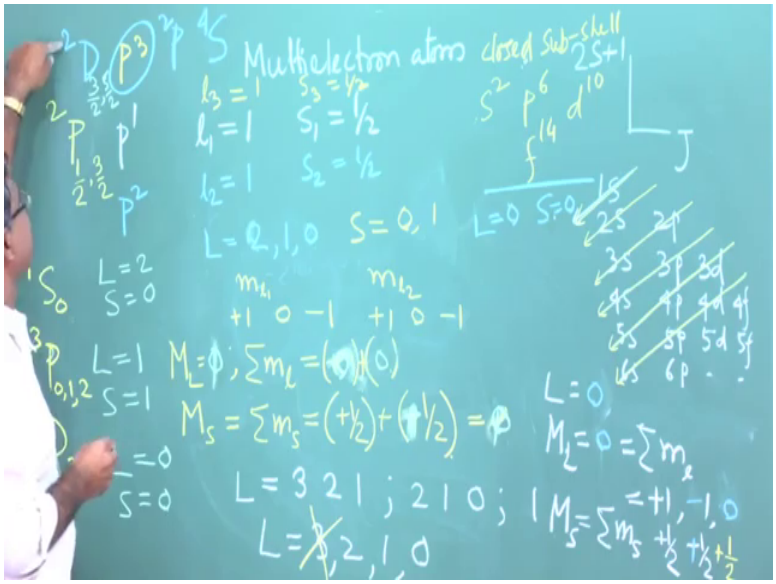
Atomic and Molecular physics
Prof. Amal Kumar Das
Department of physics
Indian Institute of Technology, Kharagpur

Lecture - 26
Multielectron atoms (Contd.)

So, we will continue our discussion.

(Refer Slide Time: 00:17)



So, for multi electron atom what we have seen so far for closed sub shell L and s are 0 that is important conclusion and then another things we have seen this equivalent electron and nonequivalent electron. Nonequivalent electron just using the vector model one can find resultant L; capital L means resultant angular momentum, orbital angular momentum, resultant spin angular momentum capital S and then this total angular momentum that is j ok.

Just using vector model one can whatever the value of L and S and J will get all are allowed it does the valid the Pauli exclusion principle because they are nonequivalent. Either n or l are different already. So, we will not bother the outer m l and m s they can be same they can be different ok.

But when it is they are equivalent electron means n and l are same then using vector model will get resultant capital L resultant capital S, but we have to find the combination

for each L each S may not be allowed. We have to see whether this any combination is validating the Pauli exclusion principle. So, that is what we are doing and this for is to, I have I have I have shown you how to calculate then p 2 is the 2 electron so, but in p we can put 6 electron maximum 6 electron ok.

Now, for p 1 I have calculated p 2 I have calculated, so for p 3 if I put one more electron. So, then you have to calculate this we have to calculate. So, we have to think, just I can I can I can start from here. So, p 2, so for that resultant L, capital L and resultant capital S I got ok, so that is here.

So, that is the from 2 I got the resultant vectors are capital L capital S and say capital J also one can get ok. So, let us check for L only first, so l 1 and l 2. So, vector sum I got the L, resultant L. Now, this resultant L is there, capital L is there. Now, I put one more electron say l 3 then ok. So, now, forget l 1, l 2. So, I have this capital L. Now, with that with that resultant one I will this do the vector sum of the third one ok, l 3. So, if I start from resultant L and S for p 2 and then only I have to add one more electron where l 3 and s 3 is one and half.

So, so basically I have to write. So, here let me write. So, additional one I am putting additional one I am putting l 3, l 1, l 2 than I will put l 3 then say here l 3; l 3 equal to 1 p s 3 equal to half ok, s 3 equal to half. Now, from this 2 already I got this one. Now, if I take let us take just this value and add the third one, so for L equal to 2, L equal to 2 ok. Now, I will add this l 3.

So, what I will get? Just vector sum, so I will get 1 and this is 2, I will get 3, I will get because summation is this resultant whatever l and then plus l 3, so from this value to l minus l 3 ok. This vector sum is same way. So, if I these 2 l l plus l 3 minus 1 l plus l 3 minus 2 l plus l 3 minus 4 etcetera up to l minus l 3 ok. So, for L, S and J for everything this as same way we do vector sum. So, then I will get resultant 1, resultant L, I will get basically. So, this is for 2 electron and this is one.

