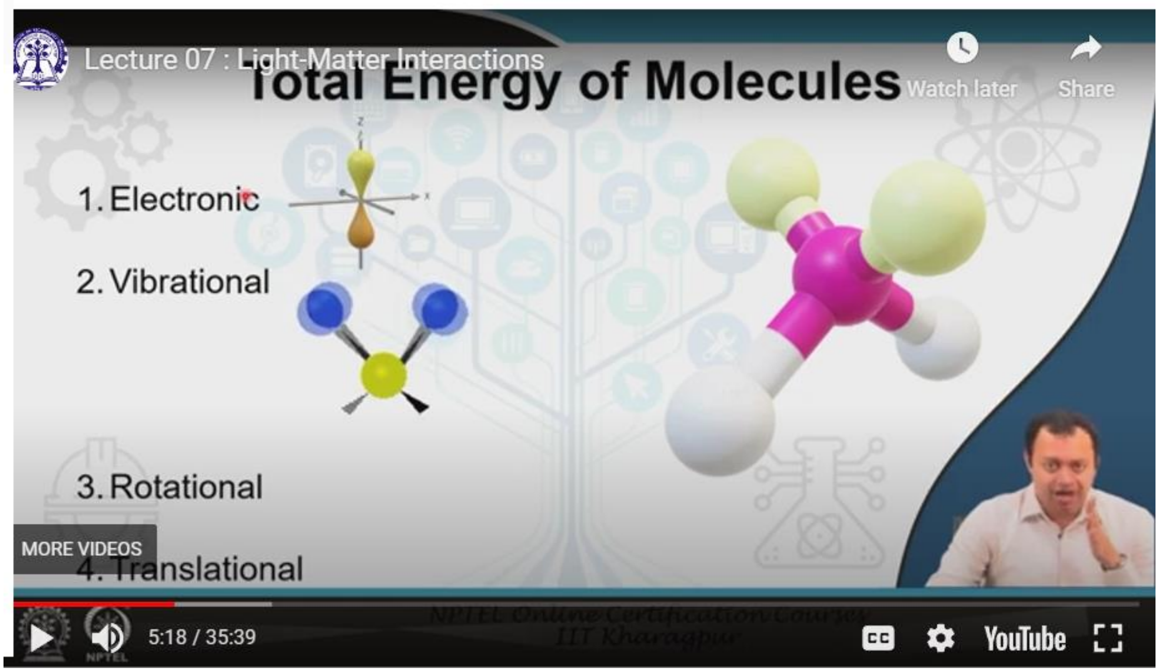
Nanobiophotonics: Touching Our Daily Life
Professor. Basudev Lahiri
Department of Electronics and Electrical Communication Engineering
Indian Institute of Technology, Kharagpur
Lecture No. 07
Light-Matter Interactions

Hello and welcome. We will continue our discussion on Light Matter Interaction. This is the preliminary basics of Photonics and Biology. So, let us get started. In the previous classes, I have described about light in general, what happens to light when it enters matter and I have also tried to classify matter according to its optical properties. Generally, we will be dealing with molecular materials.

Molecular materials simply are materials which has a variety of molecules coming together, combining with each other and forming some sort of a complicated structure. Now, as light passes through them, as light interacts with them, what are the ways in which light could be absorbed? What are the properties? What are the intricacies that get modified that get interacts when light enters the particular matter? Now, we can describe the total energy of molecules in these four categories as you see in your computer screen. First is of course, electronic. There are electrons travelling around the nucleus of an atom.



Those electrons are in discrete orbitals. Light can absorb them. They can simply then go from level 1 to level 2, one orbital to another orbital. The photon or the electromagnetic wave that is passing through it can simply be absorbed, simply be consumed, simply be eaten up. Then there is vibrational mode of molecules.

As I said, this particular process is called scissoring because they look like a scissor. Molecules absorb light. This is molecule A and these are two molecule B. You can consider it as CO_2 or H_2O or something like that and at a particular frequency of light makes them, you know, wiggle makes them scissor like this scissoring effect. Light can also in this particular case absorbed, eaten up, consumed.

There is rotational motion, rotational motion in which sciss become trans, right, a chirality the movement, the rotation of the molecule changes. There is angle associated with it. This is vibrational, very little angle is associated with it. Rotation is simply the thing is rotating along its particular axis. This moves in a particular axis.

This moves in a particular axis. Either the angle of axis changes. Here no matter what kind of movement is this. The axis of rotation remains as it is rotational motion in which the axis of rotation changes. Then there is translational in which a molecule could consume light, a matter could consume light and it translates from one particular phase to another particular phase.

