take all the eight pills at the same time. I am sure you must ask these questions. And I am also not certain that many doctors will entertain this idea. But if they do they will explain to you the reason behind why you have to do it this way. There are principles, of course medicine and the cure is established on the basis of the observations, experiments, hundreds and hundreds of years now. Quantum Mechanics is also the way I give you is a prescription, I cannot explain to you why the rules what they are. The only reason the rules are what they are they is that they seem to explain practically every phenomenon that we have come to experiment with since 1926.

There are two fundamental equations in Quantum Mechanics and in Quantum Chemistry anywhere you go that is when you study the microscopic systems, systems of atomic dimensions. There is only one fundamental equation not two but the second one is derived from the first one. One fundamental equation proposed by Erwin Schrödinger in 1926 is $+ih/2\pi\ (\partial\psi/\partial t) = \hat{H}\psi$. This is the most important equation of microscopic science and the one which governs the properties of matter. Everything that we know seems to have followed from the application of this. The h is same h as the Planck's constant. There is a partial derivative with respect to time and there is a quantity with some hat on the top this quantity has a classical analog it is known as the Hamiltonian but it is written in a specific form for the mechanics of Atoms and Molecules. Hamiltonian is an operator. But the equation we have to remember is $+ih/2\pi\ (\partial\psi/\partial t) = \hat{H}\psi$ where i is $\sqrt{-1}$ it is imaginary so we have an equation involving complex quantities. But you will not study all of this but in Chemistry you will only study this equation $\hat{H}\psi = E\psi$. The first equation is known as time dependent Schrödinger equation and the second $\hat{H}\psi = E\psi$ is known as time independent Schrödinger equation.

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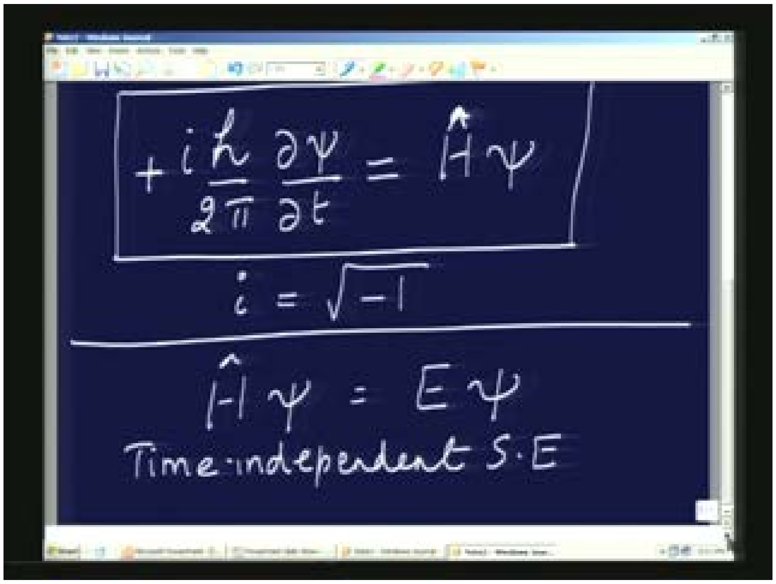

$$\boxed{+\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \hat{H}\psi}$$

$$i = \sqrt{-1}$$

$$\hat{H}\psi = E\psi$$

Time-independent S.E

What is $\hat{H}$? What is ψ? What is E? We will come to know all this things. In grade 6 or perhaps in grade 8 when somebody wrote this equation $F = ma$. We all understood the equation we studied and said this is Newton's second law for the motion of objects of macroscopic size, objects of planetary nature very large scale, force is mass times acceleration that is not the meaning of this equation but that is just the words of mathematical symbols. We never questioned what F is or what ma is. This is the equation we need to solve in order to understand the dynamics of particles, dynamics of things that we observe.

Schrödinger came up with this idea that the dynamics of Atoms and Molecules or any objects which we cannot see in microscopic dimensions has to be understood by solving an equation which looks like this: $+ih/2\pi\ (\partial\psi/\partial t) = \hat{H}\psi$. Now, do we understand this? If you ask me I do not understand this but obviously I know how to solve this equation for certain problems. And one never tries to understand Quantum Mechanics for the first time Quantum Chemistry for the first time one learns but works with the basic methods. I used to solve problems analyze the results of problems, find out what is new in the solutions of the problems as different from the solutions that one would get if one were to use classical methods and see that the quantum systems give you the answers which are actually observed in experiments. Most important experiment is spectroscopic experiments. So this is a prescription, we are going go with this, we are going to try and understand how to solve $\hat{H}\psi = E\psi$.

The entire Atoms and Molecules module is on the solution of this equation for various forms of the Hamiltonian the corresponding solutions are all known as wave functions, this is a wave equation and the quantity E are known as the energies that one can observe if one tries to measure the energy of the system under study. These are the possible energies and the entire exercise of Quantum Chemistry is to determine the wave functions and the energies through the solution of an equation called the time independent Schrödinger equation where the $\hat{H}$ is Hamiltonian.

Hamiltonian is not a quantum quantity it is a classical mechanical quantity representing the total energy of the system. Kinetic energy plus the potential energy of a system is what is known as Hamiltonian in honor of Sir William Robin Hamilton, Physicist in the 19th century. But the Hamiltonian will be written in a special form for quantum mechanical problems and therefore will require methods which are different from the methods of classical mechanics.

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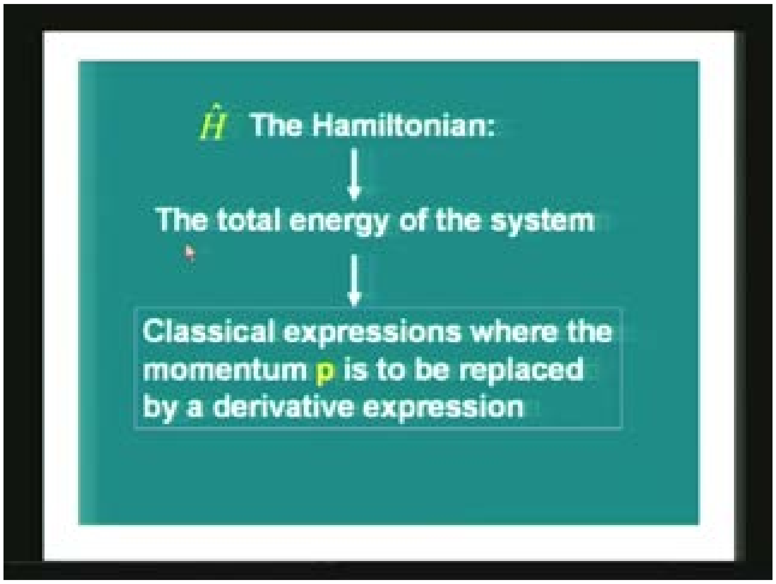

$\hat{H}$ The Hamiltonian:

↓

The total energy of the system

↓

Classical expressions where the momentum p is to be replaced by a derivative expression

As mentioned earlier $\hat{H}$ is the Hamiltonian of the system or the Hamiltonian of whatever things that we want to study. Hamiltonian is nothing but the total energy of the system. The total energy of a classical system is obviously given by the kinetic energy and the potential energy. You know, for a particle moving with a momentum p if the particle has a mass m you know its kinetic energy, its expression is given $p^2/2m$. The potential energy for example, for a particle moving in the earth's surface if there are no other forces, electric fields or anything else the potential energy is due to the height of the particle from the surface of the earth and due to the gravitational attraction of the particle with the earth. The sum of the potential energy and kinetic energy is known as Hamiltonian. But in quantum systems we are going to replace the classical expressions or the classical mechanical expressions by replacing the momentum p in a unique way.

