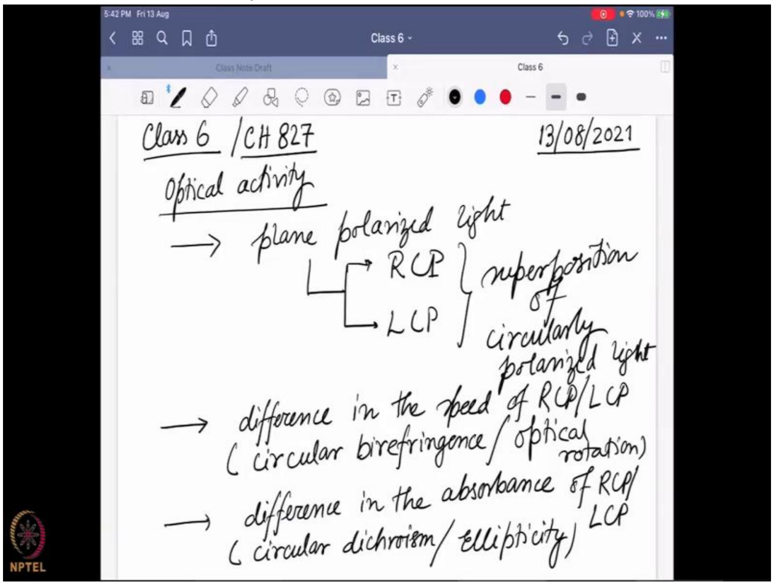
Circular Dichroism and Mossbauer Spectroscopy for Chemists

Prof. Arnab Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 22
The Physical Background of Chiral Response – V

(Refer Slide Time: 00:15)

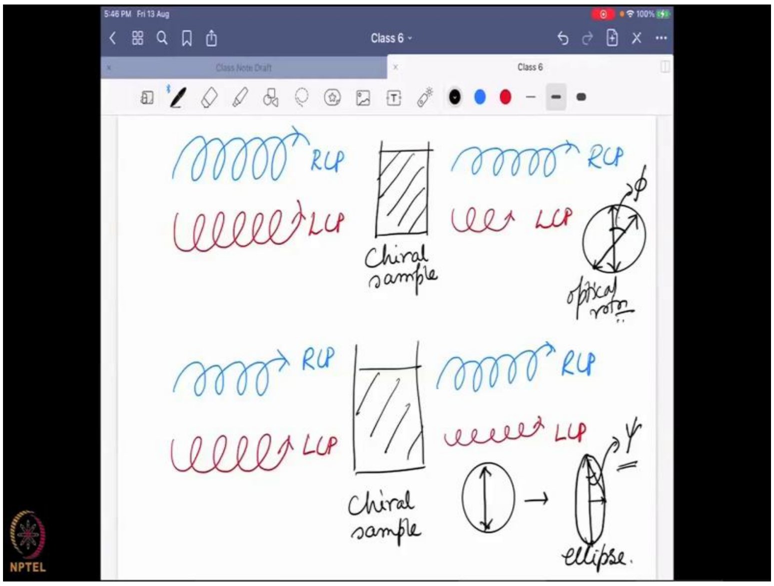


So, in the previous class we are discussing regarding the optical activity. And during this optical activity, what are the things you have gone through that this optical activity? We generally look into plane polarized lights. And you figure it out this plane polarized light can be written as a superposition of right hand circularly polarized light and left hand circularly polarized light. So, there can be explained as surplus enough circularly polarized light.

And we have gone through in details. How we can explain that thing? And then we actually looked into the details of it. And figured it out, what is actually happening? And we found there are two different effects happening over there. One is a difference in the speed of this RCP and LCP. And which we call them as circular birefringence and this end up to be affected with optical rotation.

And the other thing we found that there can be a difference in the absorbance of RCP and LCP. And that is known as circular dichroism and which is affected with the ellipticity. So, you have all studied that so, any questions up to here on this particular points? So, if not, we will go further.

(Refer Slide Time: 02:55)



So then the question, what we found that what is actually happening over there? There are two kinds of lights you can say one is the RCP and one is the LCP. And what we found? That this RCP and LCP uh to a few seconds, I am drawing it over there and again this is the chiral sample and these two lights of RCP and LCP actually come together. They are not separated but we are drawing it separately so that we can understand it better.

