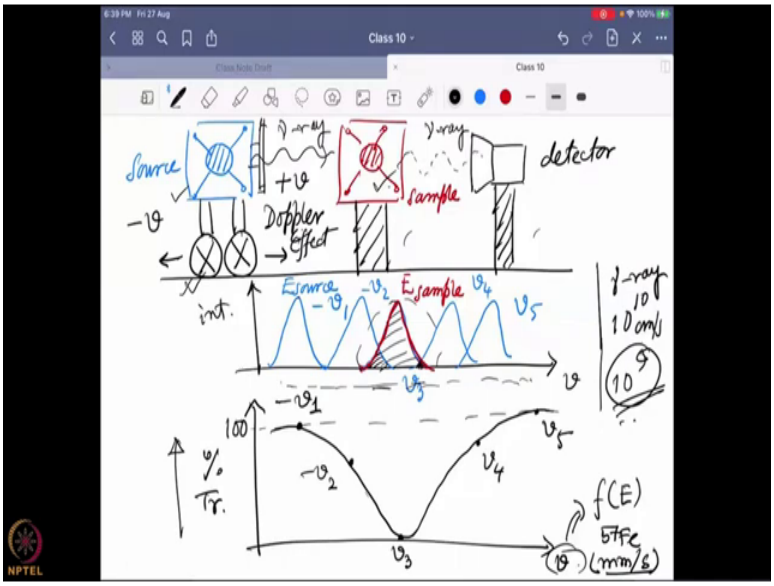
Circular Dichroism and Mossbauer and Spectroscopy for Chemists
Prof. Arnab Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

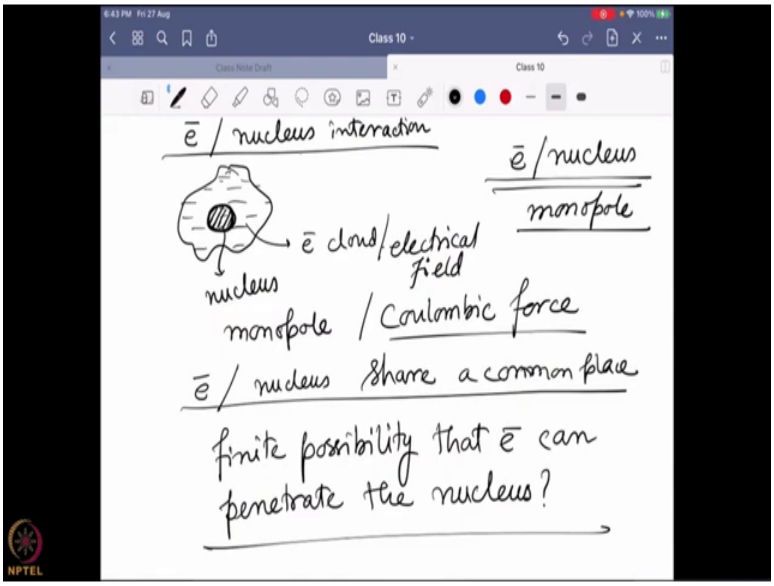
Lecture – 41
Mossbauer and Spectroscopy Fundamentals IV

(Refer Slide Time: 00:17)



Coming back to Mossbauer spectroscopy, now, we said that over here that this source and sample, although they have the similar transition happening $\frac{3}{2}$ to ½ or vice versa that energy is not actually matching. And the loose explanation I was giving that because of the electronic environment that is different.

(Refer Slide Time: 00:43)



ē / nucleus interaction

ē / nucleus

monopole

ē cloud/electrical field

nucleus

monopole / Coulombic force

ē / nucleus share a common place

finite possibility that ē can penetrate the nucleus?

Now, the question is why the electronic environment is affecting the nuclear state. So that is, we are going to cover in the final section of this class. So, electron nucleus interaction so, generally, when you look into a nuclei says that this is the nucleus. It is actually, covered by an electronic cloud and this electronic cloud it is nothing but we can say it is going to create an electrical field.

So, you can imagine, there is a positively charged system that is nucleus is sitting inside an electric field. So that is why that is going to have some electron nucleus interaction which we can define as a monopole or do an even monopole with respect to the nucleus if I see in the perspective of the nucleus, the nucleus is sitting as a positively charged and it we put it in an electrical field. So, there is no other pole over there.

