Interpretative Spectroscopy

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Lecture 24

Ground State Term Symbols

I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my previous lecture, I elaborated on different type of couplings, LS coupling or Russell-Saunders coupling and how they are related to each other, and what would happen and what is term symbol. I started talking about term symbols. So, let me continue from where I had stopped. Term symbols are very important in electronic spectroscopy. A term symbol or a spectroscopic term essentially represents the energy level of microstates.

What is microstate? Again, I would elaborate and I would calculate microstates for different electronic configuration. For a given electronic configuration that means, ground state also, you can have a term and also you have several possible excited states and each transition should be identified. That is the reason we can have different terms. This is how the term symbols have been introduced. Term symbol is nothing but represented something like this $^{2S+1}L_J$ and J can take any value between $L \pm S$.

As I mentioned earlier, for a sub shell which is less than half field L minus S (L-S) is the most stable one, that is considered as a ground state, and if for a sub shell with more than half field electronic configuration, L+S is considered. Now, how to calculate L, and what is 2S +1 and then what is J? We shall calculate for few electronic configurations, that I would do later, after little bit explaining about those things. L can have anywhere 0 to n and when we have L equal to 0 and the term symbol we are giving is S, all are capital and when 1 it is P and when it is 2 it is D when it is 3 it is F, when L value is 4 it is G and

when L value is 5 it is H and 6 it is I and so on. You know that J is total angular momentum quantum number; it can be L+S or L-S. 2S+1 is spin multiplicity. When you have no unpaired electron S is 0, 2S+1, it is a singlet. When you have one electron, it is half. So, 2S+1 will be 2 it is called doublet, when we have unpaired electrons 2, S will be 1, so, that is 1 and 2S+1 value will be 3, we call it as a triplet, and then when we have 3 electrons the $\Sigma S = 3/2$. So, it is 1 and a half and then 2S+1 will be obviously 4, and it is called quartet and then when we have 4 unpaired electrons 4, S equal to 2 (S =2) and 2S+1 equal to 5, this is called quintet. So, this is how we can identify and give the name for a state depending upon 2S+1 value is singlet, doublet, triplet, quartet, quintet and so on. Now, to make you familiar, let us find out term symbol for different electronic configuration. Let us consider a simple p^2 system. First what we have to do is, 2 electrons are there in p orbital and write electronic configuration first, you put +1, 0, -1. This is L value, azimuthal quantum number and then we have one electron here one electron is here. So, now, L can have anywhere between L can have 0, 1, 2, 3, 4, 5.

So, here L is 1, we know that S, P, D, F, G, H, I goes. Now we have S equal to 1 this is 0. So, 1 means we have to consider P here and then we have to consider 2S+1 value, it will be 3. We should consider J is L-S. So, L equal to 1, S equal to 1. So, L minus S equal to 0 (L-S = 0).

So, this is $^3P_0$. So, this will be ground term. So, easily you can calculate here then let us look into d^2 system. Of course, you have to write like this and then we have +2, +1, 0, -1, -2 are assume with the quantum numbers and then we place electron here. So, then L = sigma l this is 2S plus 1 equal to 3 (2S+1=3).

So, L equal to 3, means F will come here. Now, S is S equals sigma S equals half plus half equal to 1 then 2S plus 1 equal to 2 into 1 plus 1 equal to 3. So, that is 2S+1 is 3 and then it is less than half field, L minus S, 3-1 equal to 2. So, this is the term symbol for d^2 electron state. So, this is how you should be able to do it. If you have still doubt, let me go ahead and do it for f orbital.

So, now let us take f^3 you have to write +3, +2, +1, 0, -1, -2 and -3. Three electrons are there. So, value will be 6, 6 means basically here L equals 0 1 2 3 4 5 6. So, you should

remember which one it is. So, here S, P, D, F, G, H, I. So, I should consider I here and then 2 S plus 1 is 1 and half into 3 by 2 plus 1 is 4, 4 will be 2S this is 2S plus 1 is 3. L equal to 6 and S equal to 4. So, L minus S equal to S equals 3 by 2 here S equals 3 by 2. So, that means 3 by 2 6 minus 3 by 2 will give you L minus S value. So, that means 12 minus 3 by 2 equal to 9 by 2 this is here L minus S (L-S) which is equal 9 by 2 (9/2). So, for f^3 ground term symbol is $^4I_{9/2}$. So, this how you should be able to calculate. I hope we have learnt, if not let me go for 1 more, d^7 electronic configuration which is more than half field.

