Circular Dichroism and Mossbauer and Spectroscopy for Chemists
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Lecture – 17
The Physical Background of Chiral Response-I

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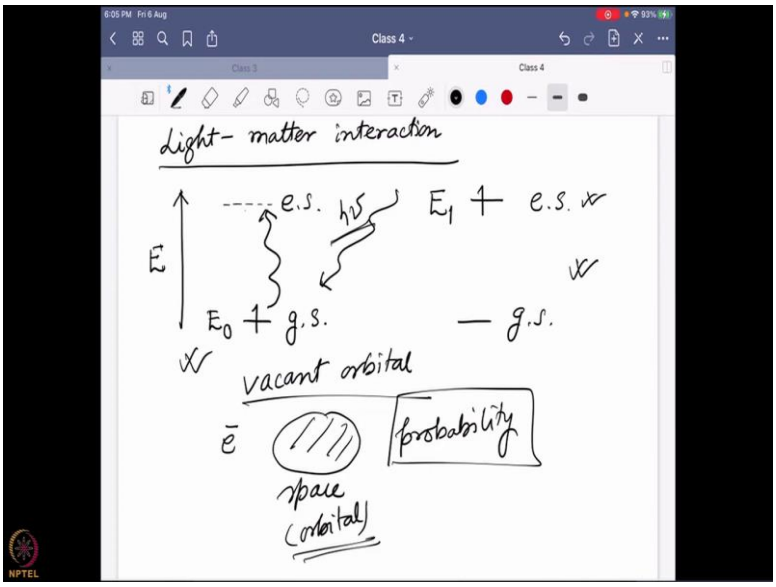

So, the discussion today we are going to have why an optically active or chiral molecule rotate the plane polarized light? That is the thing we want to understand. We know all of us that it happens. And some of you have done this experiment over and over in your lifetime take a sucrose solution pass through the plane polarized light and you see it actually changes the plane of the rotation that is fine.

The question is why? So, all these things actually begins with something called light matter interaction. So, before we go there, we are going to talk about light matter interaction and how an optical absorbance happened. So, what do we know by light matter interaction? So, this particular figure you have done a lot of time that there is an electron in the ground state, g.s. stands for ground state which has the energy of say E_0.

And then I shine light on that and this electron go to a higher excited state E_1 and generally how we draw that there there is a vacant electronic state and the electron basically, go over there. And that gives you a vacant ground state. Now, over here I am going to think a little bit does this concept of a vacant orbital that is really valid? So, what do I mean by vacant orbital? So, if I ask any one of you that what is the definition of an orbital? So, what do you say?

So, let me ask this question so, "Professor - student conversation starts" Harjit what do you say? that What is a definition of orbital according you? okay Orbital basically is a electron we can say. A little bit more, if you want to discuss electron and orbital are not the same thing right. Orbital is a space, basically the electron occupies. Yes that is very good. Rishab you want to add anything? Yes sir. Where the probability of finding an electron is maximum? okay

So, both of you are giving the right answer. So, electron is there it is moving in a finite space and we find out what is the probability of finding that electron? And wherever I am going to find it out that I will say it is my orbital. So now, if you do not even have an electron, can you have orbital? The other is probably, no. Unless you have an electron, you have no probability. The probability of finding an electron is going to be 0.

If there is no electron and that means there is no orbital present. "Professor - student conversation ends" So, why do we still say vacant orbital all the time? That is because it is very easy for us to see or visualize that the electron is sitting over here once it get excited by this incoming light. The electron goes in this particular place and we achieve the excited state. But this is actually not how the electronic transition happens. Electron transition happens a little bit different.

We are going to achieve the same starting and the same final state but the actual interaction happens in a different way. So, let us take a look how this interaction actually happens?