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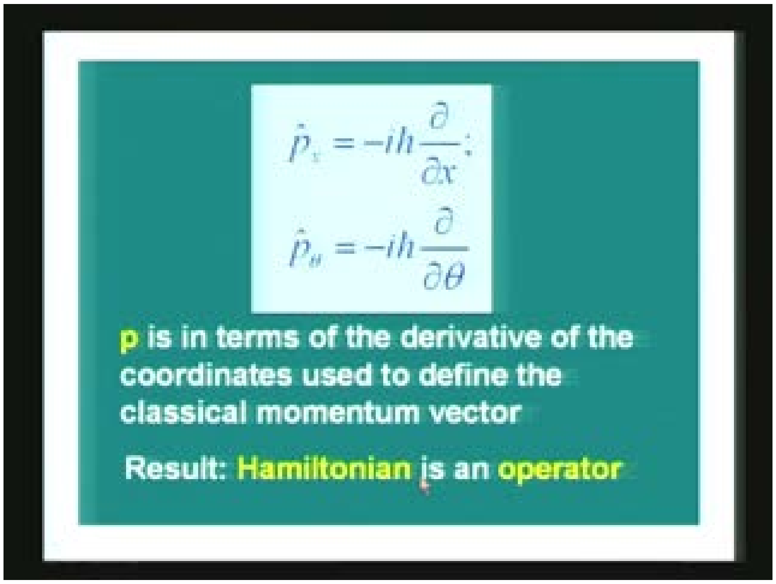

$$\hat{p}_x = -ih\frac{\partial}{\partial x};$$

$$\hat{p}_\theta = -ih\frac{\partial}{\partial \theta}$$

p is in terms of the derivative of the coordinates used to define the classical momentum vector

Result: Hamiltonian is an operator

Momentum is a vector and if we represent the vector in a certain direction the component of the vector in that direction for example along the x axis we write the momentum as the component as p_x the quantum mechanical quantity for p_x will not be p_x itself but will be given by this strange quantity $-ih/2\pi \, \partial/\partial x$. If the momentum is about a certain direction with the changing angle as the unit vector the momentum is given by $-i\hbar \, \partial/\partial\theta$ as you see here.

The momentum will be not written as p but it will be written in terms of the derivative of the coordinates used to define the classical momentum vector. Here the coordinate used is x, here the coordinate used is Θ, ψ so two things but a derivative is an operator. A derivative is to act on a function to give you something, derivative by itself does not have a meaning. So the result of this is that the Hamiltonian is not the classical quantity of sum of energies of kinetic and potential energies alone but in addition the Hamiltonian becomes an operator.

The mysterious quantity ψ, the one which troubled many Physicists, the one which was in fact misinterpreted by its founder itself, wave function, what was the meaning of the wave function? A lot of people had difficulty in understanding what the wave function was. It is a wave function associated with whatever system that you study. It depends on all the coordinates available to the system. suppose a system is moving in only one dimension or accessible positions in only one dimension, system can be found in one dimension if you do that then the coordinates available to the system is a one dimensional coordinate called the x which you represent by an axis and the values of the x as the positions. But if the system is accessing a planar area for example then there are two coordinates associated with that. So the system depends on all the coordinates that define the region of space accessible to the system. It can be a complex function, after all you have a $\sqrt{-1}$ appearing in the original Schrödinger equation. And the most important thing is after working very hard with all the solutions of the Schrödinger equations, wave functions, etc you will realize that the wave function does not have a physical meaning, does not have a physical interpretation. Then you will ask the question why I study all these things, you are telling me to solve an equation which I do not know, you are telling me to solve an equation whose solution I do not know to interpret, then what is the purpose of the entire thing.

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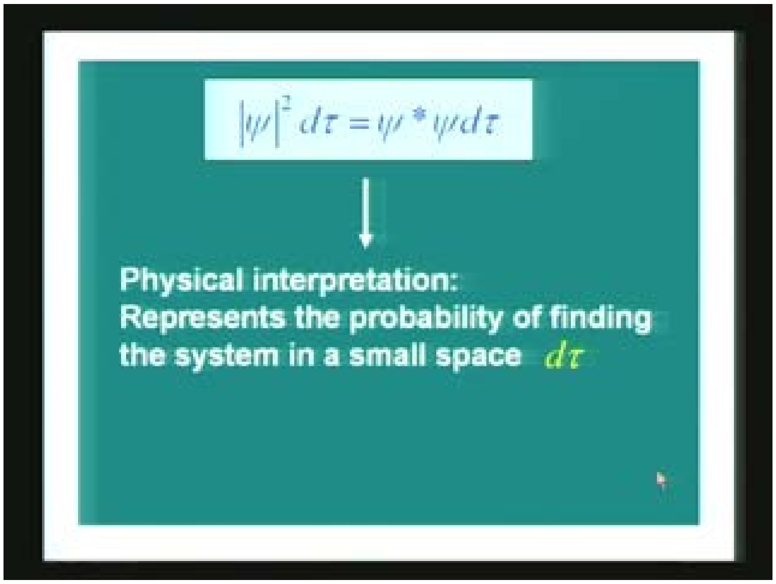

$$|\psi|^2 d\tau = \psi^* \psi d\tau$$

Physical interpretation:
Represents the probability of finding the system in a small space $d\tau$

Fortunately, there were intelligent people ahead of us who did not worry about the wave function as is as a complex function but the absolute square of the wave function $|\psi|^2 d\tau$. When you solve this $\hat{H}\psi = E\psi$ the ψ does not have a meaning, does not necessarily have a physical meaning or interpretation.

