

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

**NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)**

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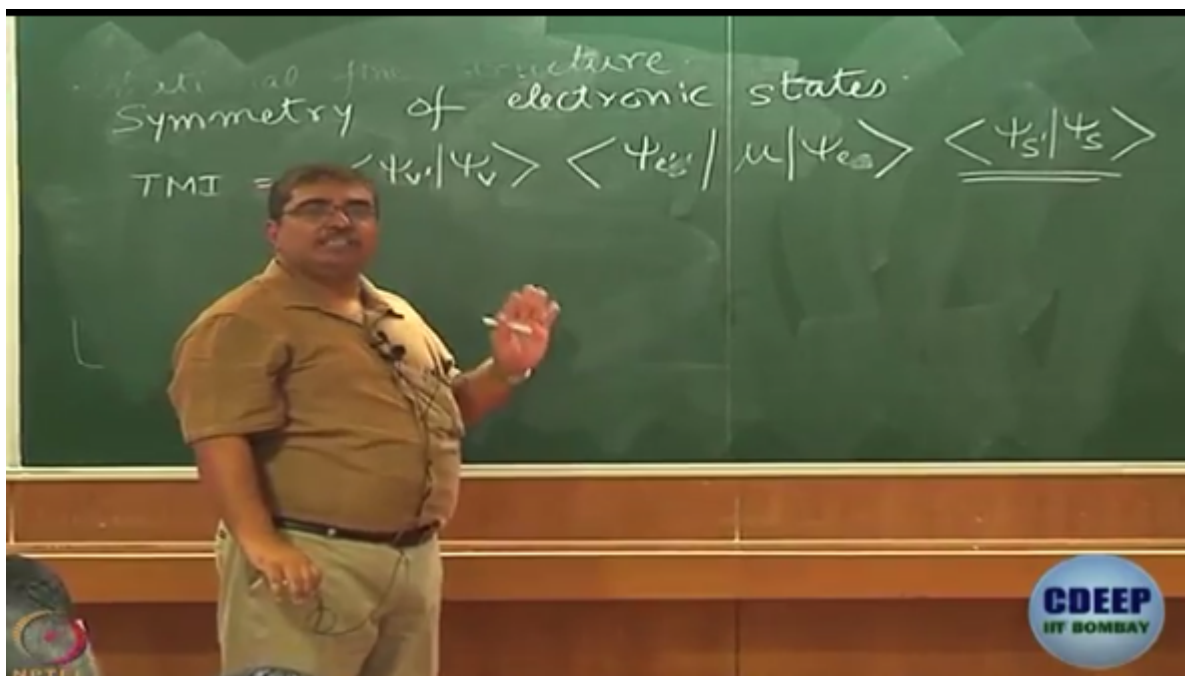
**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

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DEPARTMENT OF CHEMISTRY,
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**Lecture No. – 50
Symmetry of Electronic States**

Now let us move on to the next topic of discussion, we have taken a holiday from symmetry for a couple of days, now that holiday comes to an end. So we go back and we discuss this symmetry of electronic states. When I say symmetry of electronic states I mean symmetry of the total electronic wave function, okay, special part not total, special part of the electronic wave function, let us see what it mean.

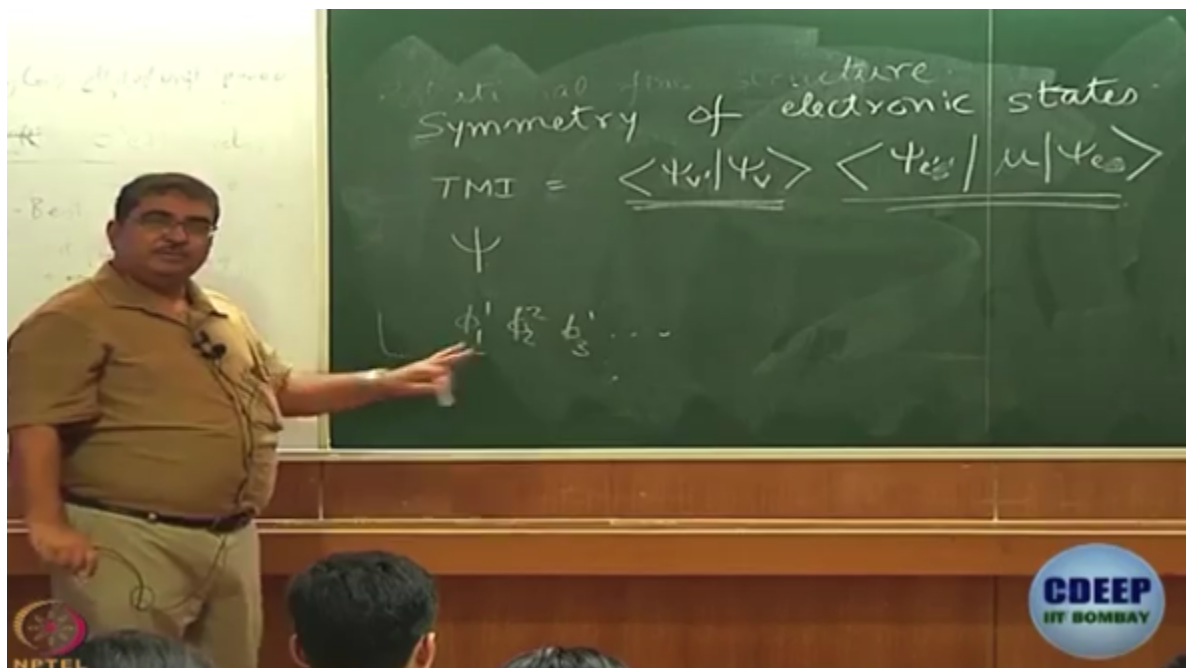
And why do we need to do this, we need to do this because we go back to our old friend transition moment integral, if Born-Oppenheimer approximation is valid if you can separate vibration from, vibrational part from electronic part you know very well that this is how we write the transition moment integral $\int \psi' \hat{V} \psi$, $\int \psi' \hat{V} \psi$ integrated overall space, $\int \psi' \hat{V} \psi$ maybe $\int \psi' \hat{V} \psi$ integrated overall space or maybe we'll write this separately as well $\int \psi' \hat{V} \psi$ $\int \psi' \hat{V} \psi$ multiplied by $\int \psi' \psi$,
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we have already dealt with this last week and we have arrived at what is called the spin selection rule. We have dealt with this, and we have got Franck Condon factor.

What we now want to talk about is this part, this is what gives us what is called the orbital selection rules very briefly we had said yesterday that this is what gives exercise to your familiar Laporte selection rule, but what we now want to do is we want to do a more systematic discussion of this orbital part of the transition moment integral, and since we have discussed vibrations already we know that for, what did we do for your vibration of poly atomic molecules, we talked about the symmetry of the vibrational wave functions, and use symmetry to evaluate whether the transition moment integral is nonzero or not, we'll adopt and exactly same strategy, identical strategy for the electronic wave functions as well, okay.

