Concepts of Chemistry for Engineering
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Lecture No. 01
Introduction to quantum theory

Welcome to the basic science course in chemistry. I am Anindya Dutta, Department of Chemistry, IIT Bombay. And I and my colleagues are delighted to be a part of this initiative, which we sincerely hope will prove to be highly beneficial for first year undergrad undergraduate students across the country.

So, in this course, we are going to take you through some rudiments of chemistry that you have studied to some extent in eleventh, twelfth perhaps, but now, we will try to answer questions that might have come to your mind while studying this in school and this is something that is going to prepare the field for further studies no matter which branch of engineering or science you are in at the moment. We will start our discussion with atomic structure. But before that, let me give credit to our institute.

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In my part, most of the things that we are going to talk about come from this course that we teach to our first year undergraduate B. Tech and BA students. It is called CH107 physical chemistry, but it is by and large about quantum chemistry. Now, this course has developed over many, many years, with a lot of contribution from many different people, the ones that you see now on your screen. So, a lot of effort has gone in to build the contents. And that is what has given the course the shape it now is in.

So, let me begin with a word of thanks to all these colleagues of mine, and also to the students, the teaching assistants, who have participated in this course. And the students who we have taught many of the things that we are going to discuss today have actually add as in out of our attempts to answer the questions asked by our students, and then we felt that this should be taught. So, that is how we learn together. It is not as if it is one-way traffic.

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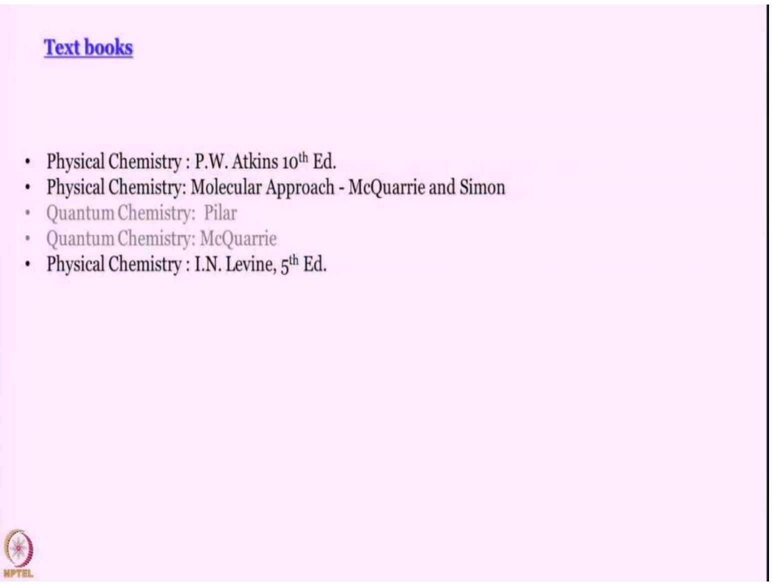

With that very, very brief forward, let us now say that what your textbooks are going to be. You already have a textbook given to you. But in addition to that, I would like to recommend physical chemistry by I.N. Levine; McQuarrie and Simon is, in my opinion, the best book in this genre, if you want to study physical chemistry a little more detail, and we will not have to refer to Pilar and McQuarrie too much in this course.

This is, these are only as reference books for those who want to learn a little more beyond this course, we sincerely hope that we will be able to rouse the curiosity among some of you, so that you will want to know more about quantum chemistry for them, Pilar and McQuarrie's quantum chemistry books are recommended.

Another book that I find, two books that I find to be very useful are Quantum Chemistry by Prasad and Quantum Chemistry by A.K. Chandra. In fact, the first book I studied on quantum chemistry was the one by A.K. Chandra when I was a student.