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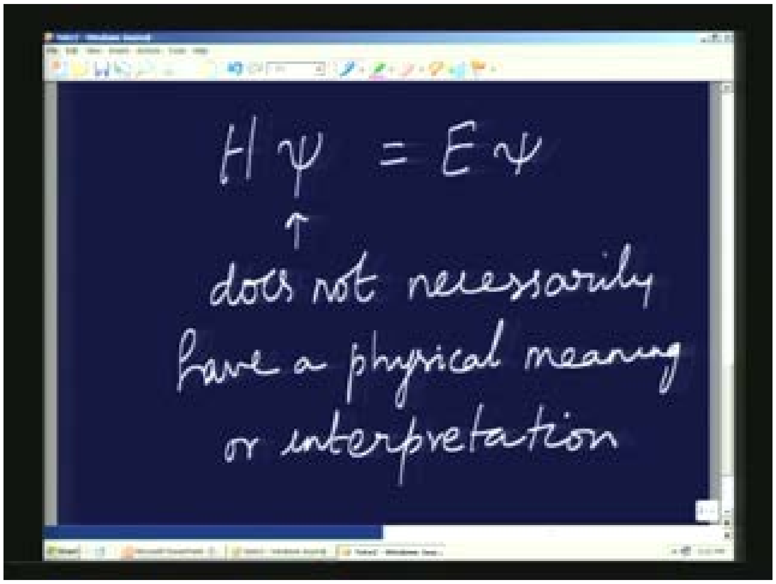

$$H\psi = E\psi$$

↑

does not necessarily have a physical meaning or interpretation

If ψ is complex then its complex conjugate is ψ*. You know what is complex conjugate, if a complex number z is written as a + i b where a is real b is real and i is √–1, you know what is the z*? z* is a – i b. That is, wherever you have i you replace i by the minus sign to get the complex conjugate. What is its role? Its role is in defining z z* or the absolute value of z^2 which if you do the simple multiplication a + ib times a – ib you get a real number $a^2 + b^2$. The ibs – ibs will get cancelled. So, even when you have complex quantity you can define a real number from the complex quantity in terms of the absolute square of the complex number.

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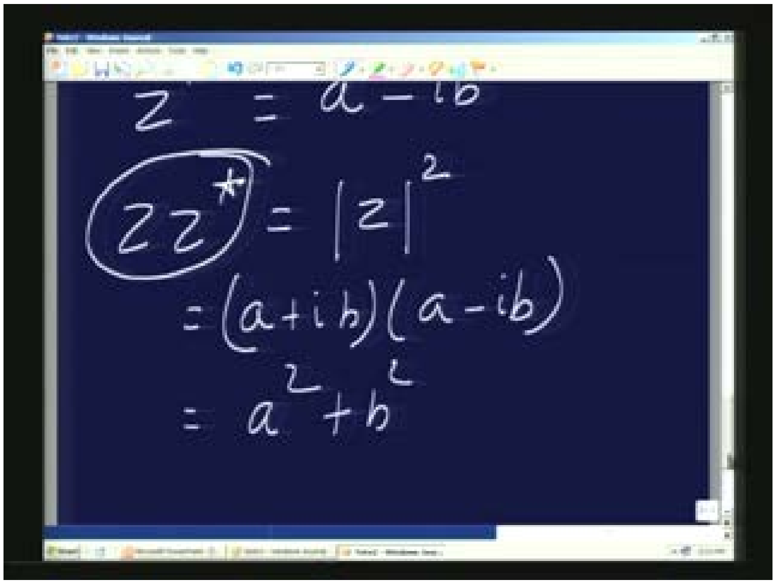

$$z = a - ib$$

$$\boxed{zz^{*}} = |z|^{2}$$

$$= (a+ib)(a-ib)$$

$$= a^{2} + b^{2}$$

And what is the relevance of this? The relevance of this is that the ψ is a complex function its complex conjugates ψ* is such that the absolute value of ψ^2 in a small interval of space has a meaning. This meaning was given by another famous Physicist Max Born, a German Physicist, what is the interpretation? The physical interpretation is that the absolute square of ψ represents the probability of finding the system in a small space dτ, dτ is a small space. For example, we will see some of the models like particles in a box, the harmonic oscillator, the hydrogen atom, molecular problem etc. We will also define what the space means, what a small interval of space means and so on. We have to remember that the absolute square of ψ times dτ that is you evaluate the function ψ in a small interval of space dτ. The ψ ψ* dτ represents the probability of finding the system in a small space. This is the only meaning that can be ascribed to the solution of the Schrödinger equation.

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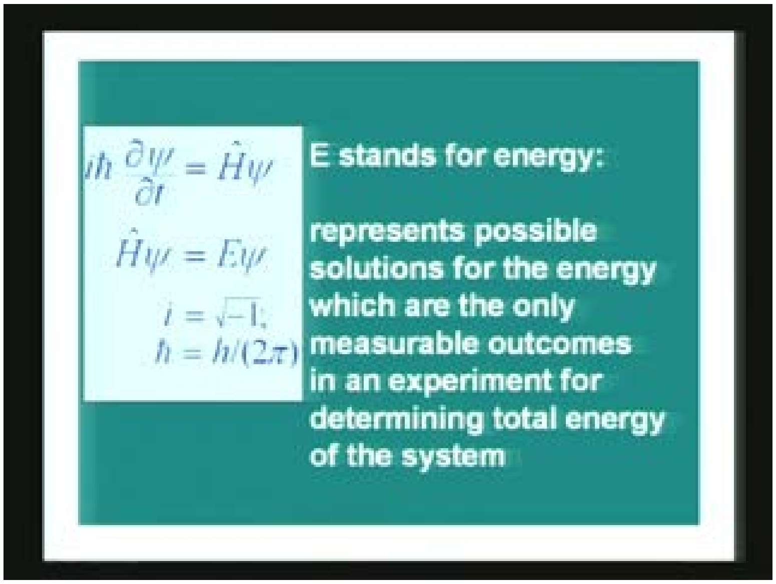

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

$$\hat{H}\psi = E\psi$$

$$i = \sqrt{-1};$$

$$\hbar = h/(2\pi)$$

E stands for energy:

represents possible solutions for the energy which are the only measurable outcomes in an experiment for determining total energy of the system

The next important fact which we have to pay attention to is the quantity E in $\hat{H}\ \psi = E\psi$. E stands for energy, you know Hamiltonian represents the total energy of the system. Therefore whatever is the dimension of ψ E must have the dimensions of energy. E represents possible solutions for the energy, what does that mean? It means that when you make a measurement for the energy of the system you will get some experimental values, what Schrödinger equation tells you is that the theory predicts certain values as the only possible values in the experimental measurement.

It is strange that when you make a measurement of energy, of a particle that is moving in a box why should you get only specific values why not any energy? A lot of what you call as practical questions will become relevant but then you will have to forget that we are talking about some things that we understand, no I am introducing you to a method we will do blindly some of these allies we will go to the allies follow through the process and hopefully we understand a little bit about that. The energy that you have here $\hat{H}\ \psi = E\psi$ where E represents the only outcomes in an experiment for determining the total energy of the system. Whenever you make a measurement on the total energy of the system the only possible value is that you will get are given by E.

