Symmetry and Group Theory

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Lecture - 58

Stationary States, Multiplicity, Ethylene

So that is what it is. Fine. Next I want to switch here and talk a little bit about stationary states because we are going to need that when we discuss naphthalene also. What is a stationary state? Yes, energy is fixed with respect to what? With respect to time, right? What is the other definition? Yeah, you are saying the same thing. Psi psi * is invariant of time. That is the other definition. Now, what is it that defines a stationary state? No, that I already said, okay.

As usual I am asking, I am looking for an easy answer. Electron configuration, right? Think of hydrogen, hydrogen atom. 1s 1 is one state. 2s 1 is another state. It is an exited state, right? So on and so forth, fine. So now what we want to know is how do we give the names of the stationary states? But before that can we give names to orbitals using symmetry. Let us think of some simple orbitals that we have come across many times.

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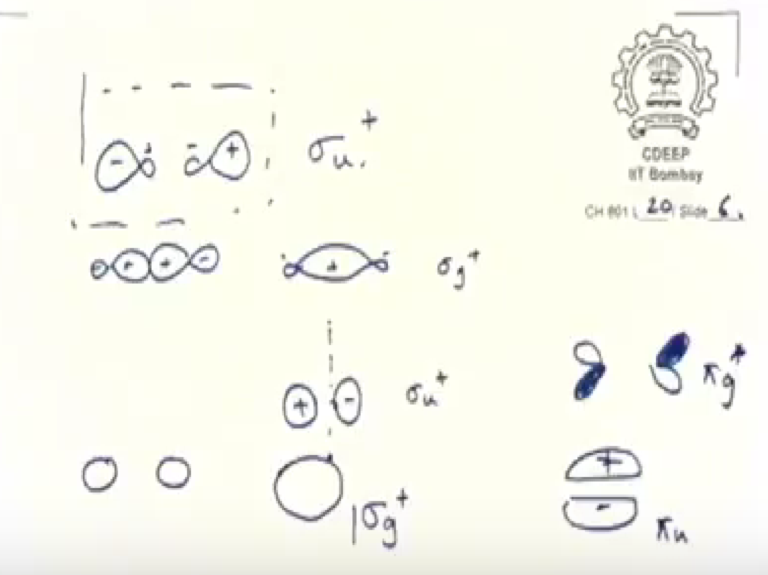

Let us talk about a linear system say hydrogen H 2 okay or N2 F2 whatever. So you have 1s orbital and you have 1s orbital okay and when you generate a molecular orbital by linear combination of these then what are they? One linear combination is plus, another linear combination is minus. Do these orbitals belong to some symmetry species of the point group? Which point group is this? Homonuclear diatomic? H 2 N 2 F 2, D infinity h. Say infinity v is HCl, heteronuclear diatomics or some other heteronuclear linear atom, linear molecule.

So even without looking at the character table I think you can see that this is totally symmetry, right? So what is the name of the totally symmetry point group , say totally symmetry reducible representation, no not in D infinity h; sigma g +. So I can call it the sigma g+ orbital. I think you are familiar with this notation. You have called one sigma orbital, right? Sigma 1s orbital, sigma g orbital also. It is just that perhaps you have not used the superscript plus so far.

Now we can use it because we know that it is the name of the symmetry species. What about this one? I will show you the character table now. Sigma u, but plus or minus; u you can see right? That is very bad way of putting it. You can see why it is (()) (03:52) could you not? So what are the symmetry operations that we need to consider.

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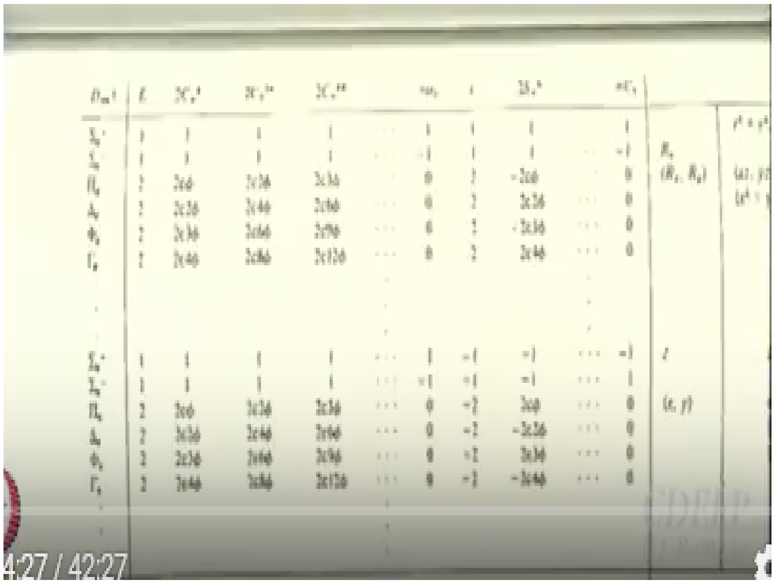

