Fundamentals of Spectroscopy

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Lecture - 57
Electronic Spectroscopy - 1

Hello all. Welcome to the lecture. In today's lecture, we will start a new module. In this module, we will discuss electronic spectroscopy. To be more specific, we will discuss molecular electronic spectroscopy. We know that electrons do not haphazardly occupy space or have arbitrary energies, but the distribution and energy are governed by well-defined natural law.

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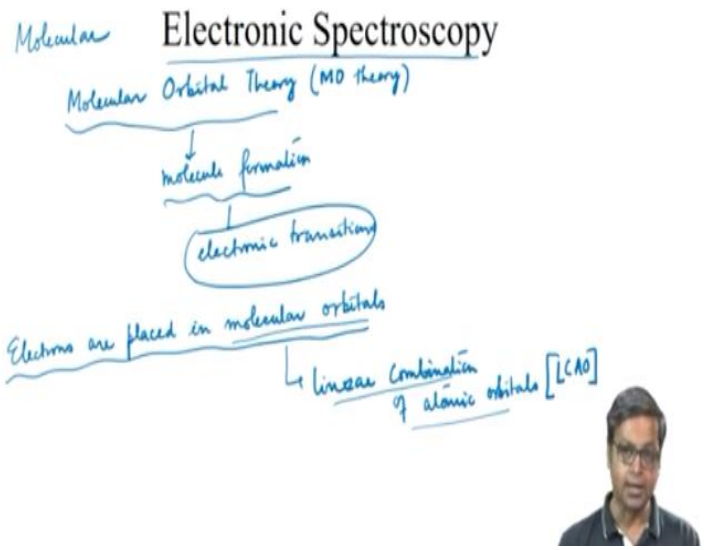

Molecular Electronic Spectroscopy

Molecular Orbital Theory (MO theory)

↓

molecule formation

↓

electronic transitions

Electrons are placed in molecular orbitals

↳ linear combination of atomic orbitals [LCAO]

So the molecular orbital theory or also known as the MO theory gives a convenient pictorial description of the molecule formation and this is well-suited to the discussion of electronic transitions and we are interested in this electronic transitions, because in this module we are discussing the molecular electronic spectroscopy. So from MO theory, we know that electrons are placed in molecular orbitals. So we can write electrons are placed in molecular orbitals.

The shape of the molecular orbital is the space within which an electron belonging to that particular orbital spends most of its time. So a good qualitative idea of the approximate shape of this molecular orbitals can be obtained if we consider that these molecular orbitals are formed by the linear combination of atomic orbitals, so which is also known as LCAO. So because molecules are formed by atoms, so if you consider the linear combination of atomic orbitals, we can get an approximate idea about the shapes of the molecular orbitals.

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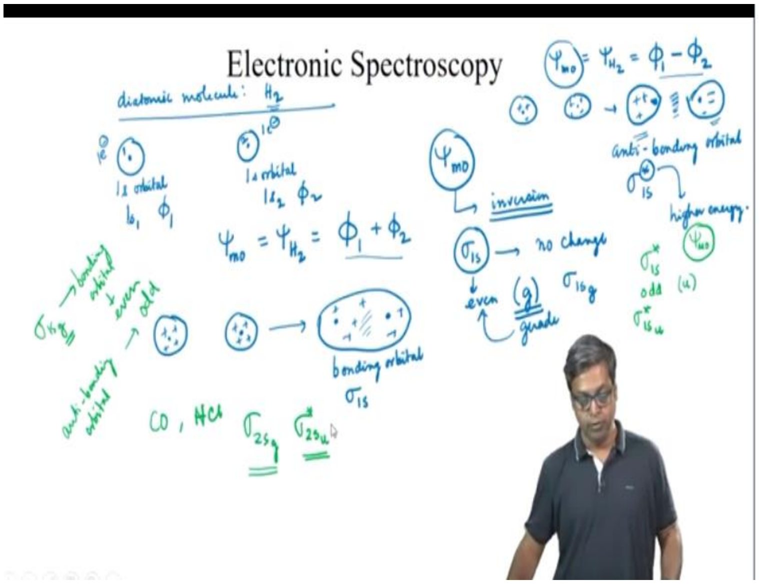

