**Quantum Chemistry of Atoms and Molecules**
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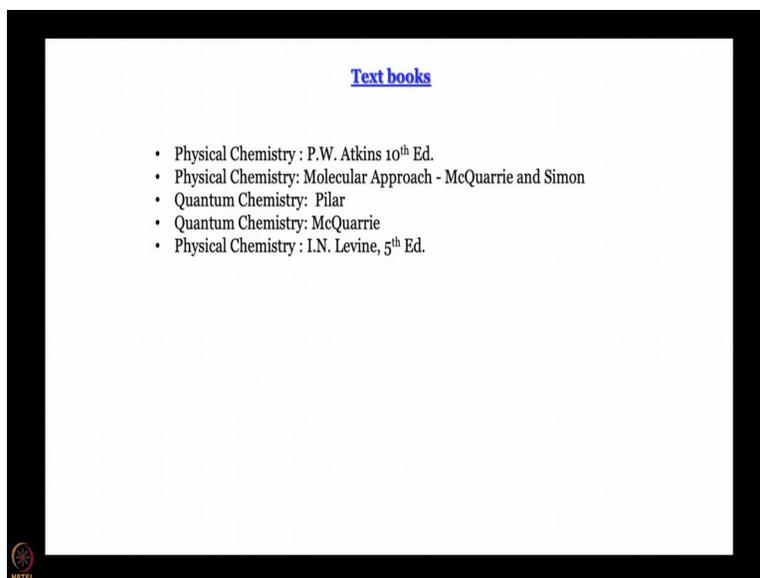
Lecture-1
Basic Introduction

Hello, welcome to the course on quantum chemistry of atoms and molecules. Before getting into the course contents and what we will discuss and what the textbooks will be. Let me first put credit where it is due. This course has developed over many years we teach most of this as our first-year course which is now called Ch107 in IIT Bombay and many people have contributed to this course.

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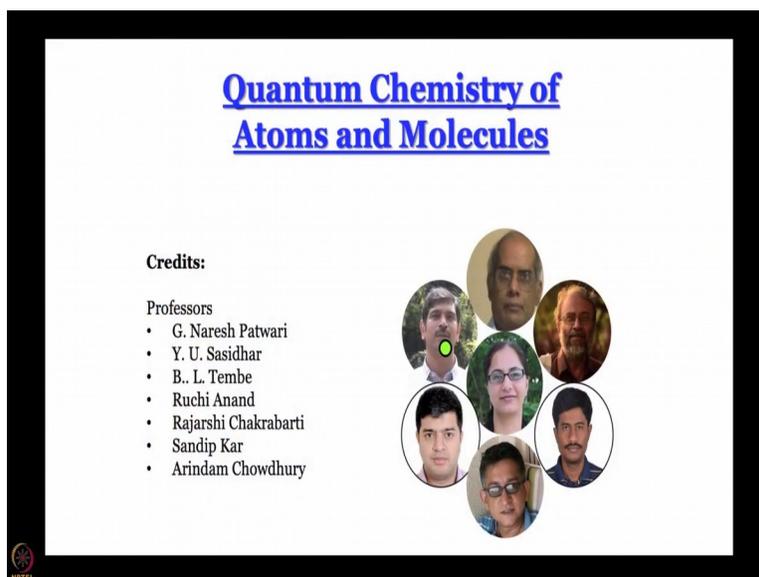
The basic slides here are actually made by professor Naresh Patwari and others like professor Sasidhar, professor Tembe, professor Ruchi Anand, professor Rajarshi Chakrabarti, professor Arindam Chowdhury and professor Sandip Kar have contributed immensely over the times for development of this course content. Let me start with expression of gratitude for all of them. Next let me tell you what the textbooks are going to be.

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Text books

- Physical Chemistry : P.W. Atkins 10th Ed.
- Physical Chemistry: Molecular Approach - McQuarrie and Simon
- Quantum Chemistry: Pilar
- Quantum Chemistry: McQuarrie
- Physical Chemistry : I.N. Levine, 5th Ed.

For this course to start with we are going to use material from textbooks on physical chemistry by P. W. Atkins and that by Macquarie and Simon. Later on as we go little deeper into the course we are going to use quantum chemistry by Pilar and quantum chemistry by McQuarrie. Occasionally you might have to refer to physical chemistry by I. N. Levine. In case we refer to any other book I will give you the specific reference.