So you see three terms is what we are talking about, one term is something we know already, your transition moment integral X, Y, Z, okay, all we need to understand now is what are the symmetries of this and this, the wave functions, electronic wave functions to do that first thing we need to understand is how do you write an electronic wave function. Suppose you have some electron configuration, you have several orbitals let us say maybe I'll write those orbitals as phi, and the electronic wave function overall sai, let us say our orbitals phi 1, phi 2, phi 3, phi 4 so on and so forth, right, and let us say for now I've one electron in each, okay, of course that is not going to be ground state at least, so let us say this is the configuration, phi 1 1, phi 2 1, phi 3 1 so on and so forth. You understand what I am saying, electron configuration open the phase or MO's don't forget that,
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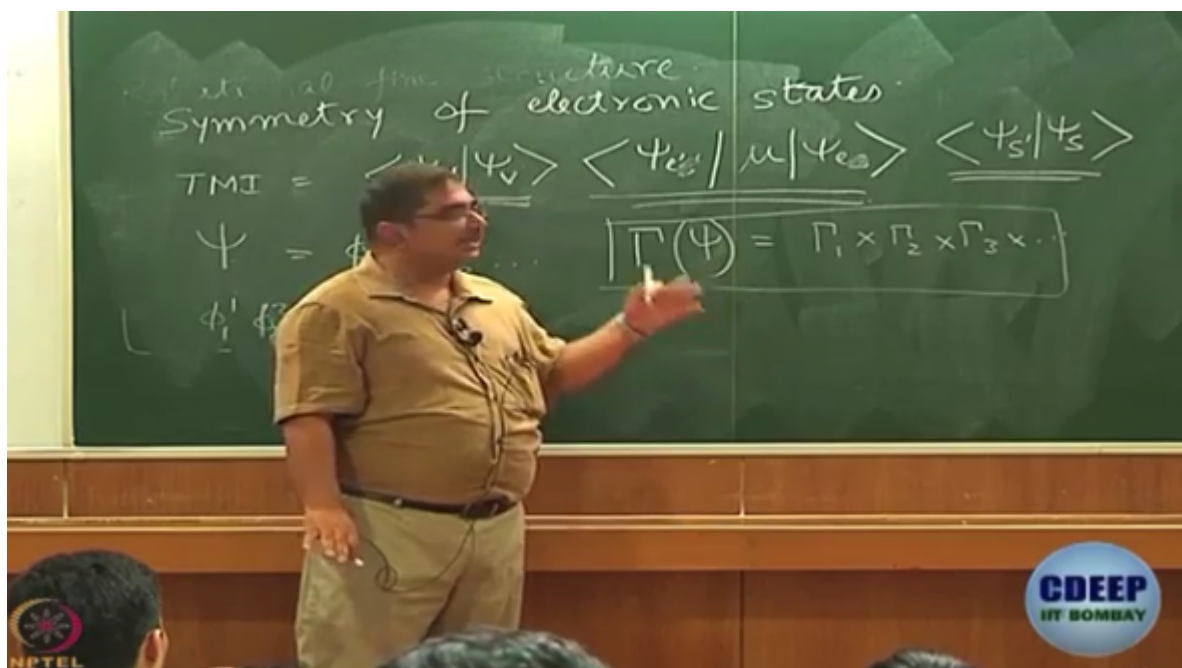


when I say orbital here I mean molecular orbital, we are discussing molecules not atoms.

So ψ will be of course ψ_1 multiplied by ψ_2 multiplied by ψ_3 and so on and so forth, so if the electron configuration is ψ_1^2 , what will ψ be? I've two electrons in ψ_1 that's all I have, say hydrogen, what is the, come on we've done this actually, what is the electronic wave function of our hydrogen? Dihydrogen ground state, what is the electronic wave function? Yes, one is dihydrogen is what I am saying, yeah so basically, whatever is the bonding orbital right, so there your $1s$ comes in, $1s + 1s$ that you multiplied twice right, and then you wrote the, wrote electron 1, electron 2 and then you proceed it, so the thing is, this also in that case all I have to write is $2 = 1$ nothing else, so this is how you write the wave function, I think we are all familiar with that, with the product of the, electronic wave function is given by product of the molecular orbitals.

So what is the symmetry of the electronic wave function? If I say this is the representation of the electronic wave function ψ of the molecule, will you agree with me that it is $\gamma_1 \times \gamma_2 \times \gamma_3$ and so on and so forth, I take every continued product of the symmetries of the molecular orbitals that are involved, okay.

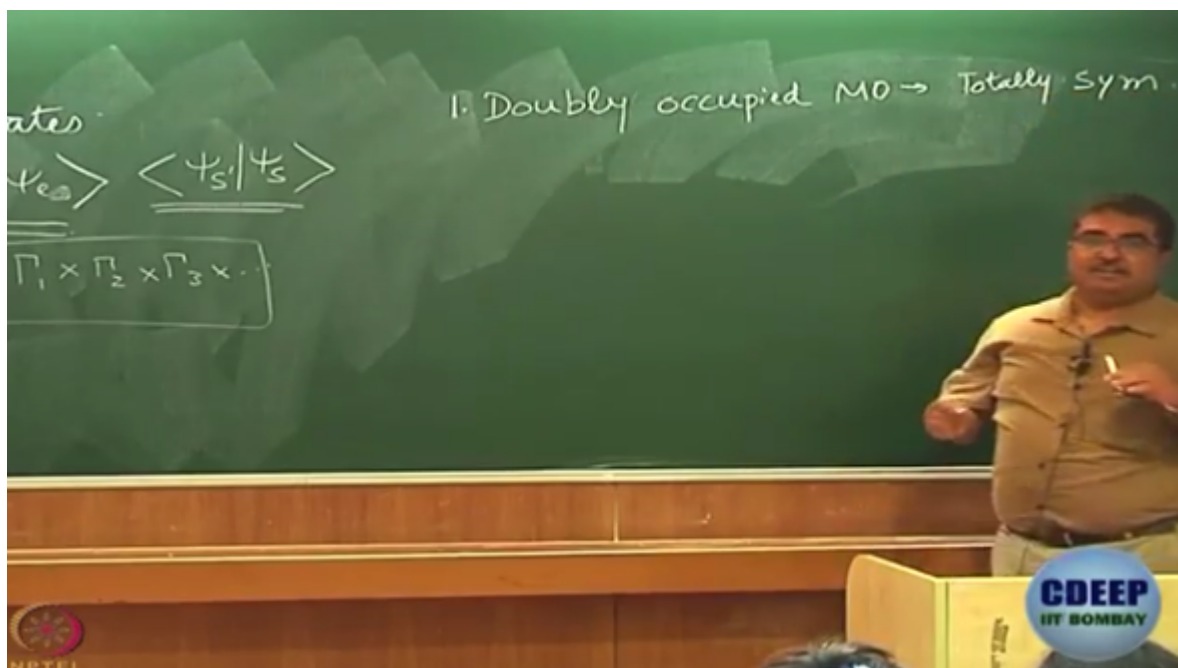
So now this is all that we need to understand to be honest, whatever we discussed for the remaining time today is based on this, okay. Let's start,
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we are going to arrive at I think 5 rules, depending on how I frame it 5 can become 3 or 6, but I think 5 rules, this part of the discussion is from Harrison Bertology, okay. So this is discussed very nicely, alright, so this is little bit, just this is what you have to remember, we take direct product, but then things can get complicated as we go along.

