Circular Dichroism and Mossbauer and Spectroscopy for Chemists
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Lecture – 42
Mossbauer Spectroscopy: Isomer Shift-I

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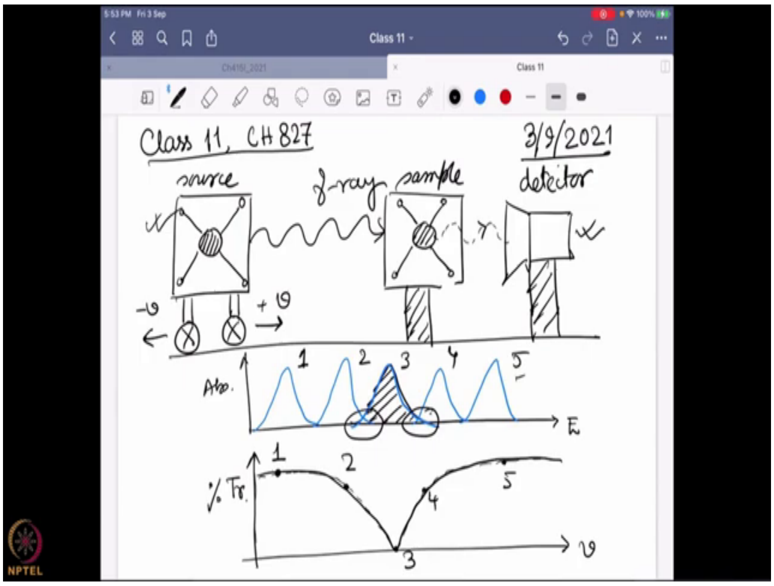

So, previously we are studying about Mossbauer Spectroscopy and we have found that if I want to have a Mossbauer spectroscopy. We actually, need to have a source and that has to be bound to a solid matrix. Otherwise, you cannot have that mossbauer effect due to the recoil. So, we want to have recoilless environment and for that I need to graft our source in a solid matrix. Similar things should be also happening to the sample.

So, this is the source, this is the sample that I am going to look into at the end, we have a detector and what is actually, happening? They are all put on a stage where the detector and the sample typically are actually, bolted. So, they do not move. However, the source is put on a wheel where you can actually, move it backward or forward and you can also even measure it is velocity +v means it is coming towards the sample –v means it is going around the sample.

And what happens? It actually, gives the γ ray and then depending on whether it is absorbing or not, you can detect it in the detector. So, what happens? What we found? That there are different possibilities, are there depending on what is the sample absorbance feature? So, this is energy versus absorbance and say this is the source one and the source energy I can module it by changing the velocity.

Because I can include a Doppler effect of that and depending on that there is say, like five different conditions, if I think about say 1, 2, 3, 4, 5 and in the fifth condition it says that it actually, matched perfectly with the absorbance feature of the sample. And then if I want to plot it with respect to %T of γ ray that has been detected in the detector versus the velocity, I am moving.

So, what I am going to see that? It is going to have a feature like this. So, say this is number 1 point position where it is nothing is happening, number 2 position a little bit of happening due to this overlap. Number 3 is the maximum because everything is absorbed number 4 again, a very little overlap and number 5 again no overlap. So that is how the signal typically looks like for mossbauer spectroscopy.

So that we have gone into the details of it and I found that we found out like how it is happening? Now, the question is why the source and sample, although they are exchanging their energy between $I = \frac{3}{2}$ and I = ½ for the source and I = ½ $I = \frac{3}{2}$ for the sample. Why they are not really matching? Why they are a little bit different for the sample and source?

