Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 1
Welcome

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

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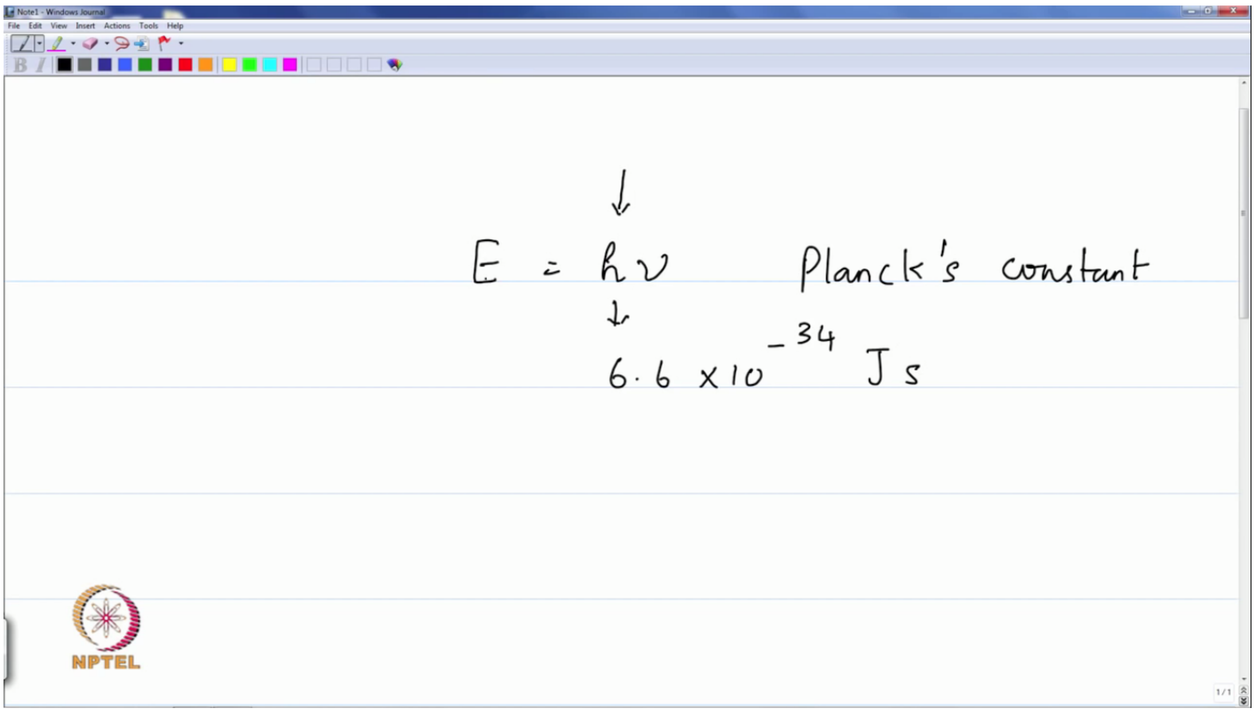
Welcome to this course. The first part of the course in chemistry which is interactively is on atomic structure and spectroscopy. What we will do in the limited period of this six to eight weeks is to introduce the basic theory and methods which are used to understand atomic and molecular structure and also to explain what we see in the experiment namely in spectroscopy.

