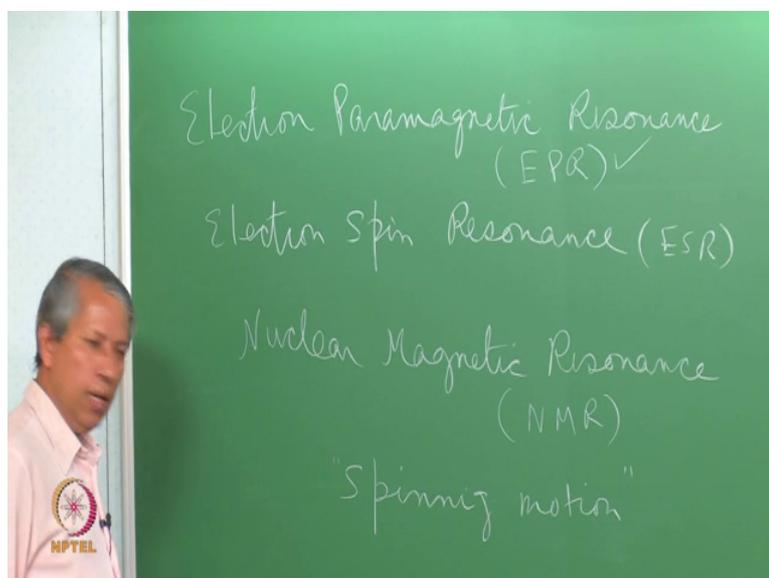


Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
Prof. Ranjan Das
Department of Chemical Sciences
Tata Institute of Fundamental Research, Mumbai

Lecture - 01
Remembering the Masters: From Zeeman to Zavoisky

Hello everyone, I am Ranjan Das. In this course of lectures, we are going to learn the Principles of Electron Paramagnetic Resonance and some of its Applications; electron paramagnetic resonance.

(Refer Slide Time: 00:36)

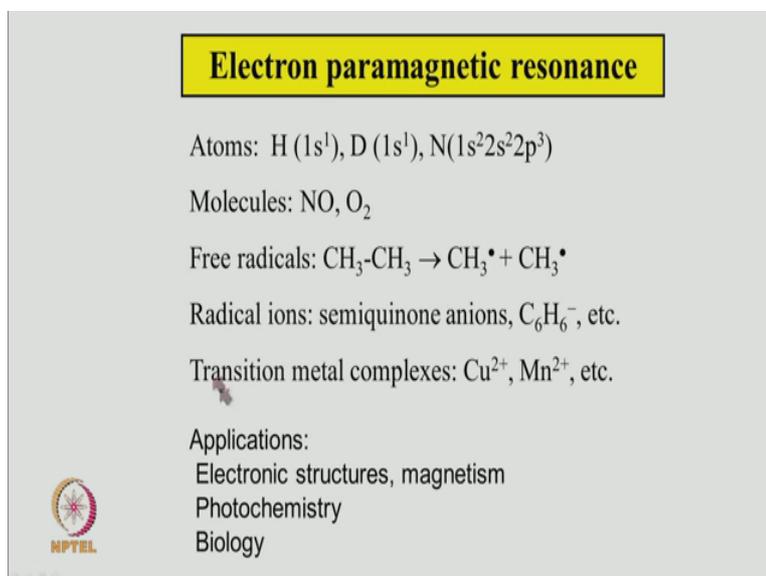


I am sure most of you have heard another spectroscopic technique called nuclear magnetic resonance. This is abbreviated as NMR and this electron paramagnetic resonance is abbreviated as EPR. There are lots of similarities in these 2 techniques. Here in NMR the key requirement is that the (Refer Time: 01:34) nuclei have magnetic moments, and because of that magnetic moments some spectroscopy can be done if they are put in magnetic field. In a very similar manner, electrons are also known to have magnetic moment. And when they are kept in a magnetic field, one can do spectroscopy on that that sense they are very similar.

In this course as we learn more of the electron paramagnetic resonance, we will see also the similarities and differences in these 2 techniques. The electron paramagnetic resonance is also known as electron spin resonance or ESR. Both are used in scientific parlance, but

do they mean the same? Or is one terminology better than the other? These things we will see later.

(Refer Slide Time: 02:56)



Electron paramagnetic resonance

Atoms: H ($1s^1$), D ($1s^1$), N ($1s^2 2s^2 2p^3$)

Molecules: NO, O₂

Free radicals: CH₃-CH₃ → CH₃• + CH₃•

Radical ions: semiquinone anions, C₆H₆⁻, etc.

Transition metal complexes: Cu²⁺, Mn²⁺, etc.

Applications:
Electronic structures, magnetism
Photochemistry
Biology



Right now, let us stick to this EPR. This spectroscopy can be used to study hosts of systems, atoms, molecules, free radicals, radical ions, transition metal complexes; in all those species which have magnetic moment associated with electron can be studied by this technique. They are wide applications in understanding electron structure, magnetism, phenomenon in photo chemistry and biology a wide range of applications.

So, before we start learning about the spectroscopy, it will be interesting to go through the history of developments of some of the key ideas that led to this spectroscopy.

(Refer Slide Time: 03:52)



Peiter Zeeman was a graduate student of Kamerlingh Onnes in the University of Leiden.

Zeeman wanted to study if magnetic field had influence on the atomic spectral lines, an experiment that Michael Faraday had attempted and not seen any.

Zeeman's initial attempts too did not show any effect. But he was keen to pursue his investigations.