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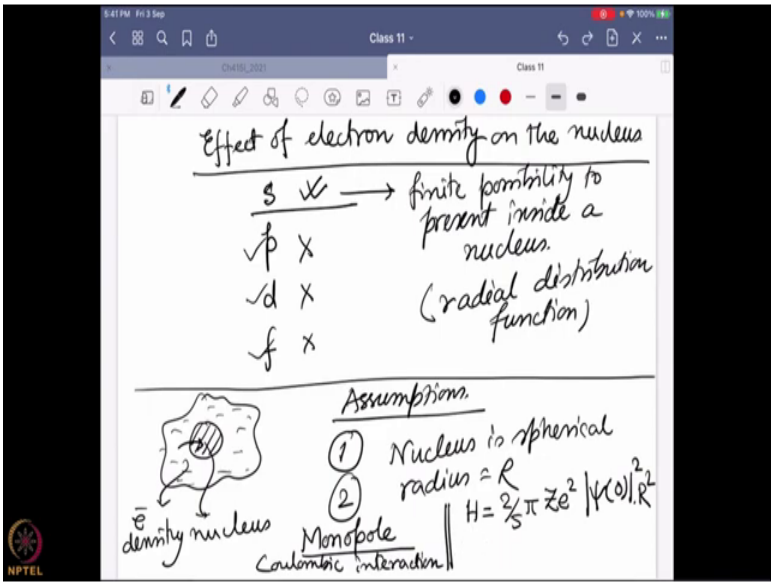

Effect of electron density on the nucleus

s ✓ ⟶ finite possibility to present inside a nucleus.

✓p ✗

✓d ✗

✓f ✗

(radial distribution function)

Assumptions.

① Nucleus is spherical

② radius = R

$H = \frac{2}{5}\pi Ze^2 |\psi(0)|^2 R^2$

$\bar{e}$ density

nucleus

Monopole

Coulombic interaction

And the answers is lying on the effect of electron density on the nucleus and last day we have gone into the details out of four different orbitals that you can have s p d f among them, only the s orbital can have some finite possibility to present inside a nucleus. And if you remember, we have gone through this thing called radial distribution function and from there we figure it out that.

Yes, there is a finite possibility for only the s orbitals and you can look into the wave functions how it is given? And you can find for the s orbitals if $r = 0$ value, if I put that means at nucleus, the wave function does not vanishes. It does vanish for p, d and f but for s orbitals it does not vanishes. So, there is a finite possibility that your electron is actually, staying inside the nucleus and that we have found.

And with respect to that we try to figure it out. the s orbital can be there. So, what is the effect of the s orbital on the nucleus? And over there, we assume this is my nucleus and this is the electron density that we are having around the nucleus. This is a nucleus and this is the electron density. And over there, only the s-electron density can be present inside this. And over here, if I have 2 assumptions, basically, there are 2 different parts of the same assumption.

First is that the nucleus is spherical and the second thing is the radius of the nucleus is R. Then what we are going to have? We are going to have something called a monopole interaction. A monopole interaction is a coulombic interaction because there is a positive charge present in that nucleus which is going to get affected by the electron density present into it and that can be represented by this Hamiltonian.

So, previously, when you talk about Hamiltonian, we think about what is the effect of nucleus on the electron? Now, we are looking into the other way? We are looking what is the effect of electron on nucleus? So, the Hamiltonian says that what you are going to have is the following $\frac{2}{5}\Pi$. These are coming for the condition that you have assumed that nucleus is spherical, so that way these particular terms are coming.

Then comes the Ze^2, is for the nucleus charge then $\psi(0)^2$ square that is the electron density inside the nucleus into R square. R is the radius of the nucleus. So, over here this Ze

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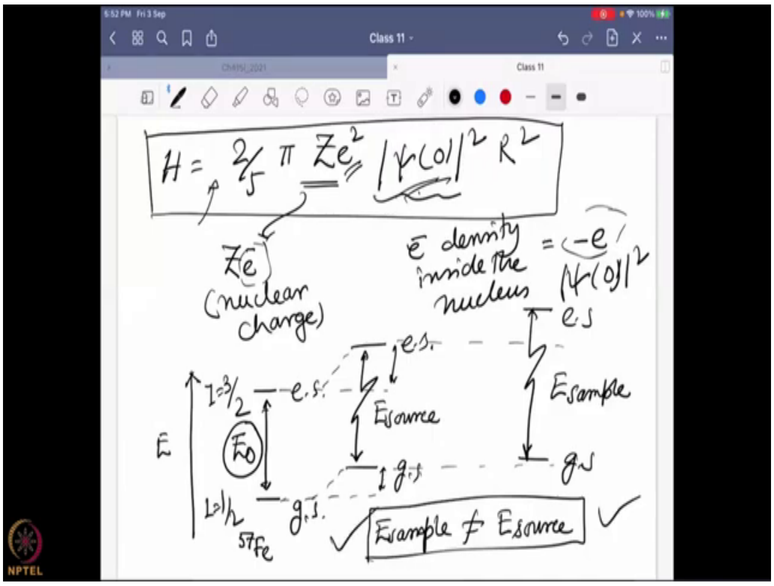