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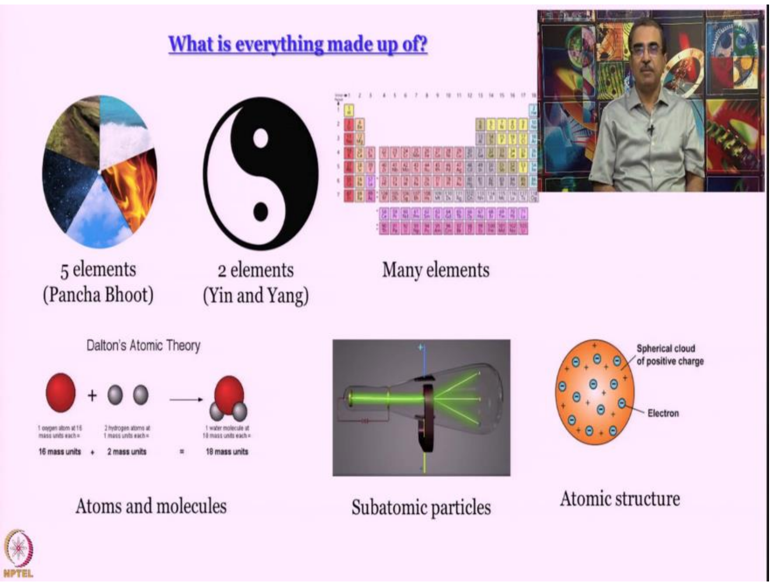

So, the question that we try to answer in this part of the course, is something that mankind has asked forever. And the question is, what is everything made up off? In our ancient Indian culture, it was felt, it was thought, it was believed that everything is made up of 5 elements or Pancha Bhoot that most of us would know about. Little philosophical way of answering this question, but actually makes sense. If you think of it in a qualitative manner, Pancha Bhoot is perhaps the best explanation that could have come at that time.

In ancient Chinese civilization, everything was believed to be made up of two opposing forces, Yin and Yang, good and bad, up and down, so on and so forth. Even that does make sense even today, as we come to the modern understanding of structure of an atom, you will see that there are two completely opposite things that apply there, apply there. Of course, with advent of time by that, by now, all of us know that it is not 5 elements or 2 elements, but in chemistry, we have many elements, 108, 118 what is the current number? I leave that to you to find out.

And in high school, I think we have all studied this periodic table, which is a nice systematic arrangement of all these elements that allow us to sort of rationalize their properties to a very great extent. But then, a question does not stop there. Element fine, let us take any one element, let us take iron or let us take hydrogen or whatever. Suppose I take a piece of iron and suppose we keep breaking it down, make smaller and smaller and smaller pieces. The question is, do I stop somewhere or can I keep on making smaller, smaller pieces?

Again, in ancient Indian civilization, an answer to this was provided by a scholar whose name is believed to be Kanada. And Kanada actually had said that everything is made up of things like ‘anu’ small fundamental particles. And that was resonated much later in Dalton's atomic theory that all of us would have studied in class 8 or something, that everything is made up of atoms. So hence, we go to the concept of atoms and molecules. But a question does not stop there.

So, the question that was there is, Dalton thought atoms are indivisible, are they really indivisible? As we know, that, towards the end of nineteenth century, by many experiments like this, a cathode ray experiment, the existence of sub atomic particles were established. So, they were called electrons. And then of course, if something that is negatively charged is present in an atom, it has to be balanced Yin and Yang, remember? It has to be balanced by something that is positively charged. So, protons and eventually, neutrons were discovered as well.

So, the next question was, how were all these subatomic particles arranged in the atom? Again, many attempts were made to answer this question. One of them had, that had some prominence, had some prominence was this Thompson's plum pudding model, where it was believed that the positive charge is delocalized over the atom, and the negative charge is embedded in this cloud, spherical cloud of positive charges.

Well, this did not hold water, because I mean, why would that happen? Why do we not get annihilation? But even this uses idea of delocalized charge we are saying spherical cloud of positive charge. So, this charge cloud is something that we go back to, eventually, we will come to that, but all this mostly was a philosophical discussion, except for this periodic table subatomic particles, Dalton’s Atomic Theory, those these things.