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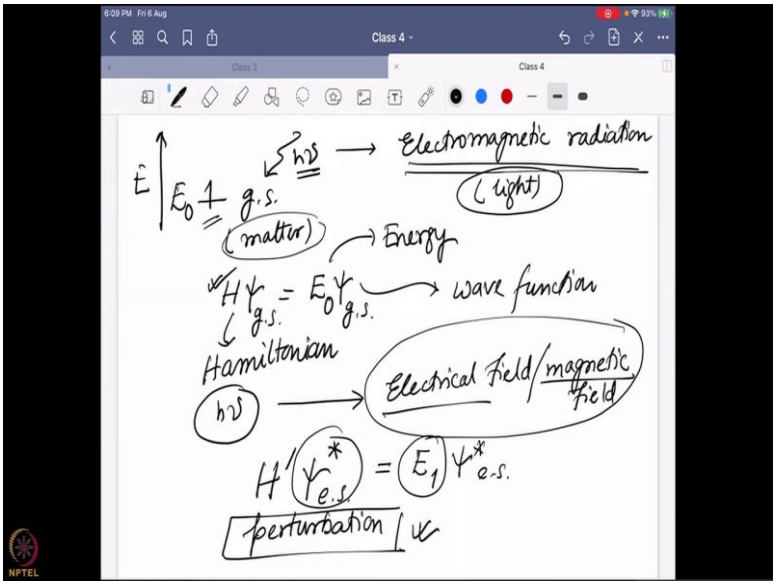


So, first of all, why this ground state system of the electron even interacts with this light? That is the first question. So, whenever we say there is a light, it is nothing but electromagnetic radiation. right And this electromagnetic radiation is going to interact with this particular electron and this electron belongs to a system or matter. And this electromagnetic radiation in general I am telling light but it can be any kind of electromagnetic radiation starting from radio wave to gamma wave.

All this electronic transition or any particular transition is actually follow the same basic theory, so that is we are going to understand. And because there is going to be an interaction between this electromagnetic radiation or light with this electron or matter. That is why we say it is a light metal interaction. okay Now, the question is why this electromagnetic radiation interacts with the electron?

So, for that again we have to go back to our favourite equation in quantum chemistry that is known as the Schrodinger equation. The equation is $H\psi = E\psi$, what is H again? Hamiltonian what is psi(ψ) wave function? And what is E is the energy of that particular electron. So, electron is moving on it is own way it is settling in a molecule with respect to the Hamiltonian or the surrounding which is given by this H.

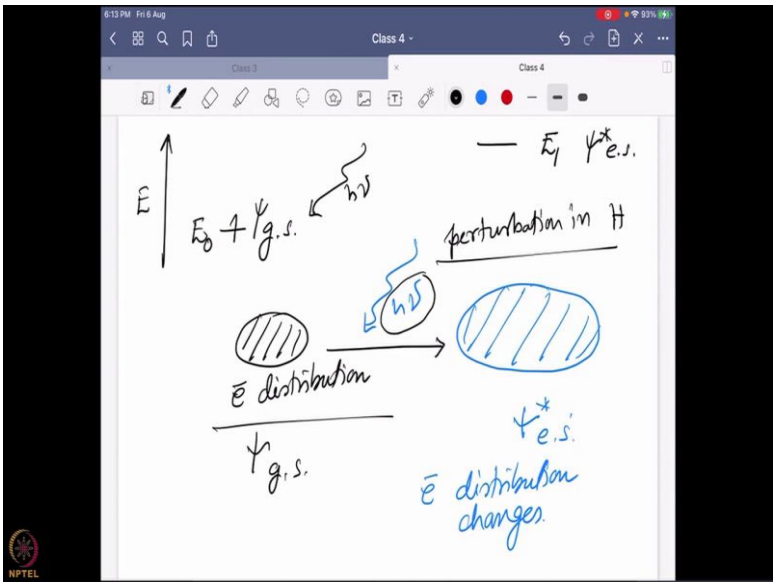
And we can say at that particular condition the ground state has energy of E_0. That means that is the Hamiltonian the wave function is defined by psi and I am writing it g.s. So that we understand it is the ground state of that wave function and the energy is easy. That is how the system is stabilized. Now, what happens? Here comes our electromagnetic radiation and this electromagnetic radiation is going to have an electrical field.

It is going to have a magnetic field. That is why it is known as the electromagnetic radiation. And this electrical and magnetic field is going to change the word of scenario because previously say the electron is moving around the nucleus. So, it is having it is just facing the interaction with the nuclei. It is facing the interaction with the other electrons present. Now, once this electromagnetic wave comes in, it changes the Hamiltonian.

It changes the surrounding. So now, I cannot define the system with the same H. It has to be a different Hamiltonian H′. If H′ is changed my psi(ψ) function will not be same, it is going to be different. And that is going to be the ψ*, star(*) generally put to define that it is an excited state. And yes, I am still writing to define that it is actually a excited

system. And obviously now, this equation is going to have a different energy.