Can you read? Now? Now can you read? Now what are the symmetry operations that we need to consider. C infinity is hopeless anyway. There is no point in talking about C infinity. But we can talk about i, i tells us that it is u, but that we have already worked out. What else? So what is the difference between the two u? What are the u's that we see? Sigma u+ and sigma u- right? The difference is in sigma v.

In sigma v+ the character of sigma v is plus and character of sigma v is minus in sigma u-; i of course both are minus, s infinity hopeless, C 2 sigma u+ is -1 and sigma u- is -1. So you have to remember these two; C 2 and sigma v. So what will be the character of sigma v for this? Where is sigma v? This sigma v what is the character? +1 or -1? +1 sure, right? So immediately we see that it has to be sigma u+ right? And as a double check what is the character of C 2?

Where is C 2? This is C 2. Man you cannot even see that. This is C 2 right? Yeah. C 2 is perpendicular to C infinity and goes to the center of the molecule. So character is -1. So what is it then? It has to be sigma u+ is it not? So I name this sigma u+. Sigma u+ convinced? Now let us talk about the other one. What happens when it is p and p sigma bond? So this is what the MO looks like basically.

I really like drawing it because you can draw it in one go without lifting the pen. What is this g or you? Of course g. And then, plus or minus? I will tell you, sigma g+, in sigma g+ the character of sigma v is +1. In sigma g- the character of sigma v is -1. That is why they are called plus and minus. What is the character of sigma v here, plus or minus? Plus. So I should call this sigma g+ also. It is the first time Dibendu has said something in this class.

So since this one of course at lower energy, I call this 1 sigma g+. Actually this is not 2 sigma g+, that comes later. This is also sigma g+, alright? Now, what about the anti-bonding one? U of course. Sigma s and u and what is the character of sigma v here? Plus or minus? Sigma v, sigma v is like this, plus or minus? Plus. Are you all convinced that it is plus. Plus, sure. So it is plus. So it is sigma u+.

“Professor - student conversation starts” How is it sigma g+? This one? The plus sign. Plus sign comes from the character of sigma v. For everything? Yeah, for D infinity h yes. **“Professor - student conversation ends”.** Then what is left? Pi interaction. This is the pi bonding orbital and this is the pi anti-bonding orbital. For some more fun I will just use filled and unfilled ones, okay. What is the character of this?

First of all you cannot assign any, no you cannot assign any one-dimensional representation is it not? You cannot assign any one-dimensional representation okay? Which one is the z direction? Z direction? Along the bond is it not? So another way of finding the symmetry species of this anti-bonding orbital would be to realize that this anti-bonding orbital is somewhat like the z axis, right lying along this direction, plus this side, minus this side. This is sigma u+.

Just a check. Where is z? Z is also sigma u+ okay? And what about these? These are like x and y. This is also plus and minus right? One orbital like this, another orbital like this. They will have the same symmetry as x and y. Where do x and y belong, x y belongs to pi u. See that pi u. x y belongs to pi u and so this is the pi u orbital and this is a pi g orbital and if you want you can call it pi g * orbital also there is no problem.

