Approximate Methods in Quantum Chemistry
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Lecture 01
Topic – Review of Quantum Chemistry

Hello students, welcome to this lecture series on approximate methods in quantum chemistry. I am Sabyashachi Mishra from Department of Chemistry, IIT Kharagpur. In next several hours we are going to discuss different approximate methods and see how we can apply them in quantum chemistry. Before we discuss any further, let us try to understand what this course would entail.

Let us, start from the definition of the terms we are using in the name of this course. We have the term Quantum Chemistry. What is it? As you know that quantum chemistry is essentially application of quantum mechanics in chemistry related problems or in the chemical world. What do I mean, when I say chemistry related problems or chemical world? Whenever we deal with atoms, molecules, large molecules, including biomolecules, solid state systems, wherever there are atoms, interactions between atoms, formation of molecules, sharing of electron, bond formation, bond breaking, in all these places chemistry is very important.

And if you notice we are discussing about the formation of bond, the breaking of bond, the sharing of electrons. You all know that these are purely quantum mechanical phenomena. Therefore, to understand these processes we must use the principles of quantum mechanics. Whenever we use principles of quantum mechanics and apply to chemical systems (including biochemical systems, extended materials, etc.) we call that field as quantum chemistry.

What are the approximate methods in quantum chemistry? You would realize by now from your earlier experience with quantum chemistry that when we say that we want to solve a system quantum mechanically, we often have the following in mind. That we want to solve the Schrödinger equation corresponding to the system. The Schrödinger equation is given by, $H\psi = E\psi$. It is very easy to write down this equation, but it is very difficult to solve it. So much so, that we could solve only a handful of problems exactly. By exact solution, I mean that whether I can solve the Schrödinger equation and obtain the eigenvalues and the eigenfunctions in the closed analytical form.

There exist only a few very simple model systems that can be exactly solved. The largest or the most complicated system that we can exactly solve quantum mechanically happens to be hydrogen atom. But as you know, as students of chemistry, hydrogen atom is perhaps the simplest of all chemical systems! Because whenever we go for larger atoms, of course they are more complicated than hydrogen atom! Whenever we talk about a molecule, even a small diatomic molecule: that is also more complex than hydrogen atom. Hence, what quantum mechanics can solve exactly is, kind of, the starting point in chemistry!

We have come to this situation where we see that quantum mechanics is invaluable and essential to describe chemical features and chemical processes. But also, the solution of a chemical problem quantum mechanically is extremely difficult. When we cannot solve them exactly what do we do? When we cannot solve a problem exactly, we see if we can find an approximate solution to it. This is exactly what we were trying to do in this course. We are going to see what are these approximate methods using which we can solve chemical problems quantum mechanically.

The approximate methods that we are going to discuss in this course, we are going to use them for smaller systems, so that we can solve them reasonably well. But these very methods are robust enough to be used for even larger systems. We are not going to always solve the problems analytically, but we would also solve these systems numerically. When we solve a system numerically it becomes straight forward to extend this method to larger systems because in that case we simply require more computational power.

With increasing access to a powerful computer, we are now able to solve quantum chemical problems for large systems. For example, we are now studying enzyme catalysis, we are studying about reactions happening at extended surfaces and also, we are studying various types of organic and inorganic reactions: their reaction mechanism, thermodynamics, and kinetics using quantum chemistry. Hence, the materials that we are going to discuss in this course are going to be fundamental in that sense and they are all used in today’s real-life modern research in quantum chemistry. So, let us get started with the discussion of our course.

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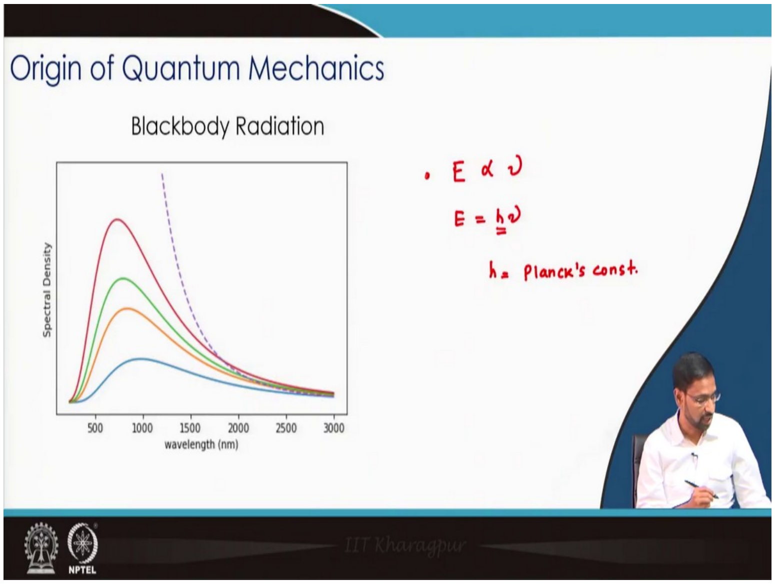