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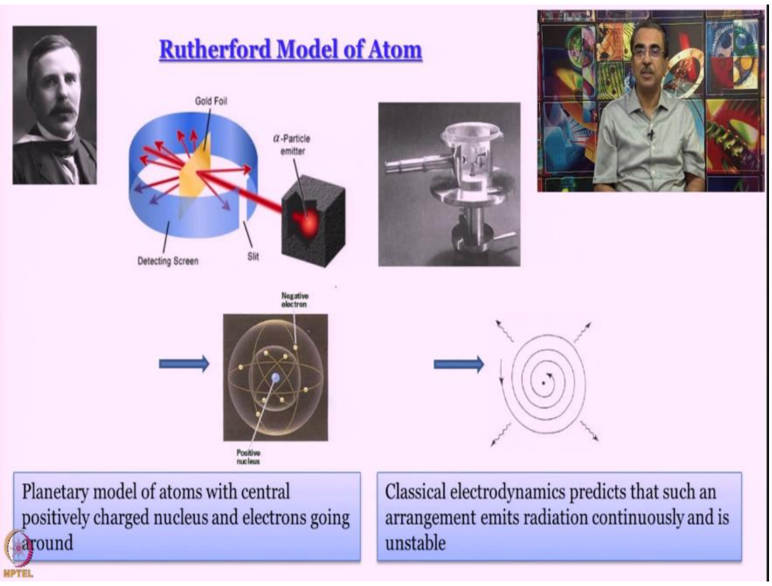

The first very, very important experiment, in my opinion, that came towards unraveling the structure within an atom was performed by a student of Rutherford actually, his name was Marsden. The experiment that was formed that was performed was at that time alpha particles had been discovered already and it was known that they were very highly energetic particles.

So, Rutherford asked Marsden to do the simple experiment, take an alpha particle emitter, keep a gold foil in front of it, and then see how many alpha particles go through straight and try to see whether there is any deviation in the path of the alpha particles. How would you know if alpha particles go straight or they bend? A photographic film was placed in this circular manner and this kind of a chamber is what was actually used for the experiment.

So, the alpha particle emitter would be here, gold foil would be here and in this empty place, the photographic film would be placed. In fact, this kind of chambers are used for modern experiments even now. So, it was expected that everything would go through straight, because alpha particles are so very highly energetic and gold foil is so thin.

And the observation was that it is true that most of them went through straight, but some of them did get deviated and 1 in 20,000 would turn back. So, these arrows that you see here, they sort of denote in a cartoon notation, what kind of paths are taken by the alpha particles, 1 in 20,000 actually turned back.

A result that is very, very easy to neglect or pushover saying that is a freak result. The greatness of Rutherford and the courage of Marsden was that they took this result seriously. And hence, this Rutherford model was proposed. What is the model? The model is that all the positive charge and most of the mass of the atom is at one point, a point that is called nucleus and the rest of the atom is practically avoid, that is why alpha particles go through straight.

But then what about the electrons, they have to be in this void space, but if they are stationary, then they would be attracted by the nucleus and they would just fall upon the nucleus and get annihilated. To explain this Rutherford invoked a planetary model. It is known that planets go around their stars, like Earth goes around the sun. Learning from that example, Rutherford proposed that these electrons actually go around the nucleus in circular orbits.

And when they do so, the centrifugal force would exactly balance the electrostatic attraction and that is what Rutherford expected would keep the electron from falling into the nucleus and resulting in annihilation of the atom. Make sense? Nice model. The problem was that, from classical electrodynamics, it is expected that a charged particle in motion would keep on emitting energy.

So, two problems with that, if you look at the emission spectrum, emission spectrum means, look at the light that comes out and see what is the intensity of light coming out of a particular color. So, if this is the situation, that you have an electron that is moving, a charged particle in motion, it would give out energy continuously, then you expect what is called a continuous spectrum, you would have all colors, no demarcation, clear demarcation between two bands. Unfortunately, as we are going to see a little later, it is known that for elements, the emission spectrum actually has discrete nature, we get what is called line spectra.