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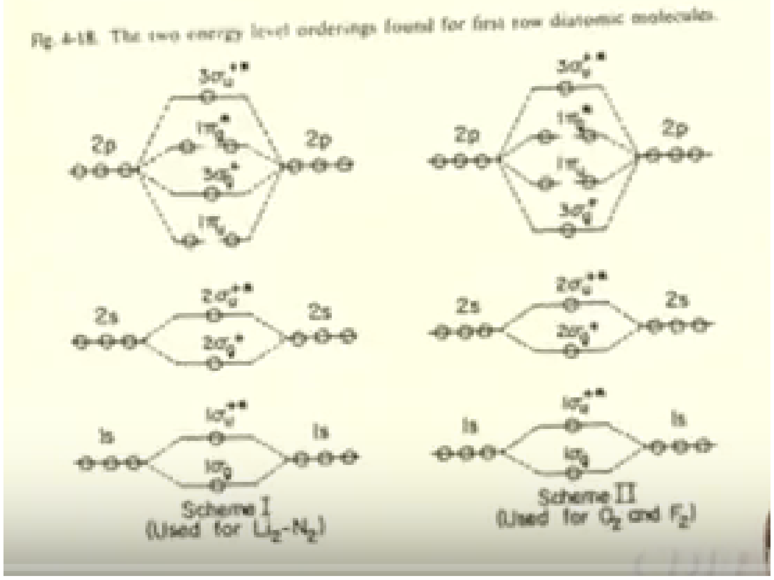

Fig. 4-18. The two energy level orderings found for first row diatomic molecules.

So with that background I think it is very easy to go back to this energy level diagram that we studied when we were children and just use the nomenclature that we just now learned. This keeps coming back to haunt us again and again, right? We studied this in class 11. But for lithium 2 2 N2 N2 this is what the sequence is. You call this 1 sigma g and the anti-bonding orbital is 1 sigma u+ *.

Then 2 sigma g+, this also has to be plus then 2 sigma u+ *, 1 pi u, 3 sigma g+, 1 pi g *, 3 sigma g+ * understand. So similarly, we can have symmetry levels for all orbitals. I can name orbitals, molecular orbitals using symmetry no matter which molecule it is, okay? Now the question is knowing the symmetries of the orbitals how do I determine the symmetries of states. Let us see. So symmetry of orbital, simple? I am going to give you assignment for this.

Well see the thing is when you work out assignments you do not have to study for end sem. End sem is a bonus. Okay. So now, now what we need to know is we need to know 5 rules. There are actually 6 rules, I will stick to 5. We do not really need the 6th one.

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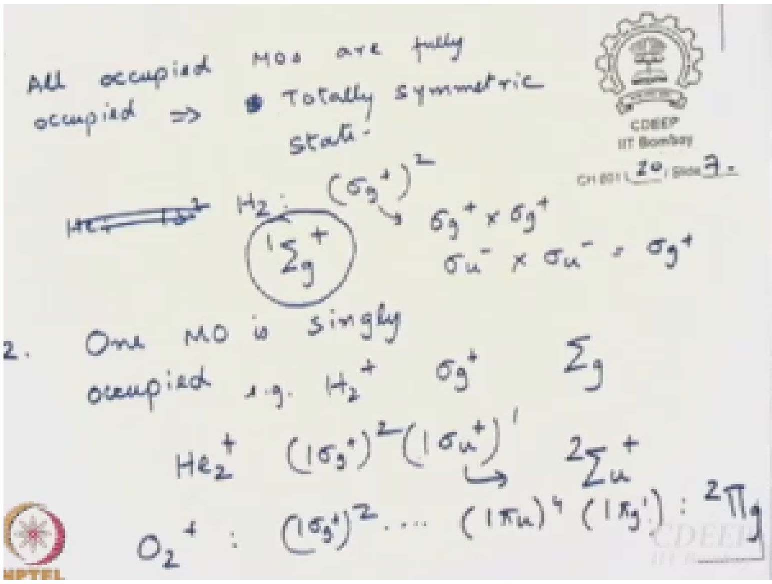

All occupied MOs are fully occupied ⇒ Totally symmetric state.

$H_2 : (\sigma_g^+)^2 \rightarrow \sigma_g^+ \times \sigma_g^+$

$^1\Sigma_g^+$

$\sigma_u^- \times \sigma_u^- = \sigma_g^+$

2. One MO is singly occupied e.g. H_2^+ σ_g^+ Σ_g

He_2^+ $(1\sigma_g^+)^2(1\sigma_u^+)^1 \rightarrow {}^2\Sigma_u^+$

$O_2^+ : (1\sigma_g^+)^2 \dots (1\pi_u)^4 (1\pi_g^1) : {}^2\Pi_g$

First is when all occupied MOs are fully occupied, I think I said this already. Then it is a totally symmetric state, right. So what will be the ground state of helium? What is the electron configuration of helium? 1s 2 right? Oh what am I saying? What will be, sorry, I suddenly had an attack of amnesia. H 2 not helium, sorry, extremely sorry, H 2. Sigma g+ 2. So all occupied orbitals are fully occupied, right? What is the symmetry of the state? Sigma g+.