Origin of Quantum Mechanics

Blackbody Radiation

- $E \propto \nu$

$E = \underline{\underline{h}}\nu$

$h =$ Planck's const.

But before we look at the approximate methods, let us try to review those simple systems where we can solve the quantum mechanical problem exactly. In fact, before that, we also want to discuss about why was there even a need for quantum mechanics. So, briefly will go through the stories of origin of quantum mechanics. There are a few experiments at the end of the 19th century and the beginning of the 20th century that puzzled the physicist of that time.

The existing knowledge in classical physics was not sufficient to explain those experimental results. One such experiment is the so-called blackbody radiation. When you look at a body and identify it with its colour, what do we understand from there? We understand that if a body has a particular colour it means that when light falls on this particular body the body absorbs all colours except for the colour that it manifests, that colour gets reflected. That is the story of a normal body that we see. Blackbody is an ideal system which absorbs and emits all radiations or all colours. Now, when you heat black body and then observe the emission spectrum or the spectral density, which shows what wavelength do they emit by what amount, we obtain the curve shown in the above diagram. This plot shows the spectral density versus wavelength. Different curves that you see in this diagram represent the blackbody radiation at different temperature.

For example, the red curve has the maximum area under it and corresponds to the black body radiation at a very high temperature. As you lower the temperature, you see the green curve, the orange and the blue curve. You should notice that at lower temperature, the area under the curve is steadily decreasing. Now, this is what we obtain from the spectral density. Why is this so important? Because we can use this concept to see what kind of bodies should be used for energy harvesting, at what temperature should we heat the body and then look at its spectral density. because this also shows how much of energy the system is trying to release.

To understand this, Max Planck took up this problem and thought that he would like to explain as to what is happening to this black body radiation at different temperature. The existing knowledge at that time from classical physics showed the expected behaviour (shown as dashed line). As you can see, this dashed line is obtained from the Rayleigh-Jean's law, which suggests that the spectral density should be inversely proportional to the fourth power of the wavelength.

When you plot the Rayleigh-Jean's curve at different wavelengths it simply goes up with decreasing wavelength, and it never comes down, which creates a strange situation that goes by the name *ultraviolet catastrophe.* At higher wavelength the Rayleigh-Jean's law matches with the experimental outcomes, but as you go for lower wavelength (or higher energy), you will see that the discrepancy is huge and this leads to the strange situation which shows that the blackbody at any temperature can emit infinite amount of energy!

This problem was resolved by Max Planck. The key idea that Max Planck invoked here was that the blackbody is made up of some oscillators that absorb and emit radiations. Classical physics said that these oscillators can absorb and emit radiation in a continuous manner. That means it can take any energy along the spectrum. But what Max Planck invoked is that, the energy of these oscillators of blackbody are quantized, so they cannot absorb/emit *any* energy rather they absorb/emit *certain* values of energy. They absorb and emit a fixed amount of energy that gets decided by the prevailing temperature of the system.

He invoked that energy of these oscillators is proportional to the frequency of the radiation. Instead of considering the energy of the oscillator as a continuous function of wavelength or frequency, he used them as a discrete set of functions. In such a case, the algebra changes (from integration to discrete sum) and he could reproduce the experimental results. He used a proportionality constant between energy and oscillator frequency as h, and this h we know as Planck's constant.