Besides the problem is, if the electron actually emits energy continually, then it is going to lose energy. So, initially you start from a situation, but some centrifugal forces there it is balancing, then when it loses energy, then it would move slower, centrifugal force would be lesser, so it would be drawn in a little closer. So, this way it would actually go round and round in a spiral and fall onto the nucleus.

And if you do that calculation, you will see that the time required for an electron to fall into the nucleus is something like pico second 10^{-12} sec, so that does not give you a stable atom. So, that is why Rutherford Model could not really make too much of headway, but it was an excellent start. Please understand that the experimental result is actually correct. It is true that there is a nucleus, it is true that the electron is in the mostly void space of the atom. But what is not true is that electron is going around in circles.

To address the situation, it required the guts of Niels Bohr. But you know, no invention, no discovery, no new observation comes without prior knowledge by and large. So, even Bohr had help. And the help came in a series of fascinating observations made in physics towards the end of nineteenth century and beginning of twentieth century. One of them we have already discussed. We said that we have lined spectra of atoms, we already said that.

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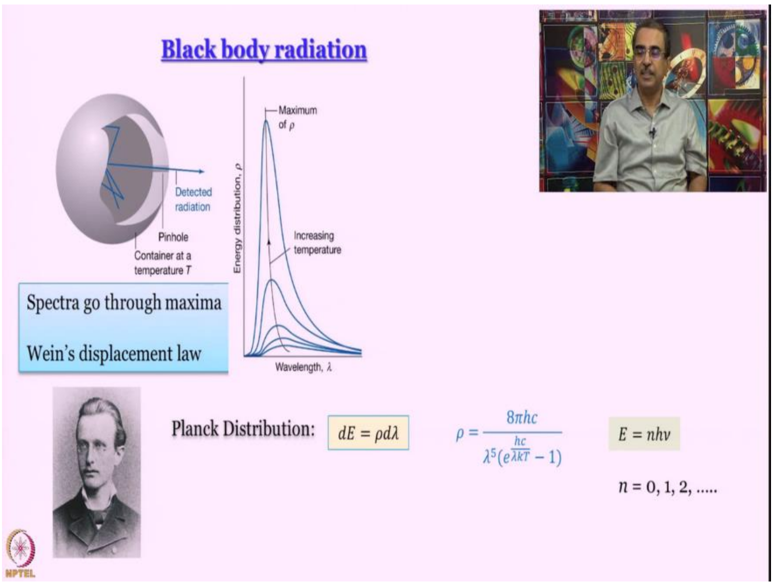

Another one was black body radiation. We have studied black body radiation in physics in class 11 and 12, I guess. So, you might be familiar with this kind of a diagram replot the energy distribution against wavelength, this is called a spectrum. It was known that if you increase the temperature, the spectrum becomes sharper and more intense and the maximum moves towards smaller wavelength that is higher energy. Why does that happen?

To explain it, there is something called Rayleigh–Jeans model, they tried to explain it by using classical oscillators within the cavity of the black body and they failed, they encounter what is called ultraviolet catastrophe. So, Rayleigh–Jeans considered large number of oscillators oscillating at whatever frequency, each can have its own frequency and their distribution is expected to give the distribution that you observe in the spectrum.

Unfortunately, the Rayleigh–Jeans model can nicely map the spectrum at longer wavelength, but it gives a monotonic increase, this turnaround is not there in Rayleigh–Jeans model. So, to answer this question, Planck proposed another model and he found that the only way you can actually provide a theoretical description of the spectrum of a black body is to consider that energy is quantized, ρ here is energy density.