So first thing what happens when I have a molecular orbital that is doubly occupied, no matter what the symmetry of that molecular orbital is, I have one molecular orbital I've two electrons in it, what will be the symmetry in such a scenario? Yes, for that we'll need to remember a small theorem or working formula that we're derived in the previous classes, and that is in the syllabus for tomorrow's quiz, so you better be able to say what it is.

What happens when I take a direct product of something with itself? Some symmetry species with itself, what do we get? We get the totally symmetric representation, does that ring a bell, totally symmetric representation, so see fully occupied orbitals that is rule number one, doubly occupied a MO's they give raise to a totally symmetric representation. What does that mean? (Refer Slide Time: 07:46)



It means that when we talk about any molecule, we don't really care about the core, right, only the valential matters, is that right or not? Say, not everything in the valential matters all MO's are doubly occupied, almost all MO's are going to be doubly occupied right, think of any say diatomic molecule, dihydrogen, well dihelium if it is there, then what is there after helium? Periodic table let's see how many of us remember? Hydrogen helium, lithium, if I have dilithium, okay, all orbitals are doubly occupied, right, so for all these the ground electronic state is totally symmetry.

What is there after lithium? Beryllium, right, all orbitals are doubly occupied in B2 as well, is that right? What is there after Beryllium? Boron, what is the case of Boron? Doubly occupied carbon, what about carbon? Accha don't forget that there this sequence also matters, where are we going to get a complication? There is no problem anywhere except for oxygen. In oxygen you will see that there are two electrons but they are in two degenerate orbitals, right, so in the simplistic picture that we write, we write two arrows like this, right, that is where we'll need to expand our discussion a little bit, before that whatever ground state we have for diatomic molecules, homonuclear diatomics they are all totally symmetry. Are we clear so far? Right.

And even for oxygen everything except for those two electrons in the pi orbitals are in orbitals that are doubly occupied right, so we don't have to worry about all those orbitals, totally symmetric + totally symmetric is totally symmetric, okay, that is the main idea that we need to understand.

Of course what happens when there is one electron, a single electron in an orbital, so do we, I hope we have not forgotten the symmetry of the MO's, remember we had worked out the symmetry of the MO's, let us draw it once again, what is the lowest energy in molecular orbital? It is formed by linear combination of 2 honest orbitals right, so if we want to draw a last case this is how we draw it, what is the symmetry of this one? Of course for that we'll need to have a look at the appropriate character table, what is the, if you are discussing homonuclear diatomic

molecules, what is the symmetry point group? What is the point group of linear, homonuclear diatomic molecule? Well, the answer is in front of you, D infinity H, we'll say H, H, that H went into the tail of your speech, so I could not hear, this is the character table, right,

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totally sym.

$D_{\infty h}$	E	$2C_{\infty}$...	∞C_2	i	$2C_2'$...	$\infty C_2''$	
Σ_g^+	1	1	...	1	1	1	...	1	x^2+y^2, z^2
Σ_g^-	1	1	...	-1	1	1	...	-1	R_z
Π_g	2	$2 \cos \phi$...	0	2	$-2 \cos \phi$...	0	(R_x, R_y)
Δ_g	2	$2 \cos 2\phi$...	0	2	$2 \cos 2\phi$...	0	$(x^2-y^2, 2xy)$
...
Σ_u^+	1	1	...	1	-1	-1	...	-1	z
Σ_u^-	1	1	...	-1	-1	-1	...	1	
Π_u	2	$2 \cos \phi$...	0	-2	$2 \cos \phi$...	0	(x, y)
Δ_u	2	$2 \cos 2\phi$...	0	-2	$-2 \cos 2\phi$...	0	
...

so for this sigma G+ is the totally symmetric representation, so everything is sigma G+, alright, and not only, it is not enough to say sigma G+, so ground state of say dihydrogen, we'll write it as sigma G+, and we write a small 1, how do I read this? Singlet sigma G+, why singlet?

Because spins are pair, okay, but of course when I say spins are pair don't forget what I mean, I mean alpha beta, -beta alpha,

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Symmetry of electronic states

TM = $\langle \psi_v | \psi_v \rangle$ $\langle \psi_{es} | \mu | \psi_{es} \rangle$ $\langle \psi_{es} | \mu | \psi_{es} \rangle$

$\Gamma(\psi) = \Gamma_1 \times \Gamma_2 \times \Gamma_3$

GS of H₂: ${}^1\Sigma_g^+$

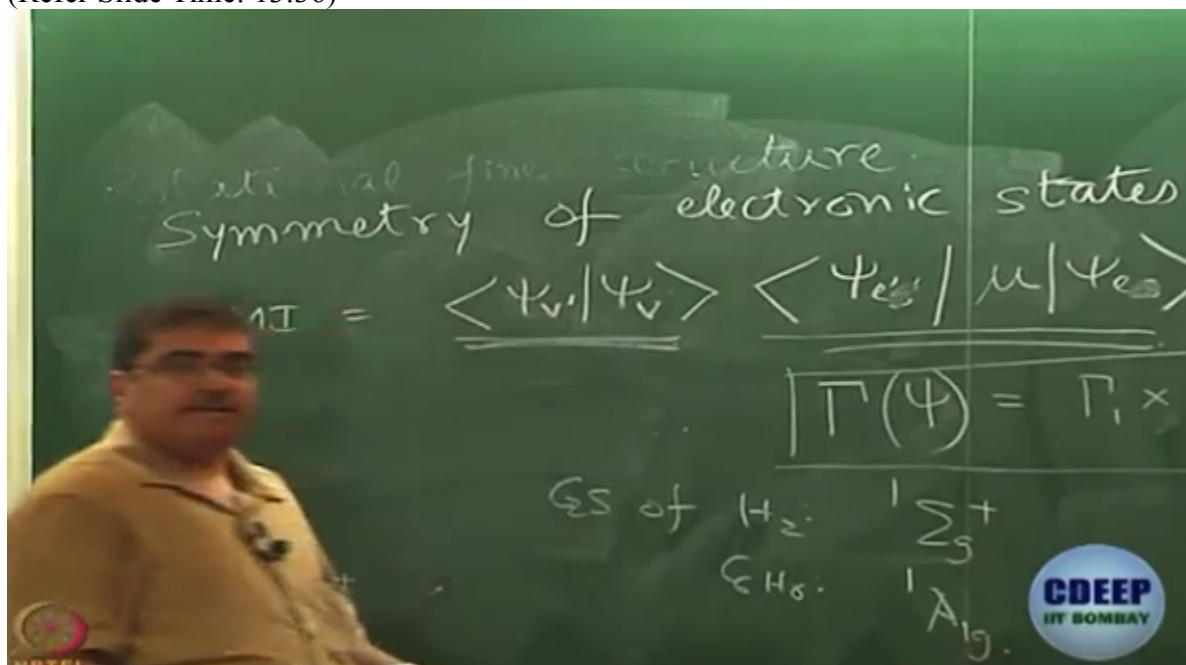
please don't forget that, we are going to use that also. Will you understand what I am saying? When I say singlet I mean alpha beta, - beta alpha please don't forget that. Don't get too obsessed with this and this picture, okay.