So let us consider one of the simplest examples. So let us start with a diatomic molecule, which is the hydrogen molecule or the H2. So in a hydrogen atom, so let us say we have a hydrogen atom and there is only one electron in the hydrogen atom and this electron is in the 1s orbital. So let us say, because we want to make this hydrogen molecule, we have two hydrogen atoms and so this hydrogen atom also has one electron and that electron is in the 1s orbital.

So let us number this hydrogen atom as 1 and the other atom as 2. So the 1s orbitals corresponding to hydrogen atom 1 and hydrogen atom 2, let us say are 1s1 and 1s2 and the corresponding wave functions are phi1 and phi2. So when these two hydrogen atoms, which are far apart kind of come close together to form this hydrogen molecule, so we can actually have two different scenarios.

So let us say we can have the wave function of the molecular orbital; that is the wave function of the hydrogen molecule can be the linear combination of the atomic orbitals, but the linear combination happens as phi 1 + phi 2. So this can be represented, let us say, we have this 1s orbital which is positive everywhere and we have the other 1s orbital and they combine to give this molecular orbital, which looks like this and it is also positive everywhere.

So here we can see the concentration of the electronic charge between the nuclei increases due to this combination of phi 1 + phi 2 and this orbital represents bond formation. So we are talking about formation of a bond between the atoms and that is why this molecular orbital is known as the bonding orbital and is represented by sigma 1s. So the other option that we can have about this linear combination is where the psi mo which is the psi of hydrogen is phi 1 - phi 2.

So let us try to draw it, so that we have a pictorial idea. So these two 1s orbitals; they combine and what we get is something like this. So when they combine this way; they kind of cancel one another. Thus, the electron density between the two nuclei will be zero, as we can see from this figure and we can see that the psi mo is positive near one nucleus and negative near the other.

So we should always remember that the probability is determined not by psi, but the psi squared and in both the cases that is phi 1 + phi 2 and phi 1 - phi 2, the probability that is psi square is positive; however, the shape of the molecule orbital shows that the electron density is not concentrated between the nuclei, but it is the greatest or concentrated outside the nucleus. So because the electron density is not concentrated between the two nuclei, the two positively charged nuclei will repel one another.

So we can think the nuclear repulsion will enhance and that is why this orbital is known as anti-bonding orbital. So this leads to an unstable state and in fact this state has energy even higher than the two separate hydrogen atoms and this orbital is labeled as sigma star 1s where the star represents higher energy. So the another thing, we should consider is that the psi molecule orbital, the wave function of this molecular orbital the psi mo may or may not change sign upon inversion operation.

So because we are talking about a homonuclear diatomic molecule, so there is center of symmetry and if we perform the inversion operation which we have discussed before, then the wave function may or may not change sign. For example, the inversion operation of the sigma 1s orbital or the bonding orbital causes no change in sign, so no change, because the sigma 1s is positive everywhere and the orbital is generally described as even or written as g.

So this g comes from gerade, which in German means even. So we write the molecular orbital as sigma 1sg. On the other hand, the sigma star 1s orbital, so if you talk about the sigma star 1s orbital, this orbital reverses sign of the psi mo upon inversion. So this orbital is odd and is represented by u, because again in German 1 gerade means odd. So we write this orbital as sigma star 1su. So in the case of hydrogen molecule, the bonding orbital is even. So sigma one is g.

So the bonding orbital is even; however, the anti-bonding orbital is odd, but for a heteronuclear molecule, for example if we have carbon monoxide or let us say if we have HCl, so there is no centre of symmetry and because there is no centre of symmetry, we cannot do this inversion operation and thus this odd-even classification of our vitals does not arise. So like the 1s orbitals if we combine two 2s atomic orbitals, we will get molecular orbitals like sigma 2sg and sigma star 2su.