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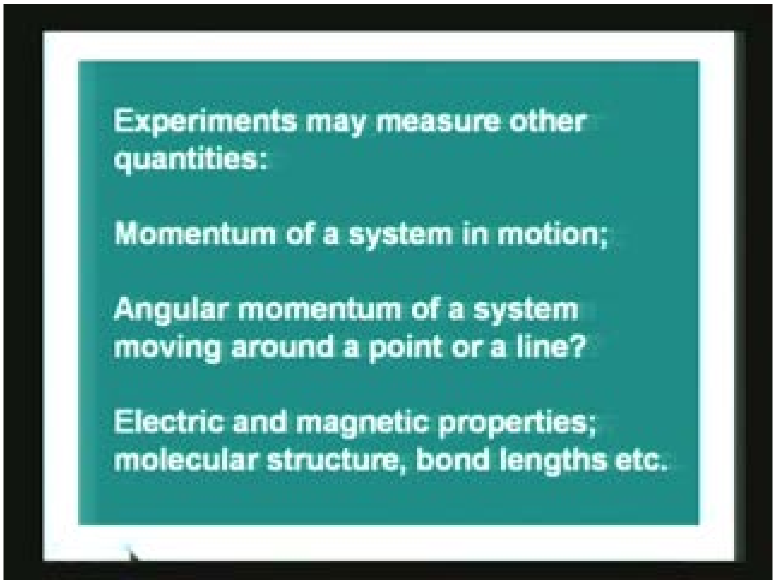

Experiments may measure other quantities:

Momentum of a system in motion;

Angular momentum of a system moving around a point or a line?

Electric and magnetic properties; molecular structure, bond lengths etc.

Energy is not only the measurable quantity you have momentum, particle's velocity, angular momentum and so on. If the particle is moving around about a point or moving about a line the electric and magnetic properties of molecules, the molecular structure, what is the size and shape and the bond lengths and bond angles. All these things are important and are called as experimental quantities. Now, the next strange thing that we have in Quantum Mechanics is, there is a 3rd strange thing, the first one was that we will have to solve the Schrödinger equation, the 2nd strange thing is that the momentum is given by an operator. The third strange thing is that the wave function does not have a meaning but the absolute square of the wave function represents a probability density or the absolute square of the wave function in a small interval of space gives you the probability of finding the system in that space that is the third strange thing.

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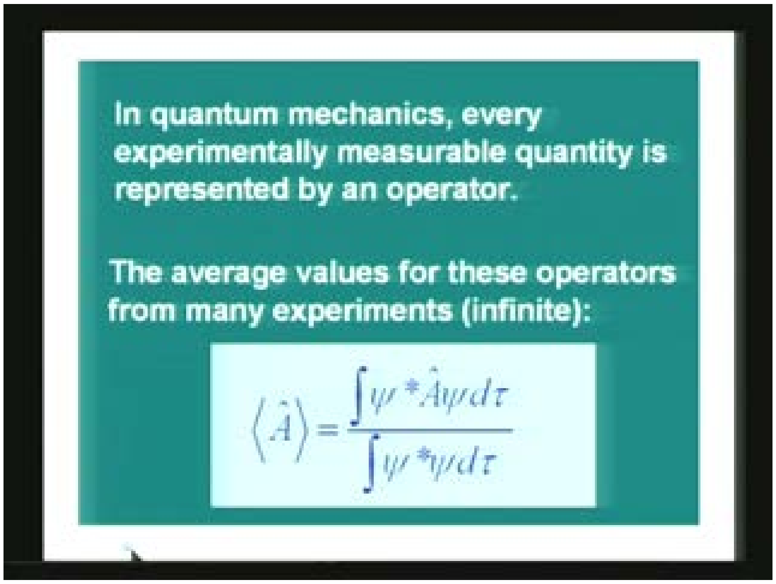

In quantum mechanics, every experimentally measurable quantity is represented by an operator.

The average values for these operators from many experiments (infinite):

$$\langle \hat{A} \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

And then the fourth strange thing is that what do we get when we make a measurement of properties of the system? We do many measurements and try to get an average, Quantum Mechanics gives an expression for the average value. The average value for any measurement of the quantity represented by $\hat{A}$ is given by $\int\psi^*\hat{A}\psi d\tau$ / $\int\psi^*\psi d\tau$. For example, if $\hat{A}$ is the momentum p in the x direction for example then it is $\int\psi^*(-i\hbar\,\partial/\partial x)\psi d\tau$ / $\int\psi^*\psi d\tau$. So, the 4th strange thing is that every measurable quantity in Quantum Mechanics is represented by an operator. The momentum by the differential operator as one of the earlier ones, likewise dipole moment, bond length, bond angle, electrical susceptibility, molecular polariazabilities and many properties are there. Every such experimentally measurable property is represented by an operator in Quantum Mechanics. And if the wave function of the system is given by ψ or if the wave function of the molecule is given by ψ then the measurement of that property on an average will give you the results as given by the formula:

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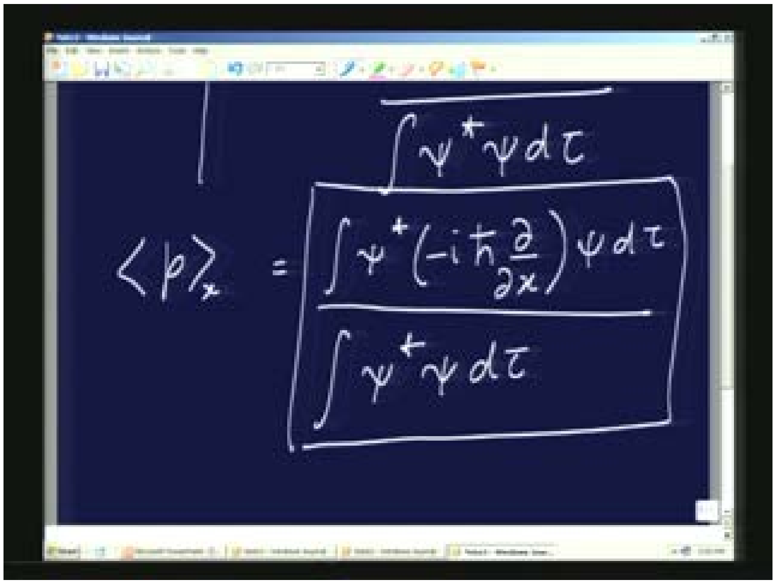

$$\int \psi^* \psi \, d\tau$$

$$\langle p \rangle_x = \boxed{\frac{\int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi \, d\tau}{\int \psi^* \psi \, d\tau}}$$

$\int\psi^*(-i\hbar\, \partial/\partial x)\psi d\tau$ / $\int\psi^*\psi d\tau$. So go back and see and the prescription is that.