So singlet sigma G+ is the ground state of things like dihydrogen, dilithium all those things. Let us say why is it singlet sigma G+, because the symmetry of this orbital is sigma G+ right, sigma G+, +sigma G+ is like that, so I have written this as small sigma G+, I've written this as capital sigma G+, this is the convention we are going to follow when we talk about orbitals we'll write sigma G+, when we talk about the state well, when we talk about orbitals we'll write small letters, when we talk about the state we write capital letters, okay.

Today's discussion we'll mainly focus on homonuclear diatomics D infinity H that will familiarize ourselves, that will familiarize us with this character table as well, but then tomorrow onwards we'll actually use simpler character tables as well.

Now but then in any case let us go ahead a little further, let us say I'm talking about the ground state of benzene, so what will be the ground state of benzene? First of all singlet or triplet? Let them think only about the 5 electrons all with sigma, singlet right, all spins appeared anyway, I was writing the spin wave function in that case it's not as easy as alpha beta - beta alpha perhaps, and what will be the symmetry of the state? For benzene it is not sigma G+, right, I agree with singlet, what will be the totally symmetric representation for benzene? A1G, so for benzene the ground state is singlet A1G, alright.

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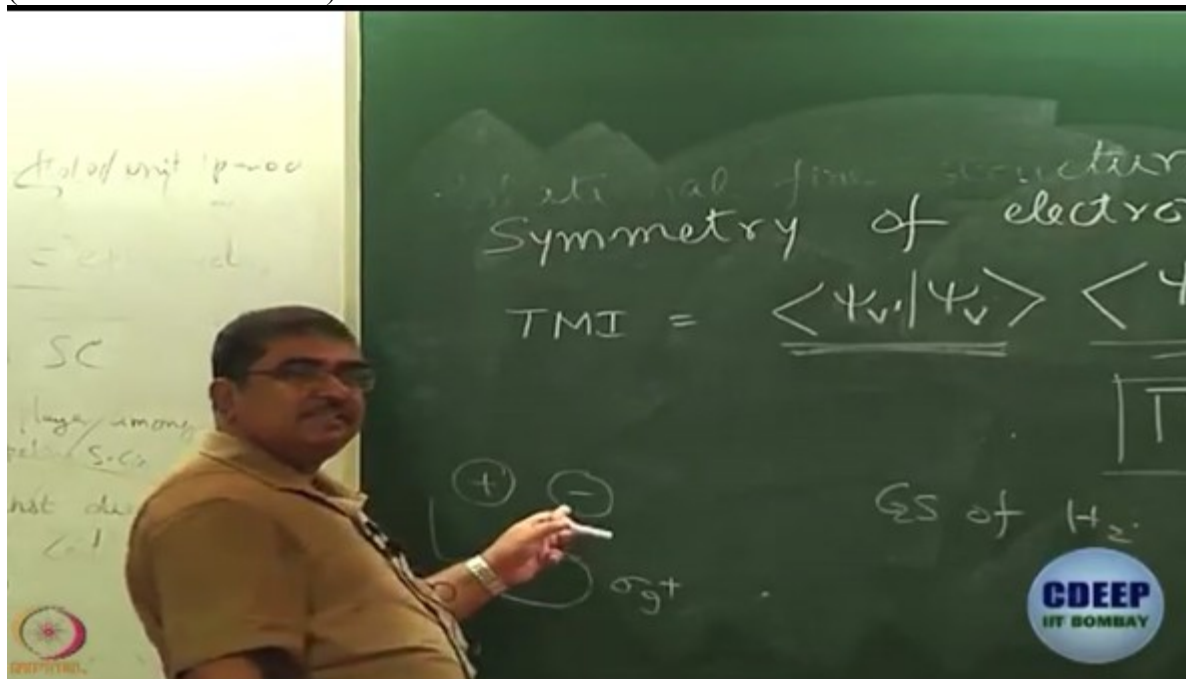


And when I write things like this, those of you who've studied term symbols will perhaps recognize that these are the terms in term symbols, alright, I had a chat with some colleagues and I have been told that inorganic chemistry they discuss LS coupling term symbols in some course I don't know in which course, so I'll not try to do that, all I want to say is this, this term symbols that we get from symmetry and term symbols that we get from LS coupling and all that they are actually the same, the reason being that there what you do is you try to use the vector model of

angular momenta and think of how they couple, okay, how they couple depends intricately on this symmetry of the electron cloud you can think, okay, that is why they are actually one and the same.

I'll not elaborate upon this further because you're supposed to learn it in some other course, but we'll go ahead with how to find out the terms from symmetry, okay, so these are the terms singlet sigma G+ in case of H2, singlet A1G in case of your benzene.

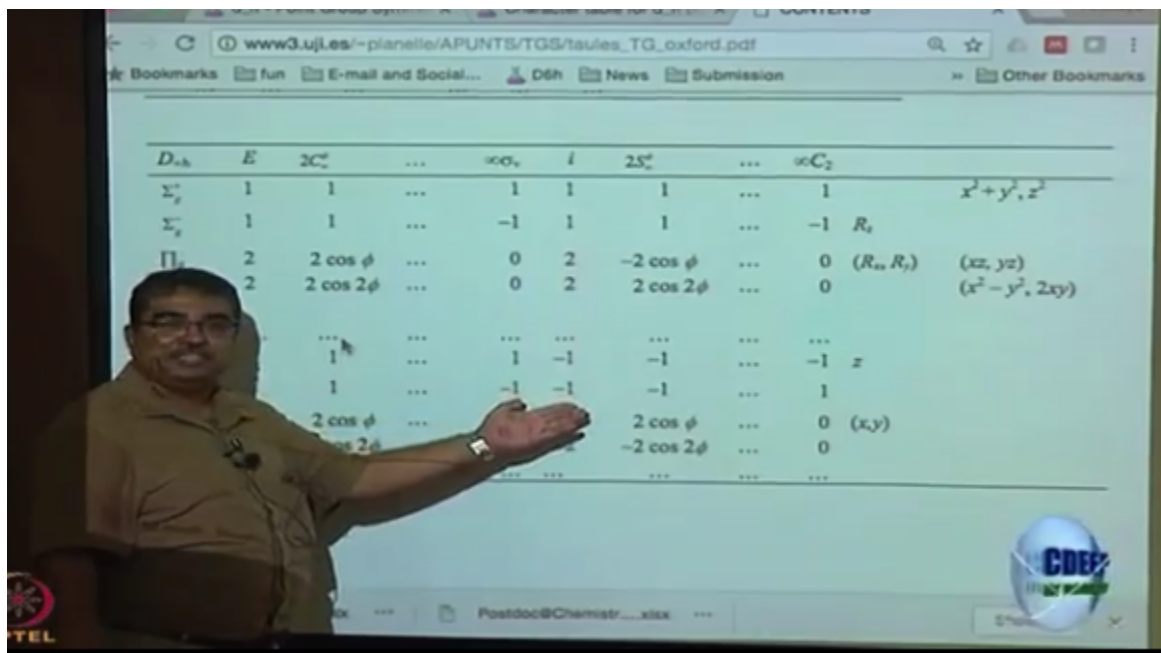
What about helium 2 if it is there? Or helium 2, what is the symmetry of this orbital?
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Character table is there, what is the symmetry of this? We're done this earlier, but first thing to ask in situations like this G or U? U, definitely U, right and it is, what will it be? Some kind of sigma of course, some kind of sigma U, which one? Sigma U- or sigma U+, why sigma U-? This is one, C infinity is 1, fine, the difference between sigma U+ and sigma U- is here, when you apply sigma V, where is sigma V? This is sigma V? What is the character, + or -? Plus, agreed? Right, so there is no need to be so negative, it is plus.