When we write orbitals we use small letters. When we write states we write capital letter, okay? But just writing this sigma g+ is not enough, two things. Let us understand why it is called sigma g+, okay. So what is the direct product of 2 sigma g+? Sigma g+ cross sigma g+. What is that? Sigma g+. What is the direct product of say sigma u- and sigma u-? That is also sigma g+ is it not? Because if it is one-dimensional representation characters are either +1 or -1 okay?

So multiply any character by itself you get 1, right? That is why if it is, if all occupied MOs are fully occupied then the direct product of the symmetries turns out to be totally symmetric. That is why it is called a totally symmetry state. Alekia, okay? Now, this is not enough. Because when I have written sigma g+ I have only taken care of the spatial part. I also have to take care of the spin part. What is the spin part here? You think in very simple terms.

Spin has to be paired; +1/2 -1/2. So capital S = 0. So 2s +1 = 1. So it is a singlet state. So this is how I write. How do I read it? Singlet sigma g+. It is not read as 1 sigma g+, alright? Singlet sigma g+. And if you want to think in a little more complicated manner then think this way. We have talked about Pauli principle in this course or not? What is Pauli principle? That for fermion the total wave function has to be antisymmetric.

So here the special part is symmetry. So what is the possible total wave or possible spin wave function here? Alpha beta minus beta alpha, right? Others will not survive, right? So alpha beta minus beta alpha. That is the only one that is possible. So total wave function is only one. Because special part is unique, spin part is also unique, okay? So it is alpha beta minus beta alpha. That is the meaning of this, okay. Number 2. Let us make it a little more complicated.

One MO is singly occupied. Ask Dibendu, he is going to tell you 1000 examples of that because you, is your project on magnetism or not, oh not. Anyway, Darwin has said that environment is also important. So he can do it. But I will give you only a very simple example. H 2+. I stick to H 2. What is the electron configuration here? Sigma g+. So what will the state be called, I think you can now figure out. It will still be called sigma g. In case, now is there only one.

You do not even have anything to get a direct product for. Okay, let us make it a little more interesting. Suppose it is He 2+. What is the electron configuration. He 2+. So 1 sigma g+ 2 1 sigma u minus or plus, + 1. Now what happens? This one, what is the direct product of sigma g+ and sigma g+? Sigma g+. That is like multiplying by 1, you do not even worry about it. You are only worried about this. Only one electron is there, right?

So there is no question of taking a double product. There is no question of taking a direct product. So whatever is the symmetry of the orbital is the symmetry of the state. Symmetry of the state is then sigma u+ okay. Using the same symmetry for both is not a good idea. Sigma u+ is a state. Now tell me there is only one electron. So what is going to be the multiplicity? Again, if you take the simple approach, +1/2 multiplied by 2 is 1; 1 + 1 is 2. So it is a doublet.

But what does doublet actually mean? It can be either alpha or beta. You do not know what it will be, right? It can be either alpha or beta. That is why two possible wave functions are there. Doublet means 2 wave functions. Triplet means 3 wave functions. Please do not forget this. Okay, simple? Let me show you another example, O 2+. 1 sigma g+ 2 then whatever it is. Then you have 1 pi u 4, 1 pi g 1. What will it be? Doublet pi g.

Do not say 2 pi g, doublet; doublet pi g. Now, lot of people say that. But it is wrong. Doublet pi g, do not forget. And this pi is capital pi. When you talk about states it is capital, okay? Moving on. And now, once you know this you can, once you know these two you can figure out the rest to be honest. So now I am only going to propose the problem, you tell me the answer.