So, what I will get? For L equal to 2 here I will get l l equal to 3 2 1 because this 2 minus 1, 1. So, 3 2 1 I will get and then for l equal to 1, here if I take l equal to 1 and then corresponding if I take the plus l 3 add for that I get basically for l equal to 1, so 1 1. So, I will get 2 1 0 right resultant l I will get 2 1 0. Now, L equal to this 0 and this have to

add with l equal to l 3 equal to 1. So, I will get basically one right I will get basically 1, I will get basically 1 ok, so basically resultant 1.

Now, you are getting, now you are getting this this the for third electron l values are this this are all. So, basically L value 3 2 1, 2 1 0 1. So, ultimately I can I can write L value we are getting 3 2 1 0 this 4 value we are getting right. Now, see that L 3, L equal to 3, I have 3 electron. So, now, L equal to 3 means capital ml it will be plus 3 2 minus 3 plus 3 plus 2 plus 1 0 minus. So, I will get 7 value right.

So, M L, capital M L is plus 3 means means. What does it mean? m l 1, m l 2 and m l 3 all has to be plus 1 right because the summation capital M L for L equal to 3 capital. So, for L equal to 3, M L 1 value of ml maximum value this will be plus 3 3 and this will come basically sum of m l individual m l, m l 1, m l 2, m l 3. So, only it will come this for plus 1 plus 1 plus 1 right. There is the other option. So, that means, M L value for 3 electrons are same M L of course, the same M L also same.

Now, S has to be different sorry M S has to be different. So, M S value already 2 choice are there M S equal to I mean this individual M S, individual M S. So, now, total M S I have to find out. So, that will come from the sum over M Ssmall m s. So, small m s it has only 2 choice plus half and minus half ok. Now, for 3 electron I have to give M S value. So, one I can give plus half, one I can give plus half, another I can give minus half ok. So, they are different file.

But what about the third one? Either I have to give plus half or minus half. I cannot give that one because then 2 of them will be identical. So, all M S has to be different ok, and that is not possible. Third one I cannot put ok. If I put plus half then this 2 will be same if I put minus half then this 2 will be same and it will valid the Pauli exclusion principle.

So, L equal to 3 that is not allowed and then you can show that L equal to 2 1 0. This 3 values are allowed ok, this 3 values are allowed and corresponding M S one has to think, so now, L equal to 2, capital L equal to 2 capital L equal to 2 means capital M L, that M L value M L capital this this are if I put this 2 now. These are 2 for L equal to 2, M L maximum, M L value 2, so 3 electrons M L 1. So, what can be the combination? Plus 1 plus 1 and another one is 0, M L value 0 right because small ml value there are 3 plus 1 0 minus 1 these are 3 allowed value. So, I can take this combination plus 1 plus 1 and 0.

So, then total M L I am getting 2 fine, then M S I have to put 3 M S, its fine. You see these 2 are same M L value same. So, I will put plus half and this is minus half, fine.

Now, these ml value 0 it is different from the other one. So, then I can put either plus half or minus half. So, generally whatever wish you can put. So, generally we put plus value plus half ok. So, when L equal 2 we are getting M S is half, this M S we are getting, capital S we are getting half so; that means, as has to be half, as has to be half. So, in this case for L equal to 2 s will be half. So, what we are getting for p 3? What is p 3 I have no written, so p 3 electron, ok.

One value we got L equal to, L equal to 2 and s equal to half. L equal 2 means D, L equal to 2 I will write D, term is D and S half means this is 2 ok, and j you can find out that will see later on. Now, L equal to 1, if I take L equal to 1, if I take L equal to 1 then M L maximum M L value will be 1 ok. So, sum of M L, sum of M L is how I can get this one. I can get plus plus 1 plus 1 minus 1, if I put minus 1 if I put minus 1 here then M L value will be plus 1.