So again this sigma 2sg is the bonding orbital and the sigma star 2su is the anti-bonding orbital. So these bonding and anti-bonding orbitals have the identical shape like we saw for sigma 1sg and sigma-star 1su; only difference is this sigma 2s orbitals are larger and higher in energy. Now similar to the s orbitals, let us go to the p orbitals.

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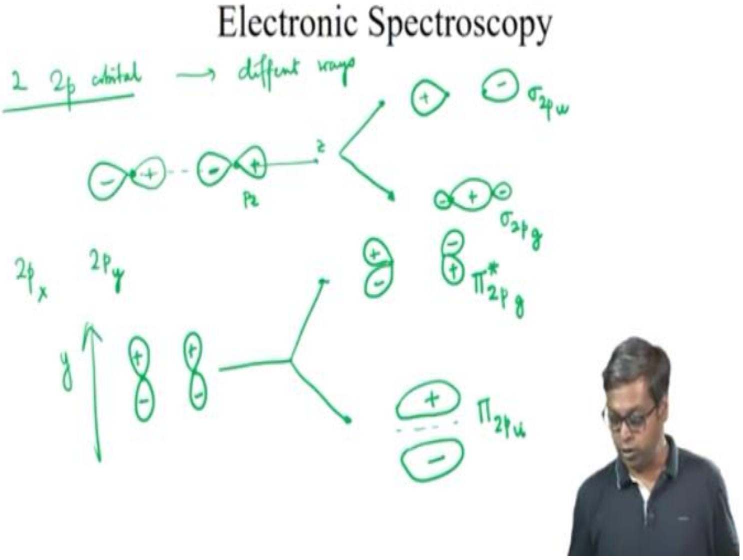

So 2 p orbitals can combine in different ways and this depends on the relative orientation. Let us say the inter nuclear axis is along the z direction or the inter-nuclear axis is the z axis and if we consider the p orbitals along the z axis, that is we are talking about the pz orbitals. Then, this pz orbitals can combine again in two different ways, like phi 1 + phi 2 and phi 1 - phi 2 and so these two different ways of combination would lead. So this would lead to something like this.

So this is positive here, negative here and these are the two nuclei and in the other case we have the two nuclei. So let us say this is positive here and this is negative here. So these are the two different combinations, if we combine pz orbitals or two pz orbitals as long as the inter nuclear axis is in the z direction. So now this is called sigma 2pg and this is sigma 2pu and again we can see this g and u comes from this inversion operation.

In one case there is no change and the other case everything changes. So the positive becomes negative; the negative becomes positive. However, now you think about the p orbitals other p orbitals. Let us say the 2px and the 2py orbitals. So their combination will be different. So let us try to draw them. So let us say this is my y-axis and we will only draw for the py and the px will be identical.

So these are my; the two nuclei and the 2 py orbitals and again when they combine, we have one with a lower energy which looks like this and the other with higher energy, which looks like this.

So this is plus, minus, minus, plus. So surprisingly, we can see here, now the anti-bonding orbital it does not change when an inversion operation is done. So now the anti-bonding orbital is even. So this is represented as pi 2pg, that is pi star and the other orbital which is odd is represented as pi 2pu. So now let us look at a different example. For example, of another homonuclear diatomic molecule that is oxygen.