Mind you in this particular topic, I am not talking phase as in a specific angular point of a travelling wave. I am talking phase as in solid liquid gas phase. Translation as in ice, yeah, it gets you bombard it with enough light energy, particular frequency, particular things. It melts and can become liquid. Further go on, it becomes steam.

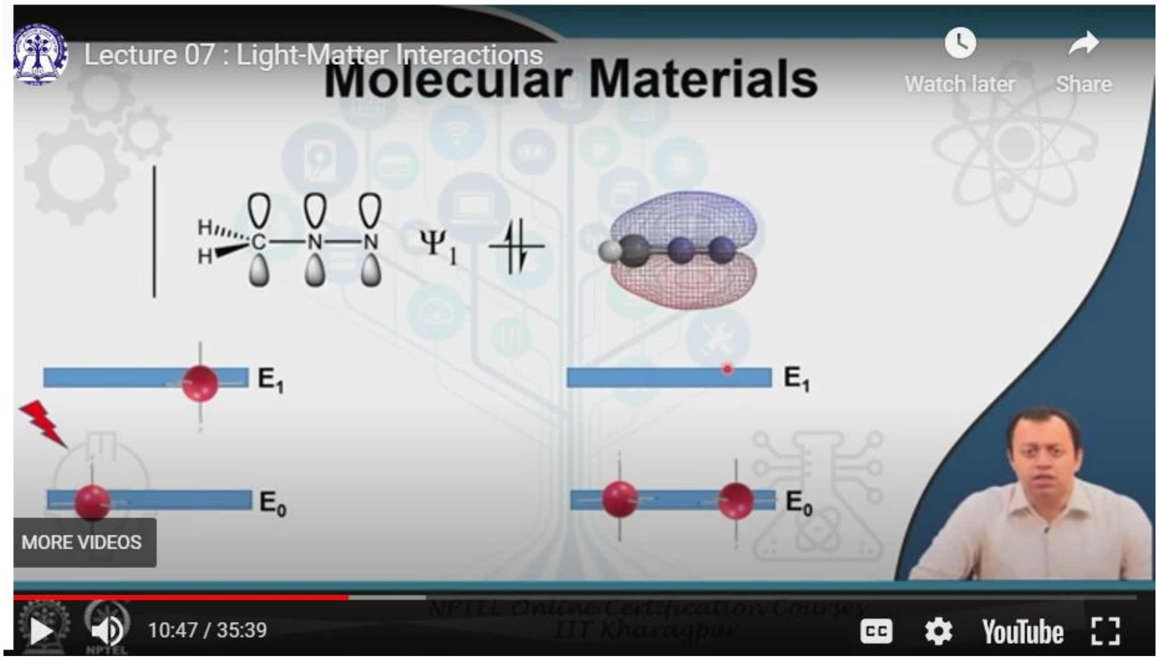
So, the coherence, the bond changes. The strength of the bonds breaks down and the material stop remaining in its particular format as it has started. Solid become liquid, liquid become gas. Translational energy is non-quantized. However, these three are quantized.

They can only electron can only absorb the light, can only absorb the energy that allows it to jump from one orbital to another orbital. It cannot have anything in between. Similarly, vibration is also at specific frequencies. It cannot randomly accept anything and go ahead. Thereby in this particular course, we will be mostly dealing with electronic absorption as well as vibrational absorption.

Light interacting mostly with the electrons or with the molecules making them vibrate. These two are something that we are not going to discuss. They are not part of biophotonic syllabus at all. Rotation can come in some chiral molecules because they are small and far between. Translational as I said is non-quantized after a particular frequency has been hit.

See different other frequencies can be given. So, that could simply not quantize. Molecular material, now here you have to pay little bit more attention than you usually do.

Molecular material has this very complex structure because they are made up of variety of different apparently completely different elements, different atoms coming together carbon, hydrogen, nitrogen not only these three, but much more complex molecules, complex elements can also come into effect. All of you have heard of this hemoglobin in blood.



Hemoglobin is a complex protein made up of carbon, hydrogen, oxygen etcetera no doubt, but it also contains heme, hematite or iron in it. Think about how complex actual molecule of hemoglobin is and we all have hemoglobin running in our body. It is part of blood RBCs red blood corpuscles have hemoglobin that allows us this pherom the iron part allows us to capture the oxygen and hence we are able to sustain life. So, hemoglobin is such a complex molecular material. It is an example of such a complex molecular material where a metallic element that is pherom that is iron is connecting with complex organic.