Other combination may be possible. Generally here we try to take the this how many shell value we can we can take here ok. So, depends value does not a matter because it will; obviously, it will dilate Pauli exclusion principle, but we should check taking the maximum number of same value of M L and M S ok. So, here this maximum M L same value plus 1 plus 1 then obviously, third one I have to I have to put minus 1, I have to put minus 1 ok.

So, then it will be 1, it will be 1 and then M S equal to, M S equal to. So, for this for this M S plus half and this minus half I have to make there is no way and this is different from the this minus 1, M L value is different from the other. So, this again I can put is plus half and minus half. So, we can take plus half. So, next am getting, M S equal to half; that means, S has to be half, S has to be half ok, yes.

So, next another term am getting L equal to 1; that means, that is that will be that will be yeah for this term another term will be p, p and S is half, so it is 2 ok. And then M L equal to then L equal to 0, then L equal to 0, L equal to 0 ok. So, M L will be 0, M L will be 0, M L will be 0. So, how you can get 0? How you can get 0? We can take plus 1 plus 1 minus 1 then it is 0 and this other one there is no option one has to take, one has to take.

So, plus 1 and another I have to take minus 1 there it is 0 then third one, third one I have to assign this 0 ml value 0, then M L 0. So, S here you see this 3 are different, plus 1 minus 1 and 0 ml value are different. So, I am take s value same because I have try to take summation sum over whatever M L or M S then we try to take maximum value one should take the maximum value.

So, M S for all I can take plus value all I can take plus value because as I told you this always you should try to take the same value of M L and M S as many as possible if they are different there is no problem it will not dilate. If they are same, so then that is the critical point one has to analyze. So, M S value I can take same then M L value will be here it is becoming different ok.

So, here it is M S value 3 by 2, so S value has to be 3 by 2 ok, maximum S value is 3 by 2. So, this S value has to be 3 by 2. So, for L equal to 0, so L equal to 0 another term we are getting is S, L equal to 0 S and this 3 by 2 means it is 4, it is 4 4 S, 4 S. So, so this here we are getting this 3 term from p equal to 3.

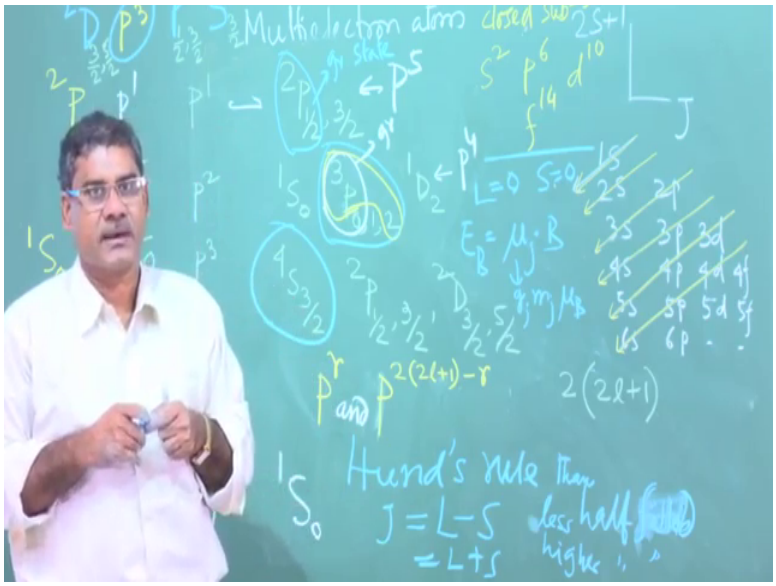
So now, here let me I will. So, here, so what will the J value? Here L equal to 2 and S equal to half, L equal 2 and S equal to half ok. So, S equal to half then; obviously, it will be 3 by 2 and 5 by 2 they will be 3 by 2 5 by 2. So, J will be 3 by 2 and 5 by 2 is it 2 again multiplicity 2 it is 2 and p it is 1 and s half. So, it will be half and 3 by 2 half and 3 by 2 and this S is 0 and S means L is 0 and S is 3 by 2; that means, this J will be 3 by 2, J will be 3 by 2.