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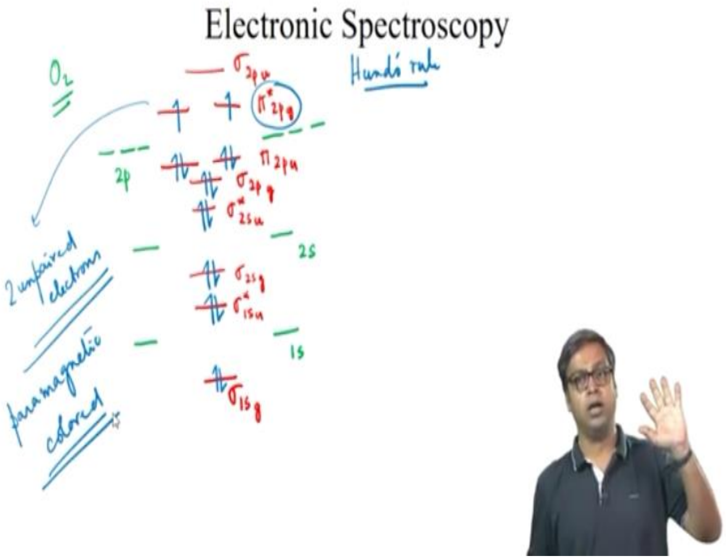

Electronic Spectroscopy

So now let us first draw the molecular orbitals. So we have the atomic orbitals. We have this 1s orbitals, then we have the 2s orbitals and then we have the degenerate 2p orbitals. So when they combine, they form two 1s orbitals forms sigma 1sg and sigma star 1su, then the two 2s orbitals will form sigma 2sg and sigma star 2su. Now this we have three degenerate p orbitals. Now we have seen when they combine and let us say the inter nuclear axis is in the z direction.

So the 2pz orbitals combine to form the sigma 2pg and that px and py orbitals of both the atoms combine to form pi 2pu. Similarly, we have pi star 2pg and sigma 2pu. So these are my molecular orbitals. So now because we are talking about oxygen and we have to put 16 electrons because the oxygen atom has 8 electron each. So if we put the 16 electrons 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16.

So we can see that we have to put electrons up to this pi star 2pg level and since these are two degenerate orbitals, the electron will occupy one each to satisfy the electron repulsion and based on this Hund’s rule, they will have spins that are parallel rather than the spins that are there. So thus oxygen will have two unpaired electrons and that we can find using this molecular orbital theory and because this oxygen has two unpaired electrons, the oxygen is para magnetic.

It is also coloured and we have discussed about this two unpaired electrons of oxygen when we were discussing ESR spectroscopy. So now let us go back to the hydrogen molecule and let us suppose that the hydrogen molecule is in the excited state.

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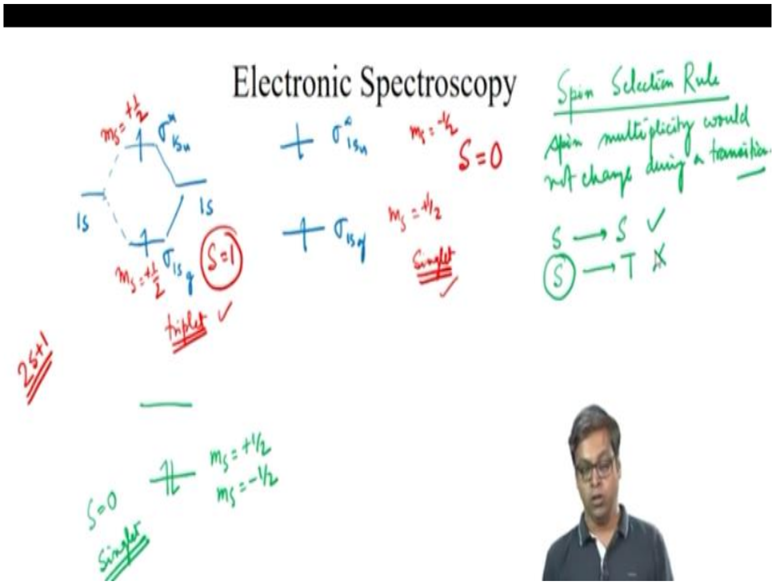

Electronic Spectroscopy

Spin Selection Rule

spin multiplicity would not change during a transition

So the hydrogen molecule, we had 1s 1s orbitals, the two atomic orbitals for the two hydrogen atoms which combine to give the sigma 1sg and the sigma star 1su orbitals. Now we are talking about the excited state. So we have one electron in the sigma 1sg and we have another electron in the sigma star 1su. Now these two unpaired electrons can have parallel spin or they can have let us say sigma 1sg sigma star 1su. So they can have anti parallel spins.