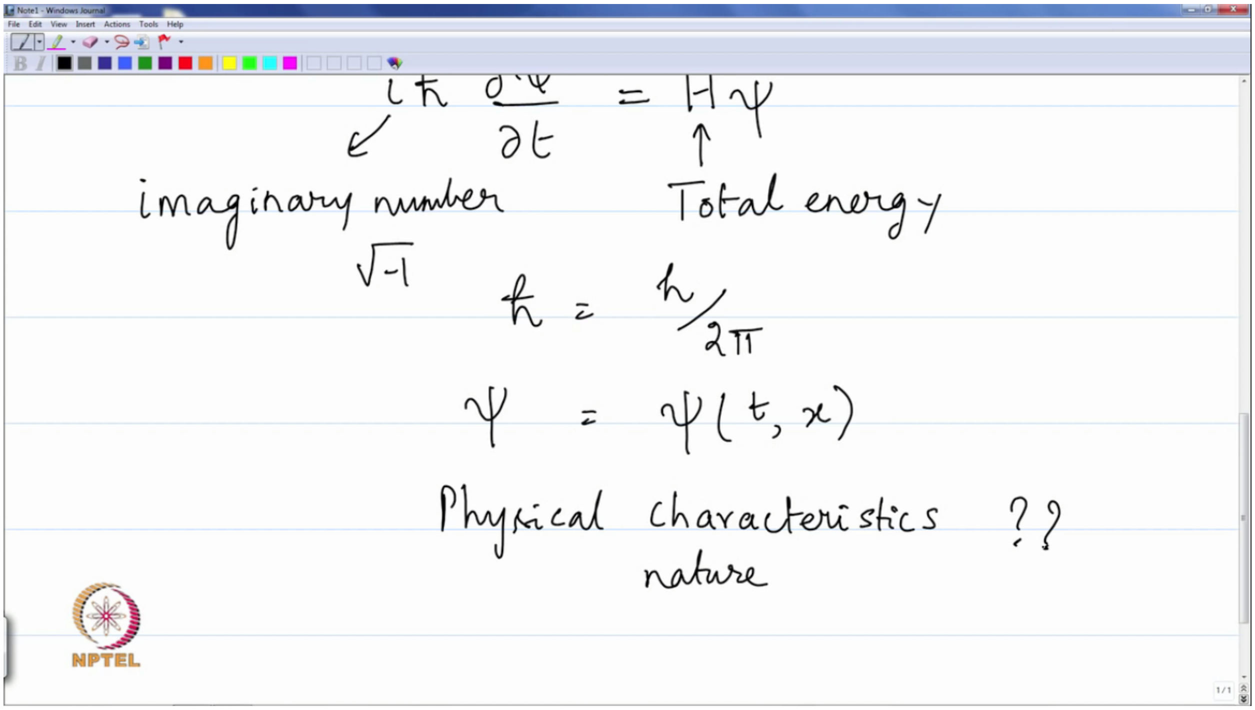
Spectroscopy is the interaction of radiation with matter and also provides the experimental tool and verification for all the things that we have understood so far in molecular and atomic quantum mechanics. Being an introductory course meant for the first or second year students entering the college I would keep the mathematics to a reasonably low level. However, I don't want to make any approximate statements as far as possible. I want to make the statements as quantitatively as I can and there are obviously exercises and assignments for you to practice that and then you can have this also discussed with your teachers in class in some sort of a reversed class mode to have the teachers interact with you and solve problems for you. The only way to learn the subject is by solving as many problems that is my learning by doing and I would very strongly recommend that you solve every problem that is proposed in this lecture series every assignment that is given and also if the in-class exercise which is provided along with the lectures.

The first introduction to quantum mechanics is something that needs a little bit of elaboration as to why it is important. Almost at the turn of the last century to be precise 1900 Max Planck came up with the hypothesis that energy emitted or absorbed by the material bodies does not happen in a continuous fashion but that it is emitted in packets, qantas and he came up with the famous formula for the energy in terms of the qantas and in terms of the frequency of light that gets emitted by the formula e is equal to h mu where mu is the frequency of the radiation that gets emitted or the radiation that is absorbed by the material bodies and he introduced a constant which was not known until then and call this as the Planck's constant. He didn't call it. All the others did since it was his fundamental contribution and he proposed the value somewhere around a 6.6 to 10 raised to minus 34 joule-seconds and since this is the energy and the frequency is per second the dimension of the constant or the Planck's constant is energy into time. There are other ways of decomposing these dimensions but after Planck introduced this I mean it wasn't something that everybody accepted it as is but they thought that with his prescription of the discretization of the transaction of energy by the material bodies he could explain at that point of time very satisfactorily what was known as the blackbody radiation phenomena which could not be explained by any classical mechanical methods.