Pieter Zeeman (1865 – 1943)

http://en.wikipedia.org/wiki/Pieter_Zeeman

To that end let us start with this person Pieter Zeeman. He was a graduate student, what we call research scholars of Kamerlingh Onnes in the University of Leiden. Now Zeeman wanted to study if magnetic field had an influence on the atomic spectral lines, those days it was already known that atomic spectra come in the form of discrete lines. So, he wanted to study if magnetic field could show any effect on them.

So, as a matter of fact Michael faraday did try to investigate this, but he could not see any effect. And Zeeman's initial attempts also did not show any effect, but he was very keen to pursue in his investing.

(Refer Slide Time: 04:50)



Kamerlingh Onnes did not want Zeeman to waste his time looking for effect that even Faraday could not see.

Heike Kamerlingh Onnes (1853 – 1926) http://en.wikipedia.org/wiki/Heike_Kamerlingh_Onnes

NPTEL

But his Professor Kamerlingh Onnes did not want Simon to waste his time looking for effect that even in faraday could not see. So, he was it discouraging him.

(Refer Slide Time: 05:03)

Zeeman was adamant. He wanted to use stronger magnets in Onnes' laboratory, but he would not give the permission.

Then Kamerlingh Onnes went to attend a conference. Zeeman took this opportunity to use his magnets and looked at the sodium spectral lines when placed in the magnetic field.

He saw that the spectral lines became a little broad.

The first indication of what was to be known as the Zeeman effect.

NPTEL

But Zeeman was adamant. He wanted to use stronger magnets. Magnets which are lying in Onnes' laboratory, but Onnes would not give him permission.

So, then Onnes went to attend a conference. So, that is opportunity that Zeeman took to use his magnets, and looked into the spectral lines of sodium atoms. And what he saw was that the spectral lines of sodium atom just become a little broad. Not a great effect,

but just a little broad. So, this was the first indication of what was to be famously known as the Zeeman Effect.

(Refer Slide Time: 05:48)

When Onnes returned after his conference, Zeeman was very excited to tell him about his observation.

How did Onnes react to Zeeman's observation?

Was he happy for the Zeeman's finding? Did he congratulate him for continuing to work where Faraday had not succeeded?

Far from it!



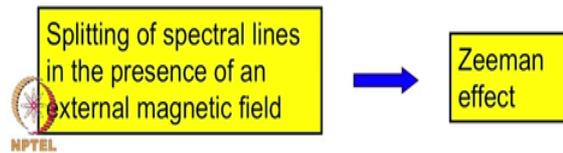
Onnes came back after his conference and Zeeman was very excited to tell him about his observation that here is the sodium lines and they are; showing some broadness if they are subjected to this magnetic field.

He has very excited about it, but how did Onnes reacted to this even excitement? Was he happy that Zeeman found something exciting? Did he congratulate him that he saw some effect which even faraday could not see? Far from it; he was in fact, very angry with Zeeman for not listening to him for wasting his time, probably even using the magnet without his permission. So, he simply is throwing out of the laboratory. He fired him.

(Refer Slide Time: 06:43)

Kamerlingh Onnes removed Zeeman from his position, and threw him out of the University of Leiden.

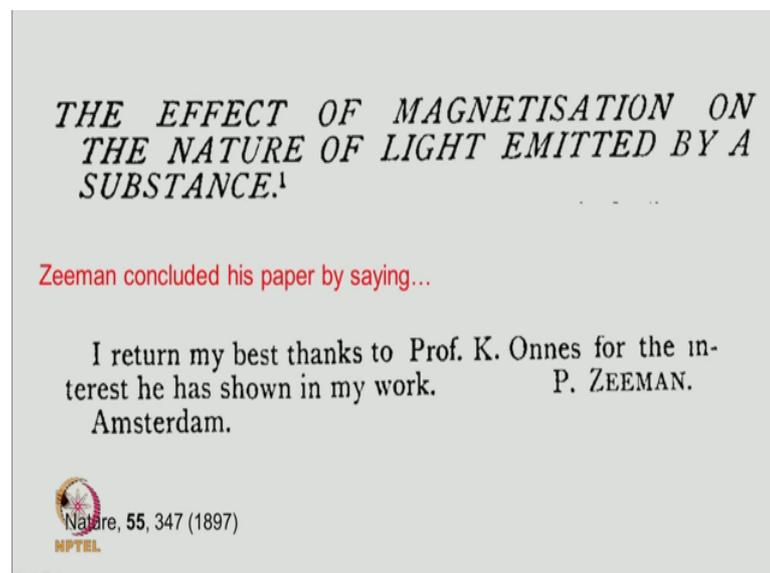
Fortunately, Zeeman found himself another position in the University of Amsterdam. There he conclusively showed that the spectral lines of sodium vapour actually split into two.



So, that could have brought an end to the scientific career of Zeeman, but fortunately Zeeman found another position in the University of Amsterdam. And there he conclusively showed the spectral lines of sodium vapor actually split into 2.

Now, this split across spectral lines in the presence of an external field is called the Zeeman Effect. Now this effect was now established and he published it in this journal, famous journal nature, and the title of the paper was the effect of magnetization on the nature of light emitted by a substance.

(Refer Slide Time: 07:15)



And in the paper, he concluded by saying I return my best thanks to Professor K Onnes for the interest he has shown in my work. I leave it to you to figure out if Zeeman was sending a message to his former supervisor. Anyhow, this work was recognized in the form of a Nobel Prize in 1902.