So that is going to be $H'\psi^*_{e.s} = E_1\psi^*_{e.s}$ the So, over here what is actually happening that when this electromagnetic radiation sets in it changes the Hamiltonian okay it changes the Hamiltonian and this particular phenomena is known as perturbation that thing most of you probably have heard or learned in your quantum chemistry class. This is known as the partial version in very like simpler way and due to this perturbation, what is the effect? Your psi(ψ) changes, your E changes and how can I define the change in this psi(ψ). **(Refer Slide Time: 08:24)**



So, previously again, I am drawing this figure again and again. E_0 is your ground state and once this h comes it changes the overall scenario. Now, your system is such that it is actually stabilizing in a totally different system in such a way that but it is happening that it is actually giving a totally different energy state. And what is this particular change? Physically means Physically means that previously you have an electronic environment that is how the electron distribution was.

That means that is how the probability was to finding that orbital. So that is $\psi_{g.s.}$ once it is interacting with this h the electronic distribution changes and that is a totally different electronic distribution. And over there what is happening? The electron distribution actually changes and that is why I go to a different state. So, over here the same state, the same electron after interacting with the electromagnetic wave changes it is orientation in the three-dimensional system.

And that is why the probability changes. That is why we say it is actually going to have a totally different orbital and what

actually is happening there. It is a change in the overall electronic distribution. The electron is not moving to a vacant orbital. What is happening? The electron is redistributing itself such a way that it is attaining a totally new system and that is what is happening during an optical absorbance this through the interaction of the electromagnetic wave.

My electronic distribution changes from one to the other and it changes because this electronic electromagnetic interaction is giving a perturbation in the Hamiltonian. okay So, anybody has any question because that is very important. That is how a electronic transition an electronic transition happens; no matter what it is an optical absorbance, vibrational, spectroscopy, rotational spectroscopy. The basic system remains the same.

It is actually change in the distribution. If it is actually, an absorption it is happening to the change the psi is defining the electronic state. If it is a vibrational state, it is actually ion, if it is a rotational state, it is happening in the microwave level, a rotational state change. But the basic thing is same through this electromagnetic radiation beat in the radio wave to the gamma ray.

It is actually changing the Hamiltonian and it is redistributing the electronic distribution. “Professor - student conversation starts” Yes, Harjit any question? Yes, please go head. Sir, if the distribution changes so, does it change the shape of the orbital? Yes, so, does the ground state an excited state orbital look same yeah, So that is what is actually happening? It is shape changes. It is symmetry changes because it is redistributing itself. Okay

Yes sir, yes sir. okay “Professor - student conversation ends” So, now we go back again and look into the electronic distribution a little bit in more details.

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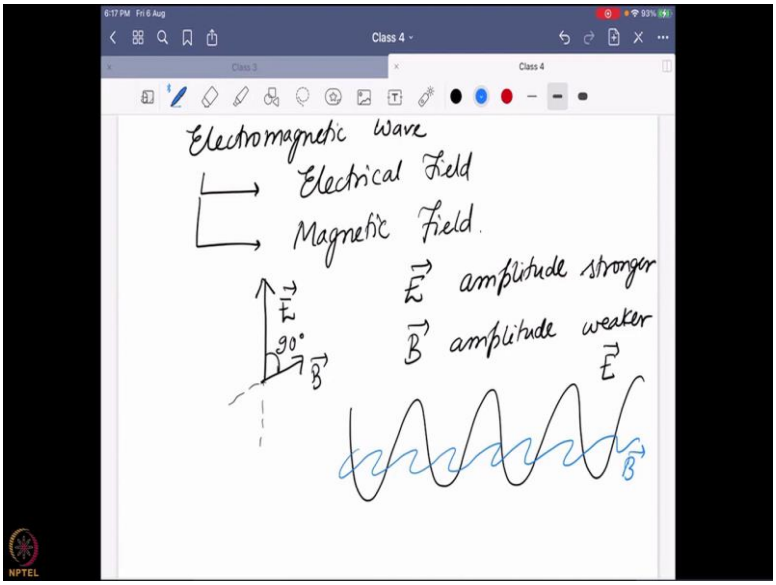

So, when we say it is an electronic electromagnetic wave, it is actually having two different segments, one is the electrical segment in electrical field and the other one is a magnetic field. And from the childhood we know this electrical field and magnetic field are perpendicular to each other. Now, say I am talking about optical absorbance. So, can anyone guess which of this field electrical or magnetic which actually triggers the change in the electronic distribution?