Now what is this course all about this course is about something that has been asked for a very, very long time but before getting there one question that especially chemistry students often ask when they are offered a course like this is do I need to know math? And the answer is yes. Because after all quantum chemistry quantum mechanics these are based on mathematics, mathematics is the backbone of science.

But then the mathematics that we need is not something that is of very high level. Mostly class 11th, 12th level mathematics is sufficient. And for those who may not have exposure to even that level of mathematics we will develop tools as we go along. But to be a very brief idea we will need to know algebra.

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Do I need to know any Math?

Algebra

$A[c_1 f_1(x) + c_2 f_2(x)] = c_1 A f_1(x) + c_2 A f_2(x)$

Trigonometry

$Sin(kx) \quad Cos(kx) \quad e^{ikx}$

Differentiation

$\dfrac{d}{dx} \quad \dfrac{d^2}{dx^2} \quad \dfrac{\partial}{\partial x} \quad \dfrac{\partial^2}{\partial x^2}$

Integration

$\int e^{ikx} dx \quad \int_a^b f(x) dx$

Differential equations

$\dfrac{\partial^2 f(x)}{\partial x^2} + \dfrac{\partial^2 f(y)}{\partial y^2} + \dfrac{\partial f(x)}{\partial x} + \dfrac{\partial f(y)}{\partial y} + m f(x) + n f(y) = k$

And we need to know a little bit of operator algebra. As you will see we are going to work with linear operators all the time they are the main tool of quantum mechanics and then we need a little bit of trigonometry we will need you to know what is sine kx, cos kx ie to the power ikx. What is the relationship between them? We will need to do basic differentiation at times we will need to do partial differentiation.

A little bit of integration not much and quantum mechanics is actually based or at least the version of quantum mechanics that we are going to talk about is based on a differential equation. So, differential equation is something that will be very, very useful for us. But then once again for those who may not have too much of preparation in mathematics there is nothing to worry this course is really meant for at least at the beginning for first-year B.Sc students.

And whatever mathematics is required one can learn or we are going to develop as we go along. Now let us come to the question that we had proposed a couple of minutes ago what is the course about.

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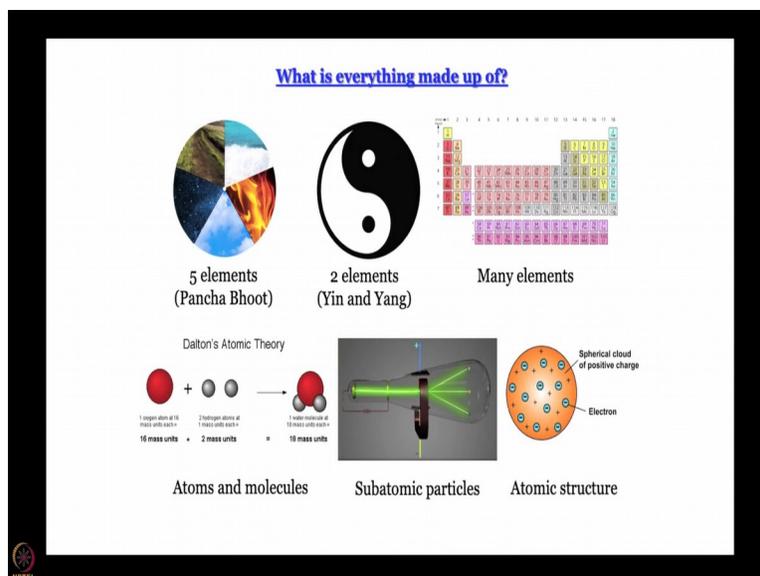
The course is about addressing a question that mankind has asked over millennia, throughout civilizations and that question is something that even a child asks and that is what is everything made up of? What am I made up of? What is the Chair, table, computer, you what is all this made up of? And humankind over 100s and 1000s of years have tried to find answer to this very basic question in different ways.

In ancient India the answer was everything is made up of 5 elements pancha bhoot as we call them. In ancient China it was believed that everything is made up of two elements yin and yang. What is Yin and Yang? Two opposing forces up and down, man and woman, good and bad and so on and so forth but they believed is that synthesis or coming together of two opposing forces makes everything up.

