Fundamentals of Spectroscopy

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Lecture 54
ESR Spectroscopy – 2

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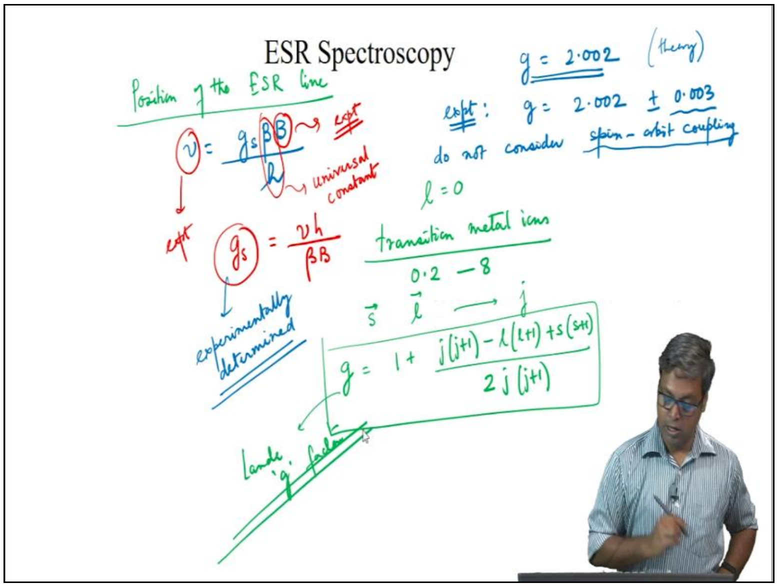

ESR Spectroscopy

Position of the ESR line

$\nu = \frac{g_s \beta B}{h}$ ~ expt ~ universal constant

expt

$g_s = \frac{\nu h}{\beta B}$

experimentally determined

$g = 2.002$ (theory)

expt: $g = 2.002 \pm 0.003$

do not consider spin-orbit coupling

$l = 0$

transition metal ions

0.2 – 8

$\vec{s}\quad \vec{l} \longrightarrow j$

$$\boxed{g = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}}$$

Lande 'g' factor

Hello all welcome to the lecture in the last lecture I started discussing electron spin resonance spectroscopy or ESR Spectroscopy. We saw that the primary condition to obtain ESR signal is the presence of an unpaired electron so the primary condition is the presence of an unpaired Electron. We will look into the energy level diagram. So in the last class we talked about the energy level diagram and also discuss some important parameters of the ESR spectrum.

So the parameters that we had discussed are we discussed intensity when we discuss the width of the spectrum and we also discussed about the peak position. So in today's lecture we sould consider the origin of the hyperfine structure. So, today we will talk about the origin of the hyperfine structures.

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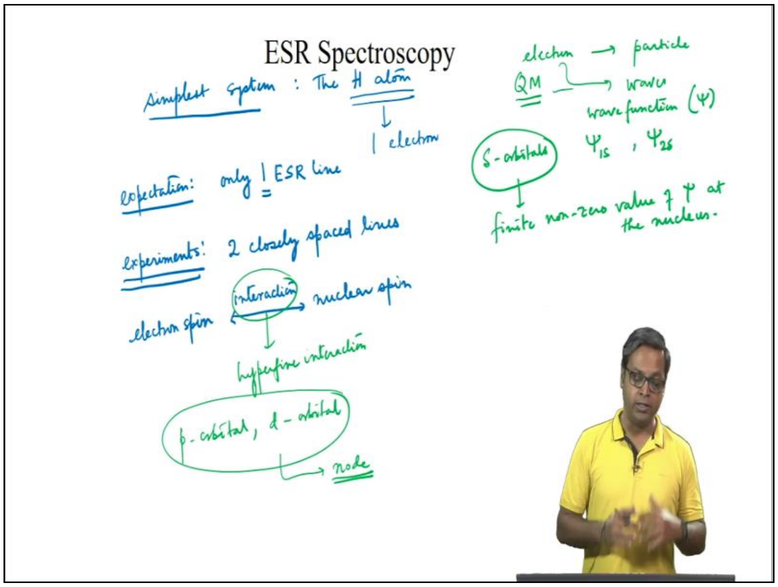