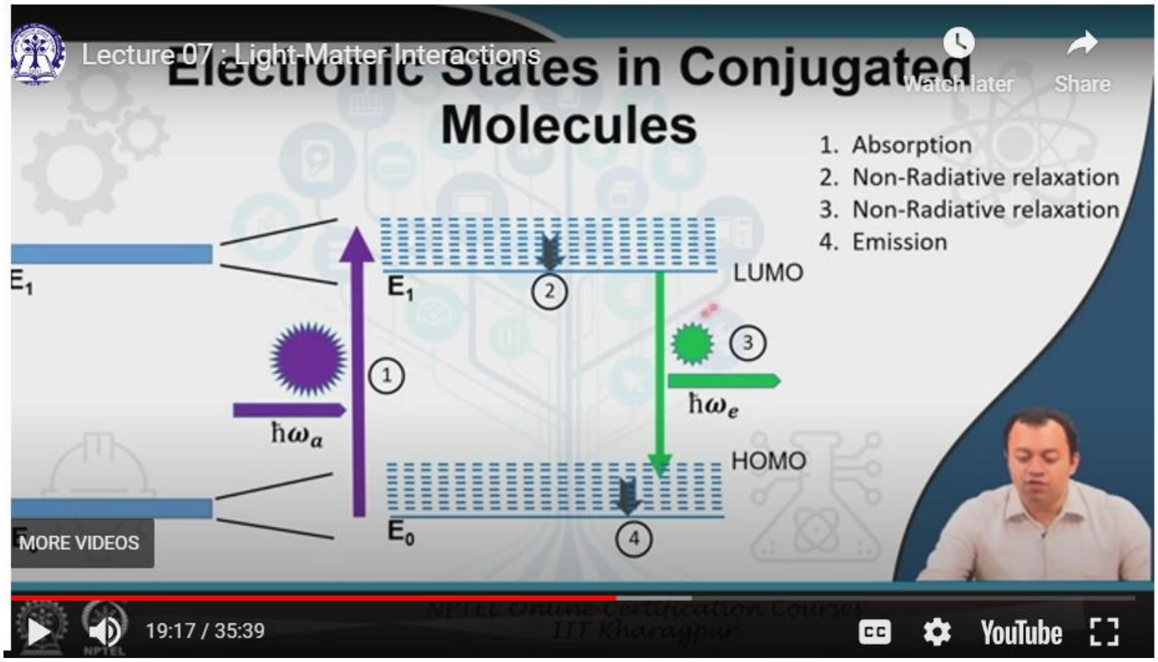
So, it is an organometallic structure, it is a organometallic substance think about it iron connecting with carbon, hydrogen, oxygen, nitrogen. Thereby the molecular orbitals that happens are much more complicated, they are much more complex, they are far more different than you normally see say for example, in semiconductors. Say for example, in semiconductors in semiconductor large number of silicones combine all of their 2S and 2P orbitals join together and form valence band and conduction band. Electronics engineers you know this medical or biological background if you do not know this do not worry too much about it is same. What I am saying is that in other optical materials semiconductors, insulators, even metal structures such as the upper level the higher energy state as well as the lower energy states are relatively easy.

Whereas, in case of molecular material the upper energy level the so-called conduction band and valence band are far more complicated. Complicated how they have their internal sub bands. A molecule absorbs light so it can be electron as well phenomena remains same this is a lower energy level, this is a higher energy level, this is non vibrating or relatively less vibrating, this was vibrating like scissor or this is an electron at S orbital it has absorbed energy and gone into P orbital. Both phenomena more or less are same basically light will be absorbed by the electron going into lower ground state to excited state molecules will absorb similar light not the same frequency light different frequency light and go from lower energy ground state to higher energy state in which they will vibrate at a particular frequency we can observe understand this frequency we can understand the molecule. Similarly after certain time after a certain time has elapsed randomly consider this as electron I think it will be easier it will return back to its original state and then it can either emit light or it can emit heat or it can emit a combination of both.

In case of semiconductors if it emits photon and returns back we call it direct semiconductor. In direct semiconductor electron is in valence band it absorbs some sort of energy goes to the conduction band after sometimes when it returns back to conduction band it can emit light and you see LEDs light emitting diodes. If it is an indirect semiconductor like silicon it can return back from conduction band to valence band and it can it basically emit phonons, phonons are this quanta vibration. Now in case of molecular material say for example in conjugated molecules these excited states and the ground state contains several sub bands of their own. In electronics you have never cared you have never cared where does the electron goes inside the conduction band as long as it has passed the band gap gone from lower level to upper level you do not care which part of upper level it has gone to because it is more or less same.