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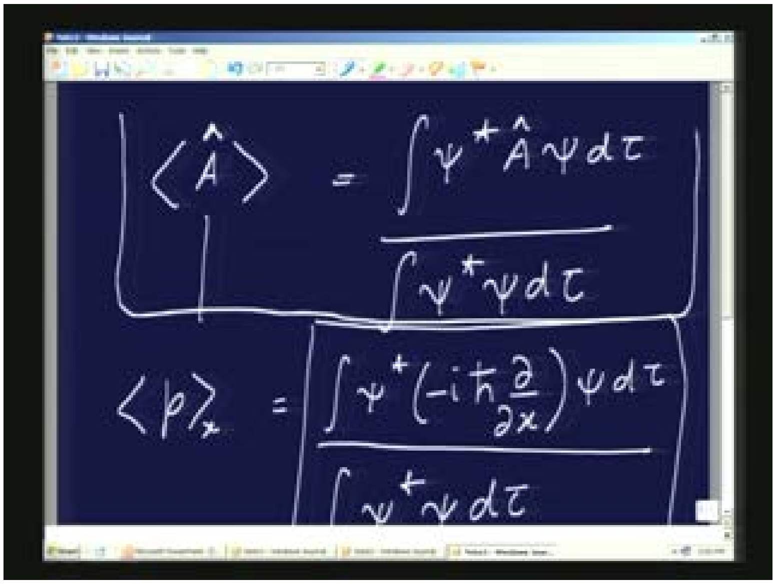

$$\boxed{\langle \hat{A} \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}}$$

$$\langle p \rangle_x = \frac{\int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

Prescription for measurement processes is that on the average what we will get for measurement of properties of the system. So, these are all things are that we come back to again and again and again.

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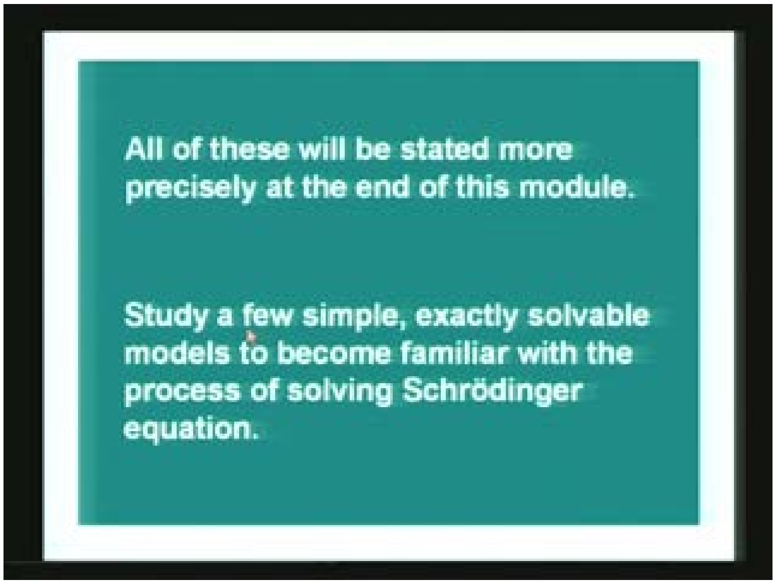

All of these will be stated more precisely at the end of this module.

Study a few simple, exactly solvable models to become familiar with the process of solving Schrödinger equation.

So let us just see what we can do for the rest of this lecture, how we go about trying to make sense out of these four strange quantities. We will understand or we will try to follow this by four simple model problems. We will study a few simple model problems, the problems can be solved mathematically exactly so that you will get functions, analytic forms for the wave functions and so on and then we will try and become familiar with the process of how to solve the Schrödinger equation for various systems.

What are the various systems? We will have four models. The first model is the most elementary model called the particle in a box. This is the simplest Schrödinger equation that we can solve, one dimensional system. The second one is a particle moving in a ring slightly more complicated. And even more complicated system is the harmonic oscillator. We will try and solve these things using the Schrödinger mechanism, the wave mechanism and then of course the hydrogen atom.

The starting point of Chemistry the Quantum Mechanics in Chemistry is the hydrogen atom the lightest and the first in the periodic table, it is the simplest atom one electron system one electron and one proton. You would see that the Quantum Mechanics of the hydrogen atom is quite difficult and you have already seen qualitatively the solutions of the hydrogen atom in terms of orbitals in your high school like wave functions, orbitals, the orbital diagrams and so on. The present method is to give you some of these pictures in a little more quantitative manner and the orbitals of hydrogen atom are extremely important for Chemists because they form the basis, the methods of solving the Schrödinger's equation for hydrogen atom form the basis for understanding molecules. Therefore, I will spend a considerable amount of time in the analysis of the hydrogen atom through the methods of Quantum Chemistry. Why do we solve these problems for a Chemistry course?

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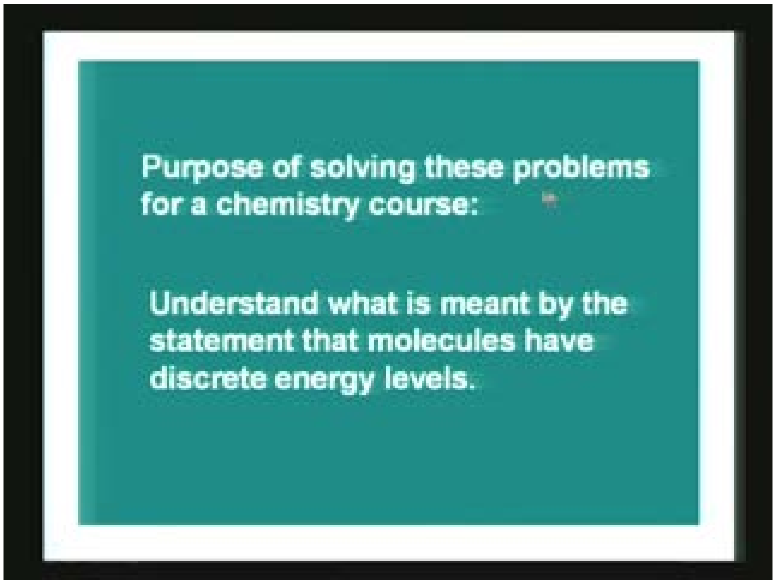

Purpose of solving these problems for a chemistry course:

Understand what is meant by the statement that molecules have discrete energy levels.

We do this because we want to understand what is meant by the statement that molecules have discrete energy levels. These are responsible for the transformations molecules undergo.