So, you see something called like $e^{\frac{hc}{\lambda kT}}$ there. Hence, we get E = nhν that means energy is quantized. These oscillators can only take up some certain fixed values of energies, integral multiples of hν, where h is a constant called Planck's constant, very small number, I leave it to you to find out what the value is and n is 0, 1, 2, 3, this kind of a number. But cannot be negative, 0 and positive numbers, whole numbers. So, quantization is something that had already come in an attempt to explain this experimental observation that was one beginning.

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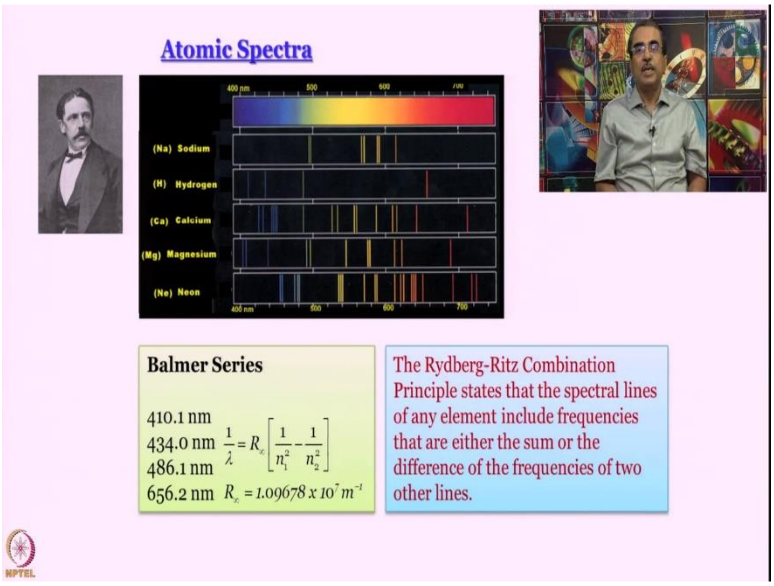

Another beginning was this line spectra. So, what you see here is, x axis is wavelength, and you get a line. Well, the color is something that is added later actually these are black and white photographs. But what you do essentially is that you place a prism or a grating in path of light that comes out of the atom and you disperse it. Remember dispersion Newton's experiment, you take sunlight and put it through a prism, it breaks down into what we call seven colors.

So, here, the emission, emitted light from an atom is made to go through a prism and it breaks down into component colors. What you expect from Rutherford model is something that is shown in the top, a continuous spectrum, what you actually get is discrete lines. For sodium, these are the lines; for hydrogen, these are the lines, in fact there are more, we will talk about that later; for calcium, magnesium, neon. So, discrete lines which means that only certain packets of energy are coming out of these atoms, another signature of quantization.

So, to explain these lines, what one can do is one can write an empirical equation like this, for each of these spectral lines here, wherever they occur, the wavelength $\frac{1}{\lambda}$ or wave number is given by R_∞. R_∞ is called Rydberg constant, multiplied by [$\frac{1}{n_1^2}$ - $\frac{1}{n_2^2}$]. n1 and n2 are two integers 1, 2, 3, 4, so on and so forth. Completely empirical. The question is why, where does this come from? And Rydberg constant you see is written it up to 1, 2, 3, 4, 5 decimal places.

So, we can actually determine it to 5 decimal places. That is the point. It is thought to be the most accurately determined physical constant. And this is the these are the lines for Balmer series, you see Balmer series is here because it is in the visible range. But I think you might know that they are actually more, Lyman, Balmer, Paschen Bracket, Pfund in different areas, different regions of electromagnetic spectrum. But all of them can be actually explained by this kind of formula. The question is why?