(Refer Slide Time: 07:48)

Zeeman was awarded the Nobel prize, in 1902, "in recognition of ... research into the influence of magnetism upon radiation phenomena."

Then after 11 years ...

Kamerlingh Onnes, too, was awarded the Nobel Prize, in 1913, "for investigations of matter at low temperatures ... [and] production of liquid helium."

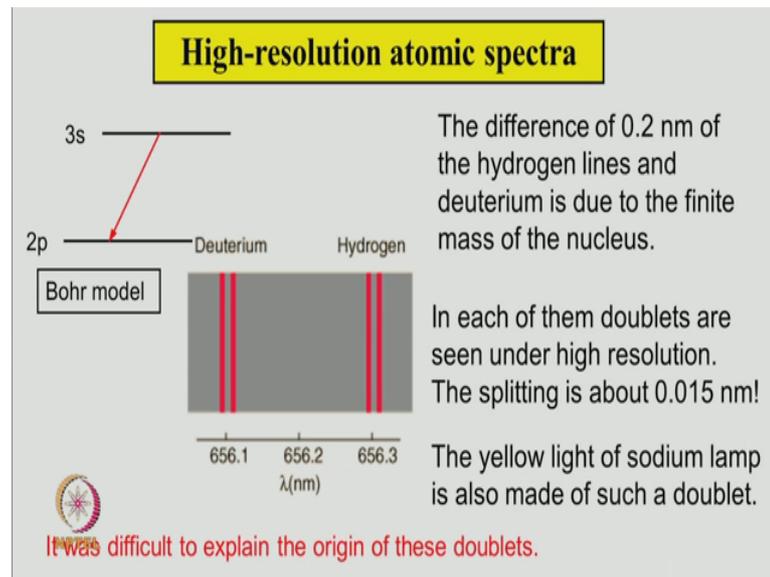


Anton Z. Capri, Quips, Quotes and Quanta – An Anecdotal
History of Physics, World Scientific (2007)

For the research into the influence of magnetism upon radiation phenomena; Kamerlingh Onnes was of course, a brilliant scientist in his own right, but he had to wait 11 years before he too could get a Nobel Prize for his investigation of matter low temperatures and production of liquid helium.

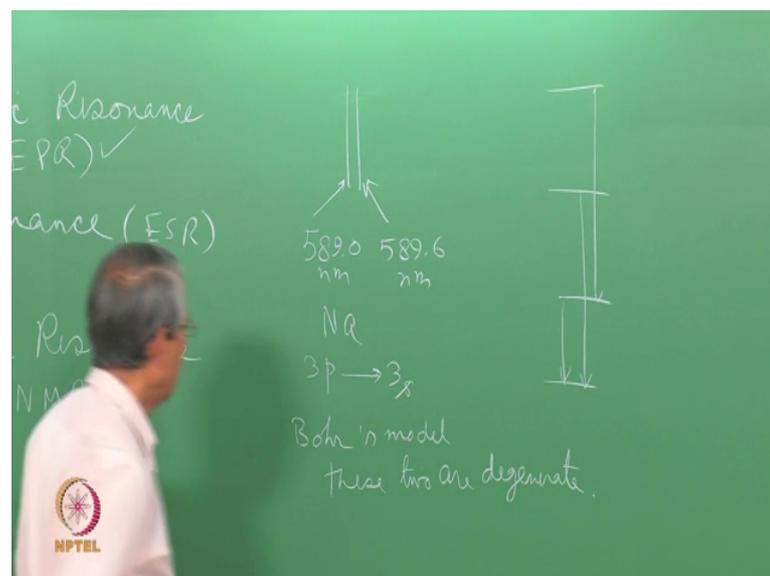
This Zeeman Effect that magnetic field caused splitting was something very difficult to explain or understand the origin of this. Also, many spectral lines were found to come in pairs.

(Refer Slide Time: 08:36)



When they are seen in high resolution, here is an example of hydrogen atom spectrum and deuterium so each of them, so this pair of lines together. The difference in their line position is due to the difference of the nuclear mass. So, that is not of serious consequence it is that these 2 doublets here and here where the separation is very small of the order of this 0.015 nanometer. That was very difficult to understand. Even sodium atom further mattered, that the bright yellow light that we see in the street lamp. That also has pair of 2 closely buying line.

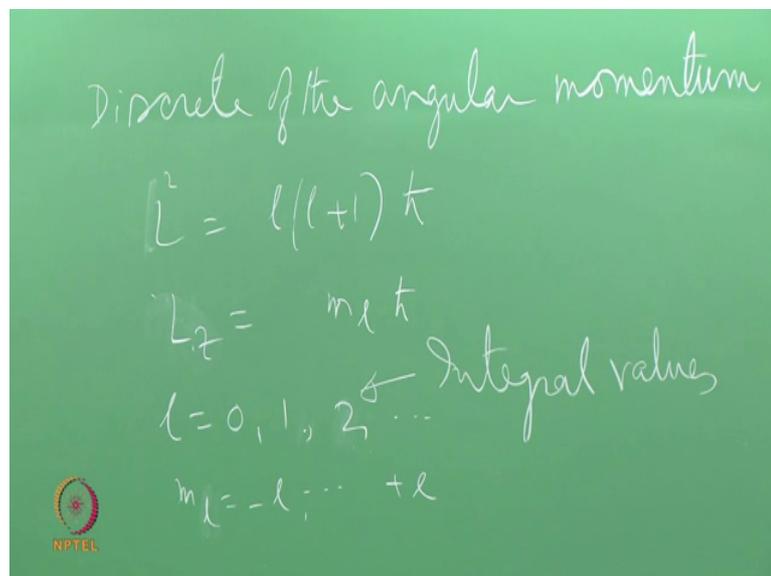
(Refer Slide Time: 09:31)



This is very close to each other. So, it is very difficult to explain these doublets. By then Bohr's model of hydrogen atom came, there the 2 revolutionary ideas were that the atoms have discrete energy levels of this kind. And the absorption emission of radiation takes place because of transition from this one discrete level to another discrete level. That is the first key proposal of Bohr.