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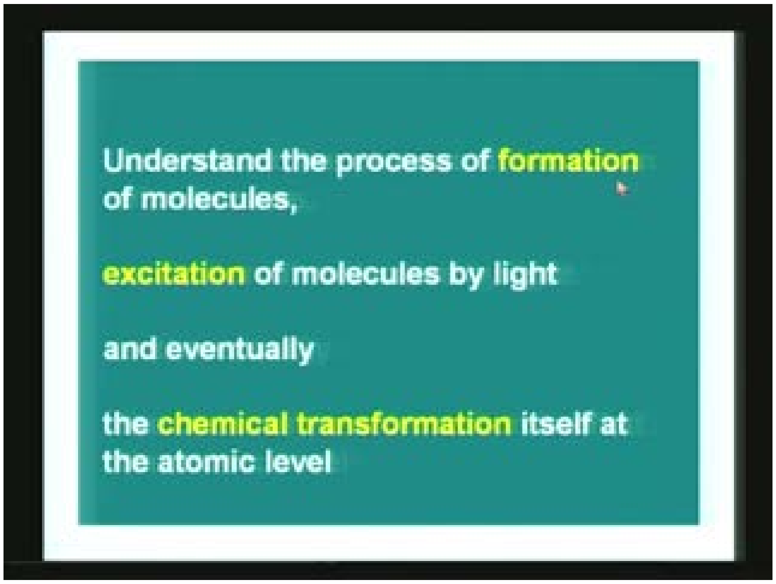

Understand the process of formation of molecules,

excitation of molecules by light

and eventually

the chemical transformation itself at the atomic level

We want to understand the process of formation of molecules. We want to understand how the molecules get excited by laser light for example or any other microwave radiation. And eventually the chemical transformation itself why molecules undergo transformations? Why some molecules are unstable the others are very stable? Why molecules rearrange? If you want to understand all these technical transformation processes at the atomic level we have to study some of these model problems. Let me go with a quick summary, we will elaborate the following models; the first one is particle in a box.

The box problem: For a particle moving inside a box in one dimension if you call this as coordinates and we imagine that the box is of length L such that the walls of the box are infinitely steep, meaning that the particle can never escape the box. It can only move inside the box and inside the box the particle is free there is no potential energy. Remember that the Hamiltonian is kinetic energy plus the potential energy. Therefore if the particle moving inside the box and if it does not have any potential energy obviously the Hamiltonian is given by its kinetic energy and the particle cannot escape the box and the mathematical conditions which imposes that is, the potentials at the two ends of the box are infinite and positive, that is steep, repulsive.

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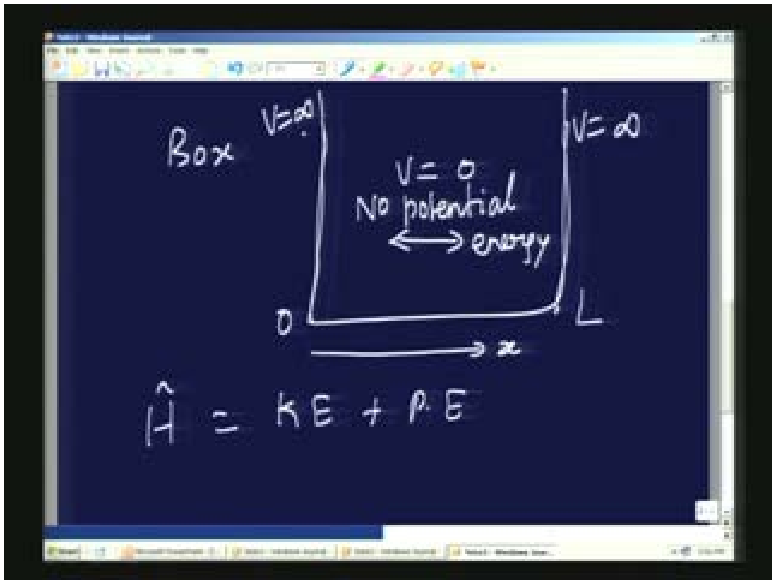

The model for this, the Hamiltonian is given by the equation $-\hbar^2/2m \, d^2/dx^2 + V$ where V is 0 if x is between 0 and L which we write by saying v = 0 for $0< x < L$ and v is infinity otherwise.

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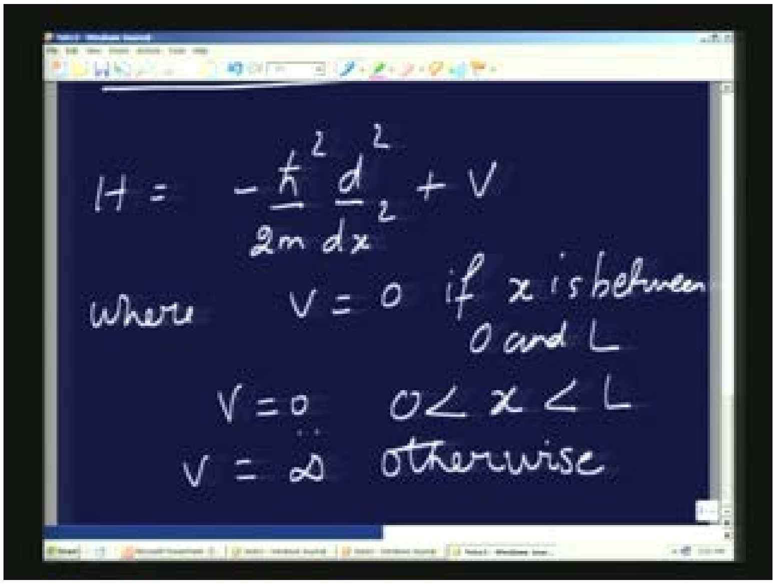

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V$$

where $V = 0$ if x is between 0 and L

$V = 0 \quad 0 < x < L$

$V = \infty$ otherwise

Therefore we want to solve this equation or this operator $\hat{H}$. What is the equation we want to solve? The equation we want to solve is with this H the differential equation $\hat{H}\psi(x) = E\psi(x)$ and E is a constant. We wanted to find out $\psi(x)$ and the energy E. This is one model, the simplest model.