The difference there also so many silicon atoms coming together and forming all these bands and forming a compact conduction band and valence band the difference between these sub bands exist there because Pauli's exclusion principle no two electron in the same in the same atom can have all four quantum numbers same. These sub bands the difference between them are 10^{-11}electron fold. So, you do not care in semiconductor physics electron going from lower level to upper level that is it you do not care which part of upper level. Whereas, in conjugated molecules conjugated molecules are part of molecular material. Molecular material can be roughly divided into saturated materials and conjugated material.

Saturated materials are more like polymers which has a strong inner core and they are strongly bonded with the other materials plastics it is polymers or nylon etcetera. Conjugated materials are biological materials, where individually they are very strong, but they are combining together making this organism as such in a very very weakly \ bonding strength. Hence my skin or my body is very very vulnerable we cannot go and absorb temperature above 60 70◦Celsius. Anyways these conjugated molecules have very complicated excited energy states and ground energy states which has large number of complicated sub bands itself. The difference between sub bands are very different from one another the averagely they are something around and correct me if I am wrong 10^{-8} to 10^{-5}electron fold.



Meaning it actually matters it actually matters where exactly in which part of the excited energy state has the original electron or the original molecule has gone to. If you have an electron at this level at this level you have submitted it with energy this goes to the upper level. You have to somehow understand which part of the upper level it has more or less gone to. The equivalent of valence band and conduction band of semiconductor physics in biology or in conjugated molecules in biochemistry is HOMO and LUMO. HOMO stand for highest occupied molecular orbital and LUMO stand for lowest unoccupied molecular orbital.

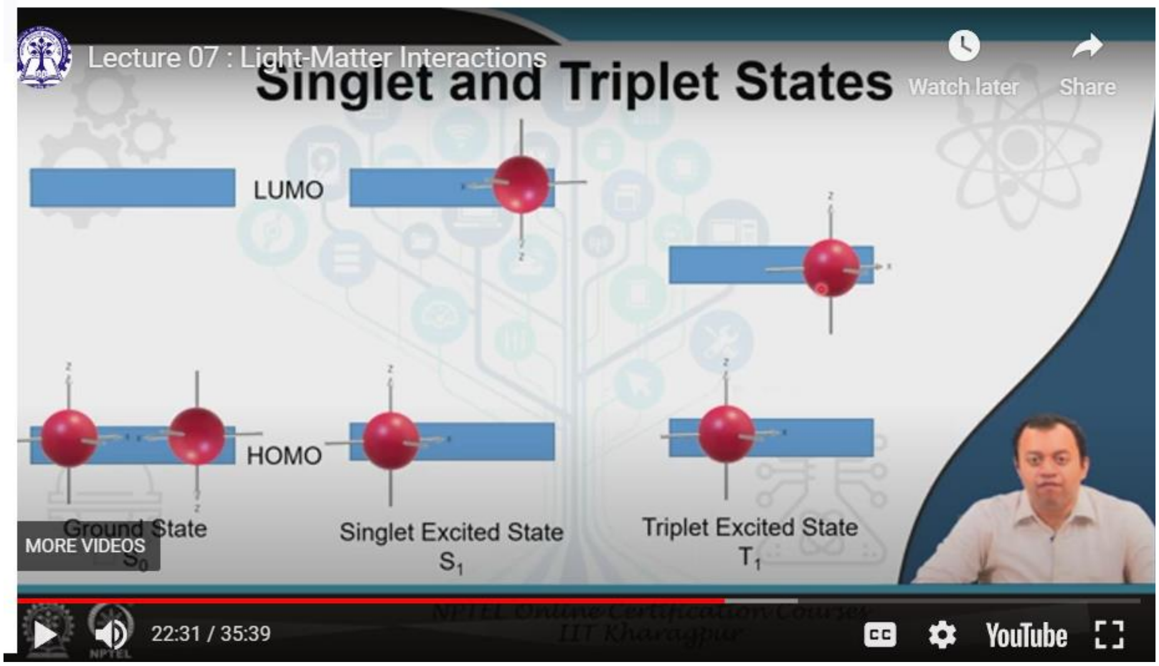
You have to put your molecule which is at HOMO highest occupied molecular orbital to lowest unoccupied molecular orbital equivalent of conduction band. Which part of LUMO from which part of HOMO it is going determines the output of emission from conjugated molecules. Let us understand this you give a particular frequency of incoming light an electron or a molecule goes at that orbital. It goes up here inside the conduction band inside the LUMO it transitions non radiatively it simply transition by vibration etcetera returns back to the lowest part of LUMO comes down to HOMO excited thing has to return back to lower state. Here also by emitting a particular frequency emitting a particular frequency of light and finally, coming back to ground state non radiatively.