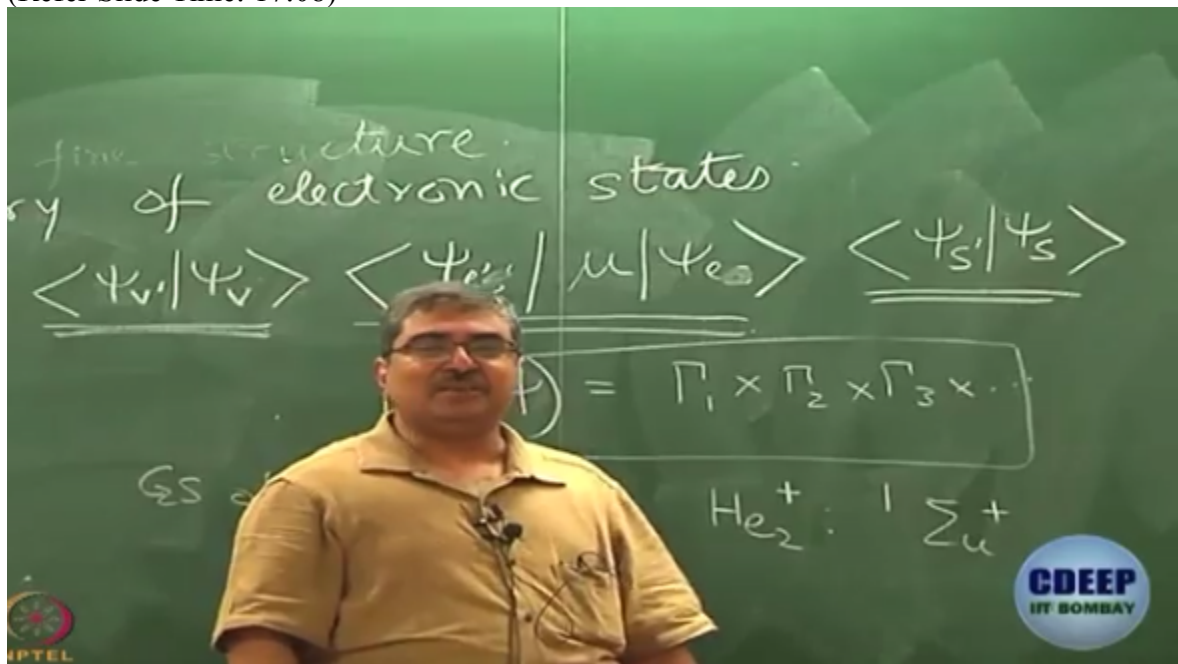
But let's check the others as well, well others is no, it doesn't make sense because they're all the same,

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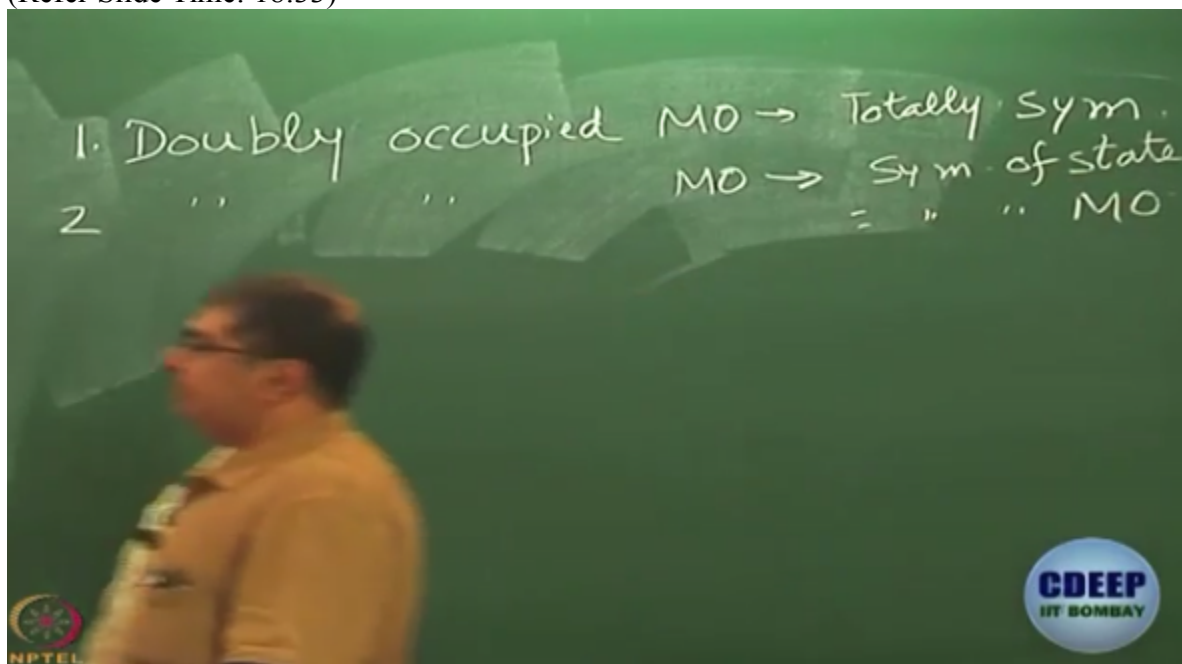


the difference come from sigma V, so this is actually sigma U+. What is the ground state of helium? Sigma G+ x sigma G+ that gives you sigma G+ anyway, what is sigma U+ x sigma U+? That is also sigma G+, isn't it? So that brings us back to this, when you have all doubly occupied MO's then it is a totally symmetric state, alright, are we all clear? Any question? Any question? No, great.