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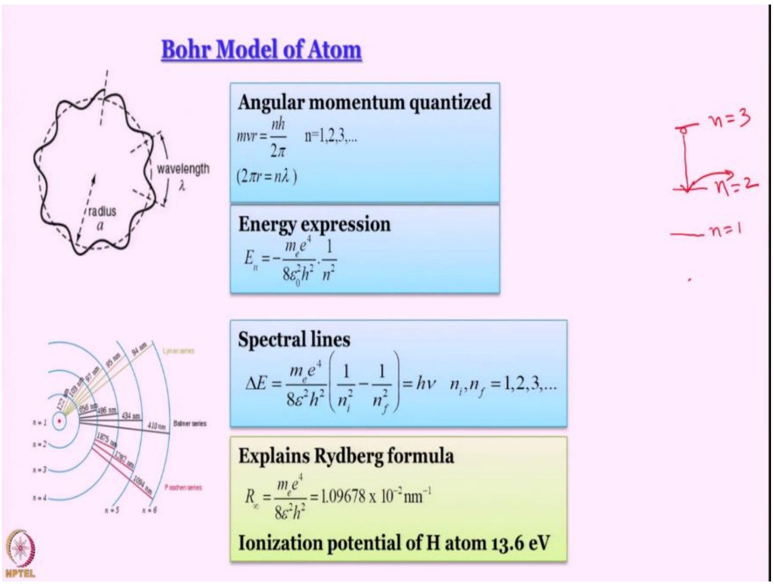

So, to explain why, and knowing that Rutherford model does not really go too far, Bohr said that I do not know why, but I can see very clearly that energies of an electron in an atom have to be quantized. And what if he figured was that the angular momentum has to be quantized, mvr = $\frac{nh}{2\pi}$

Now why angular momentum has to be quantized, that can be explained later, when we talk about de Broglie hypothesis, there is something called de Broglie wavelength associated with the electron. So, in order to have constructive interference in the wavelength, this is the condition that has to be satisfied.

The interesting thing is from here, Bohr could work out an expression for energy, which turns out to be - $-\frac{m_e e^4}{8\,\varepsilon_0^2 h^2}\ \frac{1}{n^2}$, do you have to remember this? No, these please remember, $\frac{1}{n^2}$, that is all that is required, there is no need to remember the constant. What is important is that the energy expression has something in n^2 in the denominator.

So now, what Bohr said is that, as long as this condition is satisfied that mvr = $\frac{nh}{2\pi}$, we have what he calls stationary states, stationary, not as an electron is not moving, stationary in energy, energy of electron does not change when they are in the stationary state. That is what he meant. And then what he said is that there are certain allowed stationary states, each is associated with a quantum number n, which is 1, 2, 3, so on and so forth. So, what would be the energies of these states? Maybe I will just draw even though it is drawn here, you might get confused because the orbits are shown, if I just draw the energies.

Let us say this is the energy of the lowest level n =1. Whatever its value is energy for n equal to 2. What will that be? Remember, there is a minus sign. So, it will actually go up, and the proportionality will be $\frac{1}{n^2}$, 4 times and then we have n equal to 3. So, these are the different energy levels that are there. And it is constant multiplied by 1, constant multiplied by $\frac{1}{4}$, constant multiplied by $\frac{1}{9}$ and so on and so forth. So, these are the stationary states.

Now, suppose an electron is there in n = 3, that is an excited state, it has to come down to the ground state or something. How does it come? When it jumps, Bohr said when it jumps from one stationary state to other the energy difference ΔE is emitted and this ΔE = hν. So, that is what is said by Bohr, ΔE = hν.

So, now, when you equate this ΔE = hν, you see you get [$\frac{1}{n_1^2}$ - $\frac{1}{n_2^2}$], what we have written is [$\frac{1}{n_i^2}$ - $\frac{1}{n_f^2}$]; i for initial, f for final. And that if you remember is exactly the same form as Rydberg equation. And from here that Rydberg constant that is calculated is in agreement with the experimental Rydberg constant to that seventh place or sixth place of decimal.

And the other thing that was calculated using this was the ionization potential of hydrogen atom which turns out to be 13.6 electron volt. So, Bohr theory gives us very good values of energy.