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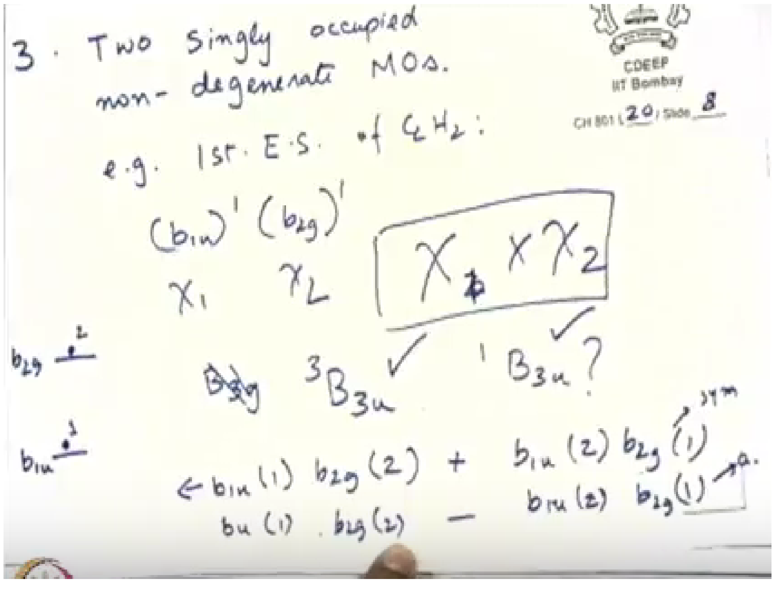

3. Two singly occupied non-degenerate MOs.

e.g. 1st. E.S. of C_2H_2:

$(b_{1u})^1 (b_{2g})^1$

$\chi_1 \quad \chi_2 \quad \boxed{\chi_1 \times \chi_2}$

$^3B_{3u}$ ✓ $\quad ^1B_{3u}$? ✓

$b_{1u}(1)\, b_{2g}(2) + b_{1u}(2)\, b_{2g}(1)$ → sym

$b_{1u}(1)\, b_{2g}(2) - b_{1u}(2)\, b_{2g}(1)$ → a.

We have two singly occupied non-degenerate operators, not operators; non-degenerate MOs. So example that I can use is first exited state of C 2 H 2. Just believe me when I write b 1u 1, b 2g 1. Of course, I will make you work out all this. I will give you some homework. So if it is b 1u 1 b

2g 1 what should it be? What is the name of the state? Why A 2u? Bean to b is a. Bean 2 b is not always equal to a no? No bean 2 b should be equal to a.

But the answer is given is different. That is why I am a little confused. Bean to b should be a. b 1u cross b 2g apparently is b 3u. Whatever it is, say this is chi 1, say this is chi 2, the state is capital chi or capital chi 1 cross capital chi 2, right? Just take a direct product of these two and I can show you the answer in a convenient form. Which point group is C 2 H 2? Ethylene. It cannot be d infinity or can be infinity. C 2 H 2 is not even ethylene.

Yeah. C 2 H 2 or C 2 H 4, what am I talking about? Hold on. It is not acetylene. Ethylene. Why am I saying C 2 H 2. Sorry, **sorry**. Bad inorganic chemistry. Ethylene. Ethylene, what is it? D 2h. I will show you the product. See the thing is what we are studying is actually very classical. It has been around for a long time. So people have worked out a lot of things. And this kind of tables of direct products is available.

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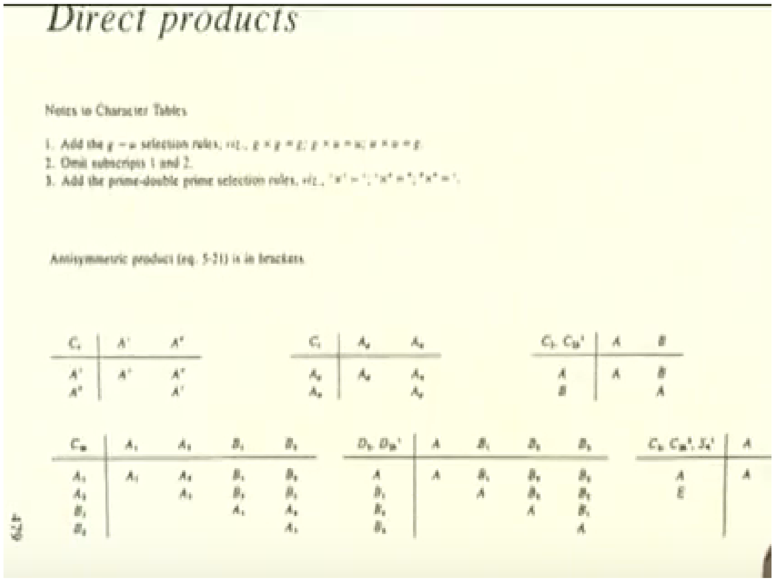

Direct products

Notes to Character Tables

Antisymmetric product (eq. 5-21) is in brackets

I am unlikely to give you such tables in 8 sem. I want you to work them out. So in D 2h, what did we want? What into what? B 1 into B 2 is B 3, okay? And then u into u is always g, u into g is always u; g into g is always g, okay? Similarly, you can write down what it is going to be. So it is a direct product. Now what will be the multiplicity? Why triplet? So this is B 3g fine. B 3u sorry. B 3u, what is the multiplicity? Should it always be triplet or can it be singlet also?