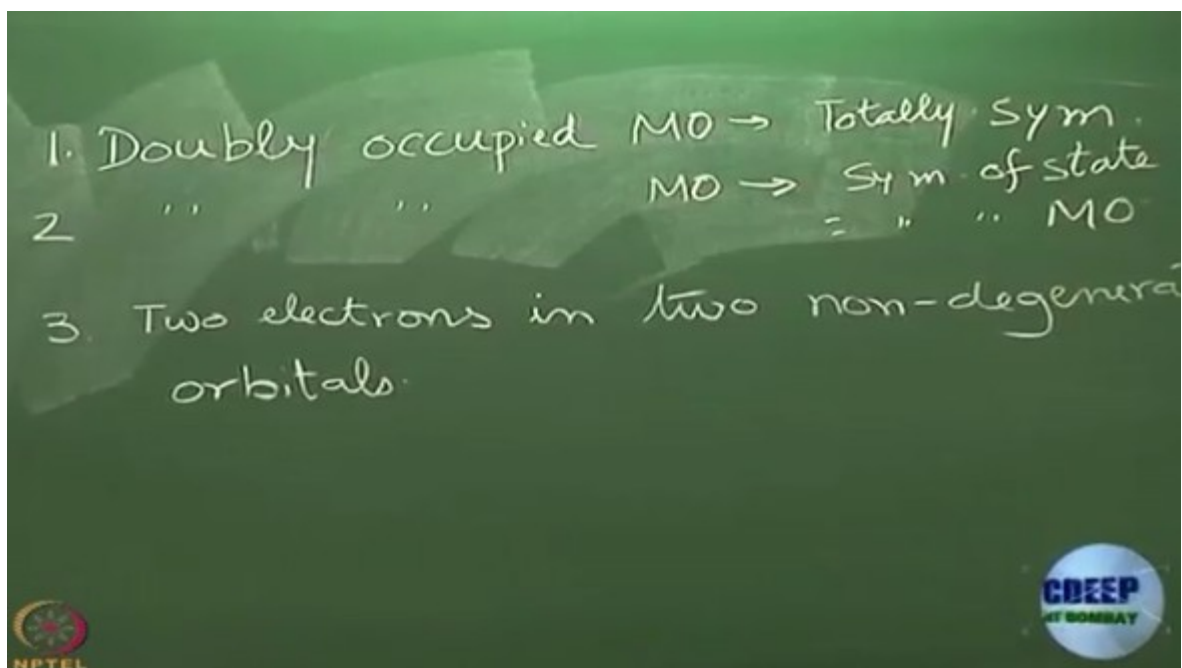
Let's get ahead, then suppose I don't have helium 2+, I have helium 2, what about HE2+? What will be the electron configuration in that case? Sigma G+2, and one electron in sigma U+, so what will be the symmetry of state? Sigma U+, simple, simple? So this ground state has singlet, singlet triplet what will it be? Sigma U+ I agree, what should I write here? (Refer Slide Time: 17:08)



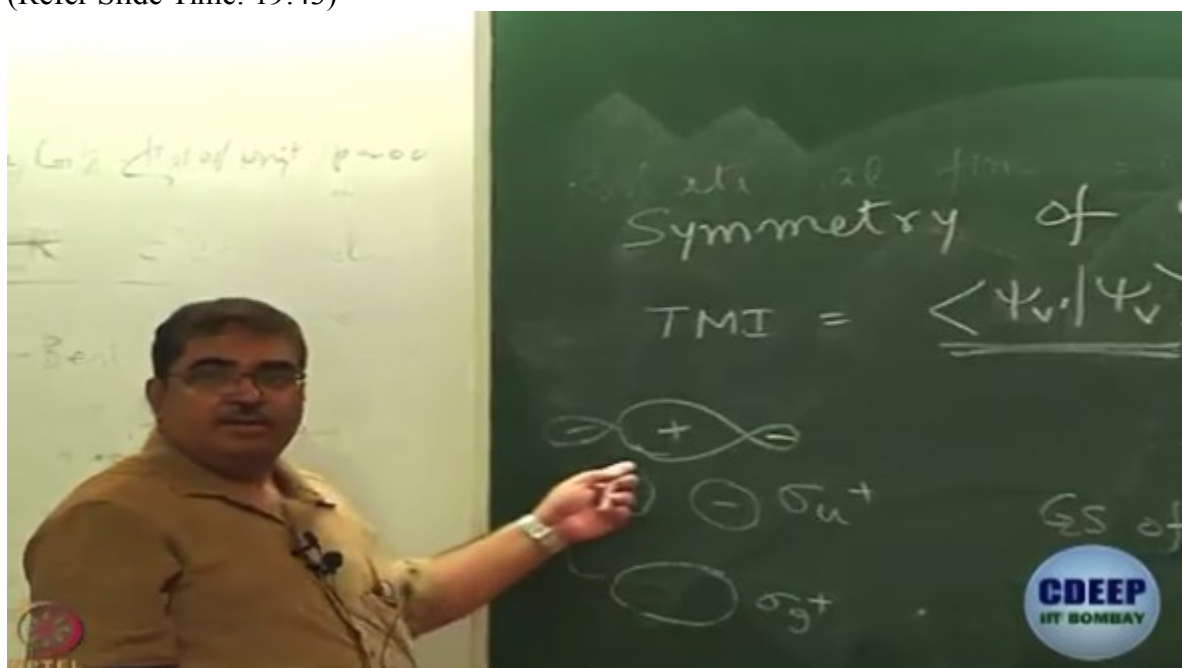
Singlet or triplet or something else? What? I have one unpaired electron, the others are paired anyway, right, I've one electron of course it makes no sense saying one unpaired electron, unless you have two, where is the question of pair and unpaired? I have one electron, what is the spin state for that? It is singlet, triplet, quartet? Yes, yes, 2 doublet, so you can either have alpha or beta right, 2 possibilities, so it's a doublet, 2 degenerate spin states are there, alright, so it's a doublet sigma U+, don't think it has to be singlet or triplet always, singlet or triplet arise when you have two electrons, when you have a lone electron it is doublet always, okay. Okay, so this is rule number 2. Singly occupied MO symmetry of state is the same as symmetry of MO, alright. (Refer Slide Time: 18:33)



Now rule number 3 is you have two electrons in two non-degenerate orbitals. Of course if you have two electrons in two non-degenerate orbitals, (Refer Slide Time: 19:15)