Now, let us consider 1 2 plus 2 plus 1 0 minus 1 minus 2 1 electron here 2, 3, 4, 5, 6, 7. So, now, the value 4 plus 2= 6, 6 are there and minus 3 equals 3, 3 means you have to consider f. So, here term is f and then 2 S plus 1 2 S plus 1 is this is 2 into 3 by 2 plus 1 =4. This is 4, and then L equals 3. So, now, J value for than half filled is L plus S. Thus, L plus S is 3 plus 3 by 2 3 plus 3 by 2, This will be 9 by 2 here $^4F_{9/2}$ will be the ground term. I hope you have understood. So, here I will tell you again here 7 electrons are there and then here we have 4 plus 2 = 6 are there. Out of 6 minus L value, if you subtract we get L equal to 3, 3 means it is F and then 2S+1 is, we have 3 electrons. It is 3 by 2 or 1.5. Then 2S + 1 will be 4. So, that 4 is 2S+1. We are putting here and since it is more than half filled, J will be having L plus S value will be the lowest energy or least energy sequence. So, here 3 plus 3 by 2 will be 9 by 2. So, this is the ground term. So, this how you should be able to calculate the term symbols.

So, now, fine we can calculate, but how to determine the ground state term? That is very important, How I wrote I will show you. So, the terms are placed in order, depending on their multiplicity, we are referring to 2S+1 value. Here the most stable state has highest S value and stability decreases as S value increases. The ground state plus the most unpaired electrons gives minimum repulsion. Why we are considering 2S+1 highest value because, when you have 2S+1 highest value, we have maximum number of unpaired electrons. So, that means, you can anticipate it has to be ground state and it gives most

stable low energy because of minimum repulsion as they are all singly occupied. For a given value of S, the state with highest L is the most stable one.

For example, two terms have the same spin multiplicity 2S+1 value, in that case we have to go to the L value, the highest L value one is the most stable one. If there is ambiguity for a given value of S and L due to some reasons, 2S+ 1 is also same, L is also same, then we have to consider the J value. The smallest J value is the most stable if the sub shell is less than half filled, and the largest J value is the most stable one, if the sub shell is more than half filled. So, we have to consider these terms here p^2 system will be ^1D. How it is ^1D. See P^2 system ^1D ^3P and ^1S are there and ^3P has a triplet state ^3P has a triplet state maximum S is 2S+1 ground state term among ^1D and ^1S. So, we have this one this is a ground state then we have ambiguity between ^1D and ^1S because both of them have the same spin multiplicity, but D has a larger L value. So, the D is the most stable.

So, then D will be the first excited state, you can consider and now, ^3P has 3 terms $^3P_0$, $^3P_1$, $^3P_2$. Since the J value for a less than half field will be L minus S, as a result, $^3P_0$ will be most stable one, least energetic one, this what I showed you $^3P_0$, while calculating I directly calculated the ground state term $^3P_0$, here, because L minus S will be 1 minus 1= 0 will come and then the next one is $^3P_1$, and $^3P_2$. So, this how you should be able to determine the ground state for any electronic configuration and as I mentioned here what is important is some similarities are there between the different electronic configuration having the same ground term that means p^n and p^{6-n}, 6 is the maximum capacity and d^n and d^{10-n} and f^n and f^{14-n} give identical terms. For exampl e, p^1 and p^5, 1 electron was less than completely filled. ^2P term is there, and p^2, p^4 again 2 electrons and 2 less than completely filled electronic configuration. ^3P. So, there is some correlation is there that we should be able to identify P^3 is unique, we have 2S+1 = 4, because here 3 unpaired electrons are there. 2S +1 will be 4 and p^6 we have ^1S and d^1 and d^9 again 1 electron, 1 less than completely filled, we have ^2D ground term and then d^2 and d^8, 2 electrons, 2 less than completely filled, we have ^3F. d^3 and d^7, 2 electron less than half filled, 2 electrons more than half filled, ^4F term we have, and d^4 1 less than half filled, 1 more than half filled for d^6. d^5 is unique, we have ^6S and then d^{10} we have ^1S. So, this is how you can see

the correlation. When you see the same ground term we can always bring some similarities as I mentioned here d^1, d^9, d^2, d^8, d^3 and d^7 or d^4, d^6 and p^1, p^5 and p^2, p^4 and we can understand and then it is easy also to remember there is no need to calculate again.

So, we have 1 and 0 values here that means and when we have L equals 2 ,1, 0, or 0 ,1 ,2, we have D, P, S and then S equal to S plus 1 then 0, 1 and we have 1 we have 3 values. So, that means the corresponding spectroscopic term can also be written in this ^{3}D we have 15 and ^{3}P we have 9 and ^{3}S we have 3 and ^{1}D we have 5 and ^{1}P we have 3 and ^{1}S we have 1. So, total of 36 are there that means ^{3}D we have, 15 what we call these are all called microstates. Number of microstates for a given term, one can calculate, that means now we have to calculate the microstates for different electronic configuration to know how many states are there, and all states, one can expect transitions from ground state to all the states, but due to the selection rules, we eliminate and make it very simple. In fact I should tell you, we come across only a two type of electronic transition as far as d-d is concerned apart from d^0, d^5 and d^{10}; they are unique d^0 do not show anything, d^5 also very special, why I would tell you later and d^{10}, there is no d-d transition because completely filled that means, leave these things, then we have d^1, d^2, d^3, d^4, d^6, d^7 and d^8, again similarities are there. We can classify into simply two categories, and then one category would show only one d-d transition, the other one would show three transitions. That means what are those things, I would tell you maybe, if possible in today's lecture or maybe in my next lecture.