Why are you saying it should always be triplet? Both are what? So let us put it like this. This is one level, this is one level. This is b 1u, this is b 2g. I have one electron here, one electron here. Is it necessarily a singlet? Is it necessarily a triplet? Can I have both the wave functions? Justify that you can have both the wave functions. Justify that you can have both the wave functions. Because those are the spin wave functions.

Alpha alpha beta beta and alpha beta + beta alpha these are symmetric and you can have alpha beta minus beta alpha. That is antisymmetric. So can you have both? Or is it necessary that you must have only one? Well let us try to write the wave functions. How do we try to write the wave functions. We write in terms of coordinates of the two electrons. In other words, we give names to electrons. I call it electron number 1, call it electron number 2.

Exactly, that is why we are, we will come to that. What is the special part of the wave function? B 1u 1 b 2g 2. Can you write this? No. Because as Shantanu said correctly 1 and 2 are indistinguishable. How will you say that it is 1 and it is not 2 that is b 1u or b 2g. So this special part is not allowed. What is allowed? A linear combination + b 1u 2, b 2g 1. This is allowed? What I was saying here. We are saying that one of the electrons is in b 1u, the other one is in b 2g. both the electrons are not in the same MO. That is all we are saying, okay?

Do you agree or not? What is the other linear combination I can write? Instead of plus I can write minus. Now see for the plus combination, is it symmetric or antisymmetric with respect to particle exchange? It is symmetric. What should the spin part be for that function, antisymmetric. Antisymmetric means alpha beta – beta alpha. And when you use the minus then the space part is antisymmetric, spin part has to be symmetric.

Spin part is antisymmetric for alpha alpha beta beta and alpha beta plus beta alpha. So you see both triplet and singlet are possible. So I can have both. This is correct, this is also correct. Is there a question? Have you all understood? Is there a confusion? Is there an objection? **“Professor - student conversation starts”** Sir, why not we have 2 electrons together. No we are saying this is the exited state. If you have it in the same orbital then that is ground state, okay. So that we can write very easily, no problem. **“Professor - student conversation ends”.**

Now I am saying that I have a situation where suppose I brought in some light and I performed an excitation okay. Now the exited state does it necessarily have to be triplet, does it necessarily have to be singlet. That is what we are discussing. So you can only use the antisymmetric wave function which is alpha beta minus beta alpha singlet. But the moment you promote an electron here you have two possibilities.

Electron number one is here, the other possibility is electron number one is here, right? So you have to write 2 terms. One term is not sufficient anymore. That is exactly, so this is what happened if you have studied say lithium exited state, the same thing happens. This is the part where we have maximum confusion. Please ask questions. Do not feel shy to ask questions now.

“Professor - student conversation starts” Sir, you said about H 2 as antisymmetric. Yeah. So which one has to be antisymmetric? Total wave function has to be antisymmetric. The product of space and spin. So if the total one has to be antisymmetric then it can be done, then you have to look at the combination. Only one looking at one is not good enough. Space part can be symmetric or antisymmetric, no problem. Spin part can be symmetric or antisymmetric no problem.

But a symmetric space part has to be combined with an antisymmetric spin part and vice versa. When you have space spin which one is antisymmetric. So in the upper one which one is antisymmetric? Upper one is upper equation? Yeah. You tell me. Antisymmetric with respect to what? No, I mean when we say symmetric or antisymmetric in this context we mean antisymmetric with respect to what? First say that. Antisymmetric with respect to the change of electrons. Exactly. **“Professor - student conversation ends”.**

Now you interchange one and two. What do you get? You get back the same function. Yeah. It is symmetric. That is symmetric. Now, if it is minus then what happens? B 1u 1 b 2g 2 - b 1u 2 b 2g 1. Now you interchange 1 and 2 what will you get? Negative. Negative of the same function.

That means it is antisymmetric with respect to particle exchange. Right? So this one is symmetric. This one is antisymmetric.