So when the spin is anti parallel. So we can think from our previous knowledge that ms = + 1/2 and ms = - 1 / 2, so which will give s = 0. On the other hand, when they have parallel spin, then ms equals, if we put this as plus half, the other one also has ms equals plus half. So in that case, we have s = 1. In other words, there can be two different states. So in one case, it is the singlet where s is 0 and the other case is the triplet, where s = 1.

So we will see later this name singlet and triplet comes from the spin multiplicity that is 2s + 1. So if s = 0, 2s + 1 is 0 + 1 is 1 and if s = 1, then 2s + 1 = 3. So s = 0 is singlet and s = 1 is triplet. So the excited state can be either in the singlet state or in the triplet state, but on the other hand the ground state where the electrons are paired and they have opposite spin, then we can say ms = + 1/2 for one spin, ms = - 1/2 for the other spin.

So we have s = 0, so the ground state is always singlet. So this brings us to something known as the spin selection rule. So the spin selection rule says that the spin multiplicity would not change during a transition, so that means a transition from a singlet state to another singlet state is allowed. On the other hand, a transition from a singlet, because we are talking about the singlet as the initial state, because we saw the ground state of hydrogen is singlet. So the singlet state to triplet state is not allowed or forbidden and we will see this again when we discuss Born–Oppenheimer approximation in detail.

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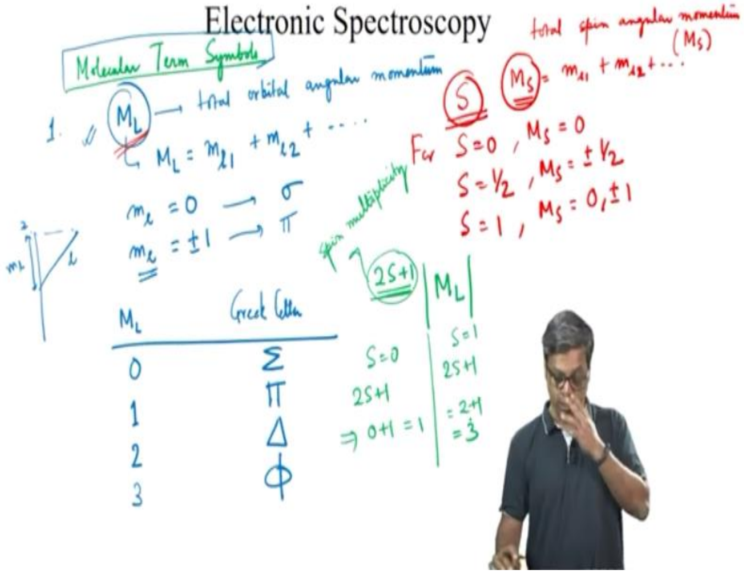

Electronic Spectroscopy

Molecular Term Symbols

1. M_L → total orbital angular momentum

$M_L = m_{l1} + m_{l2} + \dots$

$m_l = 0 \rightarrow \sigma$

$m_l = \pm 1 \rightarrow \pi$

M_L	Greek letter
0	Σ
1	Π
2	Δ
3	Φ

total spin angular momentum (M_S)

S $M_S = m_{s1} + m_{s2} + \dots$

For $S = 0$, $M_S = 0$

$S = 1/2$, $M_S = \pm 1/2$

$S = 1$, $M_S = 0, \pm 1$

spin multiplicity

$2S+1$ | M_L

$S = 0$

$2S+1$

$\Rightarrow 0+1 = 1$

$S = 1$

$2S+1$

$= 2+1$

$= 3$

So as we are discussing the ground and excited electronic states, we need to know about something known as molecular term symbols. So the electronic states of molecules are designated by term symbols. So now the question is how can we determine these term symbols? So in order to determine the term symbols first thing we need to do is to calculate the possible values of ML, where ML is the total orbital angular momentum.