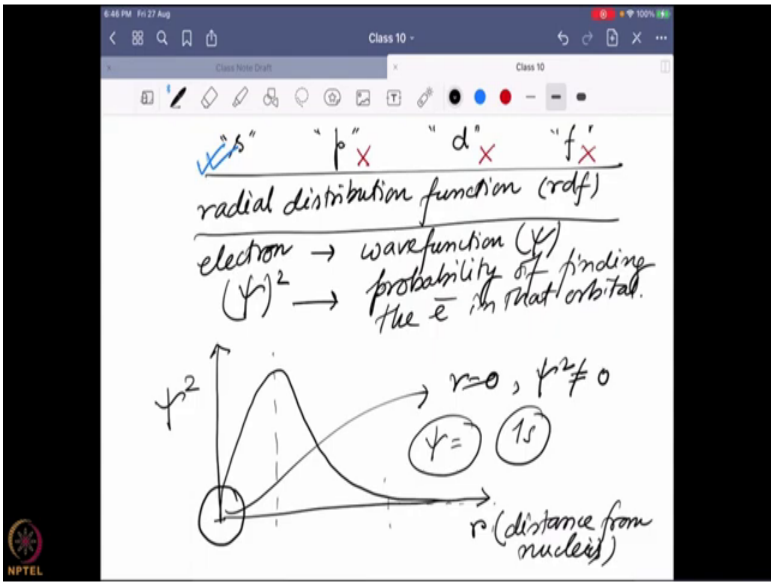
So, it is actually, taken as a monopole. And this monopole is actually, situated inside a electrical field and that I can measure the coulombic force. The coulombic force that monopole is facing. Now, before I go there, there are certain things I need to understand. First thing we need to understand that this interaction will happen once the electron and the nucleus share a common place that means they have to situate at the same place.

Now, what do I know? That electron cloud is surrounding the nucleus but the electron cannot generally go inside the nucleus but unless the electron goes inside the nucleus, there should not be any common space where they actually, sharing the space. Otherwise, there will be like a totally different field. There will be interface between them but what I want to understand? If they can share a common space.

So, for that I have to understand is there even a finite possibility that electron can penetrate the nucleus. Is it possible for the electron to go inside the nucleus? **"Professor – student Conversion Starts"** So, any suggestion on that is it even possible? **(()) (03:50).** What do you think is it possible the electron can penetrate the nucleus? Yes sir, for the radioactive nuclei it happens sometimes because electron capture is taken place from the K shell.

So, I think that is possible. So, yes, so that is true. Yes, anyone else want to add anything? **"Professor – student Conversion Ends"** Because if not so, what we are talking about is a little bit different, when you talk about the electron capture, the electron at the end is actually losing its identity. It is going inside the nucleus and becoming a part of the details. But what I am trying to understand? If the electron can still hold its identity just stay inside the nucleus for a bit and again can come out unarmed if that is possible.

(Refer Slide Time: 04:37)



✓ "s" "p" ✗ "d" ✗ "f" ✗

radial distribution function (rdf)

electron → wavefunction (ψ)

$(\psi)^2 \longrightarrow$ probability of finding the $\bar{e}$ in that orbital.

And the answer over there is actually, yes, it is possible. So now, if I look into the difference kind of electron and if I define it like what is the different orbital they stay in? These are the four different orbital we generally actually, exposed s p d f and among them only s orbital can actually, go through the nuclei. The rest of them cannot go through. Now, the question is, how do I know it?

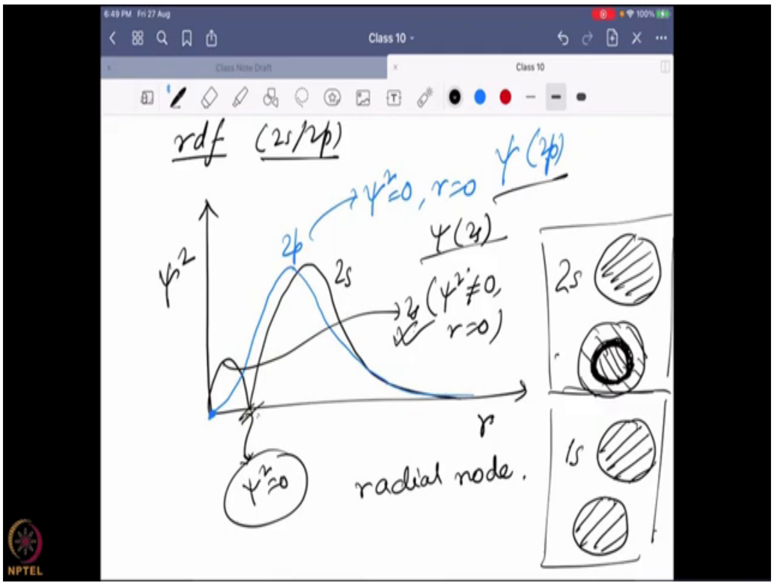
So that you know from a particular parameter which is known as radial distribution function I am quite sure most of you have gone through that in your quantum mechanical class. So, what is a radial distribution function or RDF? Now, when we have an electron, we define the electron in quantum mechanics as a wave function as a waveform ψ. And then if I take the square of that ψ^2 that actually, defines the probability of finding that electron in that particular orbital and which is not says over a particular space.