So, this discrete nature of energy levels could very easily now explain the discrete spectral lines seen in the spectra. But they are still not sufficient to explain these doublets, the way they appear here. This is the sodium atom spectrum and the one is to shown here for hydrogen and deuterium atom spectrum they are very difficult to explain. In fact, for sodium atom the transition involves 3 p to 3 s orbital. In Bohr's model these are degenerate. So, the limitation was obvious that everything is not quite understandable, but Zeeman Effect could be explained based on this model. Because Bohr had another key ingredient in this model; that is, the discrete nature of the angular momentum.

(Refer Slide Time: 11:40)



Discrete of the angular momentum

$$L^2 = l(l+1)\hbar$$
$$L_z = m_l \hbar$$

$l = 0, 1, 2, \dots$ ← Integral values

$$m_l = -l, \dots, +l$$

NPTEL

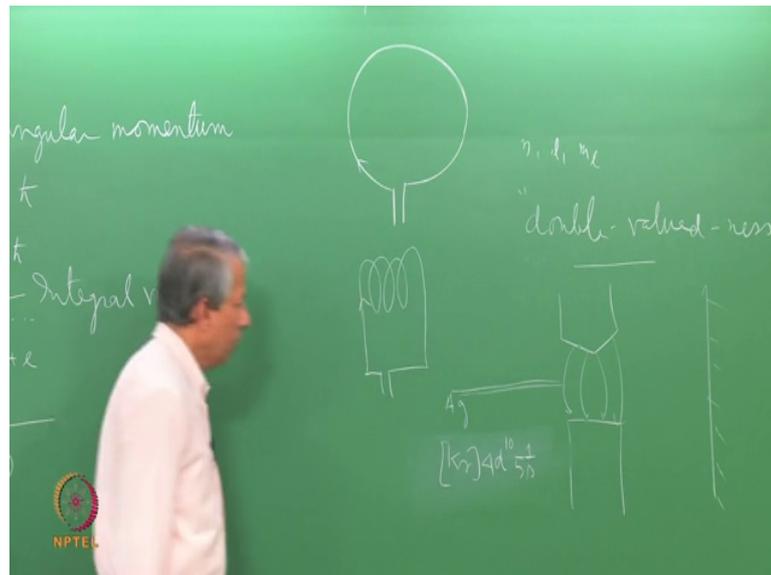
Before that it was assumed that angular momentum can take any arbitrary values. Report said that no it will take on discrete values.

Later with the Schrodinger formulation of quantum mechanics this is known to be that the angular moment value will have this kind of magnitude it is called L magnitude of L square, we will take this type of values. And the component of any arbitrary direction

will have L_z any particular z direction $m_l h$ cross. Here the value of this small L has to have this type of values.

Similarly, m_l will take minus L to plus L changing in units of one the important boundary to notice here these are all integral values. With this ad hoc requirement that Bohr has imposed, one can explain the Zeeman Effect in this way. That motion of charges produces current and current can produce magnetic field as shown by Faraday. For example, if there is a wire and through which current is flowing; it will produce a magnetic field around it and that can be easily seen by placing a let us say the magnetic compass. And depending upon the direction the current, the needle of the compass can either move this way or that way.

(Refer Slide Time: 13:57)



Or further matter we have a let us say a loop of this kind where current is flowing, then it can produce a magnetic field which will have direction either this way or that way.

In fact, solenoid is the very common example of producing magnetic field by passing current through a coil. So, that sense the orbital motion of the electron can have magnetic moment because of this sort of motion in the atom, and that magnetic moment can be influenced by the magnetic field which is the Zeeman Effect. So, it is possible to explain Zeeman Effect in this fashion, but the trouble is that not all such spectral splitting that is seen in the presence of magnetic cannot be explained by associating the orbital angular

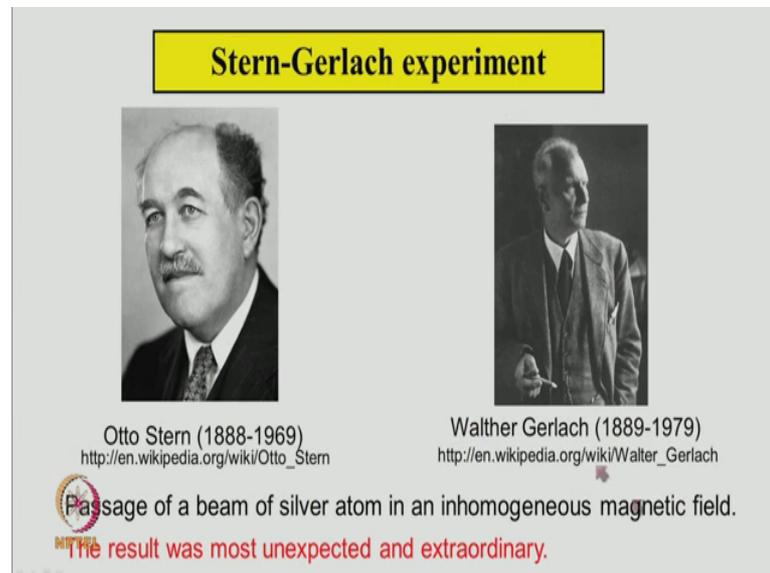
momentum and the corresponding magnetic moment, those things. Many of this spectral lines which are seen to be split cannot be explained that way. Something was missing.