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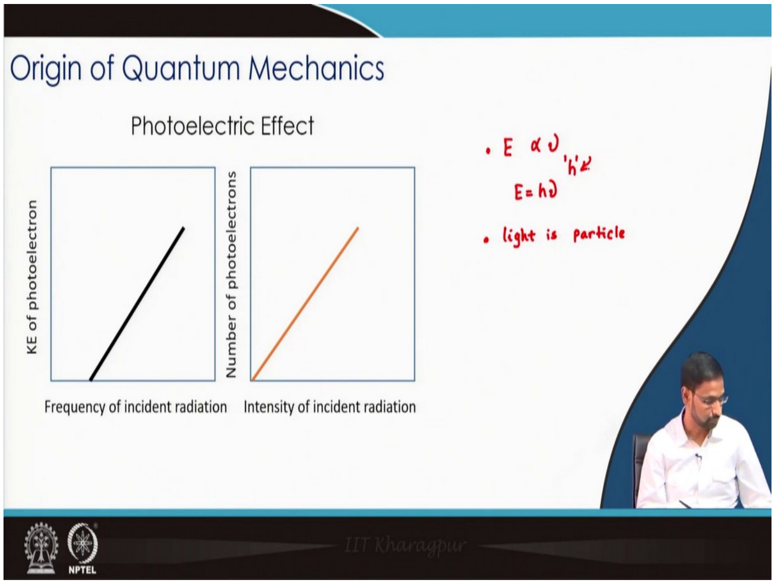

Origin of Quantum Mechanics

Photoelectric Effect

- $E \propto \nu$ 'h' ↙

  $E = h\nu$
- light is particle

Around the same time there was another experiment that was puzzling the scientists. That was the photoelectric effect. The photoelectric effect is a simple process where you shine radiation upon a metal surface and thereby the metal loses electron. This lost electron (the photoelectron) can be measured as current in a closed electric circuit. The results from the photoelectric effect experiments contained some anomalies. For example, when you plot the frequency of incident radiation in the x-axis and the kinetic energy of the emitted photoelectron in the y-axis, the experiment showed that there is a linear dependence of the kinetic energy of the photoelectron with the frequency of incident radiation. Not only that, it also showed that certain radiations (with certain values of frequency) were not able to emit any photoelectron no matter how strong or intense light was used. Some frequencies were simply unable to eject photoelectrons even if you use very high intensity light. But with some other frequencies, even when you are using a very low intensity light, those radiations could easily eject photoelectrons.

This was puzzling at that time. At that point of time it was thought that the energy of the light is determined from its intensity. It was expected that no matter which colour light you use, as long as you are using an intense light, you should see photoelectrons quickly. Also, you were expected to see the increase in kinetic energy of the photoelectrons with increasing intensity! But the experiments were not showing such result.

This is where Einstein comes into picture. Einstein proposes that we have to make some assumptions. First, the energy of the radiation is proportional to frequency (very similar to what Max Planck proposed in the blackbody radiation experiment). And again, by comparing the experimental result, this proportionality constant turned out to be the same h or Planck's constant as we saw in the blackbody radiation, i.e., $E = h\nu$. Now, where does the intensity come into picture? The intensity comes into this picture in the following way. Einstein proposed that when light falls on the matter, the energy absorption is not a continuous process, rather light of a particular colour contains a fixed amount of energy and he called them photon. The energy of these photons is determined from their frequency. Now, when you use high intensity light, you simply give increasing number of these photons. When you have a large number of these energy packets, each packet can eject one photoelectron. Einstein proposed that light, which we normally associate with a wave, is actually acting like a particle. As one particle - that is light - comes and hits the metal surface, another particle - that is electron - gets ejected. As if it is collision between two particles. Einstein's second proposal was that light which is typically known as a wave, has particle like nature.

Taken together, it means that for low frequency light, the energy of each packet is very low and this energy is not sufficient to eject even one electron. Therefore, even if you put 10,000 number of packets, since each packet is not able to eject an electron, 10,000 packets are also not going to eject even a single electron! That is why we see that even when we use high intensity for some low frequency light, we are not able to see any ejected photoelectron. Once we understand these two concepts (particle nature of light and the energy comes in fixed quantized values), the photoelectric effect experiments were easily explained. So, now we see two unrelated experiments hitting upon one constant h, which turns out to be a universal constant.