This black two arrows are vibration or could be heat. So, this purple is input 1 2 and 3 are output. So, this the emitted photon assuming it is direct assuming it has the capacity to emit some photon is not equal to the incoming or the exciting photon. The difference is lost is can be considered as loss or lost in form of non-radiative transition within HOMO and LUMO within valence band and conduction band. In semiconductor physics you never cared about which part of conduction band does the electron go to all of your conduction band is more or less same.

I know I know those who are doing PhD in solid state physics will also say that we try to do it as well in conduction band and valence band and there are these different EK diagrams that you go, but I am talking in a general master students level sense. If you are doing a PhD in quantum mechanics then again this is preliminary this is not for you I am giving a general idea. Usually bachelors' level or masters level semiconductor physics people do not care about which part of conduction band the electron goes to as long as it goes to conduction band and it is ready for conduction. In case of biology you have to deal with this you have to deal with LUMO as well as HOMO function. So, it can be and there is a mistake I figured out 3 is not non radiative relaxation 3 is actually emission.

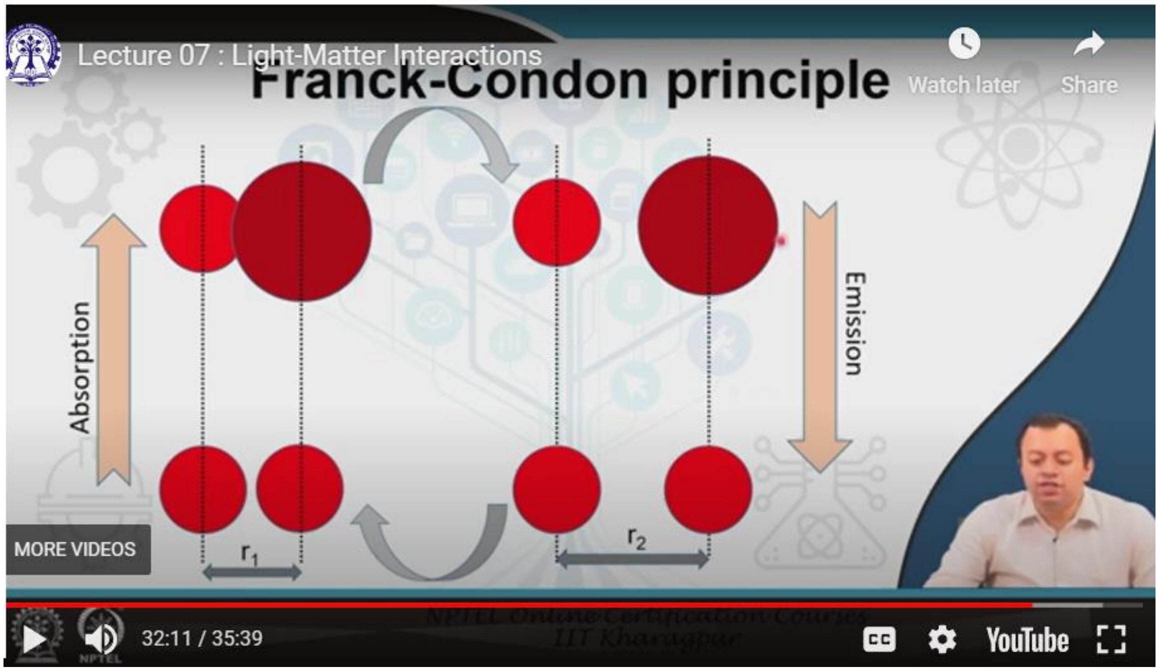
So, make sure I will try to change it 3 is again emission and non radiative relaxation is actually 4. So, one is absorption light comes it has absorbed whatever molecule or whatever orbital or whatever electron was at the ground state absorbs this particular frequency goes top at top some amount of energy that it has consumed some amount of light it has consumed is converted into non radiative relaxation non radiative transition it is vibration or it could be very well heat and then some part of it is released as some part of it is released as light. Remaining part is again converted into vibration light vibration plus light plus vibration. So, this light this energy this frequency this wavelength is not equal to this energy this frequency this wavelength some of it has been lost some of it has been lost navigating the complex excited state complex LUMO and HOMO complex conduction band and valence band. There are singlet and triplet states that is also quite important for you to know because this will help you understanding the fluorescence and phosphorescence phenomena I am just giving you an example here in the next class I will be detailing about what happens.