So, let me go to the next slide. So, again, I am writing this full equation $\frac{2}{5}\Pi Ze^2 |\psi(0)|^2 R^2$. Over here, the terms Ze is actually, coming for the nuclear charge. Where is it you can see? It is nothing but the atomic number that means how many protons are present? That is going to give you the positive charge. $\psi(0)^2$ gives you the electron density inside the nucleus.

And actually, it is given by $-e \times |\psi(0)|^2$. So, those e and this e over here that is how you get it e^2. And this negative term is actually, getting cancelled because you are talking about a monopole. So, first we have to start with a negative term over here but which is getting cancelled with the negative charge of the electron. So, they are getting gases, so, you have a positive term altogether.

So that is the Hamiltonian of a base electron density effect on the nucleus. So now, here comes the issue. So, you have a ground state and electronic state so, say we are talking about ^{57}Fe system from now on. So, ground state means $I = ½$ excited state means $I = \frac{3}{2}$. So, if there is no base electron density present, no matter what system I am taking? I am going to get the same energy gap between the excited state and the ground state.

If there is no effect of the electronic state, no effect of the electrons but in reality, there is so, there is s-electrons have finite possibility that it is actually, penetrating into the nucleus. So that is why the ground state and excited state is not going to be same. They are going to change their energy. And as they are going to change their energy, the energy gap is not going to be the same.

So, say it is the ideal energy gap what it should be? But now, my energy gap is this E source and this how much it is changing? It depends on how much is electron density you are allowing it to be. Similarly, what is happening in the sample? That can be also in a different position. So, their ground state and excited state for sure but due to the presence of this s-electron density, the energy gap is not remaining the same.

So, over here, what I am trying to say? E sample ≠E source and that is why we have to balance that energy gap between the sample and source by creating a Doppler effect by moving the source towards or away from the sample. And that is happening because of the effect of the electron density and that is why we have to know how to connect them together? How the s-electron density can be connected with respect to the energy of the nucleus state?

So far, we are already having one of the fact over there that this Hamiltonian is giving me an idea that the s-electron density has something to say on the nucleus and this nucleus over is going to be present there. Now, if I say that there are 2 different systems, one is the source and one is the sample.

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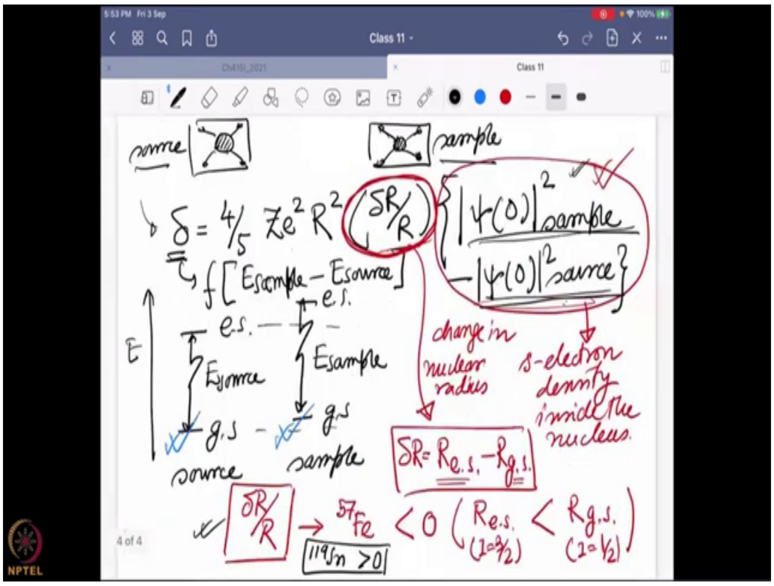

