Interpretative Spectroscopy

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Lecture 25
Calculating microstates for different electronic configuration

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. So, this is twenty fifth lecture in the series and in my previous lecture I was telling about microstates and how to determine term symbols and how to write microstates for a given electronic configuration. So, let me continue from where I had stopped to make you once again familiar with determining term symbols and also ground state term symbols and also microstates for different electronic configurations. So, you can see here I have given for $2p^1$ and $3p^1$. So, for example, if you want to determine together for two electronic configurations say one electron is $2p^1$ state and one electron in $3p^1$ state then the combined number of microstates how to determine. It is much simpler, you have to determine for both and then take the product of that one that would give you the combined number of microstates for two electronic configurations.

So, here you can see for example, $2p^1$ means you remember the formula: n factorial over r factorial into n minus r factorial [$\frac{n!}{r!(n-r)!}$], where n is the total electron capacity of the orbit we are considered or sub shell we are considering and r is number of electrons. So, here if you take 6! over 6 minus 1 factorial means you can write it as 6 factorial over 5 factorial into 6. So, and then you get 6 in both the cases, you get product is 6 * 6 = 36. So, after this one I would be writing again to make you familiar with that one and similarly you go for $3p^1$ and $3d^1$ and in case of $3d^1$, we will be having as many as 10 microstates and then 10 into 6 it would show 60.

Similarly, if you take $2s^1$ and $2p^1$ in case of $2s^1$ we will be having only two possible

ways that yourself you can look into it then we will be having 2 into 6, that will be 12. In a similar way, you can calculate for $3d^1$ and $4p^1$ that is also going to be 60 and then $3d^1$, $4d^1$, then you know that d1 system irrespective of which sub shell, it is will be having 10 microstates. So, 10 into 10 would be 100. So, this is how you can write. So, now again let me go back to simple one like d^2 system, d^2 system first what you should do is write $5d$ orbitals you write azimuthal quantum number for each subshell, then place two electrons here and then the sigma l equal to sigma l and this is the l value or m_l.

So, this will be 3, 3 means you know that L will take S, P, D, F, G, H and I, it goes like that, with values of L equal to 0 ,1, 2 ,3, 4, 5, 6 and so on. Now we have ^3F. So, F is the symbol, now then we have to take the multiplicity S equal to 1, therefore, 2S +1 equal to 3. So, this 2S +1 will come here. Recall the term symbol we are using, this J, J is L plus or minus S (L±S), and if the subshell is less than half filled, it is l minus S (L-S), and if the subshell is more than half filled, it is L plus S (L+S). For example, for d^2, L minus S has to considered, and if it is d^7 it should be L plus S. Now 2S+1 is 3 and now L we know the value L equal to 3 and S also equal to 3.

So, L minus S is 0. So, what we get is ^3F_o. This is the term symbol for ground state and similarly, we can go for ^3F. So, we put here 3 electrons, all are unpaired in the ground state. Now, we calculate the L value which is 6, 6 means, we have 3 electrons, 3 electrons S, equal to 3 by 2. So, 2S plus 1 equal to 4.

So, here multiplicity 2S +1 will be 4 and now L equal to 6 and S equal to 3/2 is there. So, L+S will be 6 minus 3 by 2, this is 9/2. So, this will be the ground state term symbol. So, this is how one should write and if you are curious.

So, it is 10! over 2!, (10 – 2)! this can be written something like this 2! is 2, this is 8!. So, we have 45 states microstates. So, this is how we should be able to determine without any problem. Let us look into one more f^2 system here f^2 system is a 14! over 2! (14-2)!. So, this can be written as 12 factorial this is 91.

So, for f^2 electronic configuration number of microstates is 91. So, this how one should be able to write. I hope you should be able to write for any given electronic configuration or any metal ion. If any metal ion is given you have to determine the ground electronic configuration, look into the oxidation state of metal and arrive at the d system. Once you arrive at the d system calculate L and identify the term symbol S, P, D, F, G, H, I and then find out multiplicity 2S +1 and then consider J value as L minus S (L-S), if the electronic configuration shows, the sub shell is less than half field and if it is more than half field consider J value of L +S. So, that is very simple.