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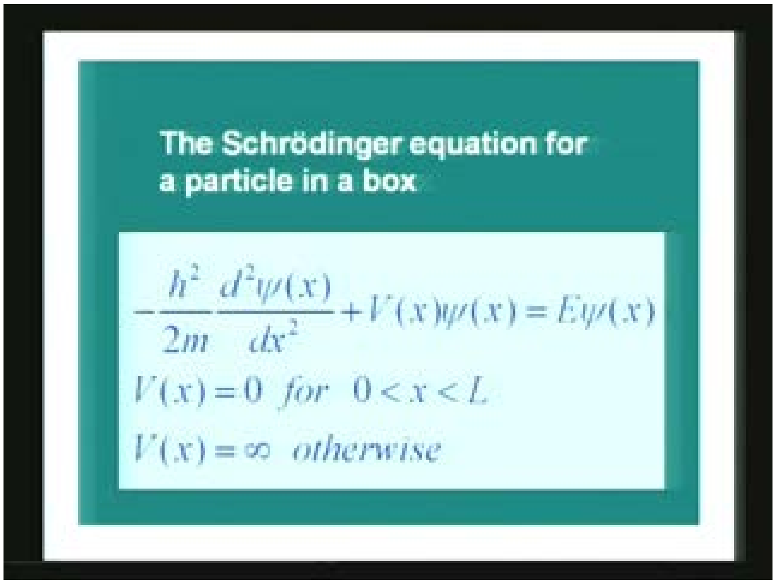

The Schrödinger equation for a particle in a box

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

$V(x) = 0 \ \ for \ \ 0 < x < L$

$V(x) = \infty \ \ otherwise$

And that is what you see in the slide here, the Schrödinger equation for a particle in a box is $-\hbar^2/2m\, d^2\psi(x)/dx^2 + V(x)\,\psi(x) = E\,\psi(x)$ where V is 0 for the particle inside the box and is infinity otherwise, this is one model.

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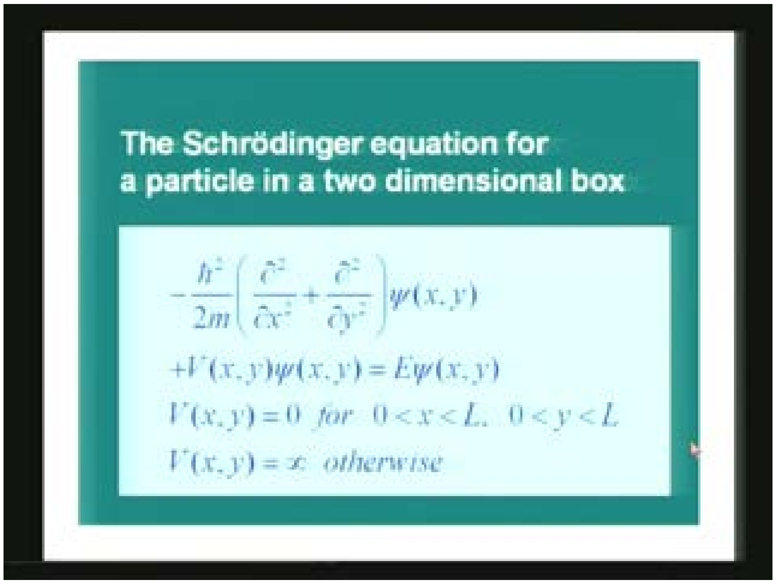

The Schrödinger equation for
a particle in a two dimensional box

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y)$$

$$+V(x,y)\psi(x,y)=E\psi(x,y)$$

$$V(x,y)=0 \ \ for \ \ 0<x<L, \ \ 0<y<L$$

$$V(x,y)=\infty \ \ otherwise$$

The second is, of course, instead of a one dimensional motion we can have a rectangular box and we can think about the particle moving in two dimensions or in three dimensions or n dimensions. Therefore how do we generalize this Schrödinger equation for a particle in a two dimensional box? We have two coordinates x and y and therefore the wave function ψ is the function of coordinates x and y and you see that this form is very similar to the one dimensional form $-\hbar^2/2m\ (\partial^2/\partial x^2+\partial^2/\partial y^2)\ \psi(x,y) + V(x,y)\ \psi(x,y)$. Now, it is a partial derivative because you have two coordinate variables. The whole term $-\hbar^2/2m(\ \partial^2/\partial x^2+\partial^2/\partial y^2)$ represents the kinetic energy of the particle and the wave function ψ and the potential energy of the particle V. The left hand side is all the Hamiltonian acting on the wave function = E times the wave function, $\psi(x,y)$. Again it is $H\psi = E\psi$. What are conditions? The conditions are very similar, here we are talking about a square box of x also between 0 to L the same length and y between 0 to L. So for a square box the potential is 0 inside the box and it is infinity otherwise. This is the second model we will do.

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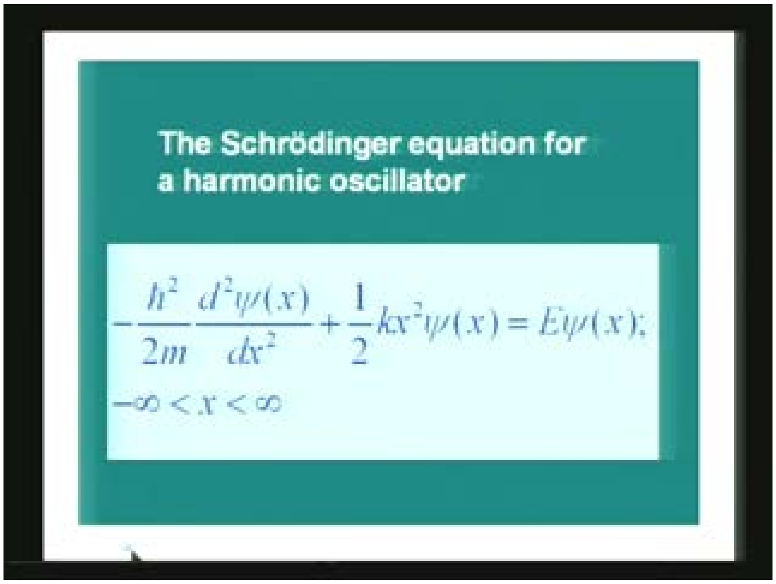

The Schrödinger equation for a harmonic oscillator

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

$$-\infty < x < \infty$$

The 3rd model we would study is the Schrödinger equation for the harmonic oscillator. The harmonic oscillator has a potential energy ½ kx^2 if x is the amplitude of the harmonic motion and k is the force constant of the harmonic oscillator system. This comes from your classical physics, the potential energy for a harmonic oscillator. The kinetic energy for the harmonic oscillator is $p^2/2m$. And that in Quantum Mechanics is now replaced by the derivative expression $-\hbar^2/2m\ \partial^2/\partial x^2$. Therefore, the potential energy plus the kinetic energy acting on the wave function ψ. Therefore, again you have is a $\hat{H}\psi = E\psi$. Now, the values of x in this problem for harmonic system are in mathematical conditions x can take any value from minus $-\infty$ to $+\infty$. That is the model we would solve.