Now that is rather a philosophical way of looking at things but if you think even in our modern way 5 elements and 2 elements are things that make sense but then our knowledge has progressed from there and we know that it is not really 5 or 2 as far as chemistry is concerned there are many elements. There are many substances which are elemental and they come together to form more complicated compounds that forms the basis of chemistry.

There are many elements and at this stage we all know that they can be arranged in a periodic table and one can even predict properties of elements that by looking at this periodic table. There

was a point of time when properties or even undiscovered elements have been predicted using this periodic table but that is one side of the story. The second part of the story is that people asked what happens in fact this answer of 5 elements and 2 elements came from there.

Okay we have a chemical element we have hydrogen let us say or we have oxygen or we have nitrogen. We start breaking them up or maybe it is easier to understand if I take a solid. Let us say I have elemental sodium I start cutting up this piece of sodium into smaller and smaller pieces and let us say that I have the power of going down to a small size as possible. What will happen? Do I keep going until there is nothing or do I stop at some level, do I stop at some particle that cannot be divided further?

Answer to this question was also there in ancient Indian science Kananth for example had proposed that there is a smallest indivisible form of element which in ancient India in Sanskrit was called kana. Later on in more modern times they were called atoms and we have all studied Dalton's atomic theory when we were in class 7-8 something. So, atoms are supposed to be the smallest entity beyond which you cannot divide further that was the understanding until Dalton's time.

But then towards the end of 19th century new discoveries were made as we know, cathode rays and anode rays were discovered. And they were found to be charged and in fact cathode rays and anode rays were found to be positive oppositely charged. Later on neutrons were discovered. So, the understanding that developed was that atoms are not the smallest indivisible units after all one could divide atoms and one could get what are called sub atomic particles.

At that time this concept of electron, proton later on Neutron came into being and then the question that arose is that inside an atom how about this subatomic particles arranged? And there were several disparate attempts to explain what the arrangement within an atom is. One of these models that survived for some time was by J.J. Thomson is called the plum pudding model. Thomson proposed that this is your atom in this we have this delocalize charge of one kind and you have the opposite charge embedded in it like seeds of pumpkin or like plum in plum cake.

But of course this could not have been a realistic model because what this model proposes is that you have positively charged and negatively charged particles in close contact. And all of us know what happens if you take a copper wire and touch one end to the positive end of a cell and touch another end to the negative end, there is shorting right and this annihilation. So, if you have this positively charged and negatively; if you have this positive and negatively charged particles in close proximity then they are going to annihilate each other, so this model did not survive the test of time.

The first plausible model of atom was proposed by Ernest Rutherford and the way Rutherford model came into being is rather interesting and instructive for students and teachers alike. So, the way it happened is that Rutherford was already a well-known scientist and in his lab came this new student named Marsden. And in any lab when a new student comes we usually give them experiments not with the purpose of making a new discovery but with the purpose of getting the acquainted with how to do experiments in the lab.

So Rutherford gave similar such experiment to Marsden and the purpose was to get his fingers wet. Alpha particles were discovered by the time and it was known that there are highly energetic particles.

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So, Rutherford handed Marsden a chamber of this kind and said that why do not you keep this alpha particle in the center and keep a gold foil and see how the alpha particles pass through the gold foil. Now while doing this experiment the idea was that a gold foil is something that is very thin. So, if you should alpha particles that are highly energetic and the gold foil then everything is expected to go through.

So Marsden's job was essentially to place a photographic plate as is shown in this cartoon he placed it all around and what he saw is that most of the alpha particles got through and that was evident in forming the spots on the photographic film in this region. Few of them got scattered to the right or to the left and most surprisingly one out of 20,000 turned right back almost 180 degrees almost reflected, one out of 20,000.

Herein lies the courage of Marsden more often than not when a student gets an unusual result like this and to say to point out how unusual this result is let me quote something that some were well-known scientists had said at that point of time. It was said that it was almost as if you shot a cannon shell at a tissue paper and it came back and hit you that is how surprising the result is and then the number was 1 in 20,000.