ESR Spectroscopy

Simplest system : The H atom
↓
1 electron

expectation: only 1 ESR line

experiments: 2 closely spaced lines

electron spin ⟵ interaction ⟶ nuclear spin
↓
hyperfine interaction

p-orbital, d-orbital ⟶ node

electron → particle
QM → wave
wave function (Ψ)

S-orbitals Ψ_{1s} , Ψ_{2s}
↓
finite non-zero value of Ψ at the nucleus.

Let us start by considering the simplest system, so what is the simplest system? The simplest system that will consider to start with his the hydrogen atom. So, this is the simplest system because the hydrogen atom contains one electron and because it contains one electron does the electron has to be unpaired. So due respect only one ESR line, so, our expectation is only one ESR line and we expect just one line because we are talking about only one electron in the hydrogen atom.

But if you look into the experimental results, so experiments predict that the ESR signal of this hydrogen atom consists of two closely spaced lines. So, now you may ask instead of one how come we have 2 closely spaced placed lines and this has been explained in terms of interaction between the electron spin and the nuclear spin. So, there is interaction between the electron spin and nuclear spin and interaction has been termed as hyperfine interaction.

So now if we consider the electron as particle it is difficult to think of interaction of the electron with the nucleus. This is because if electron is considered as a particle this interaction is difficult to think about because the nucleus is far, far away from the electron but quantum mechanics tells us that the electrons can be considered as waves and this waves represented by a wave function. So let us say it is known Psi so it is known that for a S orbital’s if think about s orbital’s it in terms of wave functions we can write psi 1s or psi 2s if you considered 2s orbital’s.

So there is a finite non zero value of psi at the nucleus this s orbital's they have finite non zero value of Psi at the nucleus however for other orbital's for example if we consider the p-orbital or if we consider the d-orbital. So these orbital's have a value of 0 at the nucleus because these orbital's at the nucleus have a node so it has a value of 0. So, thus is in the free electron is in a s-orbital it can actually interact with the nucleus and for other orbital's like d or p-orbital's this interaction will not be possible.

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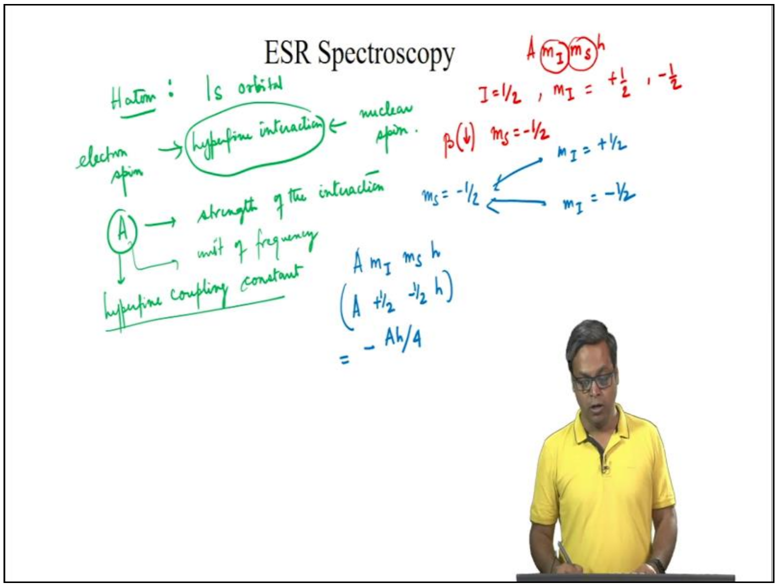

ESR Spectroscopy

H atom : 1s orbital

electron spin → $\boxed{\text{hyperfine interaction}}$ ← nuclear spin.