As I told in case of s this multiplies in number of term its its it does not follow the multiplicity ok, otherwise for other cases this number this multiplicity is this number j value, ok. So, this way one can find out. So, up to now, p 3, I showed you p 4 p 5 p 6 one can find out. So, here I will tell some rule I will tell some rule from the observation; let me ah. Yeah.

So, one observation one rule is that here I mentioned you for close sub shell or close shell L and S are 0, resultant L and S are 0, and then for nonequivalent electron all L S are allowed and corresponding spectra scopic term one can find out that is not the difficulties, but difficult is for the for the equivalent electron n and l are same those are called equivalent electron for for equivalent electron what are the state what are the state one has to or spectra scopic term one has to find out and how to find out. I told you one

way there are different way also people used. So, you can try which one is better for you, but I told you just one way. So, that can be applied for here I showed you s electron then p electrons p equivalent electron then there are d equivalent electron etcetera f equivalent electron. So, here one thing I can tell you that this here if say p 2. So, what I got?

(Refer Slide Time: 21:31)



I got basically for p 1 p 1 what are the state I got this p 1 this is the state, p 1 I got 2 p half and 3 by 2 and then I got for p 2 this is for p 2, so for p 2 electron equivalent electron. So, here this are the states this are the states what are the states 1 S 0 then 3 P 0 1 2 and then D 1 D 2. So, this are the spectra scopic term means these are the energy levels you know these are the spectra scopic these are the energy levels for the system S.

So, and then we found p 3, p 3, p 3 what you got? This I got 4 S 3 by 2, then 2 P half 3 by 2, 3 by 2 and then I got D, D its a 2 and this is 3 by 2 and 5 by 2 ok. Now, you will get basically for we have to find out for p 4 p 5 p 6 ok. So, without further calculation I can find out. So, rule is that. So, this sub shell it contains maximum 2, it contains maximum 2, 2 l plus 1 number of electrons right, 2 2 l plus 1 number of electrons ok. So, for any either p or any spectra scopic any for either s orbit orbitals, for p orbitals, d orbitals, f orbitals. So, for any orbitals, if you calculate for, so say q number of, q number of I think let me write just R one general R it can be; yes, no. Let me write I think these are l value. So, let me write l let me write this l, but it may be confusing. So, what I should anyway.

So, in case of in this case it is p. So, write p let me write p. So, p can have maximum 2 2 l plus 1. So, p we can take in general. So, p equal to one. So, one you can take 3 how many electron 6 electrons ok. If here p I have written if it is p, p in general if it is d, if it is s, so what can one can write this ok. So, for this spectra scopic term whatever I got its for p r and p this number of maximum number of electrons it can have minus r that spectra scopic term will be.

Let me write just and so p r. So, now, in case of p 1, this one and in this case it is one and this is 6 5, so whatever spectra scopic term for p 1 this same spectra scopic term will be for p 5, p 5. So, this are the, these are the spectra scopic term for p 5 also ok and then p 2 r 2. So, these will be 6 minus 2 4. So, these spectra scopic term it is are for p 4 also all right ok. So, you know p 1, p 2, p 3, p 4, p 5 and then p 6; p 6 obviously, for close sub shell it is l equal to 0 and S equal to 0; that means, its term will be its term will be S l equal to 0 this is l S equal to 0 this is 1, and J will be 0 ok.

Similarly, for d one can calculate I will not calculate. So, d is 1, d 1, d 2, d 3, d 4, d 5, right. So, if you calculate up to d 5 then d 6, d 7, d 8, d 9, d 10; d 10 obviously, it is this same 1 is 0, l equal to 0, s equal to 0, d 9 it will be same as d 1, d 8 it will be same as d 2, d 7 it will be same as d 3, d 6 it will be same as d 4 right and then d 5 ok. So, this your homework you can try to calculate the way I have calculated tenth or are there are some other method also people try to use.

Now, how to find out the spectra scopic term for multi electron atom? That I try to try to calculate, and this very important, very important this each spectra scopic electron is telling basically the basically the state of this atom state of the atom energy of the atom in which state it is ok.