can that ever be a ground state? One electron in one MO and another electron in another MO they are not of the same energy that can only be an excited state, alright, so before going there let us remind ourselves what are the kind of symmetries we have, what is this?
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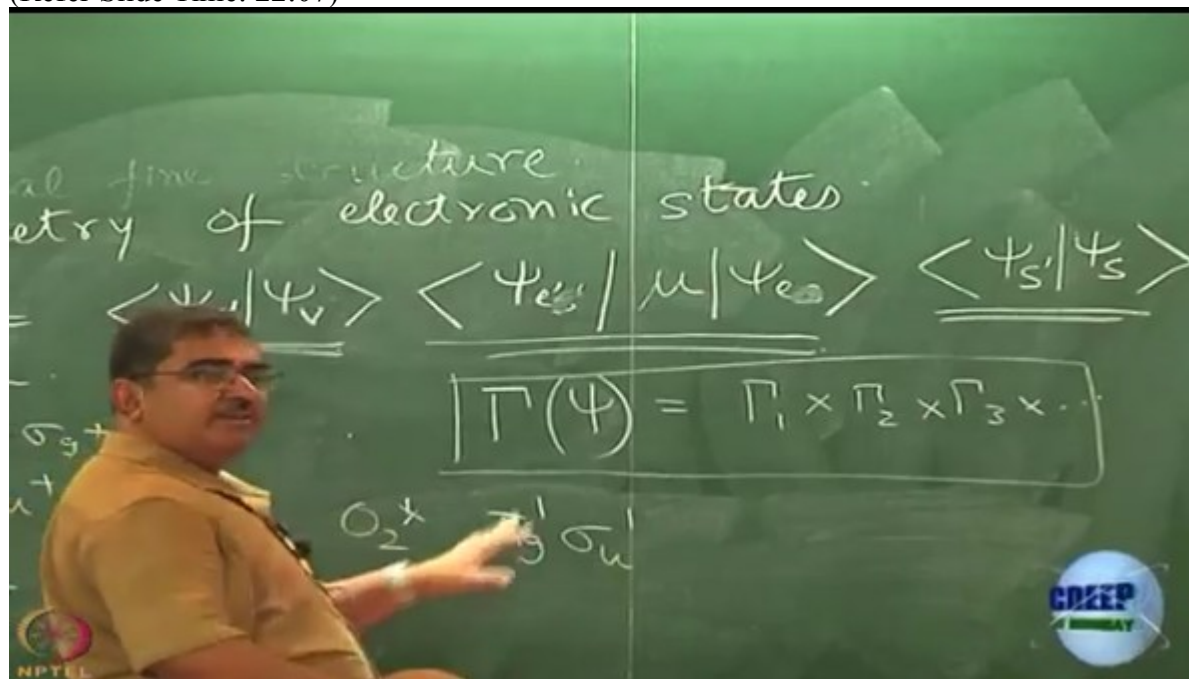


MO form by combination of PZ orbitals, this is bonding, what is the symmetry? What is the symmetry? Character of E is 1, character of C infinity? 1, what is the next thing? Sigma V, what is the character for sigma V? 1, what is the character for I, 1 or -1? 1, very good, then this is a problem of using PDF file. What is the character of S infinity? 1 sure? And what is the character of C2? 1, so it is still sigma G+.

Similarly the anti-bonding orbital will still be sigma U+, and what about the pi bonding orbital? What is the symmetry of pi? Well, symmetry of pi is pi, but which one, pi G or pi U? Pi U, right, are we clear about that?

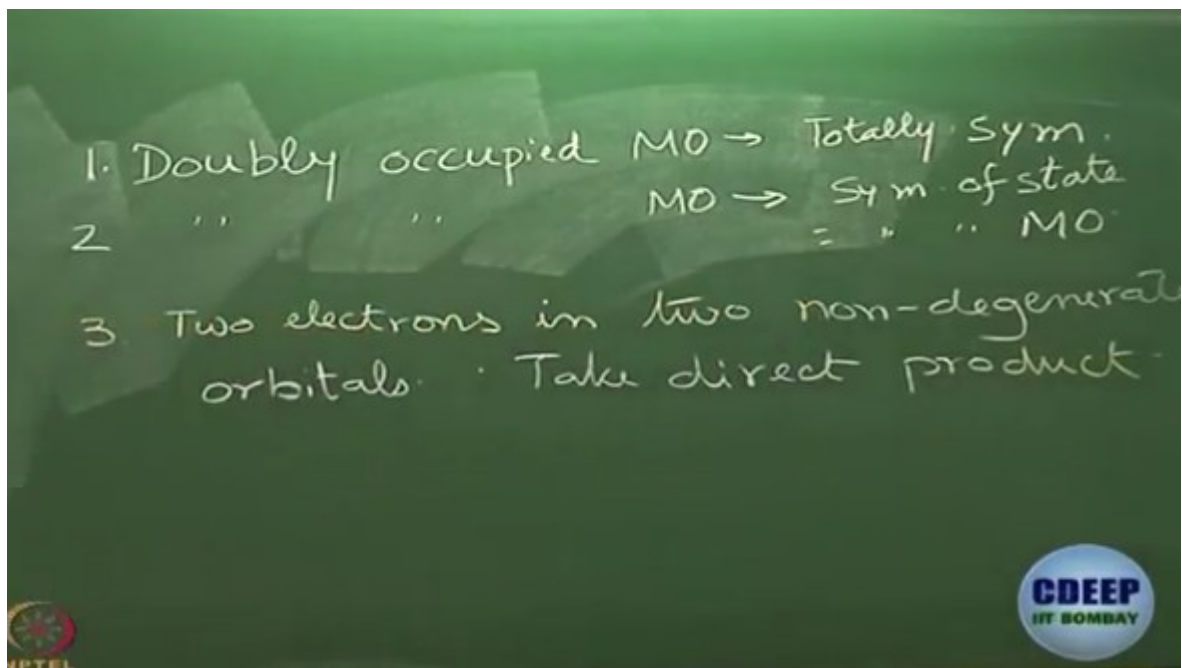
Now let us talk about then an excited state and well we can choose anything, well, let us say I have excited state of oxygen, what is the ground state of oxygen? Ground state of oxygen, what is the electron configuration? Pi G or pi U? That one, is it bonding or is it anti-bonding? So that is pi G right, anti-bonding is pi G, so ground state electron configuration will be pi G1, pi G1 we will come to that, but let us say I have performed a transition, okay, somehow I've one electron in pi G, say oxygen, dioxygen excited state, this is the electron configuration, pi G1 and let us say sigma U1, somehow I have populated a sigma, anti-bonding sigma.

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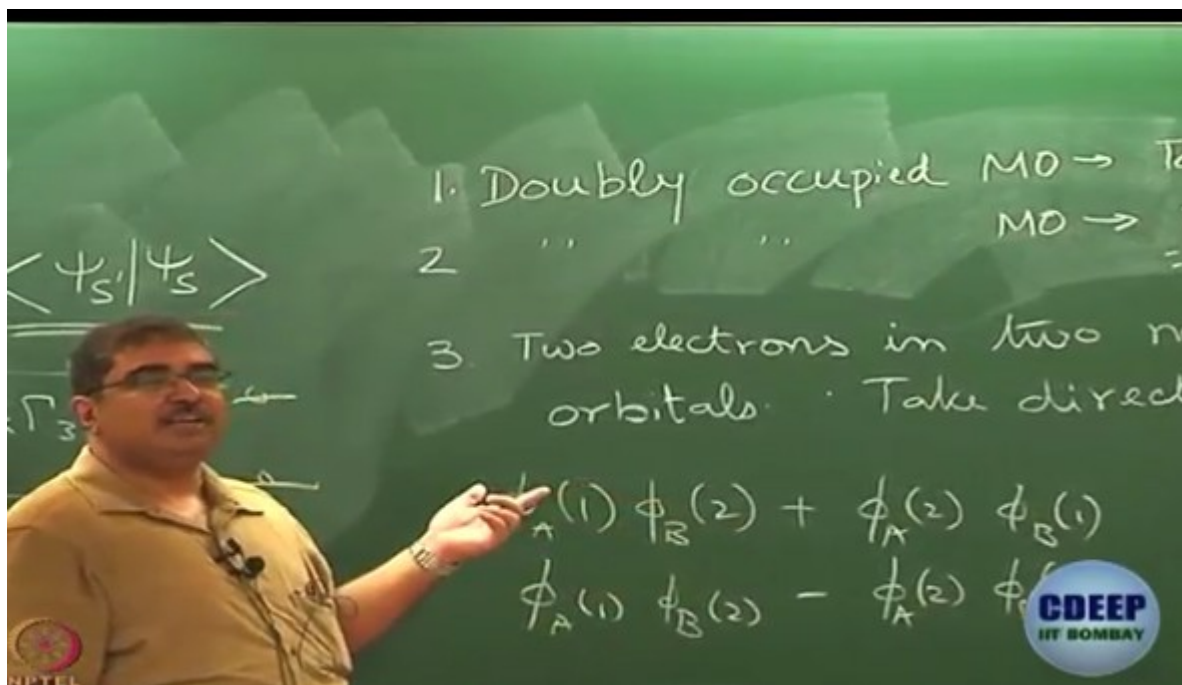


