Quantum Mechanics and Molecular Spectroscopy
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Lecture – 33
Electronic Transitions

Welcome to the lecture number 33 of the course Quantum Mechanics and Molecular Spectroscopy. Until the last class, we looked at the rotational and vibrational transitions and the associated selection rules. Today, we are going to look at the electronic transitions and the possible selection rules for them. Electronic transitions happen between two different electronic states. Now what does this two different electronic states mean?

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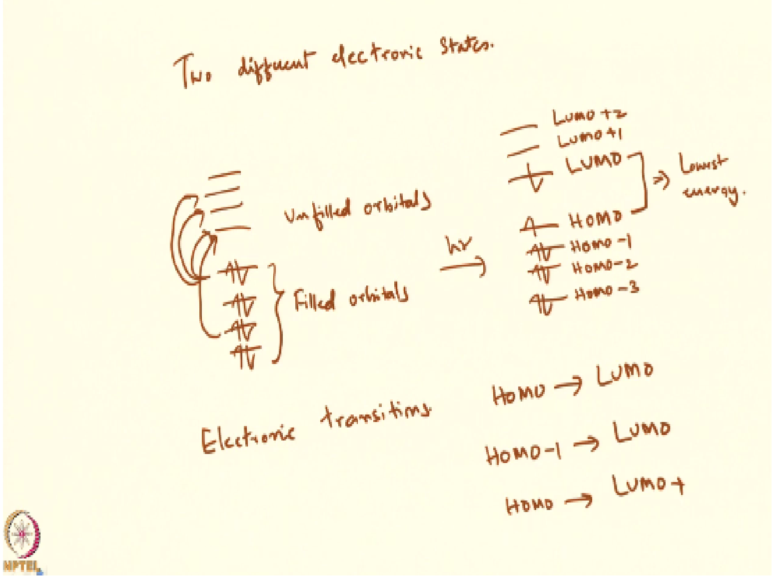

Two different electronic states mean for example you have a molecule and one can define a electronic configuration even for atoms you can define electron configuration and let us suppose there are all filled orbitals using Pauli exclusion principle or Aufbau's Principle combination of that. So these are filled orbitals and these are unfilled orbitals then what I can do is that by applying energy or putting a photon.

Then I can go in presence of h nu I can go from I have now transformed the electron or I have replaced electron from the highest occupied atomic orbital or molecular orbital to a lowest unoccupied. So, this is what we call as HOMO and this is LUMO. Of course one does not have to restrict to this one can go to LUMO + 1 to higher energy levels as well. So, one can always excite from here to here to here to various levels.

But this is the lowest energy transition. So, what I am doing in this case is that I am promoting an electron from an occupied level to an unoccupied level that is the electronic transition. So where you are displacing an electron from one orbital that is occupying to another orbital these are called electronic transitions. By the way when we have the electronic absorption or what is known as the UV visible spectroscopy in which you actually take out electron from one of the orbitals occupied orbitals and put it in the orbital that is unoccupied.

Of course you can also do from here to here you can bring in the electron that are lower than HOMO so many possibilities exist. So, electronic transitions are many such possibilities. One can have HOMO to LUMO or HOMO – 1 to LUMO or one can have HOMO to LUMO + 1 so these are this is HOMO – 1 HOMO – 2 HOMO – 3 so this is LUMO + 1, LUMO + 2 something like that.

So one can have many, many combinations and you will see that this one that is HOMO to LUMO is the lowest energy possible transition this is the lowest. Now, it turns out that when you do that.

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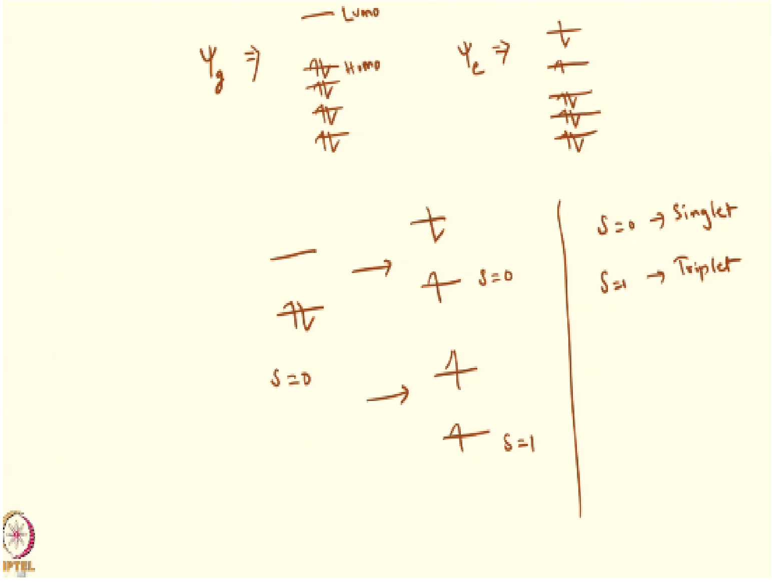