So, Pauli (Refer Time: 15:05) from Pauli said that he could explain many of these doublets here. For example, or doublets which are seen, that many of such doublets not necessarily this particular one, or this particular one, when you say doublets could be explained.

If it is assumed, that electrons are allowed to take this quantum number the n and l in pairs; that is, 2 electrons in the same values of this kind. Not more than that. So, this sort of double valuedness, double valuedness if it is accepted, then many of this doublet spectral lines can be explained. Of course, now we know that this is nothing but the Pauli Exclusion Principle. That is what is in mind.

So, why it should be so was still not clear. And not only that that does not explain all the observations of this doublets.

(Refer Slide Time: 16:25)

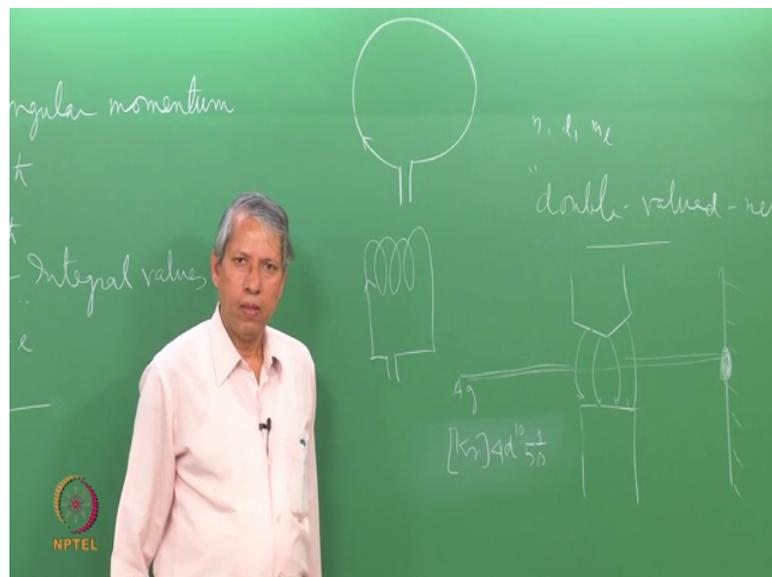


We know how important experiment was carried out by these 2 people: Otto stern and Watlther Girlach. What they did was to pass a beam of silver atom through an inhomogeneous magnetic field. In this (Refer Time: 16:53) this external is done in this way let us say. This is a magnetic field the pole pieces are made such a way that the field will be very in heaviness. Field lines will look like this, and they have a source of silver

atom. It is coming here. And they are allowed to fall on a detector size (Refer Time: 17:18) here. Silver atom is known to have this electronic configuration, $4d^{10}5s^1$. So, naturally according to this model it does not have any angular momentum.

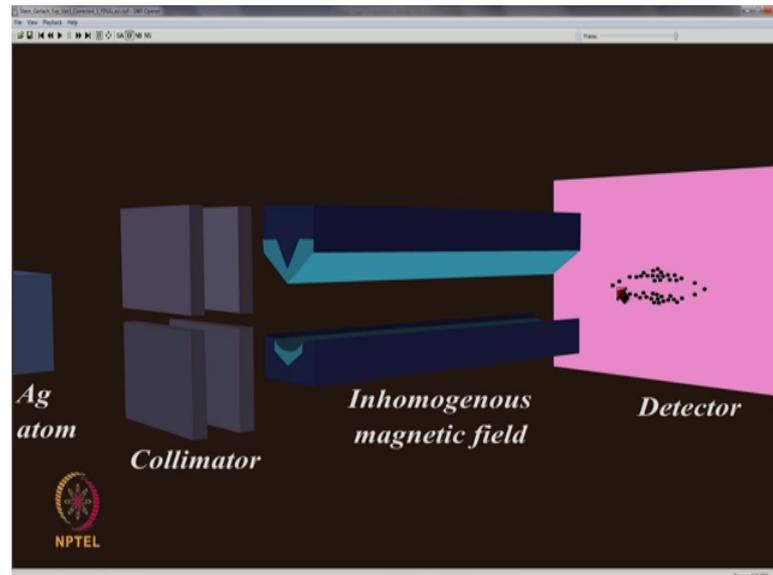
So, what is expected that since it has no angular momentum, it will also not have any magnetic moment? So, in this accounts are allowed to go through this inhomogeneous magnetic field, they will not experience any particular force. So, what is expected they will sort of fall here.

(Refer Slide Time: 18:02)



And probably form some sort on (Refer Time: 18:04) finish that is what the expectation. Let us say what they observed.