What will be the symmetry of this state? The same rule applies, no first of all you have to take a direct product of this two, what do you get if you take direct product of this two? In fact you don't even have to look at the character table for this one at least, as Vandhan is saying when you have a product of gerade and ungerade of course it is going to be ungerade, of course it is going to be ungerade, is that right? Because gerade or ungerade depends on the character of your inversion I, inversion, so for gerade it is +1, for ungerade it is -1, 1 x -1 is -1 ungerade, so it is ungerade, not only that if you have sigma and if you have pi, what will the product be? Product will also be pi, okay, think of the character of E, character of E is dimensionality of the representation, right, character of E here is 1, character of E here is 2, 2 x 1 is 2, actually it is pi U, and you can check here, this was pi G, and what was the other one? Sigma, what did I say? Sigma U+, sigma U+ and we took pi G, multiply then you are going to get back pi G, okay, if it is something else will just be the direct product, so rule 3 number is take direct product.

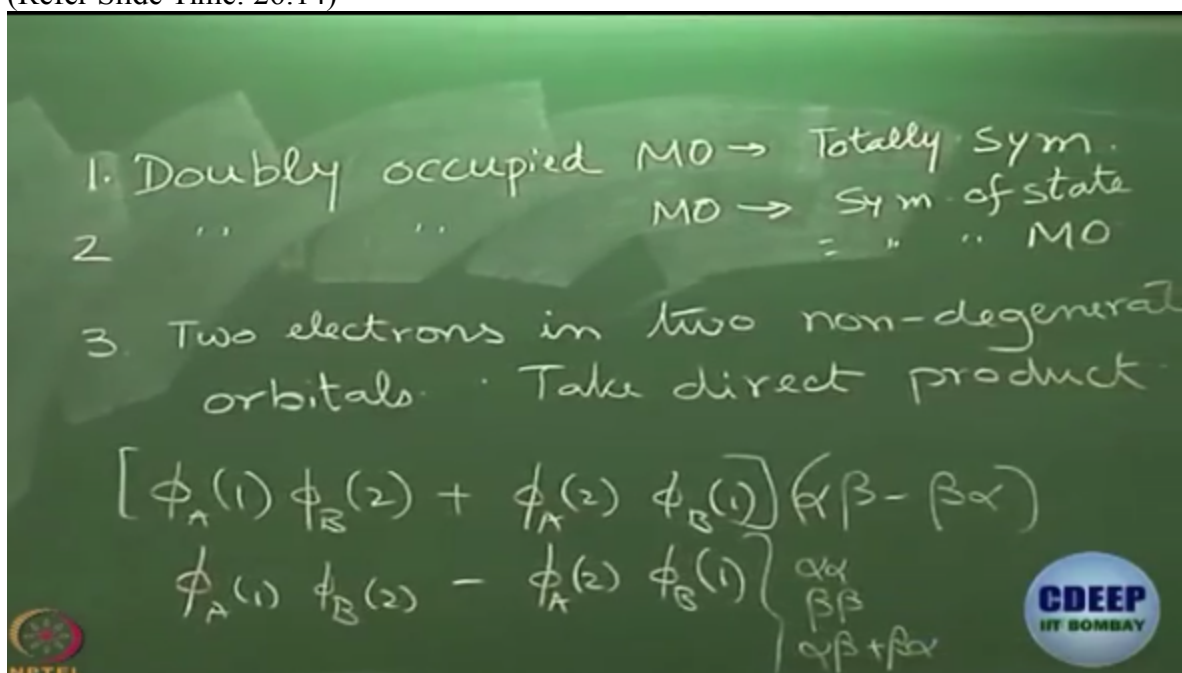
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But tell me how many states do I generate from here? First of all I don't write πU like this, I write πU like this, for state it is capital, and will I singlet πU or will I get triplet πU ? This is the situation, I have one electron here, one electron here, should I write singlet or should I write triplet? This case, can it be a doublet? No, right, two electrons singlet or triplet, so which one should I write, singlet or triplet? In this case we can write both, right, when you have two electrons in two levels, then you get singlet states as well as triplet states, right, because if you go back to the form of wave function say this is ϕ_1 , this is ϕ_2 , how do you write? $\phi_1 \phi_1$, $\phi_2 \phi_2$, but you can never just write that, you have to write $\phi_1 \phi_2$, $\phi_2 \phi_1$ as well, and you take linear combination + or -, right, so you always generate special part like this, say $\phi_{A1} \phi_{B2} + \phi_{A2} \phi_{B1}$, and you have $\phi_{A1} \phi_{B2} - \phi_{A2} \phi_{B1}$, alright, this special part is symmetric, so that will be associated with what kind of spin parts, symmetric or anti-symmetric, why?
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And that is, which rule is that? Poly principal not exclusion, poly exclusion comes from poly principal, right, so this will be your alpha beta – beta alpha, that is singlet, and this can be associated with alpha-alpha or beta-beta or alpha beta + beta alpha, that is triplet, right, (Refer Slide Time: 26:14)



so both are possible when the two orbitals involved are non-degenerate, okay.

I'll quickly write rule number 4 and then we have no more time, what is rule number 4? Rule number 4 is if you have one empty degenerate orbital, example what is electron configuration of O2 you said? How many electrons in phi G? Yes, how many electrons are there? 2 right, so I'll write O2+, then it will become pi G1, right, dioxygen with the plus sign phi G1. What will be the

symmetry of the state? Same symmetry as the orbital that is singly occupied, okay, it's sort of whole formalism, it's not whole formalism, in this case it is straight forward, because only one orbital is there, but suppose I had 3, how many total electrons can be there in phi G? 5, so if all 4 are filled for oxygen, what will be the charge? -2, if 3 are filled what is the charge? -1, right, so in that case also symmetry will be the same as the symmetry of this orbital, so in this case symmetry is going to be doublet pi G, so same symmetry, so that one vacancy you can think of it as one whole, and it will be exactly like the electron as far as symmetry is concern, alright, this is how you determine the symmetry of states.

Now when you'd have two electrons in two degenerate orbitals then the situation becomes a little more tricky because spin of one determines the spin of the other, they are not uncorrelated like it is for 2 non-degenerate orbitals, okay, so there we need to actually consider the symmetry of the total wave function including the spin part, not everything will be allowed, so on Thursday we'll start with that, we'll talk about oxygen and then we will go on to discuss the transition moment integral.

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