So, it is it was Marsden courage to have not neglected this seemingly negligible result. He walked up to the Rutherford and reported what he saw that was his courage. And it was Rutherford's greatness that he did not hand wave this new students results away saying it is just a freak observation, Rutherford took it seriously. And then after repeating the experiment many times and after putting in a lot of thought the model of Rutherford were proposed and that model was fashioned after the planetary model.

We all know that planets go around a star Rutherford proposed that similarly what you have is the analogy to the star here is the positive charge and mass. He said that first of all most of the atom is empty that is why the most of the alpha particles go through straight and he said that. Since this one in 20,000 alpha particles actually turn back most of the mass and all of the positive charge is located in a central position like the star.

And then the electron is somewhere in the void outside and now the issue is that once again if you have a static nucleus with all the positive charge and you have static electron with a negatively charge then the electron is going to go and fall on the nucleus and is going to get annihilated then we no charge anymore. To account for that Rutherford proposed that like planets go around the Sun the electrons are also going around the Sun.

And the advantage of that is that the electrostatic attraction of the electron for the nucleus can be exactly offset by the centrifugal force that would act on an electron going around in a circular orbit so that was Rutherford model, so, electrons going around. But then this model had several shortcomings and the biggest shortcoming was that in classical physics it was known that a charged particle in motion is expected to emit its energy continually that gives rise to two problems.

One problem we are going to come to a little later first problem there is that if energy is emitted continually then you expect the emission spectrum of any element of compound to be continuous but it is not as we are going to show you, one is line spectra. More important issue with this model is that if the electron keeps on losing its energy continually then what will happen is that continually it will get slowed down, so centrifugal force will decrease, electrostatic force remains the same.
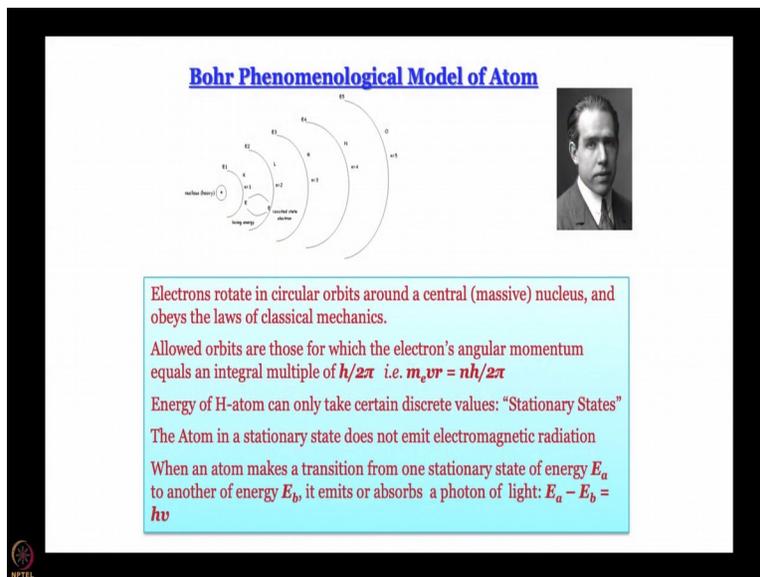
So if you keep getting closer and closer and closer to the nucleus and is going to spiral into the nucleus and once again there is going to be annihilation. And the time required for the spiraling can actually be calculated and it turns out to be about 10 to the power -12 seconds because again so that this is the major problem that you do not get a stable atom. If atoms live only for Pico seconds again then it is impossible for me to complete this half-an-hour module because atoms not exist for more than Pico seconds.

Again it is impossible for you to sit through this lecture because you would not exist for more than a Pico second so this is not a happy situation and obviously it cannot be correct. But then there was no explanation in classical theory which could circumvent this problem. So, it required the courage and foresight of Niels Bohr to propose a model that was better than Rutherford

model. Remember Bohr model is essentially; Bohr model takes Rutherford model as a starting point.

It is not as if Rutherford model is completely thrown in the sea and Bohr model comes in and it is not. Bohr model also works with circular orbits the only difference is that more remember is a phenomenological model.

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It is a model that was proposed to explain experimental results and this model involves the electron residing in certain orbits. So, what Bohr said essentially is that the electron can rotate in circular orbits only for certain values of radius well he put actually put it in a different way. He said that only those orbits are allowed where mvr equal to nh by 2pi angular momentum is quantized and it is an integral multiple of h by 2 pi of where h is Planck's constant.