It is the electrical field or magnetic field or both of them are actually placed? Anyone, which of them triggers the optical absorbance or change in the electronic distribution, electrical field or magnetic field? Anyone? It is the magnetic field I guess, good it is magnetic field. So, actually it is opposite is the electrical field actually triggers them. Why? Because, although we learned this, it is true, there is a electrical field and there is a magnetic field perpendicular to that.

How? So, let me draw that together. That will be even better idea and there is a magnetic field. But it never says that electrical and magnetic field they are have the same amplitude or same intensity. They are perpendicular to each other. The angle between them is 90 degree. That is true and I draw that in a kind of three-dimensional orientation. However, the electrical field and magnetic field intensity or amplitude is not same.

The electrical field amplitude is way too strong, okay and magnetic field amplitude is weaker. And now, you can think about that I have an electron moving in when an electron moves, what are the different fields? It creates electron field, it creates a magnetic field perpendicular to the electric field. So, it has both electronic and magnetic field

and my electromagnetic radiation also have both the speed but which of the interaction is going to affect more.

It is the electrical field versus electrical field because the amplitude is much stronger. So, for example, if I want to draw the electrical field, if the electrical field is that strong sorry say it is the electrical field and say I am drawing the magnetic field, it is going to be very weaker. So that is what is going to affect? The overall interaction because you are going to change through some perturbation, the perturbation will be much more stronger when you change it through electromagnetic. Yes Lokesh. "Professor - student conversation starts" if particle is there then electrical field will be created but if there is no particle in electromagnetic wave then how electrical field and magnetic field will create? Very good question.

So that is one of the most uh ultimate questions we have. Where does this electrical field from electromagnetic radiation on light is bringing the electrical charge. So, probably it is better to answer with the respect of the photons. All of you know this term photon right. So, these photons are such quantum mechanical uh I should not say particle but quantum mechanical system that it actually moves around with an electrical and magnetic field.

Now, if you want to find out what is the actual cause of this electrical and magnetic field, it is better to understand through the respect of electron. So, it is a very good question. So, let me take a short route on the different way and try to answer where this electrical fit and magnetic field comes from. Sir, it is meant that it is means that photon is already a charged particle. It is not charged, it has an electrical field.

You do not always need to be charged for creating electrical field. "Professor - student conversation ends" Okay You can have an electrical field but it does not always mean that you have to have a charge system but the question is where this electrical field coming from?

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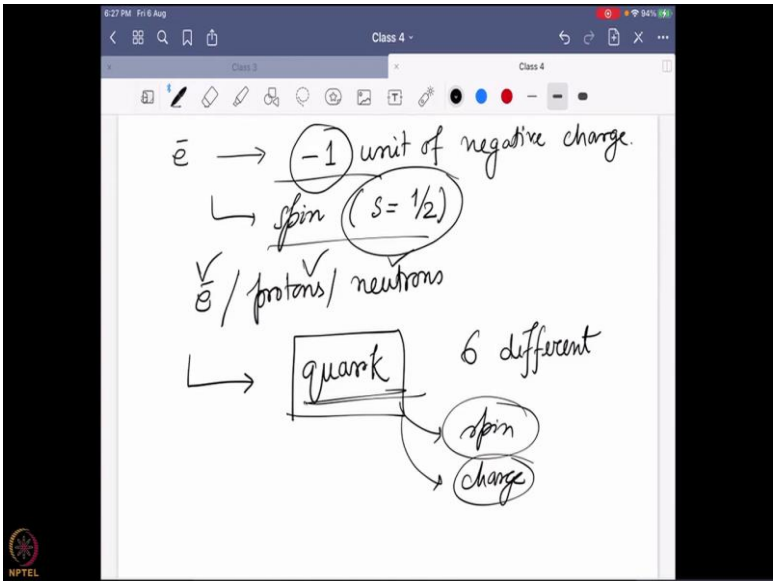

Now, say I have an electron and if I ask anyone of you, what is the charge of an electron? And each of you will say there is -1 unit of negative charge and obviously that you can explain that with respect to yes you are emu unit that you can do and that will come with a particular number. I am not worried too much about the actual value. My main concern is what is the charge? We say the charge is a negative minus 1 unit of charge.

And if I say does this electron also has any spin and what will be the answer? "Professor - student conversation starts" Lokesh, does electron has any spin? Yes, sir. What is the spin of electron? It is half plus of or minus half we can define when I actually put a magnetic field around it and with respect to that if it orients towards or against it. With respect to that I can say it is a plus half or minus half directional device but in reality, if it is just a spin, it has a half speed. "Professor - student conversation ends"

Now, the question is where does this minus 1 charge or spin half comes for the electron? And that is a question it actually take the ah sleep of many scientists, especially in the early 1900. Because around 1896 we find out we should say we discovered electron that there is something called electron and by J.J Thomson. And he found out that it has a particular charge and he defined it as minus 1 charge.