And what happens in the case of optical rotation or circular birefringence? One of them is moving faster whereas, one of them is moving slower. So that is why we see a change in the plane of the polarization of the light which end-up with the difference in the optical rotation that we have discussed earlier. So, what we noticed is the column at here is the previous one and later we say if there is a change in temptation and this particular rotation is the optical location.

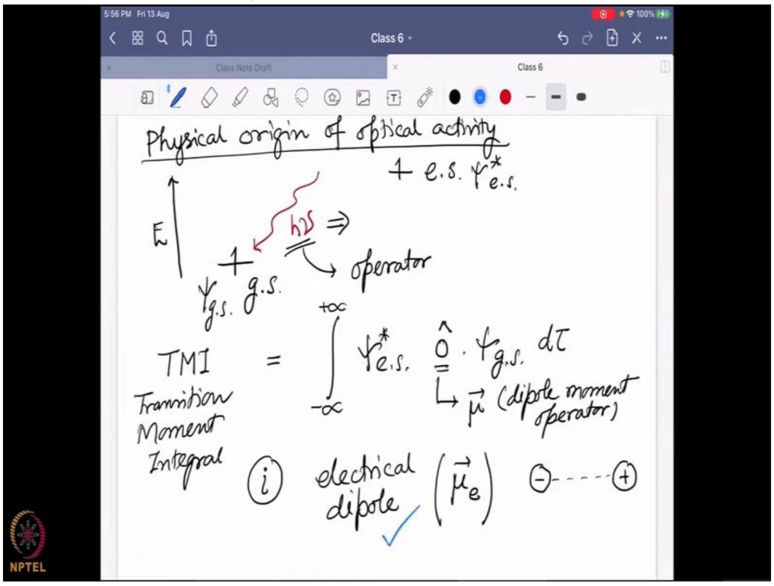
This is happening because of the difference in the speed, whereas it is possible that this is the RCP this is the LCP. Again, it is going through the chiral center and one of them is absorbed more than the other. So, the RCP is remaining almost the same. The LCP on the other hand get absorbed. So, in that case we find at, what was before a very nice plane polarized light? And superposition of RCP and LCP later on it transferred in a ellipse.

So, this is what is actually happening? And how much is the ellipse is coming down? It depends on the major and minor axis ratios minor axis ratios which is given, as this thing called ellipticity. So, this is the optical rotation in the previous one. Next, one is the electricity. So, this is what is happening. So, far we have copper and now, the question is we found that okay in the light. In the plane polarized light we have two components.

A right hand circularly polarized light and the left hand circularly polarized light which has the helicity coming over here. And which can probably create the issue with this chirality because this RCP and LCP are actually near image of each other. So, there is the reason of the light where the chirality is coming from. Now, the question is what is there in the molecule?

That can detect this particular difference in RCP and LCP or two different chiral heads of the light? So that is what we are going to cover today.

(Refer Slide Time: 06:44)



So, today we are going to cover the physical origin of optical activity. What is happening in the molecular level? Now, we have covered that earlier that if we have an electron present in a ground state of a molecule so, it is $\psi_{g.s}$. And then I actually shine light or electromagnetic radiation is hν (07:24). And that actually can create a difference in the electronic distribution of the ground state.

And bring it to an excited state configuration which I am writing at psi star excited state. And over there this whole thing is happening with this electromagnetic radiation over here. So which we can say it is the operator which actually ensures that the ground state electronic distribution transforms into an excited state electronic distribution. And if I want to cover, what is actually the probability of this thing?

And we have already discussed it which can be given as the transition moment integral or TMI $= \int_{-\infty}^{+\infty} \psi *_{e.s} \vec{\mu}\ \psi_{g.s}\, d\tau$ $(\vec{\mu}: dipole\ moment\ operator)$ transition movement integral who is actually covers up, whether this configuration will change is possible or not. So, it goes to excited state with the help of the operator from the ground state and it is happening at a small volume at $d\tau$ and say I am actually covering it for the full negative infinity to plus infinity all the possible space.