What is Planck's constant we will come to that in a minute and from there we will come back to Bohr model.

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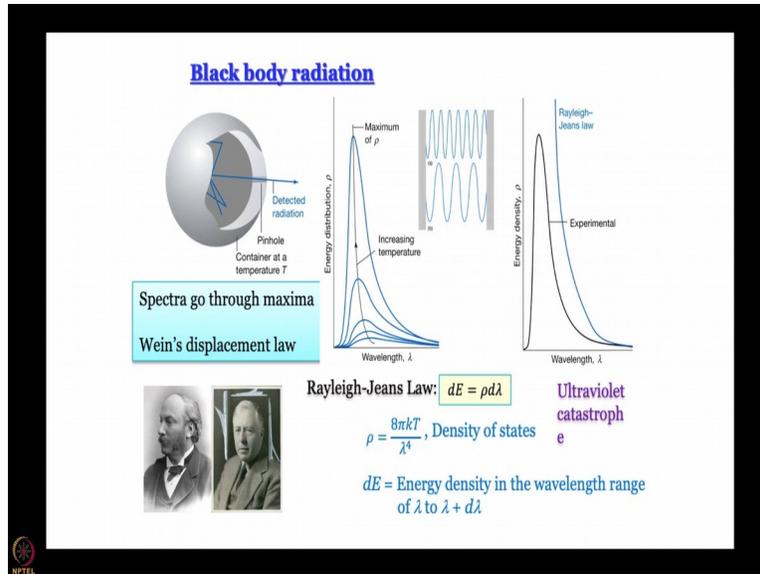
Well, to get to Planck's constant and to understand this whole quantization business one needs to look back at the end of 19th century once again and that was the time when well shortly before that time everybody thought that whatever is to be discovered in physics is discovered because Newtonian model sort of explained everything in the macro scale and everything was known things for the hunky-dory. However towards the end of 19th century indications started coming that when you try to go down to atomic or molecular level Newtonian mechanics does not really work all that well.

And there are many examples one example that we are not going to discuss in this course is Einstein's treatment of heat capacity. We, I am sure all of us have studied Dulong and Petit treatment then when Einstein looked at it then again quantization had to be invoked will not get into that we will try and restrict our discussion here to spectroscopy and to atomic structure molecular structures so on and so forth.

So, one thing that will refer to is once again something that has been introduced in class 11 physics blackbody radiation. What is a blackbody? A blackbody is something that absorbs all the energy that impinges on it and in an ideal blackbody what we have is you have an aperture through which the radiation can leak out a little bit. So, you heat the blackbody and you look at the radiation coming out of it that is seemingly a very, very simple experiment, well seemingly simple but with profound implications as we will see.

So, if one looks at the emission of the blackbody as a function of wavelength. So, if you plot intensity versus wavelength or distribution versus wavelength for example then we get an emission spectrum. And the emission spectrum of blackbody looks like this what you should see here is emission spectra at different temperatures. So, first point to note is that this is all the spectra go through a maximum.

Okay of course as you heat as you increase the temperature the intensity becomes more and more and more. You are heating means you are supplying energy. So, more energy is supplied to the body more it will emit if you do not supply any energy any energy if temperature is absolute zero or something you do not expect the blackbody to radiate anything because unless energy supplied what will it radiate. So, first one to notice spectra go through a Maxima for every temperature there is a characteristic maximal characteristic wavelength or frequency where maximum distribution or maximum intensity is obtained.

And then Wiens displacement law once again I am sure all of us have studied in class 11 physics means this weins displacement law say is that this maximum moves to higher energies as the temperature is increased there is a mathematical relationship which is not really of relevance to our us in this course so I am not going to write it weins displacement law is, what it is. Now this is the experimental observation.

To explain this there are lot of attempt to come up with theoretical models that can explain why blackbody radiation goes through a maximum and why is it that goes that the maximum moves to higher frequencies at higher temperature. Numerous attempts were made using classical physics everything failed. So, we are going to discuss a model that came close but did not succeed finally and that model is proposed by Rayleigh and Jeans Lord Rayleigh and Sir John Jeans.