And this ML is the sum of the orbital angular momentum of the electrons occupying the molecular orbitals. So we can write ML equals, let us say ml1 + ml2 + dot dot dot and ml = 0 for sigma orbital or if the electron occupies the sigma orbital and ml = +/- 1 when it occupies the pi orbital. So this ML is the projection of the angular orbital momentum on the z-axis, we have seen. So the projection of this orbital angular momentum on the z axis, this is our ml.

So different electronic configurations give rise to different values of ml and the different values of this ml are associated to different Greek letters. So if we make a table, so let us put the value of ML and the Greek letter that is associated. So we can see, we put 0 this is given by sigma and then if you put 1, it is given by PI, if it is 2m then it is delta, if it is 3, it is phi and so on and so forth. So once we have found out this ML, the next we can determine the possible values of the total spin angular momentum, which is denoted by MS.

So again Ms is given by ms1 + ms2 + dot dot and the values of this MS corresponds to the projections of the total spin that is S. So MS is the projection of the total spin of the molecule along the bond axis. So for s = 0, ms = 0 so for s = 1/2 because it is a projection, it can be + 1/2 or –1/2. So MS = +/- 1/2. For s = 1 MS = 0 +/- 1. So thus the total spin that is capital S can be obtained if we can find capital MS.

So for a particular set of ML and S, the molecular term symbol is represented by 2S + 1 mod of ML and we have discussed this before, the superscript that is 2S + 1 is the spin multiplicity and this indicates the number of values of MS party for a particular value of S. Thus the state is called a singlet when s = 0 because 2S + 1 then becomes 0 + 1, that is 1 and when S = 1, then 2S + 1 is 2 + 1 = 3. So this state is known as a triplet. Now let us go back to the hydrogen molecule.

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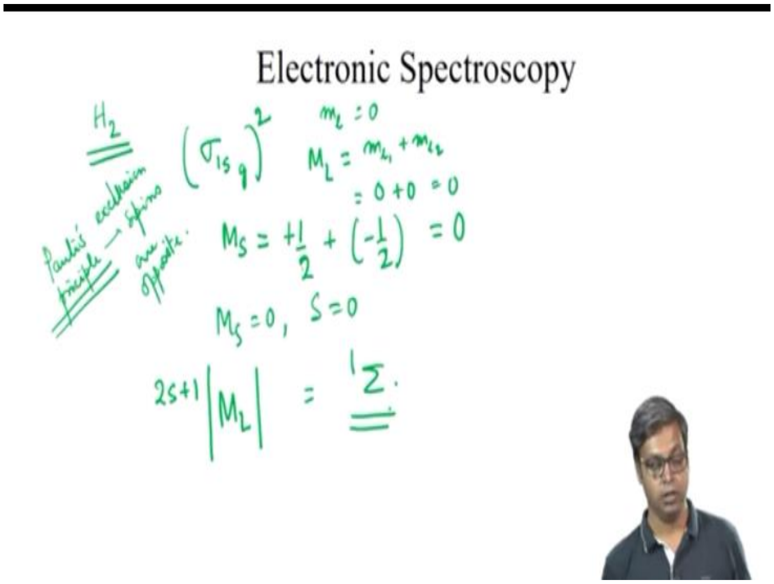

Electronic Spectroscopy

H_2

$(\sigma_{1s_g})^2$ $m_l = 0$

$M_L = m_{l_1} + m_{l_2}$

$= 0 + 0 = 0$

Pauli's exclusion principle → spins are opposite.

$M_S = +\frac{1}{2} + \left(-\frac{1}{2}\right) = 0$

$M_S = 0, \ S = 0$

$^{2S+1}|M_L| = {}^{1}\Sigma$.

So let us again revisit the hydrogen molecule. The ground state configuration is sigma 1sg2, that means that both electrons are in this orbital and because both the electrons occupy the sigma orbital so for each electron ML = 0. So we can write ML = ml1 + ml2 that is 0 + 0 = 0 and we know the spins are opposite. This is due to the Pauli’s exclusion principle. So the Pauli’s exclusion principle tells us that the spins are opposite.