$$\delta = \frac{4}{5} Z e^2 R^2 \left(\frac{\delta R}{R}\right) \left\{ |\psi(0)|^2_{sample} - |\psi(0)|^2_{source} \right\}$$

$$= f[E_{sample} - E_{source}]$$

$$\boxed{\delta R = R_{e.s.} - R_{g.s.}}$$

$$\boxed{\frac{\delta R}{R}} \rightarrow {}^{57}Fe < 0 \left(\underset{(I=3/2)}{R_{e.s.}} < \underset{(I=1/2)}{R_{g.s.}} \right)$$

$$\boxed{{}^{119}Sn > 0}$$

So, say there is my source and here is my sample and say they are not the same molecular identity. They are both iron but not molecularly same say one is iron chloride, one is iron sulphate. So, how much that is going to affect it? So that what we can do specifically differentiate that energy with respect to the s-electron density? And what I am going to get is a difference in energy of the source and sample?

And that is given by this equation, $\frac{4}{5}$ Ze^2R^2 $\frac{\delta R}{R}|\psi(0)|^2$of sample – $|\psi(0)|^2$of source. So, let us go slowly what do I mean by this particular equation? This equation is saying that if you have a sample and source and if there is an energy difference present between the energy gap of the source and sample. So, this δ value is nothing but what it is saying? That say this is my ground state and excited state.

So, what I am basically drawing the ground state and excited state related difference for the source and say the sample is different. So, say this is E source and this is E sample. So, this δ value is a function of this $E_{sample} – E_{source}$. So that is what I am trying to figure it out over here. And that is given by this term delta, what is the actual name of that? I have come into a little bit later.

But this δ value defines what will be the difference of energy between the sample and source? And what are the parameters that is going to be different over here? So, if you look into here, what are the parameters that is going to be differ at these 2 terms? One is this one and one is this one. So, first come into this particular term $|\psi(0)|^2_{sample} – |\psi(0)|^2_{source}$. What is giving it?

Basically, it is saying, what is the difference of s-electron density inside the nucleus? Say if you can measure this electron density between the sample and also the electron density inside the source, whatever the difference is that is going to be this particular term. And say your source and samples are actually, basically the same thing these terms becomes 0 and you will not see any difference between the source and sample in energy gap.

So that is given by this particular term. Now, what is $\frac{\delta R}{R}$ now that is very interesting? What it is actually given? δR value is that difference in the radius in the excited state – ground state. So, what it is saying? That when you are changing the nuclear state from I= ½ to I= $\frac{3}{2}$, is it always true that the nucleus remaining almost same? Can it also change it is nuclear radius?

And the answer is yes, it can changes nuclear radius, it can shrink down or it can expand if it expands that means excited, state radius will be higher than the ground state. So, δR will be a positive term. But if it shrinks down that means excited state is smaller than the ground state it will be negative term. And over here, this $\frac{\delta R}{R}$ term defines whatever the changes you are seeing with respect to the nuclear size.

So, it is a change in the nuclear size or nuclear radius. And this term depends on the particular atom you are taking because depending on the particular atom or isotope, I should say particular isotope so, like ^{57}Fe in the case of ^{57}Fe this value is negative. Why? Because, in case of ^{57}Fe that excited state radius that means at I = $\frac{3}{2}$ is actually, smaller in size than in the ground state I = ½ . So that is why this value will be negative.

So, these are the 2 parameters that can be changed during the transition one is the s-electron density difference, one is the change in the radii of the system. Any question so, far. Please go ahead. So, this is very important like what are the changes can happen? That can affect that the excited state and the ground state energy cap can be different from source to sample. And what we found? There are 2 important factors.

One is this $\frac{\delta R}{R}$ and one is this difference in the s-electron density? Now, $\frac{\delta R}{R}$ can be changed but that has minimal effect with respect to what is happening around the nucleus, whether the electron density is changing increasing that does not matter. It only says that the $\frac{\delta R}{R}$, whether it will be positive or negative for Fe it is negative. If you go for ^{119}Sn it is positive.