Now if you use build a principle and you can have a wavefunction called as psi ground and this wavefunction will correspond to the electronic configuration and one could have a psi excited as two electronic configuration. So this is HOMO, this is LUMO. Now there is one thing that I am trying to do here. If you see concentration HOMO and LUMO what I have done I have started from here and I have left to this.

The other possibility is this. Now this state is represented by S = 0 this state also is represented by S = 0, this is state is written as S = 1. So, when we have S = 0 this we call it as a singlet state anyway this is a singlet state and when you have S = 1 we have triplet state. Now S = 0, S = 1 triplet state, singlet state this is because of the degeneracy of the wavefunctions.

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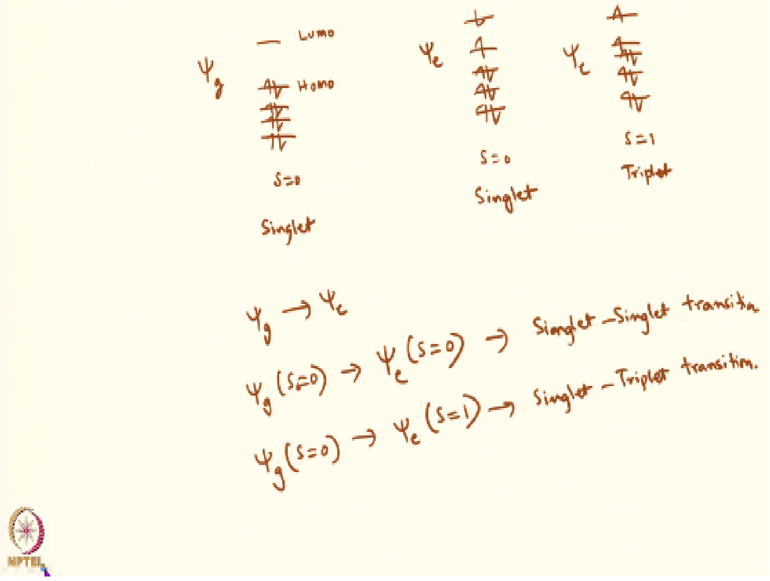

Now there are two things that are possible. So when you have psi g when you have this combination, this is HOMO, this is LUMO. So, you could go to psi excited state in two possibilities one is this 1, 2, 3 where S = 0 or one would have psi so that is S = 1 so this is singlet, this is triplet. So, one could have this is also singlet so when I go from psi ground to psi excited state I can go from psi ground S = 0 to psi excited S = 0.

Or I could go from a psi ground S = 0 to psi excited S = 1. So this is called singlet-singlet transition and this is called singlet triplet transition. Now I have the exact wavefunction will depend on the molecule or atom in consideration.

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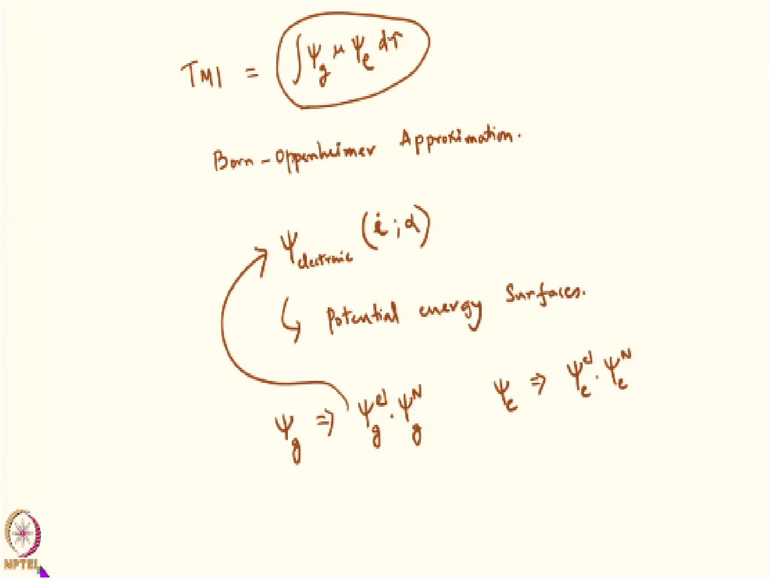

$TMI = \boxed{\int \psi_g \mu \psi_e \, d\tau}$

Born-Oppenheimer Approximation.