So, suppose in a ground state you have 2 electrons these 2 electrons are paired you know Pauli's exclusion principle no 2 electron in the same atom can have all 4 quantum number same this has all 3 quantum number since these 2 electrons except the spin quantum number. So, when you have spin up and spin down we can consider them as paired this has an up spin this has a different spin high school physics I do not need to tell you what quantum numbers are you should be knowing even if you are from biological background this was taught to you in class 11 12 that is high school physics what spin is the spin is opposite to one another no 2 electrons can have all 4 quantum number same tell me what are the quantum numbers please tell me you know this. When one of the electron absorbs light and goes top the spin is more or less maintained. So, they are still opposite spin they are still opposite spin and this is called singlet state basically the dipole has increased basically the dipole has increased a bit and the spin is still paired this is spin up and this is spin down and this is called singlet excited state this is ground state this is a singlet excited state. Sometimes so happen that if you have a quantum defect state by doping or some other way it may so happen that the spin are unpaired this spin and this spin are same if that is the case then this electron cannot return to ground state unless it has changed its spin back.



So, this is at a suspended animation position this cannot remain forever at an excited state nothing can remain forever at an excited state it has to return to the lowest energy state that is the phenomena everything every matter wants to return to its lowest energy state it wants to return to its lowest energy state, but it cannot come because if it is coming it is violating Pauli's exclusion principle. So, what happens to this well you tell me what happens to this it cannot go out it cannot come in it stays as it is like a ghost and this ghost gives you a ghostly light this ghostly light is called phosphorescence we will discuss in next class phosphorescence. Let us discuss about Franck Condon principle. Franck Condon principle is the exact principle that determine what physically transformation happens when light is absorbed by a particular atom. Understand this interaction of light with matter in this particular case I am considering matter as an atom result in a physical change in the atom.

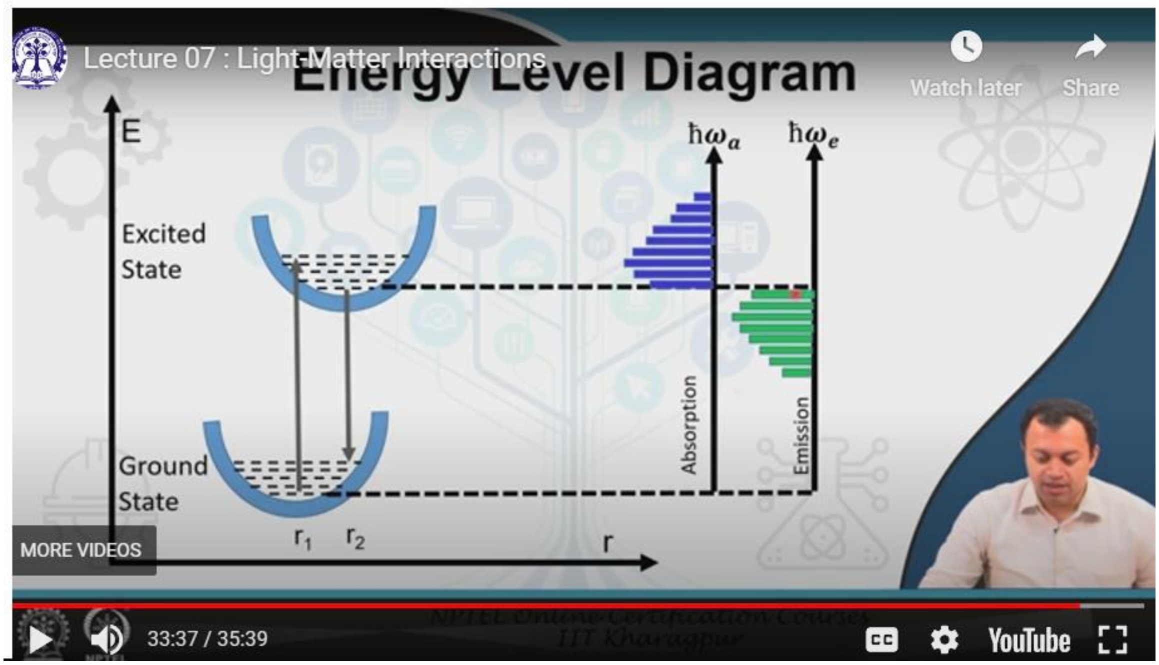
If light has been absorbed by the molecule or by the electron there is a physical change just like by absorbing water your paper swells up or your cloth changes its structure a little bit similarly when mostly in case of conjugated material biological material upon absorption upon interaction of with light upon absorption the physical property of the atom changes. Suppose we have a simply 2 hydrogen atom 2 hydrogen atom very similar to one another this is one proton and one electron orbiting it same both of them have come together. What are the forces of attraction and repulsion we have the nucleus of this hydrogen atom is attractive towards the electron of its own as well as electron of its neighbour. The nucleus of this is also attractive towards the electron of its own as well as electron of its neighbour. These 2 electrons are repelling each other these 2 nucleuses are repelling each other.