So the symmetric space part has to be combined with the antisymmetric spin part for the total wave function to be antisymmetric, right? What is the antisymmetric spin part? Alpha beta – beta alpha. Right and when the space part is symmetric, antisymmetric sorry it has to be combined with symmetric spin part. There are 3 possibilities there alpha alpha, beta beta, and alpha beta plus beta alpha. That is why this gives rise to a singlet state, this gives rise to a triplet state. So you can have singlet B 3u. You can also have triplet B 3u. This is extremely important to understand.

“Professor - student conversation starts” How will the molecule be spread, presented in state? Okay I will come to that. First tell me whether you agree with this or not. You agree with this? Is there any doubt, please get it cleared that is the next very important question I will come to that, and what we will do is after this perhaps I do not want to take the last one at least, it is almost 7. Hold on, we will talk about that tomorrow. P x and p y right? P x and p y are degenerate. Is it possible only to have a, no that is p x and p y are degenerate. **“Professor - student conversation ends”.**

We are talking about non-degenerate MOs now. P x and p y is 15 times more complicated than this. That is why I do not want to take it at quarter to seven. We will talk about that also. Instead of p x and p y we will talk about pi and pi u and pi u pi j and pi g whatever it is. Then we will have some fun. Was it about p x and p y or was it about pi? P x and p y. What is the topic that is going on now? Multielectron atoms or what?

Basically same thing but atomic orbitals or molecular orbitals? So I think we are doing the same thing. Wait. We have to answer his question. Are you okay so far? Then I will go ahead and answer his question.

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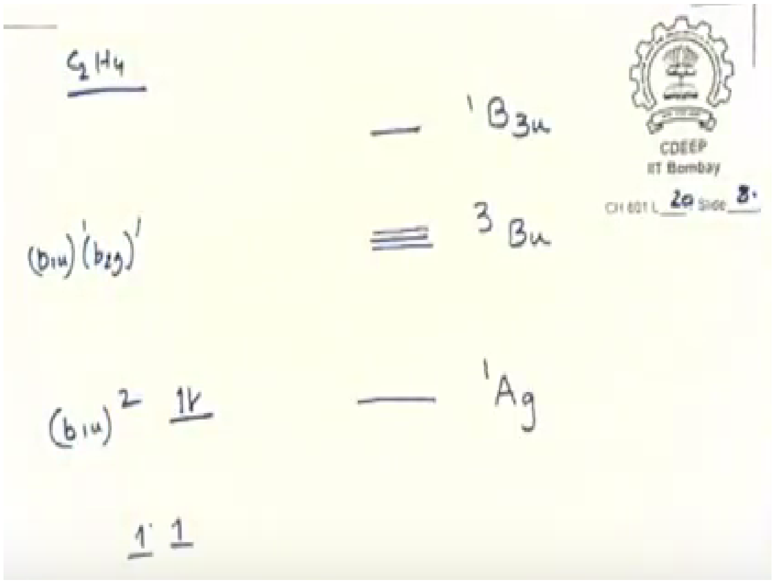

Which molecule are we talking about? Ethylene. What is the formula? We are not talking about acetylene. I get confused between ethylene and acetylene. So what is the ground state you said? B 1u 2, right? What is the spin function? Alpha beta – minus beta. So in simple terms we write it like this, here it spins. But the point I am trying to make is that triplet state is not necessarily unpaired spin. And triplet state actually means 3 spin wave functions all of which are symmetric.

In two of those spins are parallel, alpha alpha and beta beta. In the third one alpha beta – beta alpha spins are actually paired. So when I draw something like this it is really an approximate way of trying it, okay? Looking at spin wave function is a little better, anyway. What is this state you told me? Alpha beta – beta alpha cannot say. What is the name of the state? What is the symmetry of the state? Singlet, doublet, triplet something you said no? Singlet A, A g or A 1g?

D 2h A g not A 1g. There is no A 1g, A g. Because I am not going to zoom it again. A g, A g and A u. Then you have b 1 g, b 2g, b 3g and b 1u, b 2u, b 3u. okay, I think we discussed this some time. It is A g, not A 1g. So singlet A g. So now you know the meaning of singlet A g. If anybody graduates from here goes somewhere and says what is singlet A g then to put it in polite terms I will be very sad.