$\psi_{electronic}(i;\alpha)$

↳ Potential energy Surfaces.

$\psi_g \Rightarrow \psi_g^{el} \cdot \psi_g^{N}$ $\qquad \psi_e \Rightarrow \psi_e^{el} \cdot \psi_e^{N}$

Now let us think of a transition moment integral so TMI will be equal to integral psi ground mu psi excited d tau that is going to be my transition moment integral. However, the way this transition moment integral has written has a problem because you see there is something called Born-Oppenheimer Approximation. Now what does Born-Oppenheimer Approximation says?

It says that the electronic wavefunction parametrically depends on a nuclear coordinates. So psi electronic is dependent on the electron coordinate I would call it as i and nuclear coordinates alpha. So that means whenever the nucleus changes its position the electronic wavefunction will change and this gives rise to concept of potential energy surfaces. Therefore, your psi g will consist of two things.

This will consist of psi g electronic multiplied by psi g nuclear and this comes out of the electronic transition or Born-Oppenheimer Approximation. Therefore, it is similarly you have psi excited will have two possibilities psi excited. Let me call it as electronic and psi excited nuclear. So, this wavefunction that you use in the transition moment integral it is bit more complicated.

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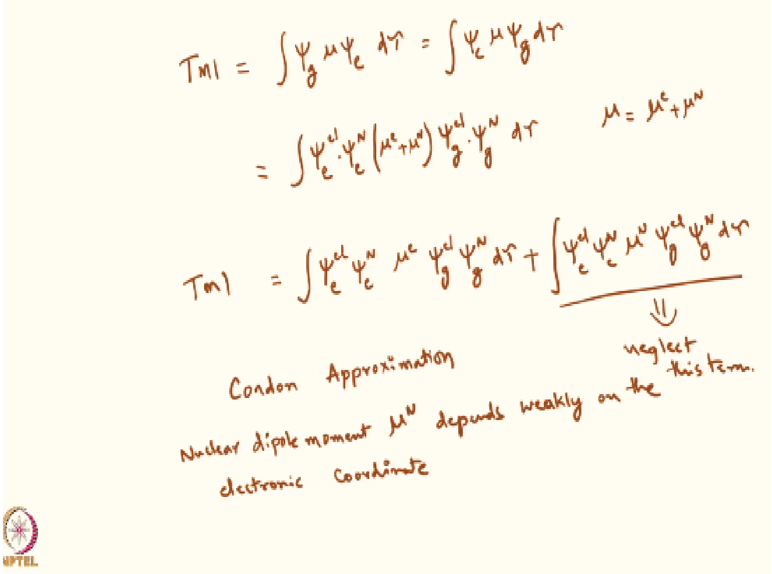

$$\mathrm{TMI} = \int \psi_g \mu \psi_e \, d\tau = \int \psi_e \mu \psi_g \, d\tau$$

$$= \int \psi_e^{el} \cdot \psi_e^{N} (\mu^e + \mu^N) \psi_g^{el} \cdot \psi_g^{N} \, d\tau \qquad \mu = \mu^e + \mu^N$$

$$\mathrm{TMI} = \int \psi_e^{el} \psi_e^{N} \mu^e \psi_g^{el} \psi_g^{N} \, d\tau + \underbrace{\int \psi_e^{el} \psi_e^{N} \mu^N \psi_g^{el} \psi_g^{N} \, d\tau}_{\Downarrow \text{ neglect this term.}}$$

Condon Approximation

Nuclear dipole moment μ^N depends weakly on the electronic coordinate

So, one can therefore write your TMI will be equal to psi g mu psi e or rather other way round d tau in fact this should be equal to the mu acts on psi g psi e mu psi g d tau, but you know this is a Hermitian operators so it does not really matter because overall the transition moment integral must be the transition moment integral square which is equal to, which is proportional to the probability of transition this is square and it has to be positive number.