Now, here for nonequivalent electron there is no problem for equivalent electron one has to be careful to calculate that is also here able to calculate. Now, here whatever I have data. Now, if I ask you are if you if you if you try to find out that here this for p 1 electron, p 1 electron for ground configuration of the, so it is p 1 electron it may be it may be atom say lithium alkali atom, lithium atom lithium atom, potassium atom, sodium atom ok.

So, because 1 s to 2 s to 2 p 1 right that will be for no sorry, it is a not lithium, not alkali atom because that is S electron for alkali atom that is S electron. So, S that I do not have

here so, but I have calculated. So, for p electron this is basically 1 is to 2 S 2 to p 1. So, that is that is boron right its boron and this for other we have to seen it that in that column of the of the puric table, so whatever the other in that column. So, basically this column form with this of the electron you know. So, all p 1 that will be in one column, p 2 electron this another column itself, and yes and there is not last column is for inner gas, and for inner gas this the outer most electron outer most sub shell is closed ok. So, all sub shell are closed. So, that basically, so unit table is arranged in different row depending on the outermost electron whether it is S 1 or it is p 1 or it is others ok.

So, here what I am trying to find out electric configuration it is whatever this way this is the minimum energy configuration for any atom you can give minimum energy configuration. And for a particular atom ok, so outer shell is p and in that p if it is one electron before that it is close sub shell are close. So, there is the contribution of L and S because they are 0.

Now, only contribution from p 1, then put one more electron then you will get the next atom that is p 2 p 3 p 4 p 5 p 6 etcetera right. So, but when this for this atom it will have 2 states p half and p 3 by 2 ok. Now, again 2 states, now above this 2 states which one will be the down state which one will be the minimum energy state or on both are having the minimum energy. It cannot be, because you know this energy depends on J value, in J we have seen.

So, lowest J value is the lowest J value will have lower energy state and higher J value will have the higher value. So obviously, this one means 2 p half, 2 p half this is one will be the ground state, this one will be the ground state ok. And 2 p 3 by 2 is energy is higher than the 2 p half. So, one can if someone ask which one is the down state. So, out of this 2 we can find out ok.

So, similarly we can find out here there are see for p 2 there are many states. So, how to find out the down state? So, here s is same, l is same, so depending on j we could find out. And here how to find out here different types are there? Now, is important rule to find out the ground state and for equivalent for equivalent electron ok. So, this called this is a Hund's rule you know Hund's rule to find out the ground state of multi electron system and its and for non equivalent electron configure, for equivalent electron

configuration these are for equivalent electron configuration what is the ground state that we can find out taking the help of Hund's rule.

What is Hund's rule? Hund's rule is that to get the lowest energy state ground state first we have to which this term is having L S right, and J, L S and J, right. So, out of them how to find out. Out of them how to find out? Say Hund's rule is telling first we have to maximize S ok, which will have the lower energy. Whatever the terms are available, so maximize S. So, here whatever terms are available; what is the maximum S? These are the having maximum S, S equal to 1 in this case.

So, now, I select this one ok. Then next is after selecting this S then I should maximize L, I should maximize L ok. So, now, here you see I have only one L, if if another term would be there. So, 3 p and here also 3 D kind of things then maximize S means out of out of them. So, 3 would be the maximum then I have to maximize L. So, then whether p I will consider or D I will consider if it is 3 D 3 D 2. So, then I will consider D ok. Since here I do not have any choice only one term only one L value. So, I will choose. I have to choose this ok.

So, maximize S passed then maximize L. So, this is the term and then out of this 3, p 0, p 1 and p 2 which one you should consider ok. So, then this Hund's rule is telling that that basically this for less for equivalent electron I told for this valid for equivalent electron configuration. So, lower J will have the lower energy when will get will get.

So, basically is telling will get lower energy lowest J value will give the lower energy for less than half filled shell or sub shell for less than half filled sub shell and higher J value, higher J value will give the lower energy for higher than half filled shell sub shell ok. What does it mean? So, I will get lower energy J value, J value lower low lowest J value will give the lowest energy state when it is. So, J value L minus S that will be the lowest energy state for less than when is for less half filled shell less half filled shell ok.