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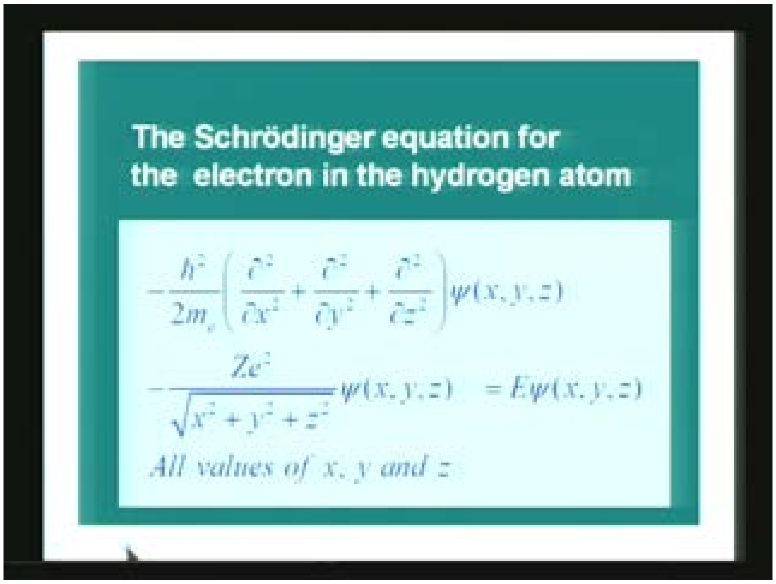

The Schrödinger equation for the electron in the hydrogen atom

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)$$

$$-\frac{Ze^2}{\sqrt{x^2+y^2+z^2}}\psi(x,y,z) \quad = E\psi(x,y,z)$$

All values of x, y and z

And the last, is of course the most important one for the chemist namely the Schrödinger equation for the electron in the hydrogen atom. The Bohr model if you recall you are used to drawing a circle with the electron on the circle and the proton in the middle and drawing the potential energy as the columbic interaction energy of the negatively charged electron and the positively charged proton. You recall that if the distance between the two is r, if you draw a circle, if the electron is on the circle and the proton is at middle of the circle and if distance between two is r. The proton has a charge + z the electron has the charge –e, z is 1 for a proton and for other nuclei depends on the number of protons you have. What is the columbic energy of attraction between these two electrically charged particles? It is $-ze^2/4\pi\varepsilon_0 r$ in classical electrodynamics in the si units. You must have remembered this from your electromagnetism in high school. So, this is the columbic attraction but the electron is of course is not stationary you remember from the Bohr model that it is moving around and the Bohr model introduces something like a planetary motion for the electrons.

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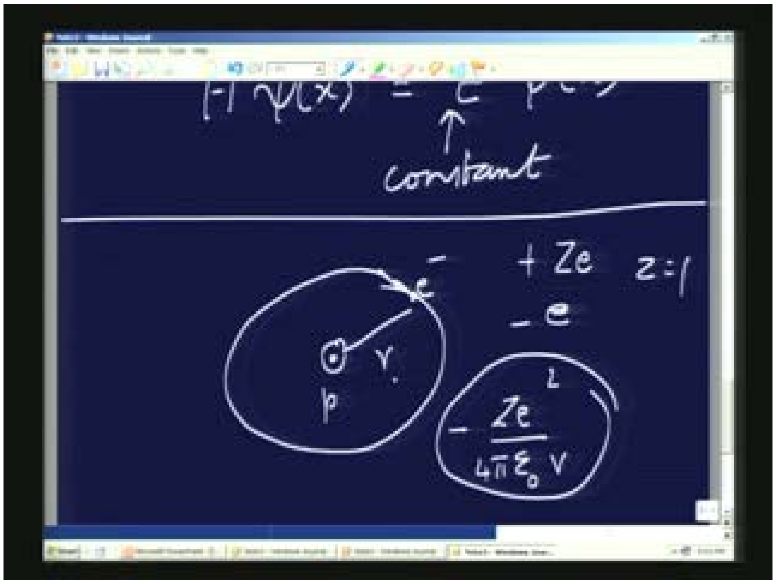

Bohr’s picture is also quantum mechanical in the sense that he was able to explain the line spectra of the hydrogen atoms through this planetary model. Now, we have the Schrödinger equation for the solution of the hydrogen atom which is hopefully much more general than the solution to the hydrogen atom that Bohr proposed and the potential energy for the hydrogen atom system is $-ze^2/4\pi\varepsilon_0 r$.

What is the kinetic energy? The kinetic energy is $p^2/2m$ again. But now, p is that since the electron is moving around in a three dimensional sphere with the proton in the middle. The momentum has three components in a three dimensional world the x, y, z components. And those components are written in such a way that you have the kinetic energy of the system given by $-\hbar^2/2m_e(\partial^2/\partial x^2+\partial^2/\partial y^2+\partial^2/\partial z^2)$. Now, this is the kinetic energy expression in mechanics. And $-ze^2/\sqrt{(x^2+y^2+z^2)}$ is the potential energy because you know the distance r is given in terms of the distance from the origin. If the origin is at the centre of the nucleus then it is $-ze^2/r$ so what you have is the potential energy given by $-ze^2/r$ hence it is H times ψ = E times ψ.

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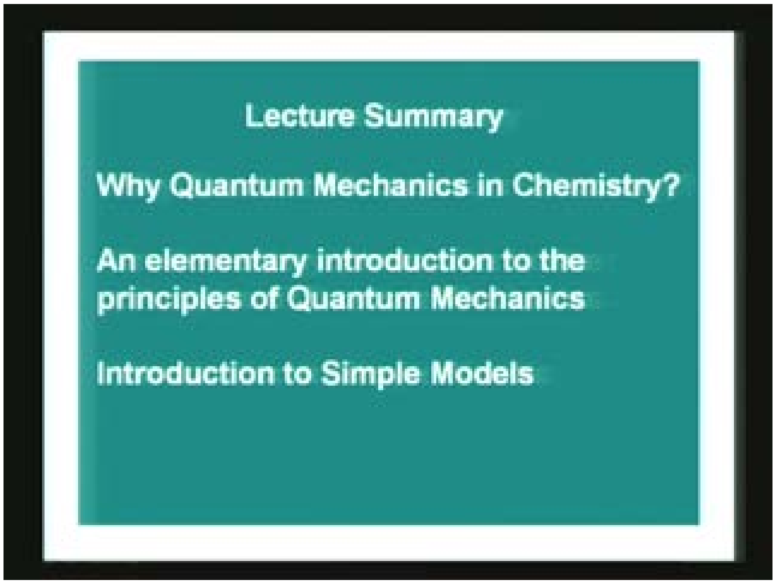

Lecture Summary

Why Quantum Mechanics in Chemistry?

An elementary introduction to the principles of Quantum Mechanics

Introduction to Simple Models

So let we summarize this lecture. We learnt about why we need Quantum Mechanics in Chemistry? We went through some explanations and then an elementary introduction to the principles of Quantum Mechanics. We also looked at the introduction of some simple models.