$\textcircled{A}$ → strength of the interaction

→ unit of frequency

↓

hyperfine coupling constant

$A \, \textcircled{m_I} \textcircled{m_s} \, h$

$I = 1/2 \, , \, m_I = +\frac{1}{2} \, , -\frac{1}{2}$

$\beta(\downarrow) \quad m_s = -1/2$

$m_s = -1/2 \leftarrow m_I = +1/2$

$m_s = -1/2 \leftarrow m_I = -1/2$

$A \, m_I \, m_s \, h$

$(A \; +1/2 \; -1/2 \; h)$

$= - Ah/4$

So, in the case of hydrogen atom we know the electron for the hydrogen atom resides in the 1s-orbital and because it is in the is-orbital thus this hyperfine interaction is possible. So, again this hyperfine interaction is the interaction between the electron spin and the nuclear spin. So, strength of this interaction is denoted by parameter A so we will write A where A is the strength of the interaction and this A is known as the hyperfine coupling constant.

So the hyperfine coupling constant A stands or gives us the strength of interaction and the unit of A is the same as the unit of frequency. So, the interaction energy is given by the expression A m I m s h where is A is the hyperfine coupling constant m I comes from the nuclear spin and m s comes from electron spin. So, for hydrogen atom we have one proton in the nucleus and for a Proton We know that I equals 1/2 and because I equals 1/2 that means m I can take 2 values m I can +1/2 or -1/2 and let us say the electron is in the beta state.

So beta state means that down spin state that means m s equals -1/2. So if the electron is in the beta state this electron can internet with both m I equals +1/2 and -1/2 in other words if we write it pictorially this m s equals –1/2 can interact with m I equals +1/2 and m I equals -1/2 and so we can actually calculate the energy. So now if we put A m I m s and let us see that m I equals +1/2 and the electrons in the beta state so m s = -1/2 then we have energy that is –Ah by 4 in other words for interaction between an electron in the beta state with m I = + 1/2 there will be a negative energy. So, now let us consider all the possible interaction and draw a schematic energy level diagram.

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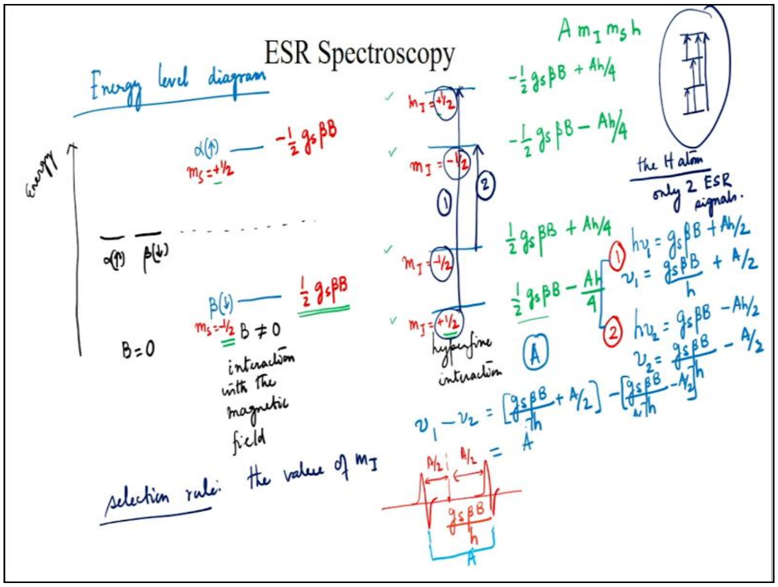

ESR Spectroscopy

So, let us look into the energy level diagram. So, our vertical axis is energy and we have two states Alpha that is the up spin state and beta that is the down spin state and this two states are degenerate when there is no magnetic field that is B = 0 however when we have an externally applied magnetic field that is B is not equal to 0 then we have interaction of electron spin with the magnetic field and because of this interaction the degeneracy which was there at B = 0 is lifted and now we have 2 states one is alpha, which is the higher energy state up spin state and the other is beta, which is the lower energy state or the this is the down spin state.