So that actually covers up this overall possibility of this transition. And previously, when we discuss about, we discussed that this operator is nothing but the dipole moment operator. The transition dipole moment that is created by this incoming electromagnetic wave. Now, over here, when you say it is a dipole moment operator and presumably we are saying it is an electric dipole. We are actually neglecting all the different possibilities.

So, today we are going to say about, what are the different operators possible which can create this particular change to take an electronic distribution from the ground state and redistribute it to the excited state? So, it is not only the electrical diagram. So, there are three different possibilities which can ensure this particular transition. The first one is the electrical dipole moment which you already know it is given as $\overrightarrow{\mu_e}$, e:for the electron.

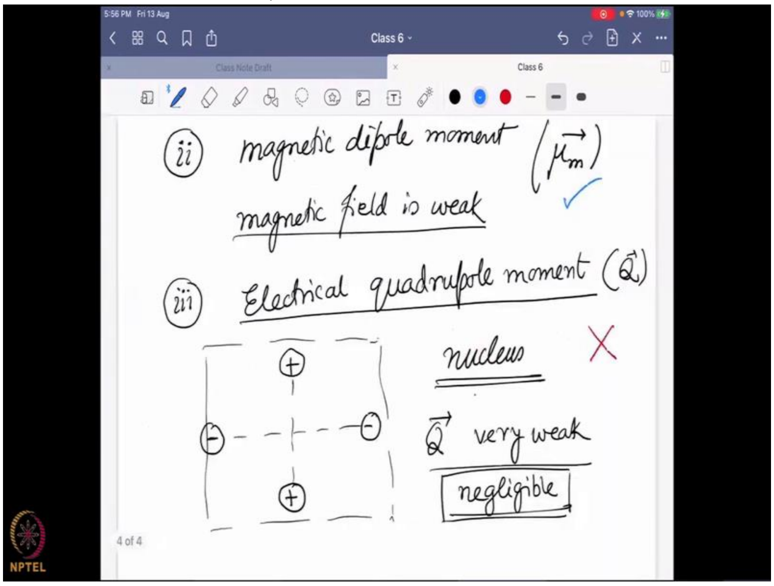
So, over here, what happens? You have a negative region, we have a positive region, we create a dipole. So that is why there are two different dipoles and that is actually let us say, electric type. So, whenever you have an electronic distribution, if you make it an asymmetric shape, it will create an electrical type. If it is a shear of an electronic field, you can say there is no difference in the electronic distribution. But now, say it is actually irregular shape.

So, irregular shape is in somewhere you have more electron density than the other region. So, you can say in one particular region. You have more electron density negative to the other region lack of electron density are positive so, you create a dipole. So that kind of thing can happen and this electrical dipole is the easiest thing to develop in a molecule. So that is why, this is the most dominant one when we come to this transition moment integral operator.

But this is not the only thing. The other thing which can affect it, it is the magnetic dipole moment. So, there is a possibility. You can have a magnetic dipole moment. Obviously, when you are talking about an electromagnetic radiation it also have a magnetic direction. Although, it is pretty weak the magnetic moment, as we just said, the magnetic field intensity is weak but it is a non-zero entity.

So, what happens when there is a magnetic field? Again, the magnetic field can have two different directions, as we generally try to say it is a north pole but the south pole but we mean to say there are two different, totally exactly opposite characteristics. And this to create the other two poles and that is known as magnetic dipole moment. And this magnetic dipole moment operator can also create this particular change of this ground state to the excited state when it comes to an operator. okay.

(Refer Slide Time: 12:06)



So, this magnetic dipole moment operator is created by the magnetic field. And in the molecule also you have electron density. So, if you have electron density, you have electrical field, obviously perpendicular to that. You are going to create a magnetic field and this magnetic field can create an magnetic dipole and that can also create and electronic transition. And the third one is known as an electrical quadrupole moment.

So, what is an electrical quadrupole? It is only given as $\vec{Q}$ electrical quadruple is that you actually create instead of two different poles, you can create even four poles. So, how it actually looks like? So, it generally looks like it is created as a positive, exactly opposite here you are going to be positive and perpendicular to that 90 degree angle. You are going to get two negative regions.