So, this values becomes positive that means, in this case of ^{119}Sn, the excited state has a higher radii compared to the ground state that is all. So, it actually, defines what will be just a signature of it like it is a negative or positive? However, it does not really matter too much what will be the absolute value of it? It just defined it this will be positive or negative. But the absolute value will be depend on the difference between the sample and source s-electron density.

So that is why the electron density or less electron density can matter and can affect that the value can be different. And that is why, if I go back a little bit over there, you can see the sample and the source will be different and that is why we are actually, have to move the source back and forth to match the sample because the source and sample cannot be same all the time due to the change in the s-electron density.

So now, if I want to find out, if I have an Fe, what should be the trend of this change? Whose side I should move around that will be totally dependent on this particular value of the s-electron density.

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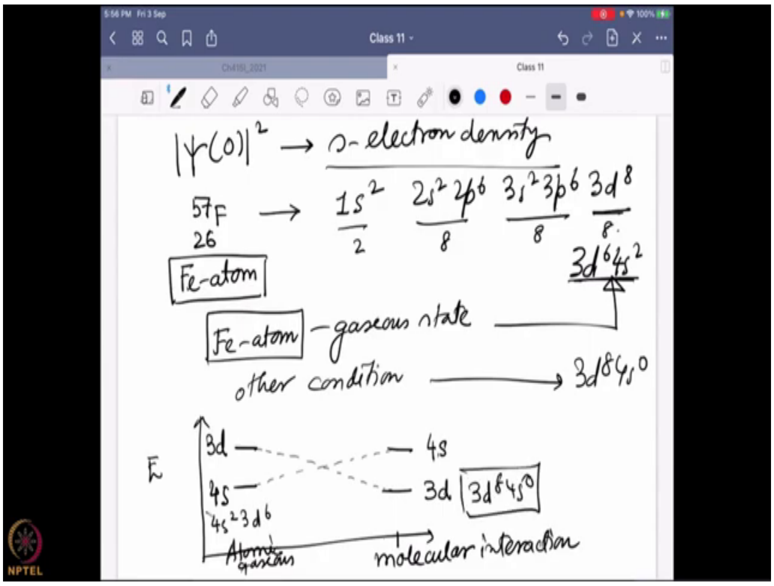

So that will be our concern from now on so, this one s-electron density that I am going to look into. Now, how the s-electron density can matter. So, again, I am taking iron as an example. So, if I look into Fe, there are 26 electrons if I start from the atomic state of the Fe atom. So, say, I am taking an Fe atom, a single Fe atom in gaseous state with 26 electrons. What would be the electronic configuration?

You are doing that from 7 standard right now it is so, it will be $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^8$ that we actually, write it down. So, if I did not correctly so, let me write down 2 to 4, 10, 12, 16 electrons 10, 8, 8 so that is the 26 electrons you can have over there. However, when I am writing it, I am writing at $3d^8$ but previously you guys have published studied it. It is $3d^6$ $4s^2$ because you are also writing $4s^2$.

So, over here you have to understand it depends on which particular condition I am talking about. If it is a Fe atom in gaseous state in such a way that this ion atom is not interacting with anything else then only it can be $3d^6$ $4s^2$. Any other condition, even in metallic state it is going to have a configuration of $3d^8$ $4s^0$. Why? Because it depends on the energy of the orbitals so, say I am looking into 2 different states.

One is the atomic gaseous state and one in a molecular interaction when the atom is following a molecule. So, in the atomic condition, what happens? The 4s orbital has lower energy than 3d. So that is why 4s orbitals get accumulated first. So that is why we get over here $4s^2$ $3d^6$. However, as you start forming the molecules, the d orbitals have better overlap, higher interaction.

So, it gets stabilized. On the other hand 4s orbital is not so much so, it gets higher in energy. So, in a molecule 3d has lower energy compared to 4s. So that is why it goes to $3d^8$ $4s^0$ system. And that is why we are going to look into this configuration mostly.