(Refer Slide Time: 18:10)



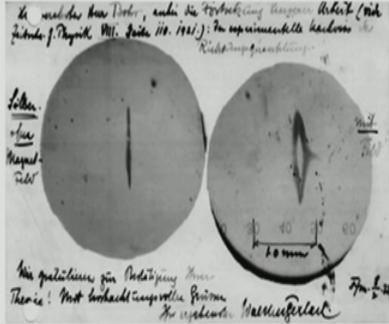
So, here is an animation we sort of tries to describe this experiment. Here is the source of silver atom their collimator. So, that we get a narrow beam of silver atoms, and this long thing is the inhomogeneous magnetic field. And this is the screen, which detects the silver atom. So, let us see what happens. So, a silver atoms are coming from left, and going through this magnetic field and see they are following apparently randomly on the screen. So, you see that they seem to be piling up in 2 places. Now is piling up. It is very obvious that the beams are falling in 2 places and 2 piles are formed there. So, it is not what was expected here, that they fall expected that maybe they will fall only one lump.

So, this is again very extraordinary finding. It cannot be explained by the known electronic structure.

(Refer Slide Time: 19:24)

Stern-Gerlach experiment

Gerlach sent a postcard to Bohr.



The atomic beam split into two!

The atom has no orbital angular momentum.

Magnetic field OFF Magnetic field ON

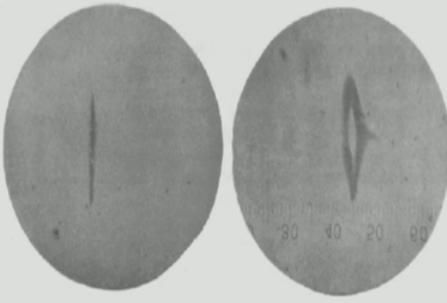
So, they send this finding to Niels Bohr in a postcard, announcing that at end they found the splitting of this silver beam particularly because the silver atoms did not have any angular momentum. Here is the actual photograph, and the magnetic field was off all the atoms fail here. A single lump or the magnetic field is on the so splitting.

(Refer Slide Time: 19:49)

Stern-Gerlach experiment

Stern and Gerlach published their work in *Zeitschrift für Physik*, 1922.

Title of their paper: Experimental Proof of Directional Quantization (or Space quantization)

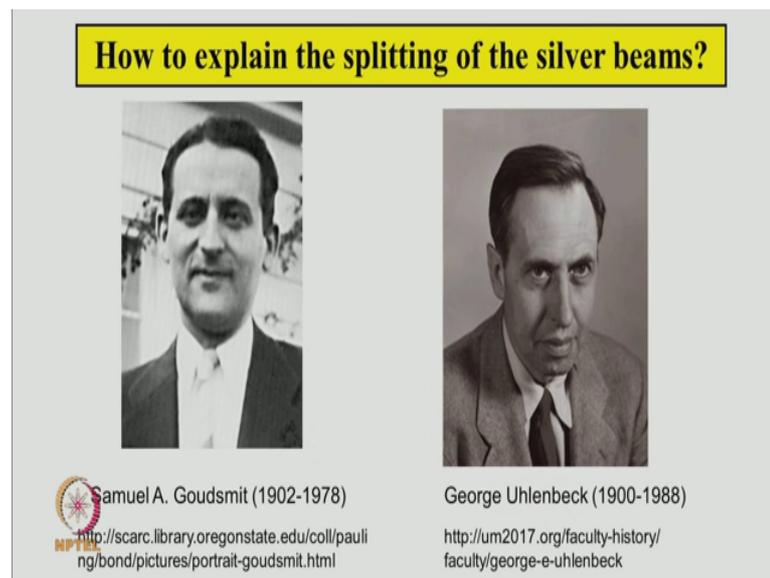


W. Gerlach, W. & O. Stern, *Z. Phys.* **9**, 349–352 (1922)

They publish their result in this journal *Zeitschrift Fur Physik*, the title the experimental proof of directional quantization. So, this is the famous here yet again this is a very difficult experiment that erection.

Once again it is very difficult to explain this observation, because this silver atom with this configuration does not have any suppose you have no magnetic moment, no angular momentum, no magnetic moment. But even then, it is so splitting, I mean this must have got something to do with the magnetic field that is experienced by this and this is causing splitting and it was splitting on 2 lines; so yet another extraordinary finding without any explanation.

(Refer Slide Time: 20:42)



Then these 2 persons said that they have a way to explain the splitting of silver atoms. There are 2 young graduate students of they had a very extraordinary and rather novel model of silver atom, sorry.

They come up with a very novel proposal. They said that this Pauli's double occupancy of electrons or the stern Gerlach experiment result both could be explained.

(Refer Slide Time: 21:13)

Uhlenbeck and Goudsmit were two young graduate students of Paul Ehrenfest.

Samual Goudsmit (Experimentalist)
George Uhlenbeck (Theoretician)

Pauli's double occupancy of electrons and the Stern-Gerlach result.