So, let us continue now. So, as I mentioned just now we found out that there will be 15 states for p^2 system, then we can examine them. You can see here I have written all possible states for the given electronic configuration of p^2. So, initially you can have something like this. 2 electrons this is the one we are considering as ground term, and next what you have, you can shift this one here, another possibility and then you can have these are the possibilities, then we can reverse the spin in this fashion and we get another 3 here and then we can have one upward spin and one downward spin. We can have this 3 and another one is for example, if it is downward spin, this can be downward spin you can go like this. We have another 3 and then we can pair both the electrons and then we can arrange them either in minus 1 or l equal to 0 or l equal to plus 1 value. So, this is how we can write as possible microstates. It is very lengthy and laborious, if you want to write for 120 to 110 or 45 microstates, but nevertheless if you are curious, you can always start writing and check whether the determined value is correct or not experimentally. So, why these arrangements have different energies there is a question the mean distance between the electrons may vary from one arrangement to the another average interelectron repulsions will vary.

So, that means the arrangement and the mean distance between the electrons may vary because of interelectronic repulsions and hence these levels will be split into a number of levels of different interelectronic repulsions and hence they will be possessing different

energies. Although *p* orbitals degenerate and have the same energy, the electrons present in them interact with each other and result in the formation of a ground state and one or more excited states. The first one we determine ground state and then because of interaction or coupling what you can have is you can have several excited states. So, besides electrostatic repulsion following factors influence each other what are those factors by interaction or coupling of magnetic fields produced by their spins by coupling of the magnetic fields produced by the orbital motion of the electrons that is called orbital angular momentum and when several electrons occupy a soft shell the energy states obtained on the result of the orbital angular quantum number of the electrons. So, these points should be remembered the resultant of all the l values is denoted by a new quantum number L that is called resultant angular quantum number, it can take values from 0 to n and for 0 the term is S, for 1 P, for 2 D, and 3 F, 4 G, 5 H, 6 I, 7 K, J is excluded because J we are taking for spin orbit coupling that is the reason the term is omitted while considering the term for resultant angular quantum number depending upon the values. For example, L equal to +1, 0, -1. One can have L equal to 1 0 2 values.

So, now let us come back again to p^2 configuration what you should remember is angular momenta is quantized into packets of magnitude of h over 2 pi ($\frac{h}{2\pi}$). This is governed by quantum mechanical rules for p electron l equal to 1. So, orbital angular moment will be 1 into h over 2pi ($\frac{h}{2\pi}$) that is shown by an arrow of unit length. So, this will be shown by an arrow of unit length for 2p electrons, the way in which the l value may interact with each other can be shown diagrammatically in this fashion. For example, all these 3 interactions are possible since the angular momentum is quantized. So, that means whether we can arrange in different ways to have different resultant values. The permissible arrangements are those where the resultant is a whole number of quanta, this we should remember.

So, the resultant interaction is such that the resultant will be a whole number of quanta for p state, the vector l must be at an angle to each other such that the resultant is a whole number. So, this we should remember that means for example, let us take l equal to 1

and l equal to 1 we have 2. So, that means the resultant will be l equal to 2 when l equal to 2 is there. We have D state and then they can also interact in such a way that the resultant will be l equal to 1 here in this one we get P state of course, you can recall l equal to 0 1 2 3 4; S P D F G it goes like that. So, l equal to 1, it is the P state when they interact in this fashion l can have value of 0 in that case what we get is S state. So, this how we can arrive at the different microstates by looking into the resultant, all these 3 interactions are possible since the angular moment is quantized.

So, all these things are resulting in whole number of quanta. That is the reason this is quite possible. Now what is spin orbit coupling when several electrons are present in a sub shell, the overall effect of the individual orbital angular momentum l is given by the resultant angular quanta number capital L. Similarly, the overall effect of the individual spins m_s is given by the result spin quanta number S = sigma m_s (Σm_s). In an atom, the magnetic effects of L and S may interact or couple giving a new quanta number called J that is called total angular quanta number this is essentially the vectorial combination of L and S that is also called as Russell-Saunders coupling or spin orbital coupling. For example, in case of p^2 case we know that l values will be 2 1 0 and corresponding terms will be D, P and S and have values of 1 and 0.