So, it does not really matter, but technically this should be like this. So this will be equal to your psi e will be equal to psi e electronic multiplied by psi e nuclear and your psi g will be equal to psi g electronic multiplied by psi g nuclear and the transition moment integral or the dipole moment vector can also see there is electronic charge distribution and there is a nuclear charge distribution.

So one can always write mu as the sum of mu e + mu N d tau. Now I can separate this into two things this is equal to integral psi e electronic psi e nuclear mu e rather I can psi g electronic psi g nuclear d tau + integral. So your total mu is written as mu e electronic + mu nuclear and psi e electronic psi e nuclear mu N psi g electronic, psi g nuclear d tau. So now the total transition moment integral can be now divided into two such integrals.

One because of the electronic dipole moment and the other is the nuclear dipole moment. Now, evaluation of these two integrals is not very it is going to be challenging. So one makes another approximation called Condon approximation. So, essentially what are we looking at this in this we are looking at how the electron wavefunction changes with respect to the nuclear coordinates.

The electronic function does change with respect to nuclear coordinates however what we figure out is the dipole moment the nuclear dipole moment or the dipole moment or it is a nuclear dipole moment mu N depends weakly on the electronic coordinates. So that means this dependence on these coordinates is very weak that is why we can neglect this term and this neglection is called Condon approximation.

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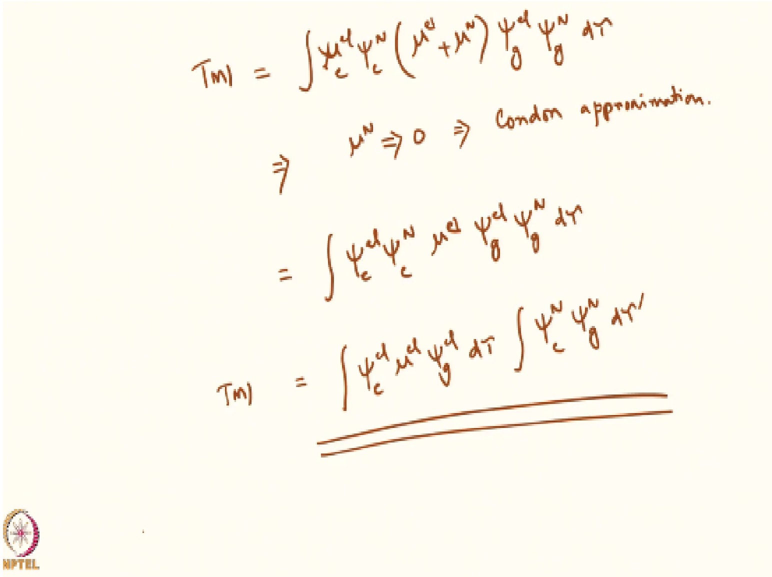

$$TMI = \int \mu_e^{el} \psi_e^{N} (\mu^{el} + \mu^{N}) \psi_g^{el} \psi_g^{N} \, d\tau$$

$$\Rightarrow \quad \mu^{N} \Rightarrow 0 \Rightarrow \text{Condon approximation.}$$

$$= \int \psi_e^{el} \psi_e^{N} \mu^{el} \psi_g^{el} \psi_g^{N} \, d\tau$$

$$TMI = \underline{\underline{\int \psi_e^{el} \mu^{el} \psi_g^{el} \, d\tau \int \psi_e^{N} \psi_g^{N} \, d\tau'}}$$

So, your transition moment integral so your TMI or other way to do it is the following is that when you have integral mu electronic excited mu electronic nuclear mu e + mu N psi ground electronic psi ground nuclear d tau = now what in this what we do is mu N be equal this goes to 0 and this is the Condon approximation. So, essentially the dipole moment is enhanced or contribution comes from only the electronic coordinates.

So this means what you have is mu e electronic sorry this must be psi electronic not mu psi e electronic psi e nuclear mu e psi g electronic psi g nuclear d tau. Now, we will see that the mu e electronic will only act on the psi e and psi g electronic. So that means this will be equal to integral psi e electronic mu electronic psi g electronic d tau and integral over psi e nuclear psi g nuclear d tau prime.

Because the nuclear coordinates are different than the electronic coordinates so they are separate. So, these two are the integral that need to be evaluated. So, for getting the electronic transitions one need to evaluate these two integrals. Evaluation of these two integrals I will take up in the next lecture. We will stop it here now. Thank you.