So what Rayleigh and Jeans did is that they considered this oscillation of electromagnetic field within the cavity of the blackbody. This oscillation can take place with several frequencies. What they did is, they did a classical mechanical treatment and came up with this kind of a law where

dE equal to Rho d lambda, Rho is a proportionality constant Rho is actually what is called density of states and is given by the formula in Rayleigh and Jeans model 8 pi kt divided by lambda to the power 4 dE is the energy density in the wavelength range of lambda to plus d lambda.

Now the problem is this, this Rho is what you have on the y-axis of the experimental spectra and if you look at the expression for Rho it has lambda to the power 4 in the denominator. So, what happens at what happens as lambda becomes smaller and smaller Rho becomes larger and larger and larger and larger, it does not go through a maximum. So, the problem is in using Rayleigh and Jeans model one can actually get a good match at longer wavelengths.

But for shorter wavelengths the mismatch starts creeping in and it keeps getting larger and larger and larger as we go to smaller wavelengths that is higher energies. And in the ultraviolet region there is a very big mismatch between the theoretical prediction of Rayleigh Jeans model and the experimental observation. This goes by the name of ultraviolet catastrophe, it completely breaks down in the UV region.

To address this problem Max Planck tried a different approach we are not going to do any of these derivations here because it is derivations generally are done in quantum physics courses not very difficult if you go through any of basic physics or quantum chemistry, quantum mechanics book one can understand without much difficulty because it is explained nicely.

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So, Max Planck came up with this distribution where Rho is equal to 8 pi hc divided by lambda to the power 5 multiplied by e to the power hc by lambda kT − 1. To arrive at this distribution he had to make an assumption. He showed that this is only going to happen when energy is quantized E equal to n h nu where nu is a frequency of light, h is a constant named after Planck and n is a whole number positive or not well 0 1 2.

Where did this quantization come from? It was a assumed so this is really one of the beginnings of quantum mechanics. And the reason why Planck's distribution is a great thing is that; well let us see what happens to it when we work in long wavelength regime. For long wavelength one can assume that e to the power hc by lambda kT is going to be much, much smaller than 1. In that case one can write e to the power hc by lambda kT as 1 + hc by lambda kT once again this is something that we learned in class 11 & 12 math.

So what happens well what is there in the denominator in the denominator we have this exponential term -1, so let us subtract 1 from both sides what do we get we get hc by lambda kT so this entire exponential term becomes hc by lambda kT you multiply it by lambda to the power 5 what do you get you get Rho equal to 8 pi kT divided by lambda by lambda to the power 4 same expression as what we saw in Rayleigh Jeans distribution.

And remember Rayleigh Jeans distribution works well for long wavelength. So, in long wavelength Planck's distribution is the same as Rayleigh Jeans distribution and things are good but more importantly at short wavelength e to the power hc by lambda kT has to be much, much larger than 1 what happens then it is a large number. So, if you go to short enough wavelength then this denominator is going to be huge close to infinity and Rho is going to become 0.

So what I am saying is that this Planck's distribution actually goes through a maximum and becomes 0 at very high frequency and you look at this distribution and the experimental spectrum at a given temperature they match perfectly that is why Planck's distribution is widely accepted. And this attempt of Planck, what was Planck goal? Planck's goal was simply to get a distribution that can explain blackbody radiation.

While doing so two important things came up first is, we get to learn that at atomic and molecular level energy is quantized. We get to know what Planck's constant is and as we will see over the course Planck's constant is a fundamental constant that we use all the time in quantum mechanics. And the other important thing is an Indian scientist Professor S. N. Bose; if you know this life story of S. N. Bose he was very good in mathematics.

And in his childhood he once scored 110 out of 100 because not only had he solved all the problems correctly he had solved them in many different ways and the teacher felt that he deserves more credit for that. So, solving a problem in many different ways was his forte and that is exactly what he did with Planck's derivation. Bose tried to derive Planck's law in a different way and in doing so he arrived at something that gave rise to something that is much more profound and that is called Bose Einstein statistics.

As most of us would know Bose is the only Indian scientist after a fundamental class of particles is named bosons. We have bosons and your fermions. So, what we have discussed in this introductory module is the early days the early dawn of quantum mechanics where many discoveries were made great minds were sort of grouping in the dark and they were finding treasure that was yet unknown to humankind which we are going to have profound implication in

the years to come. So, we stop here now and in the next module we are to talk about atomic spectra.