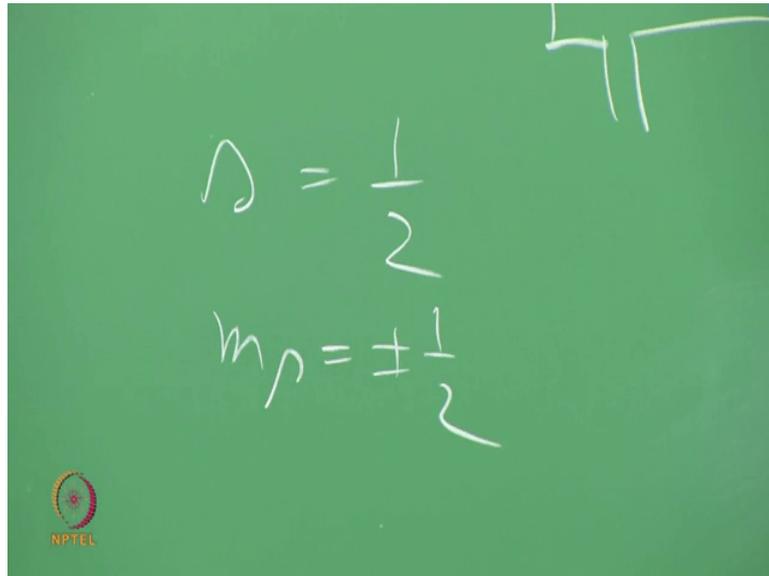
Electron has an angular momentum that takes only two values.

The spinning motion of electron is a new degree of freedom.

If they make an ad hoc assumption that electrons have another degree of freedom which is they are sort of spinning about its own axis. So, then this let us say spinning in this way clockwise fashion or anti clockwise fashion, it can give a magnetic moment in this direction or that direction. These 2 types of magnetic moment can interact with a magnetic field here, and it can split into 2.

And similarly, it can also explain the double valuedness of Pauli. Important thing is that the angular momentum that the silver atoms would have we will have integral values, but half-integral values.

(Refer Slide Time: 22:17)


$$S = \frac{1}{2}$$
$$m_s = \pm \frac{1}{2}$$

If I call them let us say s this will have value of half, m m is equal to plus minus half which is quite different from what has been accepted till them.

(Refer Slide Time: 22:34)

A spinning electron?

Uhlenbeck and Goudsmit's idea did not find favour in the scientific community.

Wolfgang Pauli was a towering figure in science then. He used to be a severe critic of his own, as well as others', work. He damned the claim of Uhlenbeck and Goudsmit. Their result was off by a factor of 2!

Ehrenfest then sent these two young men to discuss with Hendrick Lorentz.

Lorentz, too, dismissed their model of spinning electron.



So, Ehrenfest suggested that they discuss this with Pauli. Now Pauli was a towering figure in science, and he was a very severe critic of his own work as well as work of others. So, when he uhlenbeck and goudsmit (Refer Time: 22:48) goes and talk to him about their model, he simply said this is nonsense. He damned in their work. It is also true that the calculation of uhlenbeck and goudsmit was differing by a factor of 2 from

the observation. So, there then Ehrenfest and these 2 young men discussed with Hendrik Lorentz. Lorentz too dismissed their model of spinning electron.

(Refer Slide Time: 23:19)

A spinning electron?

Nuclear sizes are exceedingly small: of the order of $10^{-15} \text{ m} = 1 \text{ fermi (f)}$

The size of an electron is even smaller, of order of $10^{-18} \text{ m} = 10^{-3} \text{ fermi}$

If the spinning motion is to produce the observed effect, the surface of the electron has to move at 10 times the speed of light. **Clearly nonsensical!**

The diagram shows a circle representing an electron with a vertical axis and a curved arrow indicating rotation. A small red arrow points to the left, and a blue arrow points to the right. The text is in black and red, with a blue arrow pointing to the red text.

What is a novel Lorentz complaint? Here it is if the charge is rotating it can produce magnetic field fine, but let us estimate what type of situation one needs to produce a situation which can explain this deflection. So, if so, this is the spinning model of electron which is spinning in this fashion this electron, negative charges here. Nuclear charges are exceedingly small of the order of 10 to the power minus 5 meter what is called one fermi. And electron size even smaller about thousand times smaller than this.

So, if the electrons rotation of this kind is actually producing the observed effect. The surface of the electron has to move at 10 times the speed of light.

(Refer Slide Time: 24:13)

Uhlenbeck and Goudsmit became very dejected and came back to Ehrenfest saying that they wanted to withdraw their manuscript from publication.

Ehrenfest replied that their paper was either very important or nonsense, and he had already sent the manuscript for publication. He added, "You are both young enough without a reputation to lose and can permit yourself a folly."

Their paper was published in Naturwissenschaften.

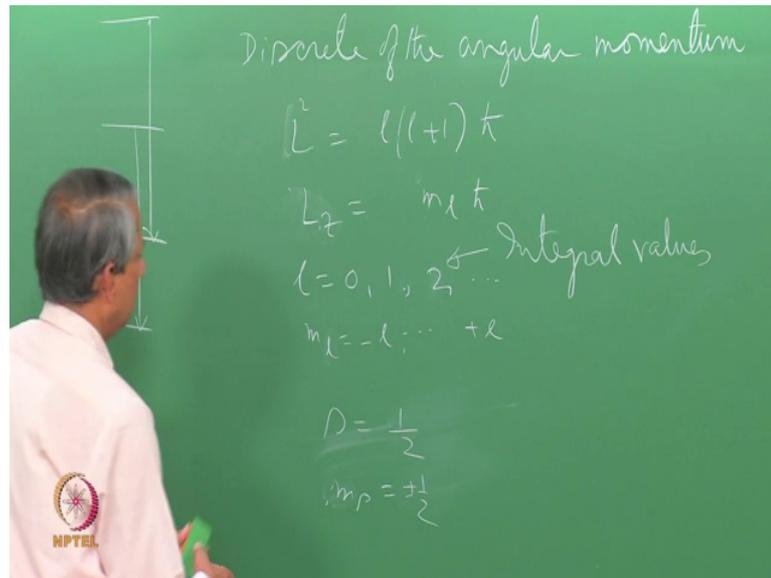


Later, relativistic calculations took care of the error of factor of 2.