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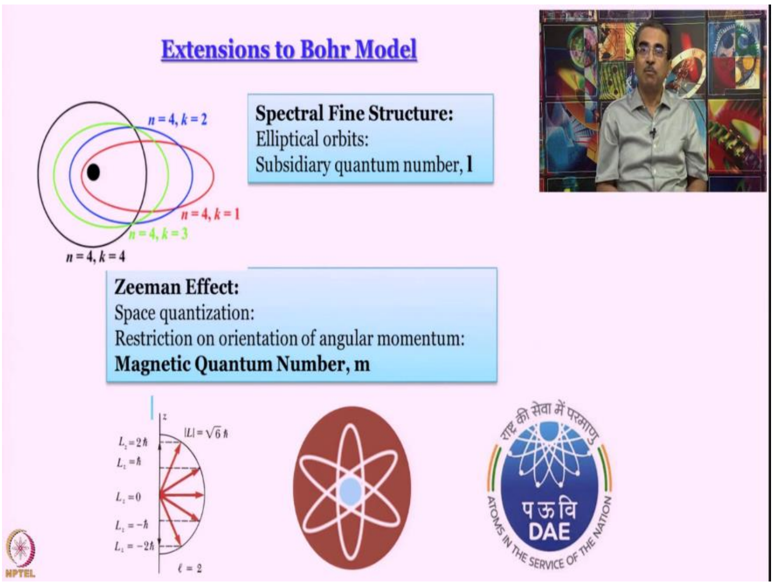

But then, when people took a closer look at it, it turned out that Bohr theory was incomplete. So, with better spectrometers, it was found that the spectral lines that were thought to be 1 are actually many, this is what is called fine structure. To explain this, Sommerfeld did an extension of Bohr model taking hints from Einstein's work. Now, plenty of non-mathematical popular literature is available on Bohr model and Sommerfeld model, I encourage you to read those.

So, what Sommerfeld said was that corresponding to each value of n, it is not necessary that the orbits are always circular, you can have elliptical orbits, and depending on the ellipticity of the orbits, the energies will change a little bit, will not be just dependent on n, this secondary quantum number k is what Sommerfeld used, that is also going to have some effect on the energy.

Then, the Zeeman effect experiment was done. Magnetic field was applied and it was found that now the spectral lines increase in number, you are splitting our spectral lines. That was explained by saying that you have situation like this. For any given value of n and k combination, it is not necessary that there is only one circular, well, there is only one elliptical orbit. You can have more than one and the number is 2L + 1 where L is the modified secondary quantum number.

So, the range goes from + L to -L. So, here we see 1, 2, 3; 3 orbits, so, +1, 0, -1. So, for this the L value is actually 1 and magnetic quantum number m values are 1, 0, -1. And if we have this orbits that are oriented in different direction, discrete different directions, angular momentum vector is perpendicular to the plane of the orbit.

So, the angular momentum vector can also take up discrete orientations in space. This is called space quantization, I am going a little fast, because I think you have studied all this in class eleventh, twelfth. And how many values of m can be there, that was also determined that you can have 2L+ 1 values. So, what does m determine? m determines the z component of angular momentum. Remember, we are going to come back to this.

So, this model gave rise to a lot of excitement. You can see this kind of picture in many places, including the logo of our department of atomic energy. However, end of the day, this model had to be scrapped. Why? Because, first of all, it is evident that Bohr theory by itself is incomplete. You make a new observation, you have to extend it, that is a problem. Secondly, the major tool that Bohr use was calculus, integration, which is the tool of classical mechanics.

So, on one hand, you are saying that classical mechanics does not work. But you use this tool as long as it works. The moment it does not work; you say that classical mechanics does not work. So, there is a little bit of dichotomy here. But the most important objection against Bohr theory, spin is something that I did not talk about. We will talk about that later.