Now, how if I can draw that in a graph? We can draw the orbital fine but if I want to draw that with respect to a graph. Over there, I am drawing ψ^2 that means, what is the probability of finding the electron? And in this x axis I am drawing r, r is nothing but distance from the nuclei or nucleus. Now, when we look into what we found for 1s orbital, I am going to draw that for each on one orbital for 1s orbital is looks like this.

What does it mean? That over there I have the maxima after a while it is almost non-zero existence, so that is everything fine. But one important thing we found over there. Here we found at r = 0 ψ^2 value is actually $\neq 0$. Why? I am not going into the details it depends on, how I define the ψ function? Look into the ψ function of 1s orbital. And over there, if you put r = 0, you will find ψ^2 value is not going to be 0.

It is a non-zero value, what that means? That means there is a finite possibility, just for even for some time that electron can stay inside the nucleus r = 0 means you are inside the nucleus. That is what is actually, happening?

(Refer Slide Time: 07:41)



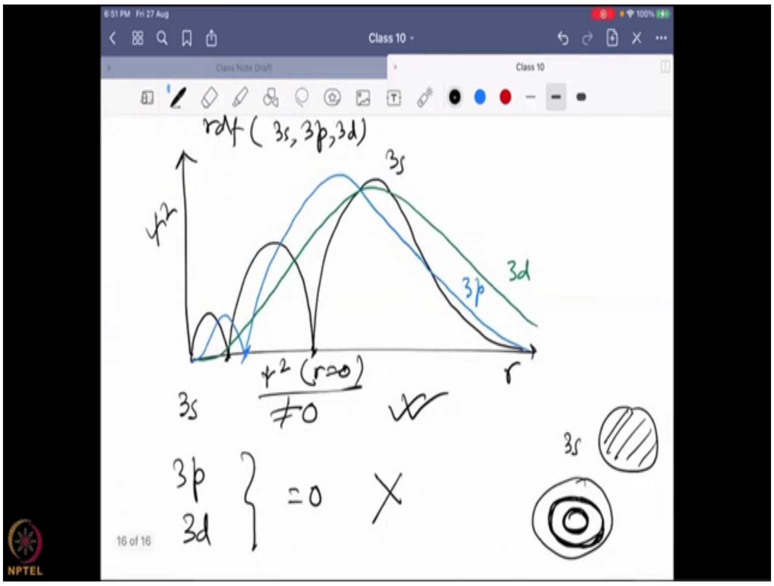
Now, if I draw the 2s orbital, I am drawing the radial distribution function for the 2s and the 2p set of orbitals. Again, I am drawing the ψ^2 and and the internuclear distance from the sorry the internet the electron distance from the nucleus and if I draw the 2s orbital. The 2s orbital looks like this. So, over there, there is a particular point where ψ^2 becomes 0 at a finite alternative this is something known as a radial node.

So, in 1s orbital you do not see such kind of $\psi^2 = 0$ value over here but over here you see that that is called node and how the radial node looks like? So, if I want to draw 1s orbital, this looks like a sphere and if you cut down the sphere in half, you will find it is still a total sphere. But if you look into the 2s orbital from outside, it looks like a sphere. If you cut it half you will find this following that at one particular place, there is 0 electron density.

And outside that there is 1. So, there is a hollow region at particular r value. There is no electron density is present. So that is called as a node and a radial and this is present in the 2s orbital. So that is why, when you are drawing the RDF we found this is 0. What about the 2p orbital? 2p orbital looks like this. So, this is 2s.this is 2p and now, over here you can see the 2p value is saying that it has a $\psi^2 = 0$ value at $r = 0$.

Because look into the wave function of ψ = 2p. And then if you look into the wave function of 2s, you find ψ^2 = non-zero = r = 0, again look into the wave function of ψ = 2s and compare that with 2p. You will find that if you put $r = 0$ ψ^2 not = 0 for 2s. Similarly that means 2s has finite probability to be inside the nucleus but 2p is not.