And because the spins are opposite, we can write MS = +1/2 + - 1/2 that is equals 0 and because MS = 0, then S = 0 and so the term symbol that we have is denoted by 2S + 1 mod of ML and because ML = 0 that is the sigma state. So this is 1 sigma. So this is the term symbol for the ground state of hydrogen molecule.

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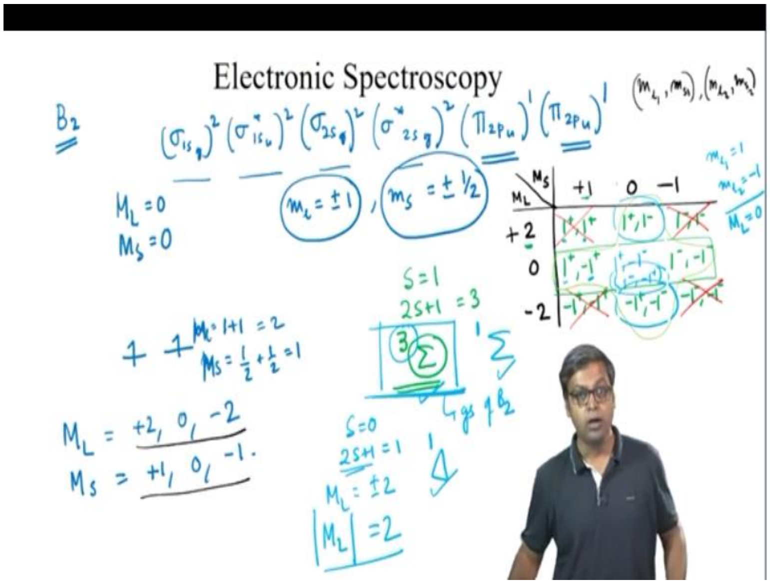

So now let us consider another molecule which is more complex that is B2. So the ground state electronic configuration is sigma 1sg2, sigma star 1su2, sigma 2sg2, two electrons are there, then sigma star 2sg2 electrons are there. So we are done with 8 electrons but there are 10. So we have pi 2pu and pi 2pu, one each, so in total we have 10 electrons, so because if you think about the first four molecular orbitals, they are full and they are of sigma type.

And because they are of sigma type then ML = 0 and because they are full that means MS = 0, because the two spins are paired up. So we should consider only the last two electrons which are in this pi molecular orbitals. So the highest occupied molecular orbital here is a doubly degenerate orbital and according to Hund’s rule, we can see that ML equals +/- 1 and MS = +/- 1/2. So ML = +/- 1 because it is the pi orbital and MS = +/- 1/2.

So we can show that let us draw the possibilities. One possibility is this and let us say in this case one is 1 + 1 that is 2 ML and MS = 1/2 + 1/2 that is 1. So we can show in this way that the possible values of ML are +2, 0, -2 and the possible values of MS are +1, 0 and -1. So now once we know this we can make a table for all combinations or all possible combinations of let us say ml1, ms1, ml2, ms2. So all these different combinations we will make.

So let us make the table here. Here we have ML values and we have the MS values here. So this ML values are 2, 0 and -2 we have seen here and this is +1, 0 and -1, what we are seeing here. So what are the different possible combinations that we can have, because this is +2, we can write 1 + 1 +, that means this 1 +1 = 2 and because both are plus, so this is plus 1. Then we can have right here 1 + 1 - and here 1 - 1 -, so these are the three possible combinations that we have.

Here we can write – 1 + -1+, -1- -1- and -1+ -1-, so we can write for +2 and -2 and for 0, we have to write 1 + - 1 +, this is one option and for this -1, you have 1 - and - 1 -, but for this middle part we have 2 options, which is 1 + - 1 - or we can write 1 - -1 +, so here this + and - denotes the MS values, that is the up spin, down spin in all these cases and the ML are denoted by this 1s here.