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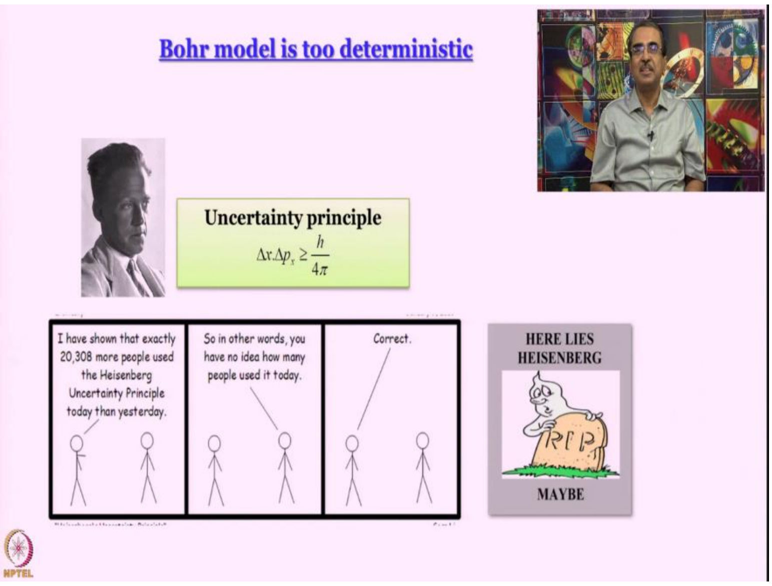

The biggest problem of Bohr theory came from Heisenberg's work. Heisenberg showed that for atomic particles, subatomic particles, this kind of uncertainty holds, $\Delta x.\Delta p_x \geq \frac{h}{4\pi}$. So, you cannot determine the position and momentum accurately like what Bohr model tries to do. So, Bohr model is too deterministic in nature.

And remember, uncertainty principle is not about not being able to do the right experiment, it is about a natural threshold, something that you cannot cross, no matter how good an instrument you build. If you study high level courses in quantum physics or quantum chemistry, you will learn more about uncertainty principle. But for now, let us just say that uncertainty principle was the final nail in the coffin of Bohr model. So, even though it gives us very good agreement with many experimental results, one has to discard Bohr theory and move on to something else, look for something else.

In fact, this uncertainty principle gave rise to a lot of interest beyond the world of science. So, you get so this kind of cartoons and all came up. But the biggest problem is that uncertainty principle says that you cannot really continue with this nice logic that we have of the classical world, you cannot take it too deep into atomic world.

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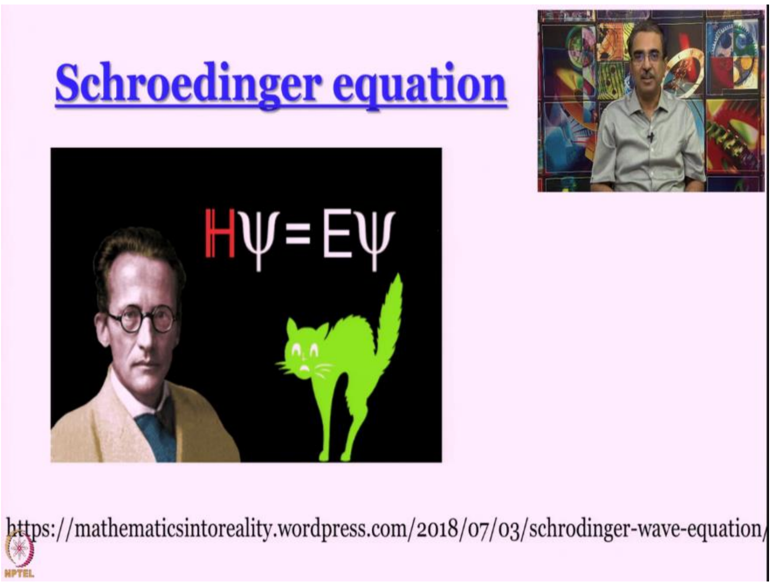

So, Bohr model has to be discarded, you have to look for something else. This something else was provided by Schrodinger in his famous equation. This is what we will discuss in the next module.