So, now let us look into the coupling of spin orbit. So, that means coupling of spin angular momenta is m_s equal to plus half then they can couple with each other. So, that is equals 1 interaction and now they can oppose each other in this fashion. So, S equals 0. So, this is how we get S equal to 1 and S equal to 0 value through coupling of spin angular momentum.

So, now let us look into p^2 case again to see in the spin orbit interactions. So, l equal to we know the value 2, 1, 0 and corresponding terms will be D, P, S and then S equal to 1 and 0 values are there. Now, let us look into the interactions assuming their vectors. So, we should remember, this resultant should be having a whole quantum number, quanta.

So, l equal to 2 and s equal to 1 can interact in such a way that the net resultant will be J equals 3.

In this case 3 will come here $^3D_3$ will be the state and then they can also interact in this fashion L=2 that is the reason we have taken double the value of this 1 here and then L=2 and S can interact in such a way that resultant will be J equals 2 and then we have here $^3D_2$ state and then they can also interact in this fashion. Now, the J value will be 1 the resultant and then we will be having $^3D_1$ state. So, next we go for this is S equal to 1 and L equal to 1. Now, L equal to 1, this is L equal to 2 and S equal to 1, we are considering here. Now, let us consider l equal to 1 and S equal to 1.

Now, the net resultant will be J equal to 2 and this will be $^3P_2$ state, and now we can have interaction in this way. So, that J value equal to 1 and here we get $^3P_1$ state, and now if you interact in this fashion the J equal to 0, we get $^3P_0$ state, this is the ground state, we call it as L minus S and we call here L plus S here. Similarly, now we can consider L equal to 2 and S equal to 0. This is the last one and in L equal to 2 and S equal to 0, J equal to 2 and L equal to 1 and S equal to 0, J equal to 1 and L equal to 0, and S equal to J equal to 0. So, what we get is here $^1D_2$ state and $^1P_1$ state and then $^1S_0$ state. So, this is how you can also show diagrammatically by considering this as vectors and then you can arrive at the different ground state term symbols along with J values. J values you can clearly see how we are getting the values here.

So, each of these arrangements corresponds to an electronic arrangement spectroscopic state represented by a term symbol here. This is a typical term symbol. So, now, let us come back to again electronic spectra of transition metal complexes. In transition metal complexes, electrons may be promoted from one energy level to another one; those two energy levels between which electronic transition occurs are essentially called as HOMO and LUMO, highest occupied molecular orbital and the lowest unoccupied molecular orbital. Such electronic transitions you know require high energy and during electronic transitions low energy vibrational rotational transition will also occur because each

energy electronic state is composed of several vibration levels and which in turn composed of several rotational levels as a result what will happen we can see as possible vibration rotational excitation accompanying in electronic transition. So, in electronic spectra such transitions are too close in energy to be resolved into separate absorption bands. As a result, this would cause broadening of absorption bands in *d-d* spectra. So, bandwidths for the same reason the bandwidths in electronic spectra are in the order of about 1000 to 3000 centimeter minus 1.

So, in a free gaseous metal ion *d* orbitals degenerate, all d orbitals would be having the same energy. As a result, no *d-d* transition is observed in a complex; degeneracy is lost and splitting can be seen in case of octahedral complex t_{2g} ground state and e_g excited state and of course, in case of tetrahedral complexes opposite of octahedral happens and will be having e as ground state and t_2 as the excited state and depending upon the ligand field what would happen? We will be having different orbitals coming into the picture as HOMO and LUMO. So, in between, we can see electronic transition, that is called as *d-d* transition. The magnitude of $delta_o$ (Δ_o) depends on the nature of the ligands and affects the energy of electronic transitions and hence the frequency of absorption maxima. In spectrochemical series, we know the position of each ligand by considering its donor and acceptor properties, and then if the ligands are of weak field in nature then the HOMO-LUMO gap will be smaller. Crystal field energy will be smaller and delta (Δ_o) would be smaller and require very less energy for the promotion of the electrons or excitation of the electrons. So, extent of splitting is related to ligand position in the spectrochemical series. From that point of view, we have to remember several factors and the most important factor is the spectrochemical series and the rank provided to a ligand in the spectrochemical series whether it is increasing order or decreasing order of crystal field stabilization energy or crystal field strength.

So, let me continue in my next lecture more information about electronic spectra of transmittal complexes, until then have an excellent time. Thank you.