What is the exited state? B 1u 1 b 2 g 1 right and you said you can have both triplet as well as singlet, right? Now to answer your question. In the ground state the molecule is in singlet A g state. In the exited state it can be in both triplet B 3u state or singlet B 3u state. **"Professor - student conversation starts"** In the triplet state it would not be 3 state or 1 state? It will be 3 states, 3 degenerate states. You can actually separate them by applying a magnetic field, okay? **"Professor - student conversation ends".**

Now, why have I drawn the triplet state lower in energy? Can I say Hund's rule. Everything else being the same, the state with higher multiplicity has a lower energy. And I would like to stop there because exchange energy and all that are very confusing to me at least. It is not really exchange, it is something else. Let us not go there. So see what has happened? These two states have originated from the same electron configuration is it not?

If you just look at the space part, the space part is same between this and this. The reason why they are two states is spin. But space part is the same. So just because of spin also, you can get separate parts. What we will do is that tomorrow we will have a little longish class. We will have to break in between. I want to talk about oxygen. So I will take that example first. Then we will talk about naphthalene, right? Fine. We stop here but maybe let us take this, the next one at least and it will take 1 minute only.

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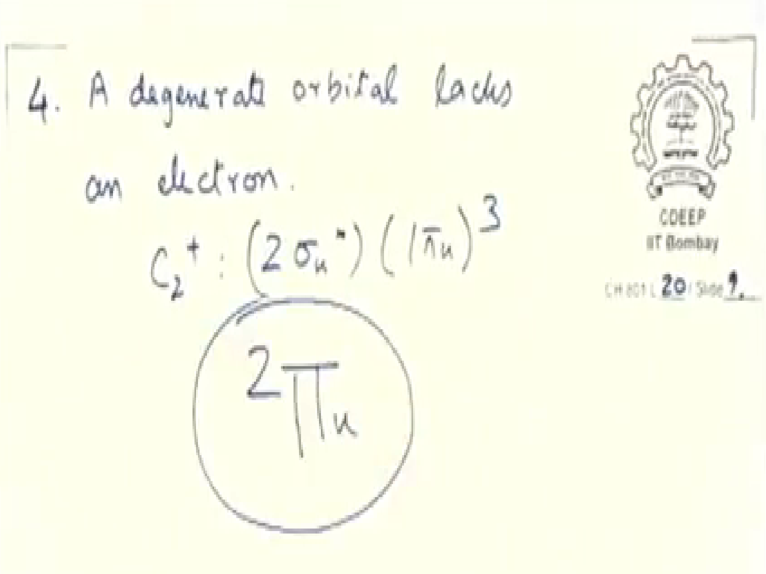

4. A degenerate orbital lacks an electron.

$C_2^+ : (2\sigma_u^*)(1\pi_u)^3$

$^2\Pi_u$

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Rule No. 3 is done. Rule No. 4. A degenerate orbitals, the degenerate orbital lacks an electron. Example is C 2+ but after this I want to answer this question a little more detail. Configuration is

2 sigma u * 1 pi u 3. So how many pi u orbitals are there? How many 1 pi u orbitals are there? It is a doubly degenerate state right? So 2, so one electron is missing. What will be the name? One electron is missing. There should have been 4 electrons right?

If it is C 2 then it would have been 1 pi u 4. Instead of that it is C 2+ so it is 1 pi u 3. One electron is missing. How do we handle this situation? We use hole formalism. There is one deficiency, right? One deficiency means 1 hole, right. So I call this state pi u capital pi u. what will be the multiplicity? 1 hole. So can be +1/2 can be -1/2? Doublet. Doublet pi u, okay. To conclude, let me provide one more answer to his question.

So what we showed you was a case where the ground state is singlet, exited state can be singlet or triplet. Tomorrow we are going to talk about oxygen, right? It is too bad that it would not be recorded. I cannot help it. We will see in oxygen, the ground state itself is triplet. That is something that you can arrive at using your simple treatment also. We will see how by using our treatment we can arrive at the singlet and triplet ground and exited states of oxygen.

And in case of radicals for example, radicals have what, 1 electron sometimes, right? There you can have triplet ground states, okay? So that is why I asked Dibendu what he is working on. So in the field of molecular magnetism this radicals are ubiquitous. So there you have molecules with triplet ground state also. But for usual organic molecules, it is always singlet ground state. For inorganic complexes of course you can have other than singlet. But we will take the simplest example tomorrow that is of oxygen, okay.