So, you can see all together when you look into that there are four different poles. So that is why it is called the quadrupole. And over here a little bit different from the dipole the opposite ends are not the different but the same charge you would. So, there are two positive and two negative opposite to each other and that is what is known as the electrical quadrupole.

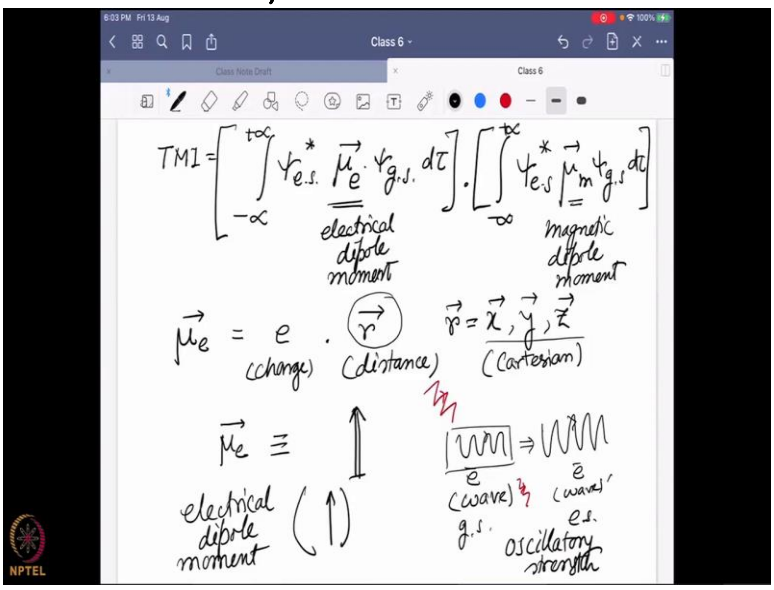
And the electrical quadrupole moment when it generates a big chunk of this electrical quadruple quadrupole moment is influenced by the nucleus actually. So, the presence of the nucleus in the molecule actually plays a huge role to create this quadrupole moment. However, very similar to the magnetic type magnetic dipole the electrical quadrupole moment is also very weak, is even weaker than the magnetic field in most of the cases.

So that is why even this one, although it can create an electronic transition but generally we neglect it because the value is so low. However, there are some particular spectroscopic experiments where this quadrupole moment can play a huge role. So, one of them actually depends on the nuclear quadrupole moment very similar to NMR. You can also follow that and find out some very interesting uh features of a molecule.

And the other one is Mossbauer spectroscopy by this quadrupole moment plays a important role. So, this role of quadrupole moment in the Mossbauer spectroscopy will cover in the later part of the class. But this quadrupole moment spectroscopic that will not cover but if anyone is interested, please go through and find a way that even you can follow the quadrupole moment generated in a molecule, especially from the nucleus.

And find out very important factors about molecule. So, anyway so, over there this particular feature the electrical quadrupole moment we are going to neglect. We are going to mostly look into this magnetic dipole moment, although it is weak but what is the effect? And obviously, this electrical dipole moment these are the two important factors which is actually going to happen.

(Refer Slide Time: 15:38)



So now, if we look back to this transition moment integral one more time, I want to break it down, break it down one factor from the electric dipole and one factor from the magnetic dipole. So, this whole TMI $= \square \int_{-\infty}^{+\infty} \psi *_{e.s}\, \overrightarrow{\mu_e}\, \psi_{g.s}\, d\tau \square\square\square \int_{-\infty}^{+\infty} \psi *_{e.s}\, \overrightarrow{\mu_m}\, \psi_{g.s}\, d\tau]$, $\overrightarrow{\mu_m}$: *magnetic dipole moment.* I am going to break it down and they are going to be interrelated with respect to dot product. I am not going in details why this is due to their physical properties. So, over there they are this is the, how we actually write it down?

But over here instead of $\vec{\mu}$, I am going to write $\overrightarrow{\mu_e}$. That means this is the electrical dipole moment. And very similarly this is factor number one and very similarly I can run another one which will be controlled by the magnetic dipole moment. So, these are the two operators can be activated. Now, what we are going to look into? How these operators actually look like? So, when you talk about these operators, what does this operator means?