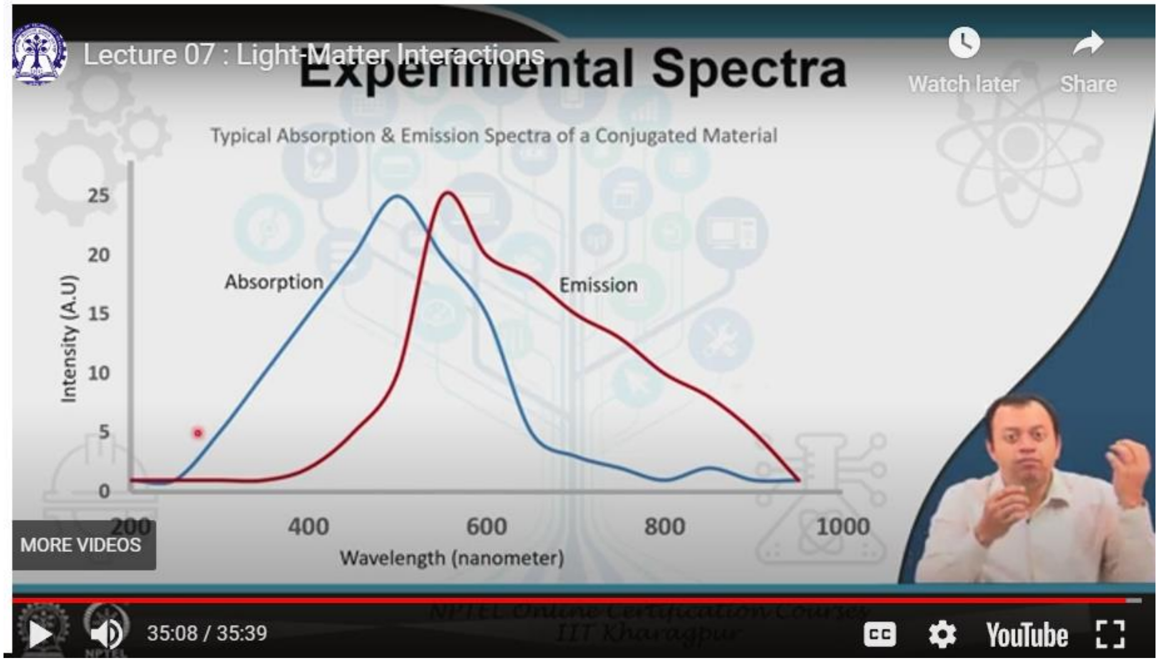
So, there is a combination of repulsive forces as well as attractive forces. If the attractive forces prevails then you have a bond if the repulsive forces are prevailing then you have anti bonding or no bonding that is how it is bonding is basically the attractive forces prevailing the overall total forces and in order to in order for the attractive forces to prevail atoms arranged in peculiar manner in 3 dimensional space in 3 dimensional space electromagnetic force has some amount of direction. So, this attractive electromagnetic force to happen in a particular direction they arrange themselves in 3 dimensional space and hence you have molecular shapes complicated molecular shapes the more complicated the molecule becomes the more complicated shape it has to be and complicated molecules are thereby also easier to break if you can make the attractive forces go down and the repulsive forces come up. Now, they have an intermolecular distance between r 1, r 1 is the distance which allows these 2 molecules this is hydrogen this is hydrogen combined together to form H 2 yeah H 2 O's H 2 easiest thing and they have an inter atomic distance r 1, r 1 is the most thermodynamically stable reduces the energy per say why do atoms forms molecules simply to reduce energy. So, that the electron have larger area to move around.