So, clearly this is nonsensical. So, when Uhlenbeck and Goudsmit become very dejected and came back to Ehrenfest saying that they wanted to withdraw their paper from publication. But Ehrenfest replied that their paper was either very important or nonsense. And he has already sent the manuscript for publication, and then he added that you are both young enough and you have no reputation so far to lose. So, you can permit yourself a folly that is if the suggestion of yours turns out to be important you will become famous, but if it does turn out to be nonsense then you do not lose anything hence the paper was published in the journal naturwissenschaften and later calculation using relativistic correction also took care of the factor of 2 which initially they had trouble explaining.

So, this suggestion of uhlenbeck and goudsmit did turn out to be very, very important. Now angular momentum integral kind angular momentum can also be half integral.

(Refer Slide Time: 25:17)



That is s equal to half m_s equal to plus minus half is also possible. Here it is (Refer Time: 25:28) integral to non-integral that is a very drastic difference. Therefore, electrons do have a magnetic moment; which arising because of this motion. So, everything really fell into places, but the Lorentz complained that electrons have spinning this way, that complaint is still valid.

So, what is now accepted that? One must not take this spinning motion. One must not take the spinning motion very literally. Though it is very easy to visualize the motion of the electron, electrons are not really spinning around the axis. The way earth rotates around this axis to produce day and night electrons are not doing that kind of motion. One must take it to be an intrinsic property of the electron that has angular momentum of this type of magnitude, and it takes 2 components and also it has no internal motion to really give us a visual picture of what is happening there.

We just take it to be intrinsic property angular momentum of this kind and the intrinsic magnetic moment. So, these 2 are intrinsic property. We may not feel very comfortable about that accepting these as intrinsic property, but we do get used to such ideas, when you keep using them often. For example, in our daily life we have really accepted many of these things as an intrinsic property without questioning them, mass for example. What is mass? Mass is amount to matter. What is the matter? That is more difficult then,

that what the amount of masters present. So, you see we are not making any progress by explaining the concept of mass.

Similarly, what is charge? Electron has negative charge, proton has positive charge, what are they? What are these charges? Can you really explain them? We really do not have any experience and except that we take them to be a property of the particles which shows how they interact; that is, positive charge and positive charge they repel each other. That is the way it is. So, once we know that they have certain properties and to explain the properties we have to have this concept. In the same way intrinsic properties of spin angle momentum and magnetic moment can be accepted to say that no host of things are explained and we get used to using them. Intrinsic properties like mass and charge.

Anyhow coming back to now spectroscopy that Zeeman showed the splitting of energy levels, now if the energy level is a split one can look at the transition among the split lines and that is nothing but the electron parametric resonance spectroscopy.

(Refer Slide Time: 28:50)



 Yevgeny Konstantinovich Zavoisky
(1907–1976)

First observation of Electron Paramagnetic Resonance of copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in 1944 in Kazan Physical-Technical Institute, USSR.

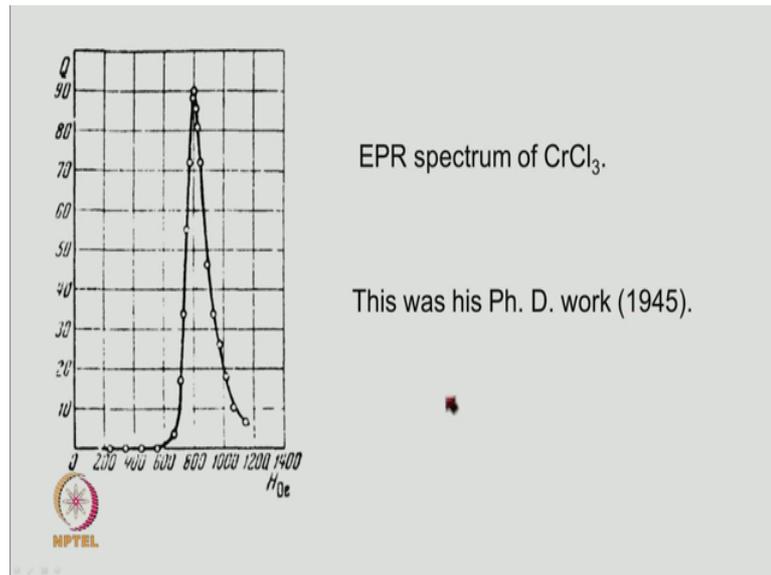
Not many, even among the Soviet scientists, believed his finding.

E. Zavoisky, J. Phys. USSR **9**, 245 (1945)

http://en.wikipedia.org/wiki/Yevgeny_Zavoisky

So, this was first observed by the Russian scientist Zavoisky in 1944 in Kubrick law right not many people believed his finding not even soviet scientists he published his work in 1945 in Russian journal. So, it took time before it was noticed by the international scientific community. Nevertheless, this was his PhD work, PhD thesis work.

(Refer Slide Time: 29:18)



And he got his PhD in in 1945. This is the one EPR spectrum they recorded in chromium chloride. So, these are the way the history of science and particularly led to the properties of electron, and how it leads to the existence of magnetic moment which can be which can be influenced by magnetic field. And that can give rise to different energy levels, and that can give rise to spectroscopy. And that is the EPR spectroscopy.