When shell or sub shell is shell or half filled less than half filled, when shell is less than less than half filled ok. Means is less than p 3, so up to less than for p 1 p 2. So, lower J value L minus S and for higher than higher than J value higher than half filled higher than half filled higher than half filled so that that is for J equal to L plus S ok.

So, that means, for p 2 this one will be the, this one will be the S is maximize and then L there is no choice and out of them low this, the J value lowest value. So, this will be the ground state. This will be the ground state for p 2, but for p 4 it is higher than the half filled because p 3 it is higher than the half filled. So, for that L plus S means maximum L maximum J. So, for that for that one, so this will be the I think I will use. So, this will be the, so p 3 p 2 that will be the ground state for p 4 ok.

So, if we put this we have to find out which atom it is depending on this n value ok. So, this way one has to find out ok. So, how to find out the ground state? It is it is whether it is less than half filled or higher than half filled depending on that it this ground state will be different ok. So, that is that is valid for all sub shell whether it is d or this f ok.

So, so I think this the how to find out the ground state of an multi electron atom ok. So, this is the way one has to find out for any atom having many electrons you know this say chromium. Chromium is 24 number of electrons, copper is 29 number of electrons ok, for all of atoms one has to find out first if take this take the electronic configuration of that atom 1 S 2, 2 S 2, 2 p 6 etcetera etcetera ok. Then close sub shell L S value are 0, so neglect it. Then only unfired, unfilled sub shell, so un filled sub shell will be s one p 1, p 2, p 3, p 4, p 5, p 6 again close d 1, d 2, d 3, d 4, d 5 etcetera ok.

So, for that we have to find out, we have to find spectra scopic term for equivalent electron how to calculate for nonequivalent electron that is all terms are allowed. Now, you will get many terms for this electronic configuration for a particular electron configuration and out of them we have to find out ground state which one is ground state. So, we have to take helps of Hund's rule, Hund's rule is telling first maximize L maximize S we have to find out what is maximize S. So, in this case this is the maximum p 3 maximum S, then I will select this term. So, there is no 4 other. So, L is same. Now, here is 3 by 2, there is the other choice. So, it is interesting.

So, here we talk about the less than half filled and higher than half filled ok. So, what about this half filled? Interestingly for half filled for half filled only one term ok. So, you will not need to do anything and that is happened ok; maximize S and then L then that is having only one term ok. So, we say one has to find out the.

So, if I can find out the spectra scopic term for an atom then everything is done if I know the spectra scopic as I mentioned earlier for a single electron or atom if I know the

spectra scopic term then I can do everything spectra scopic study I can do everything right. I can I can I can I can what I want to do I want to I want to study the spectral lines. So, if I know the spectra scopic term. So, I can find out the corresponding condition and I get the spectral lines. If I if I apply magnetic field then I can find out the g 1, g 1 effect. If I apply g 1 if a 5, so I can calculate the I can calculate the basically have to this energy have to calculate E B equal to mu j, mu j dot B right. So, mu j is a, mu j. What is the mu j? Mu j is g j; mu j is mu j is will be g j m j m j g j m j mu b right, ok, yes.

So, g j you know 1 plus j square plus l square minus s square divide by no, 1 plus j square plus s square minus l square divide by 2 j s ok. So, g j 1 can find out. So, n j you know everything you know, if we know the spectra scopic term. So, you can find out the effect of magnetic, effect of magnetic, effect of magnetic, effect of magnetic field similarly you can find out the effect of electric field on that atom. So, to find out the effect of electric field magnetic field are light or the transition transitions of electrons in the in the in the atom for which we get the spectral lines ok. So, everything we can find out if we know the spectra scopic term and that is what we have done for multi electron system.

So, here we have, we have seen we have consider some rules Pauli exclusion principle, Hund's rule, etcetera (Refer Time: 46:14) principle this etcetera. So, these all are valid, these are simple rules, but everything one can find out from quantum mechanical treatment. If you use quantum mechanics then all things can be expand, but there are difficulties for single electronic it is easy for multi electronics is difficult, but one can qualitatively one can one can explain them, qualitatively whether it is it is difficult.

So, I think I will stop here. Next I will try to use quantum mechanics.