Just about five years later it was Albert Einstein who threw in the next tantrum if I may say so, to the whole field of physics with his hypothesis that or his proposition that light itself consisted of packets of energy. If you recall elementary physics Newton many many years ago I mean hundreds of years ago proposed that light consists of corpuscles or particles particulate that was disputed later by Huygens and many others through the experiments of diffraction, interference and many well-established physical experiments and they proposed that light had to be wave. later the fact that light was wave was further generalized by Maxwell through his theory for electromagnetic radiation in which he considered light to be a part of the general field called the electromagnetic radiation in which electric and magnetic fields oscillate in time. So the property that light is a wave was well established for more than 200 years. But then Einstein in explaining the photoelectric effect of the emission of electrons by metals when light falls on the metals he came up with this proposal that light itself consists of packets of energy and he used exactly the same formula that Plank had except two that know I will put the subscript light and the packet of energy also is given by this formula that h mu where h was the Planck's constant which was introduced by Max Planck five years before that and mu is the frequency of light. So there was this difficulty that how can light be both wave and particle and this discussion continues for some time and it was Louis de Broglie who added some more light into this whole process of description namely that all material particles which are in motion can be ascribed with a wavelength in addition to a momentum which involves the mass and the mass is of course localized therefore all material particles which are localized while they are traveling when they are moving can be associated with a wavelength and he called it as the matter wave. In this process he introduced the wavelength lambda to be again involving the Planck's constant and the momentum of the particle this is for particles which travel not with the speed of light but much less than the speed of light which you can write as the mass times the velocity. So here is again the Planck's constant and this idea that particles in motion can actually be associated with a wavelength now brought into question by someone who would contribute to the most fundamental equation of matter for the next 100 years by Erwin Schroedinger. Schroedinger asked himself the question what these the dynamical equations governing such matter waves would be. Why this question because Newton and many others had described the planetary motion and the motion of macroscopic particles through their equations of motion, the dynamics in time that is how things change in time. That dynamics was unknown to Newton's equations of motion. Then the dynamics of electromagnetic radiation. I mean the properties of electromagnetic radiation were obviously described by Maxwell known as the theory of classical electromagnetic electromagnetism.

So there were theories for the time evolution of waves and the time evolution of particles but things which behave particle and wavelength is there a separate dynamical equation that will govern their evolution in time and Schrodinger came up with a proposal and an answer which became the most famous equation of the last century called the Schrodinger equation and I will write that out. The Schrodinger equation comes up with a function psi which is a function of time and a quantity called the Hamiltonian or the total energy of the system and it involves the imaginary number square root of -1 and h bar is again Planck's constant h divided by 2 pi. Schroedinger proposed to this equation as the equation that the matter waves would satisfy and he proposed the function psi as a property of the system and since it's the property which describes how the system evolves in time, psi itself is a function of time but in addition to time it is also a function of the position or the momentum but not both. The X here represents position in one dimension or one dimensional motion but if the motion happens in three dimensions it's a function of all the three positional coordinates of that system or the particle but if also a function of time. Schroedinger proposed the wave function and then the question was asked what does this wave function mean even he had difficulty explaining the physical property or the physical characteristics of the wave function or nature. What is it? In fact Schroedinger made the mistake.



His interpretation was proved to be wrong and later it was professor Max Born who came up with the correct interpretation that most of us accepted today that it's not the wave function which is important given that this equation is an equation containing you see this particular one that you have here. Let me highlight it. See this particular equation which has the total energy on one side and it has a wave function on the other side but it also contains the imaginary number and therefore it's possible that the wave function psi itself is imaginary or complex and if it is complex than we do not have a physical interpretation for the wave function itself but it was Max Born who said it's not the wave function psi but if the complex conjugate times the wave function itself the product. That can be interpreted through probability statements. It is associated with the probability of something. We will see all of this in this whole course. The entire course it would be, in the entire course it would be nice for me to actually solve the time-dependent equation but I'm not going to. I would limit myself to a much smaller subset of Schrodinger equation known as the time independent Schrodinger equation which is given by the symbol H let me write it with a different wave function psi as a constant times psi and this is time independent in the sense the Hamiltonian or the total energy associated with that system is not time dependent or it's time independent. If radiation interacts with matter for a brief time as we do in spectroscopy during the interaction period the system total energy is dependent on time because the radiation itself is an oscillating electric and magnetic field in some approximation in the wave approximation. Therefore, the Hamiltonian can in principle be dependent on time or we may introduce a force for a short period a changing force therefore the Hamiltonian which represents the total energy of the system may actually depend on time but we will not consider those cases we will consider those problems in this particular course of short 15 I mean two weeks or eight weeks or ten weeks period we would study only the time independent Schrodinger equation and this would be done with simple model problems in the entire course models and these models will later be associated with the chemical systems in order to give you the – I mean the feel for why chemists are interested in it.

I welcome you on to this course and I hope that you will enjoy the learning process in the next eight weeks or so but please do answer all the assignments please do attempt all the assignments please do answer all the questions which are discussed either in your class related to the subject or given to you for your own attempt. Without solving those problems you will not even be able to appreciate what all of this is about and I wish you all the best.

We will continue that in the next lecture. Thank you.