Now, they have this energy state and they have this inter atomic distance. Now, this particular atom has absorbed a photon this was the electrons orbital it has now absorbed a photon it has swirled up this was the distance from the center to the outer periphery this was the nucleus and this was the orbit s 1 s now it has absorbed photon and has gone jumped to the next orbit. So, physically the atomic radius has increased. So, the atom has swollen up previously it was like this now it has swollen up the size the direction everything is changing electromagnetic force is inversely proportional to radius remember q 1 q 2 by r square 1 by 4 pi epsilon epsilon r epsilon naught. So, now, the distance have changed now this entire phenomena has simply this r 1 is no longer sustainable r 1 was at a specific case when both the electrons were at a specific orbital.

Now, this electrons orbital has moved it has absorbed light it has gone to an excited state it has gone to an excited state and this particular excited state they are no longer bonding they have the repulsion the forces of repulsion comes forward and they separate from one another they separate from one another at a distance which is different than r 1 at a distance which is different than r 1, but it cannot stay at an excited state forever it cannot stay at excited state forever it soon ejects this photon either in the form of light or in the form of heat returns back after emission to its original size it returns back after emission to its original size. Now, the distance is still different now the distance is still different, but it has returned back to its original size the swelling the swelling up of the atom has reduced hydrogen atoms swelled up because the electron moved from here this orbit to this orbit the bigger orbit because why it has gone to the next level it cannot stay in the next level for long it emitted the photon returned back. Once this is done the restoring forces will come back and it will return to its original position some of you may ask what if this states keep on happening we give more and more light well if you give more and more heat if you give more and more light the translation occurs the bonding is broken the bond is broken and it simply excites and go away why do you think your clothes fade your shirts your trousers fade when you put it in sun for a very long time for over a year think about it touching your daily lives this is part of your part of you the title. So, I am not talking something abstract I am simply saying that when light interacts with matter there is a physical modification taking place in the matter the physical modification the physical change results in modifying the bond structure if that modification prevails if the modification prevails if the modification remain as it is either the bond breaks down either the bond breaks down the material changes its property completely or if it has returned back to its original position before much damage could be done we can restore it back to its original position our task here will remain to absorb take it to an excited position understand what is happening and then quickly return it back we do not want to do any permanent damage we do not want to do any permanent damage why photonics because photonics precisely allows you to control this particular phenomena it takes it to the edge breaks the bond, but then restores the bond immediately sending sound or heat or electric current may not be allowing you to go for restoring forces may not not as a Frank Condon principle simply states that if we know R 1 and if we know R 2 we can figure out what are the time these molecules state at different positions R 1 and R 2 how much time it takes for it to relax what are the phenomena what are the emission properties and based on that we can calculate the overall HOMO and LUMO the molecular orbitals of this particular molecule I have taken a very very simple molecule H 2 this is hydrogen atom 1 hydrogen atom 2 it can so happen that you will have a plethora of different atoms complicated atoms hemoglobin per se and then interaction of light with them result in a physical deformation a physical change a physical modification in its properties.



Thereby when you have a complex structure you get an energy level diagram which has an absorption frequency and an emission frequency at two different level these are excited state and ground state I have particularly not given you box upon box electronics engineers have this incredibly bad habit to consider simply box upon box they make a box which is a conduction band they make another box below it which is a valence band electron going from upper level to lower level you are no longer studying electronics you are studying photonics and biophotonics and though this is also not correct bow shaped go and see some complicated EK diagram they have their individual subgroups individual sub bands depending on from which sub band which sub band of atom 1 it has gone to the deformation takes place in the molecule from R 1 to R 2 R 1 is the original case R 2 is the excited case R 1 is the original case R 2 is the excited case and you have discrete values of emission taking place these they are discrete because these sub energy levels are discrete and these ground state and excited state are discrete electrons can only exist or molecules can only exist at this state or at this state and nothing in between and



this is the final experimental spectra where absorption is at a higher wave lower wavelength higher frequency that is higher energy emission is at a lower frequency higher wavelength lower energy what happens in the overlap period you can ask yourself this question what happens in the overlap period I want some answer speculated answer from you in the forum we have a forum in which you can discuss or ask me questions about something you have doubt on I will immediately try to answer so in the forum you can answer your question what happens in the absorption in the overlapping part but in biology when we are trying to interact biological matter with light light will absorb higher frequency and biological matter will absorb higher frequency will emit lower frequency if it emits it's not going to be exactly the same thing in fluorescence we absorb blue or green light or ultraviolet light emit yellow and red light and thereby we see things in a much clearer manner in fluorescence spectroscopy fluorescence microscopy which is going to be the next chapter so these are the concepts covered I know I try to take a bit more time than you expected these are my references and I shall see you in the next class thank you very much