Later one when other physicist comes on around that time, they found proton, they found neutron. And they always found out that each of them has a particular charge, has a particular spin. Now, the question is what is the origin of this electronic spin, electronic charge or the neutron or the proton? What is actually coming from? So, where all of these are actually coming from? So, then people actually have different theories for that.

This is happening for that reason or those reasons and later on people figure it out that whenever we actually studied still class or even bachelor that we said that electron, proton, neutron that is the latest or the smallest thing you can find in an atom. So, these are the sub atomic particles you cannot break down further. But later on people find out no, it is not probably true. You can break them further down.

Obviously, not that straight forward but it can be break down and you find out that this electron, protons and neutrons they are made out of a very similar looking unit and that is known as quark. And there are six different quarks present. I should say we have found so far. And these six different quarks can combine in different combinations. It is like a permutation combination and the most stable three combinations give you electron, protons and neutrons.

And each of this quark has a particular spin has a particular charge and when they combine together, they give you this particular charge and this particular spin. So, this electronic spin, the electronic charge it is actually a very natural phenomena coming to it. So, how should we think about it? For an example, if I say I have a mass of that x kilogram. So, if you say why I have this particular mass?

You say because I have this particular different system in our body blood, then bones, other cellular system and all those things combined together I have this mass. So, then the question comes why do you have the mass in bones or cells or in blood? You go down and down and down and at the end you find you have some atoms and each of the atoms has some mass. So, it is a natural phenomenon. It has this mass obviously that is why you have this mass.

Similarly, the quarks combine such a way that it actually comes out with it is original mass, charge, spin and all the basic properties and that actually represented in it is combined form in the form of electron, protons neutrons. And these are the not the only ones you can have neutrinos, you can have neurons and all those things. And probably all of you heard this story about this experiment in the CERN where they actually created a system, where they actually collided these particles, these very simple particles to each other.

And try to find out when they collide if they are going to their original forms of quarks or something like that. And then the fire find out that yes, probably you can see a few glimpses of that and from there we actually confirmed from the theory and the experiment that these things actually exist.

And the presences of this quartz are the principal reason why do you have a charge and spin for an electron?

Similarly, when you talk about a photon that photon is also made out of this particular original quartz at a particular combination which actually does not have any overall charge or an overall spin but the quartz are there. So that means in in their hard they have some electrical field and that electrical field is the main reason for this electromagnetic radiation. "Professor - student conversation starts" Does it give you a little bit of idea Lokesh why it is happening? Yes sir, yes sir, yes, yes, thank you, thank you sir.

Sir, Yes. Sir basically, photons have energy but it has no mass sir, how is it possible? So, it is actually combined with such particular quartz which actually mass is actually pretty low. So, sometimes, if I cannot define like we do not have any system to measure, it is mass. So, we say that it is almost close to 0 mass, for example, when we compare between electron and proton. Can we measure a mass of an electron? Yes, probably we can measure.

How much difference the difference between the mass of an electron and proton is such that an electron is almost close to 1836 times lower than that. But if I say the electrons say it is one millionth time lower mass compared to proton. So, compared to proton what it would look like that it is almost a mass less quantity. So, mass is such that it does not really affect any phenomena combined to mass. Okay "Professor - student conversation ends"

So that means this system does not have, uh what kind of parameter I should say? For example, a physical momentum so, for example, if a light hits you, you do not feel the light hitting you but you can get the heat or some sensation over there. But a light cannot just push you around because it has a so low mass almost close to 0. But in a similar system a photon with a photon can you shift a very low mass system with a photon?

Yes, you can so, where this particular momentum is coming. It is coming there because it have to compare with such a system with a very low mass. okay So, although we say very in an overview that it is a mass less system but does it means it is mass is actually 0 unit or it is so much of a low mass that I cannot actually measure with our current scale. So that is the question. okay So, I do not want to go into further in the discussion of this uh uh particle physics.

So, for that mindset yeah So, for that you have to take a class of particle physics or look into some uh I say some

books or some literatures on particle physics. Those are very interesting actually and put as a question acquired. Everything actually starts from and it is coming from big bang and all those things you can go and look into that. But it is a little bit out of the scope of this class. So, I am actually going back to our original discussion. okay