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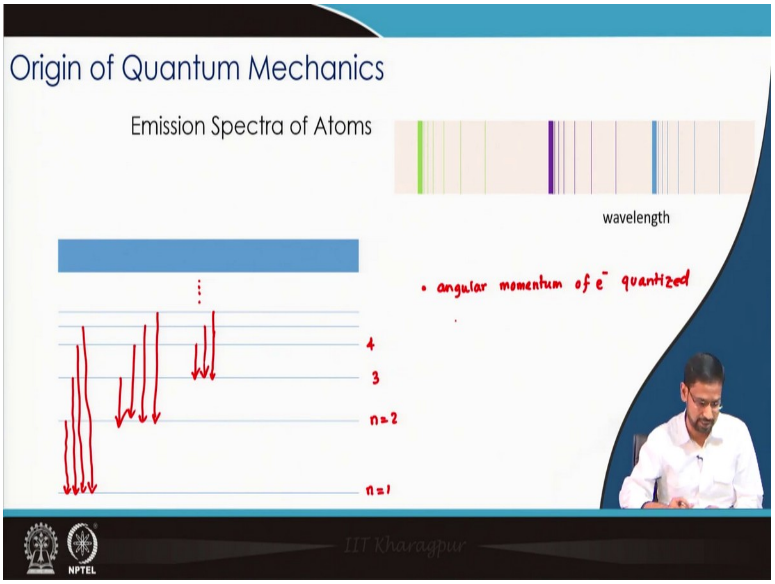

Origin of Quantum Mechanics

Emission Spectra of Atoms

- angular momentum of e^- quantized

Now, we go to another experiment which puzzled the scientists at that time and this relates to the emission spectra of atom. The picture that you see above is a cartoon representation of a typical emission spectrum of an atom where you see several discrete lines followed by a bunch of closely spaced lines looking like a continuum, then again, some separated lines followed by continuous lines and so on so forth.

For hydrogen atom when the emission spectra were recorded, the results were very puzzling. But as you know, Lyman, Balmer, Paschen etc. could fit a group of these lines by using some mathematical equations and finally Rydberg provided a single set of equations that could reproduce all these bands together for the hydrogen atoms emission spectrum. But this did not give us any physical insight. What was required was to understand what might be happening in the system when we record emission spectra so that we get this kind of features. This was given by Bohr in his Bohr's atomic model. In Bohr's atomic model, Bohr assumed *again* something to be quantized! Bohr proposed that the angular momentum of electrons is quantized. How does this angular momentum come in? In the Bohr's atomic model, you see that there is a central nucleus the electron go around the nucleus. Bohr suggested that the electron goes around the nucleus in fixed stationary orbits and while it moves around, the angular momentum is quantized (not continuous value, rather some discrete value of angular momentum is allowed).

Once Bohr made this assumption, and carried out some simple algebra of balancing of forces operating in the atom (these are small exercises I am sure you have done earlier), the Bohr's atomic model ends up with some discrete energy levels, with quantum numbers n = 1, 2, 3, …

After some discrete lines when you go sufficiently higher energy, the spacing between two neighbouring lines is very small. The emission spectrum is obtained when the electron jumps from one higher energy stationary orbit to a lower energy stationary orbit. From this energy difference, this model could reproduce different series, e.g., the Lyman series, Balmer series, Paschen series, etc. Hence, Bohr's atomic model could give a physical interpretation of Rydberg's formula. Of course, Bohr’s atomic model had its own shortcomings. But the success of Bohr's atomic model, in at least explaining the emission spectrum of hydrogen atom was primarily due to this interesting assumption that the angular momentum of electron is quantized and of course that also leads to the situation that the radius of the stationary orbits is also discrete. So, now again and again, we are experiencing that things are quantized! That was quite puzzling because we see that n = 1, 2, 3, …, as if these natural numbers are very important to mother nature! We always thought that human beings invented the natural numbers to count our sheep! We thought that they are no different from any other real number 1.1, 1.2 etc. But now here we see again and again that the systems, in its nature, in its various forms, various manifestations, use them. For the oscillators of blackbody radiation, the energy is quantized; energy of electromagnetic radiation is quantized; angular momentum is quantized. The quantization of many different observables are coming into picture. These are three ground breaking experiments that clearly exposed the limitation of classical physics as it existed back then.