Now, before that I shall show you how to calculate microstates. For example, here total number of microstates, now for these terms are given has ^{3}D, ^{3}P, ^{3}S, ^{1}D, ^{1}P and ^{1}S for this combination non-equivalent electrons, then the total number of microstates is 6*6 =36. We have calculated here 36. So, how we arrived at that one also let us look into it now again before we proceed to calculate microstates for different electronic configuration whether it is P or D or F. The way we determine term symbols for a ground state, let us look into it. First L1 = 1, and L2 = 2, here now again, if you see L1+L2 to L1-L2 ,it goes that way and we have L equal to 3 to 1 values are there, when you have L=3 to 1 values

are there, we can look into the term symbols P, D and F and then two electrons are there and one electron is there when the two electrons are there, S equal to 1, it will be 3. So, we have to consider 2S+1 value of 1 and 3 for this system. We have one electron in $^3P_1$ and $^3D_1$ also we have one electron. Similarly, S_1 equal to half and S_2 equal to half and then S will be 1 and 0. So, the total number of microstates possible here is 3 of ^3D, ^3P and ^1F, ^1D and ^1P and this multiplicity is 2S+1 is 3, whereas here multiplicity is because of 0 electrons. So, here 0 spin, that means no unpaired electrons.

So, that means total number of microstates will be 6*10= 60. So, that is shown here ^3F, we have 3(2*3+1) = 21 and then here ^3D, we have 15 and ^3P we have 9 and ^1F we have 7 and ^1D we have 5 and ^1P we have 3. It is basically L-S coupling, we have shown here and then we get a total of 60 here. So, then how we got these things, we can go back to microstates and look into it. So, what is microstate? So, here the number of arrangements of electrons in a given sub shell for a given electronic configuration. So, that means in the ground state we can write only one electronic configuration in such a way that the maximum number of unpaired electrons are there and if it exceeds, we will start pairing, but when you go to excited states, they need not have to obey Aufbau principle and Hund's rule.

You can have anything in that case. What happens, several possible excited states, one can think of sum of all possible excited states along with ground state are nothing, but the microstates and to determine the microstate for a given electronic configuration. We use this formula that is n factorial over r factorial into n minus r factorial $[\frac{n!}{r!(n-r)!}]$. n factorial is nothing, but the total electron capacity of an orbital, if it is a d^2 is 10, if it is f it is 14, if it is g it is 18, if it is p it is 6 electrons. So, this is how we go and L is azimuthal quantum number and r is number of electrons in the sub shell d^2, if r equal to 2 and n equal to 10, this is how we determine that one. So, some values are shown here. So, number of microstates for p^2 =6!, the p orbital capacity is 6 electrons, then 2 is r, is 2 factorial and then this is n minus r. So, it comes around 15, how it comes 15, also I will show you and d^2 similarly 10! over 2! into 10 minus 2!, it comes around 45 and here for d^5 system 10! and then here we have 5! and then 10 minus 5!.

So, we have 252 comes here I will calculate again showing you in more detail d^1 we have 10 factorial and p^1 we have 6 and then p^3 we have 20. d^1 we have 10 microstate and p^1, we have 6 and p^3 we have 20. If it is not clear here let me do it here let us consider simple p^2 here, if you consider the total number of electrons, r equal to 2, and then n equals 6. So, what we will do is the formula is n factorial over r factorial into n minus r factorial $[\frac{n!}{r!(n-r)!}]$. So, here 6! and then 2! and then 6 minus 2 is 4!. So, this one I can write 4! *5 * 6 and 4! *2 goes we have 15. So, the microstates for p^2 is 15.

Let us look into d^2 here. So, d^2 here r factorial equal to 2 again and then n factorial equal to 10, the total capacity is 10. So, here if you use the same 10 factorial over 2 factorial into 10 minus 2!. So, this can be written as 8! into 9 into 10 and here 2!.. So, it goes 45. So, this is how you can calculate just look into it, I would come up with few more electronic configurations for both P and D and also with F orbital to make you familiar with calculating microstates and also determine the ground term.

Again, in my next lecture, I will show you a few ground state term determination, and also microstates for several other electronic configuration until then, go through this course and then try to make familiar yourself to get some confidence about interpretation and elucidation of the structures. Thank you.