So we can see if we add up this 1 and minus 1, then that is the ml1 = 1 and ml2 = - 1, then we add up the ML becomes 0. So we know the Pauli exclusion principle requires that two electrons in the same orbital, they cannot have the same set of quantum numbers and because they cannot have the same set of quantum numbers, these options the four options are cancelled out and so because the four options are canceled out, we are only left with these options.

Now let us carefully look into these options. So if we only consider this, so if we consider this along the horizontal direction what we have? We have there are three possible image values for ML = 0. So we know that ML = 0 gives rise to the sigma state and because there are 3 possible MS values that is +1, 0 and -1 that means S = 1. If S = 1 2S + 1 = 3. So one of the states is 3 sigma and now if we consider these two cases, here we have only one MS value that is 0 that means S = 0 that means 2S + 1 = 1.

But the ML value = +/- 2, so mod of ML is 2 so another state we have is delta because ML = 2 that is a singlet and similarly if we do the final one, we will find it is a sigma state, which is singlet. So the three possibilities are a triplet sigma, a singular sigma and a singlet delta. So now the state with the largest multiplicity that is the 2S + 1 is the ground state. So the 2S + 1 or the spin multiplicity is written in this state.

So this triplet sigma this is the ground state of B2. So this term symbols are also used to denote symmetry or symmetry properties of a molecular wave function. For a homonuclear diatomic molecule, inversion is possible and we have discussed about this inversion before in this lecture, so because a molecular electronic wave function is a product of the molecular orbitals.

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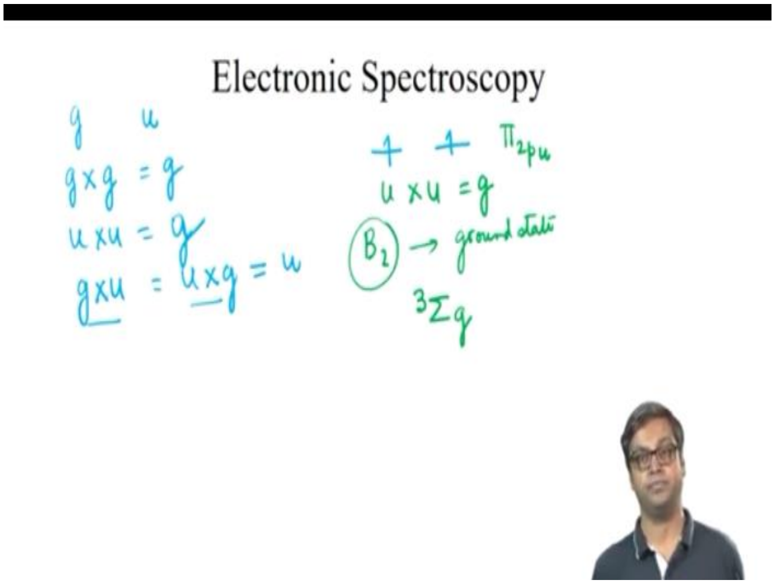

Electronic Spectroscopy

$g \quad u$

$g \times g = g$

$u \times u = g$

$\underline{g \times u} = \underline{u} \times g = u$

$+ \quad + \quad \pi_{2pu}$

$u \times u = g$

$\boxed{B_2} \rightarrow$ ground state

${}^3\Sigma_g$

The symmetry of the molecular electronic wave function of a homonuclear diatomic molecule can either be g or it can be u. So we should remember, because we are multiplying or is a product of these molecular orbitals, so the rule of thumb is g times g is g, u times u is g, but g times u or u times g is u. So for B2, we have to consider the two states which have these two unpaired electrons. So these two states are pi 2pu. So that means we have u times u equals g.

So the final term symbol for the ground state of the B2, the ground state is given by triplet sigma g. So this brings us to the end of the lecture and in the next lecture, we would look into the characteristics of electronic transitions and characteristics of electronic spectrum.