The operator means, is the formula. So, this $\overrightarrow{\mu_e}$, we first take a look. So, what is an electrical dipole moment? So, electrical dipole moment is nothing but as simple as the way we defined a dipole, it is that we created a charge difference between two poles which are separated by a particular distance. So that means there are two important factors that is going to control it.

One is the charge and one is the distance and among them this distance is a factorial. This charge does not have any particular direction. But when it moves to a particular direction then it creates a vector. So, electrical field is created when the charge is moving at a particular direction, so that directional system is coming from this distance. Now, if I want to define a system present in a three-dimensional space and type to find out which direction it is moving, how we can define?

As you know, we can define it in three different ways. We can either do that by Cartesian axis. We can define this $\vec{r} = \vec{x}, \vec{y}, \vec{z}$ and putting the factorial system because that is how the r can be defined or you can do that with the spherical terms. But there is a distance and the angles theta and phi. So, over there for the simplicity, I am taking it as a Cartesian axis. You can also do that with spherical coordinates.

But Cartesian axis we are looking into because that is going to connect it with the molecular structure. So, over here what I am saying? That if a dipole moment is created it is going to have a directionality. And this directionality can be defined as a combination of $\vec{x}, \vec{y}$ *or* $\vec{z}$. So that means, what I am saying?

That whatever the dipole moment I am generating if I want to look it physically.

How it looks that means it is going to be a charge which is having a particular direction. And what the direction important because if you remember, what I said earlier? That we have an electron present and that is in a wave function, I am actually imagining. And when an electromagnetic radiation falls on that they actually exchange energy. And if you remember, we talk about the oscillatory strength which is connected to the molar extension coefficient of an absorbance.

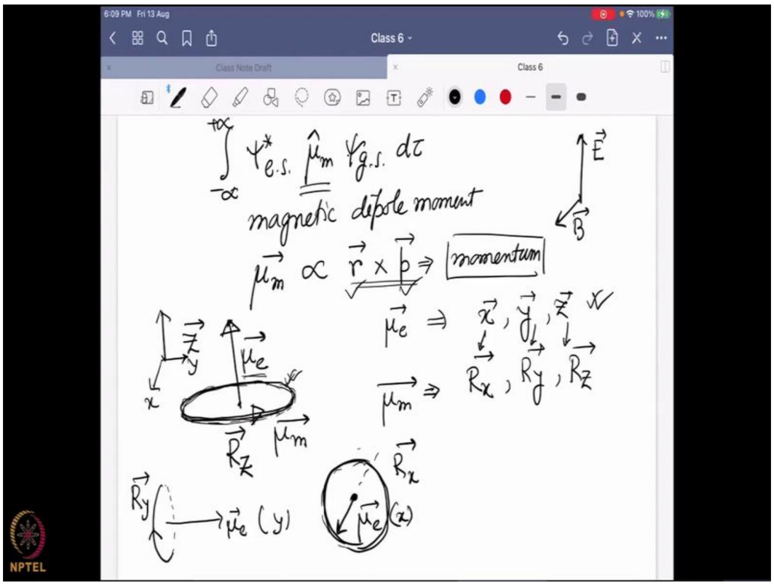
Which says that this particular wave over here which is present in a molecule that is going to change it is waveform. Now, say it is a little bit large. So, waveform is now different from the other. So, say it is the down state. It is the excited state and why is happening? Because this is incoming electronic radiation is actually giving some energy in exchanging some energy to this electron.

And you can imagine in a way that an already existing wave it is increasing in it is amplitude by taking some oscillation or oscillatory power from the incoming electromagnetic radiation. So that is what is happening? And that is why you talk about the oscillatory strength. Now, it is happening. Now, over there if two waves have to merge and interact, you can imagine, how important will be the direction?

Because depending on the direction, whether they are totally in the 0 degree angle or 90 degree angle, depending on that that will define how much possibly oscillatory strength can be exchanged? So that is why the directionality how they are interacting is very much important. And as we just discussed that it is actually going to have two different component. One is the electrical dipole and one is the magnetic dipole, the electrical dipole component interacts through a $\vec{x}$, $\vec{y}$, $\vec{z}$ directionality type function.