Now in alpha we know that m s equals +1/2 and for beta m s = -1/2 and if you look into the energies of these states the beta state has energy 1/2 gs beta B and alpha state as energy that is -1/2 gs beta B. So far we have not considered the interaction of the electron spin with the nuclear spin or in other words we did not considered the hyperfine interaction. So, now if you considered the hyperfine interaction then these energy levels will further split, so because m I can take two values so will have 4 levels here.

And let us put m I values here so here m I equals +1/2 for the lowest level and m I = - 1/2 for the highest level m I = +1/2 and for the second highest level that is the lower level for Alpha spin interaction m I equals -1/2. So what we can see here, we have 4 levels and now let us put down energy. So, the energy here so this is 1/2 gs beta B and then hyperfine energy is given by A m I m s h for this case this is m s equals +1/2. So, if I multiply -1/2 into +1/2 we get - 1 by 4 so here it is A h by 4.

Similarly for this level 1/2 gs beta B but then now your multiplying -1/2 which is m s and -1/2 that is m I so we get h by 4. So, we can think That we had the energy before the hyperfine interaction that is 1/2 gs beta B and now it splits so one level goes up by h by 4 and the other level goes down by h by 4. So, we have 1/2 gs beta B is - 4 and 1/2 gs beta B + h by 4 and for the other two levels we can write this is -1/2 gs beta B this is the highest level then we are multiplied plus with plus so we have + h by 4.

And similarly level has -1/2 gs beta B – A h by 4 so this is energy level diagram. Now, if you see you can see we have 4 energy levels. This is one, this is the next one third and because of this hyperfine interaction instead of two now have 4 energy levels and because your phone which can expect more than one condition that is possible. So, let us try to draw randomly 4 energies level and let us say there is no rule we should restrict ask from having any transition.

So, I can have transition from here to here, here to here so you can see many, many transition are possible. if you see here the number of possible transition is actually more than 2, however from experiments we know that the hydrogen atom shows only 2 ESR signal. So, at this point we need to understand why instead of ESR line for hydrogen atom. We have only two lines in the spectrum. So at this point we need to focus what is known as the selection rule for ESR transition.

And the selection rule for such transitions states that the value of m I should not change. So if the m I value does not change so what are the different transitions we can have? So, we have m I equals +1/2 and we also have in m I equals +1/2 one possible transition. And the other possible transition is m I equals -1/2 and m I equals -1/2 so this is the other possible transition. So, these are only two possible transition that we have.

So we have one transition which is of larger energy and we say this is number 1 and we another transition of smaller energy difference this we label as 2. So, now latest let us look into this energy difference of the transition energies, so if we look into one that is from m I goes from +1/2 to -1/2 then the energy involved in the transition is given h nu = gs beta B + A h by 2. So, this h nu is energy, but if we want to know about the frequency then we have to divide it by hnu equals gs beta B divided by h + A by 2 this is for the process one m I goes to +1/2 and m I goes to -1/2.

Now if you think about the process 2 then what we have we have h nu equals gs beta B –A h by 2 or in other words nu equals gs beta B divided by h – A by 2. So, now if we compare 2 transition we can see that the energy difference that means energy difference between 1 and 2 is nothing but A because this is h nu1and that is nu1 and h nu2 that is nu 2 and what we do it is let say nu 1 – nu 2 so what we get here we have gs beta B divided by h + A by 2 - gs beta B divided by h – A by 2 and if you do this difference is better be cancelled out and so what we get here is A.

So, we can see that if we compare this transitions these two transitions are separated by A so what does this mean in terms of spectrum. So, this means this was my energy let us say gs beta B divided by h and because ESR is shown as first derivative plot. So, the first derivative of the peaks so will have one peak here and will have another peak here and such that this difference is A by 2 and this difference is also A by 2.

In other words what it means the difference from one peak to another peak is A. So, this brings us to the end of the lecture and in the next lecture would look into more details of the ESR spectrum.