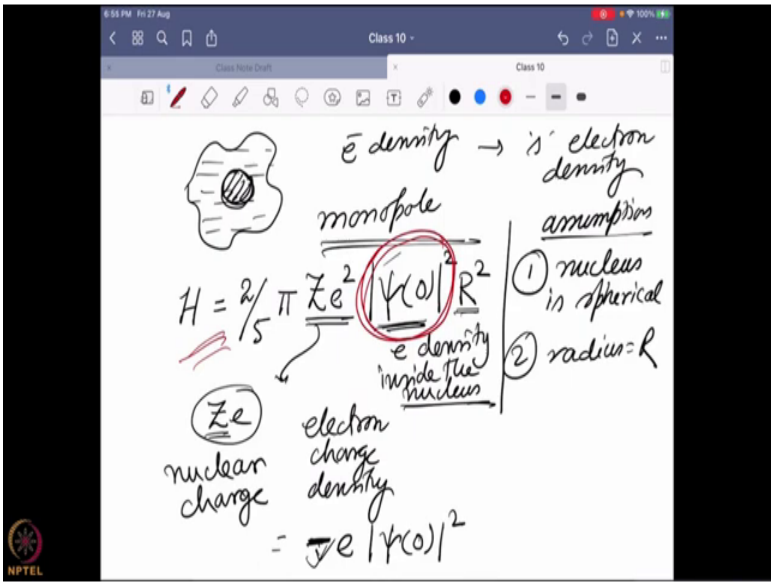
(Refer Slide Time: 10:20)



Now, very quickly I will go to 3s, 3p and 3d. So, 3s looks like this, so now, it has 2 nodes. You probably learned it earlier that how many nodes you expect it is n – l – 1 n = primary quantum number, l = azimuthal quantum number, all those things. So, there will be 2 nodes. So that means, if I take a 3s orbital which looks like a sphere, if I cut it in half, you will find 2 regions where there no electron density present that is how it is going to look like.

Now, if you look into 2p that is, how it is going to look like? So, 2p Sorry 3p is going to have 1 node and then you probably can have say 3d that is, how 3d is going to look like? So that is how it is going to look like? And over here again, you are going to see for 3s at r = 0. It is non-zero for 3p and 3d value they are = 0. So, they cannot be present inside the nuclei but 3s can and that is why we suggested that yes it is possible to have some electron density present inside the nucleus. If you have s orbital but not p or d or f orbital.

(Refer Slide Time: 12:23)



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

$$= -\cancel{z}e|\psi(0)|^2$$

Now, with respect to that we come to this thing that so, we are talking about a nucleus, we have some electron density outside and we are trying to find out **(()) (12:33)** what is the effect of this electron density on the nuclei. And over there, the electron density we are concerned about is only the s electron density. Now, because as we discussed earlier, it is a monopole and we are trying to find, what is the effect of this electron field on the nucleus?

And if I want to draw the Hamiltonian because that is how we define the surrounding, how this electrical field is affecting the nuclei? We are going to find an equation and for before finding the equation, I am taking 2 assumptions. First assumption is this nucleus is we are talking about is spherical and the radius of this nucleus is R. These are the 2 assumption I am taking it as a sphere, not any other particular 3D shape which is possible but at this moment we are taking only spherical.

If that is the case, the Hamiltonian will be given by this equation $\frac{2}{5}\Pi Ze^2 |\psi(0)|^2 R^2$ now, I will go slowly but each of these terms believe. So, over there, the Ze^2 is actually, a mixture of Ze which actually, define what is the nuclear charge. Z is the number of protons present in the system. So, it will surely define the monopole energy with respect to, what is the nucleus I am talking about?

And then the electron you have the electron charge density that we also have to think about and that is given as –e that is the charge of an electron into $\psi(0)^2$ square. What is $\psi(0)^2$? $\psi(0)^2$

is that electron density inside the nucleus. As you just said, it is electron density possible to spend some time inside the nucleus, how much electron density is present inside the nucleus?

That is given by $\psi(0)^2$, $\psi(0)$ is the wave function inside the nucleus, $\psi(0)^2$ is the probability and if I multiply that with the –e sign that will be the electron charge density. And in the Hamiltonian previously, it should have a negative sign because I am talking about a positive charge nucleus with an electron. So, there should be a negative charge in the beginning but that negative sign is cancelled by this electron charge density.

So that is why it is not there and R is the radius of the system. So that is how the equation comes. So now, I can have an Hamiltonian, how the system is behaving with some electron density present inside the nucleus? Now, imagine this is not going to be the same for the sample and the solution and that is why this Hamiltonian is going to change that means it is very similar to some perturbation and that is going to affect my energy states.

Now, how they are going to be happening? What will be the parameters we have to look into? That we will cover next week on Friday. So, we are going to stop it over here. Any questions up to this point please go ahead.