So, our electrical dipole moment which is going to interact with my electron density present in a molecule that will basically, follow a line. It can be x axis, y axis, z axis or any of the combination but it will be a line. That is how the electrical dipole will interact find up to this point. okay So, over here we take care of this particular part of electrical dipole moment. Now, what about this magnetic dipole moment?

(Refer Slide Time: 22:38)



So, magnetic dipole moment is also very important because it also has, $\int_{-\infty}^{+\infty} \psi *_{e.s} \overrightarrow{\mu_m} \psi_{g.s} d\tau$, the probability to excite a ground state to this excited state. Now, we talk about this magnetic dipole moment. So, already we know that if we have a electrical field like this, a magnetic dipole generally will be on the perpendicular to it that you already know. But how this magnetic dipole moment actually physically stays in the system?

For example, we just find out the electrical development is going to follow a line. How this magnetic dipole moment will follow? Now, this magnetic dipole moment if I want to find out how it is going to behave? This magnetic dipole moment is proportional to two different factors. One is the r which is the same as the directionality factor of the electrical dipole moment and then cross p, p is the moment momentum. $\overrightarrow{\mu_m} \propto \vec{r} \times \vec{p}$

So, these are the two vectors which comes together and create this magnetic. So, the moment of the charge has a lot of the things to do for the creation of this magnetic problem. So that is the basis of the electro dynamic electromagnetic theory from Maxwell. So, you can now, go back and look into the equations, how they behave? But the basic form was that the magnetic moment for the change of the electrical field is one of the main reasons for creating the magnetic field.

And over there this magnetic moment is going to be connected with the directionality in this session $\vec{r} \times \vec{p}$ and because of the, this particular factorial diagram interaction the magnetic field actually is created in the perpendicular and not only that it is going to be created not only in the perpendicular but in a circular. So that is, how the magnetic dipole moment will be created? Perpendicular to the electrical that moment we just talked about and it will move in a circular.

So, previously we have connected the electrical dipole moment because of directional axis system that we can connect it to the $\vec{x}, \vec{y}$ *or* $\vec{z}$ axis motions. Over here, how we can define this moment of this magnetic moment? You can see we can define it as a rotational motion. What do I mean? So, for a moment you define that this is actually z axis this direction. So, this is a $\vec{z}$ direction this electrical dipole moment that we created it is created in the $\vec{z}$ axis.

And this rotational motion is happening around that $\vec{z}$ axis in the xy plane. So, this particular rotation can be defined as a rotational along the $\vec{z}$ axis. Similarly, you can have a $\vec{\mu_e}$ say this is y sorry this is y this is x direction. So, it can have in this direction. You can say it is y and you can have a rotational motion in this direction. You can say it is a R_y. Similarly, you can have and $\vec{\mu_e}$ in this direction which is the x direction.

And you can create a magnetic field now in the plane of this pole, we are using, it will be R_x. So, what I am trying to say? The magnetic field which is going to be created over here it will be perpendicular to the axis of the electrical dipole moment. And it will show a rotational behaviour and that is why a magnetic dipole moment can be defined as R_x, R_y or R_z or a combination of them. So, this is very important.

So, we will wait for a minute to grasp this idea one more time. So, magnetic dipole moment can affect an electronic It is exciting Excite excitation. And this magnetic dipole moment is directly connected to the electric dipole moment created over here. So, this electric dipole moment behaves as a function of charge into distance. Because is it only one particular motion over there, the distance it follows that $\vec{x}, \vec{y}$ *or* $\vec{z}$ axis motion are their combination.

A magnetic moment on the other hand follow a combination of the direction and the momentum physical momentum, linear momentum. And that is why all together it comes out we in a rotational motion that is shown over here. And that will be exactly perpendicular to the electrical dipole moment we are discussing about. So that is why they will be correspondingly can be defined as R_x, R_y, R_z with respect to $\vec{x}, \vec{y}$ & $\vec{z}$direction.

So, magnetic moment if it is going to be created, it is actually going to be in a rotational motion. Any doubt or any issue over here, please, let me know before you go further.