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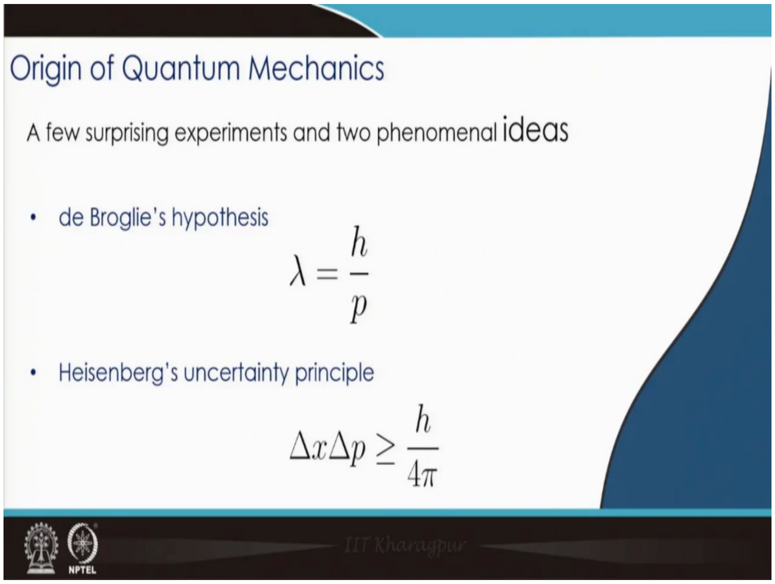

Origin of Quantum Mechanics

A few surprising experiments and two phenomenal ideas

- de Broglie's hypothesis

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

- Heisenberg's uncertainty principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

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Now, we will discuss that, apart from these three experiments, there are two great theoretical ideas, which are not really inspired by or compelled by experiment, but they were ideas of their own which were ground breaking and phenomenal.

The first of them is the so-called de Broglie's hypothesis. Remember, when we were discussing the photoelectron effect, we said that Einstein suggested that light which is regularly is typically believed as a wave has particle-like nature. Now, de Broglie, in his hypothesis, suggested that like light, any other particle that we see are of course particles, but they also have wave-like nature! That was very puzzling. That was against our intuition. de Broglie's was suggesting that these electrons, the nucleus, or even you extend it to classical world - everything that we see as a particle which has a mass, which is moving at a velocity v, therefore has got a momentum p = mv, has a wave-like nature.

Now, if all particles have wave-like nature, how do you explain that wave, how would you characterize that wave? The answer to that question is that, if a particle with mass m moving with speed v (or in other words has momentum p), it is associated with a wavelength (we call it as a de Broglie wavelength), which is given by $\lambda = h/p$, where h is *again* the Planck's constant. This was a great idea! de Broglie's hypothesis actually helped prove Bohr's atomic model even in a more systematic way.

But more importantly, now the wave particle duality gets a complete shape, Einstein's proposition was light which has both wave-like and particle-like nature. Now de Broglie's hypothesis is that any particle that we see has also a wave-like nature. Of course, when you look at the classical world, where the mass is very large, the momentum is also very large. Hence, lambda or the de Broglie’s wavelength is very small. For classical objects, the de Broglie is so small that it does not make sense to be called as a wave.

The second ground breaking idea was the Heisenberg's uncertainty principle, where Heisenberg suggested this great concept that you cannot simultaneously and precisely measure some quantities. For example, position and momentum. We will discuss about the mathematical argument behind this. In short, Heisenberg's uncertainty principle said that if you want to determine the position of a particle precisely, you have to give away your right to know the momentum of the particle exactly. Thus, simultaneous and precise determination of position and momentum is forbidden! It is not an experimental limitation, so that one day someone would build a better machine with which you can determine the position and momentum of the particle simultaneously and precisely! It is inherent nature of the quantum mechanical systems that position and momentum cannot be simultaneously and precisely determined. They would have to follow a minimum uncertainty.

This minimum uncertainty is given by this $h/4\pi$. The uncertainty has to be always greater than this value. You can easily imagine this. Because when you try to locate a particular particle in space, you would probe it with a certain light with certain wavelength and the wavelength of that light with which you are probing the position of the particle must be very small, so that you can locate the particle precisely. But when you make the wavelength of the probe very small the momentum of that light, which also has a particle-like nature according to de Broglie's hypothesis, will be very large. This particle which has a large momentum when it goes and interacts with the particle whose position you are trying to determine, there would be a transfer of momentum. This transport of momentum will simply change the momentum of the particle that you are initially trying to find the position of. So, therefore if you want to precisely determine the position there will be an uncertainty in momentum, because the very act of measurement of the position will compromise the momentum of the particle.

The three experiments: the blackbody radiation, photoelectric effect, the emission spectra atoms plus these two ground breaking ideas: the de Broglie’s hypothesis and the Heisenberg's uncertainty principle, exposed the limitations of classical physics. Then there was a need of a new mechanics and that is how quantum mechanics originated. With the growth of quantum mechanics, how we have come forward, that is the story that we would continue in our next lecture. Thank you for your attention.