Spectroscopic Techniques for Pharmaceutical and Biopharmaceutical Industries
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Lecture 15: Atomic Spectroscopy--3

Hello students, welcome to lecture 15 of this course. In the last two lectures I have discussed about how to calculate energy of different atomic orbitals and I discussed about how does spectra of hydrogen look like. We looked at the gross spectra of hydrogen atom and then we also looked at the fine spectra of hydrogen atom which is due to spin orbit coupling, the spin orbit coupling. Now I will go to discuss atoms having more than one electron.

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For example helium atom, so helium atom consists of a nucleus and two electron and if I try to solve Schrodinger wave equation to get the energy of different energy levels associated with helium atom, we will not be able to get the analytics solution and this is because of interelectronic repulsion term between two electron is given by e square divided by 4 Pi epsilon knot r12 where r12 is distance between two electrons.

So what generally we do is to use different methods to calculate the energy of different levels associated with helium atom. One of the most common method is approximate method. In this

method what we do is first we assume that electrons do not interact with one another and then we can ignore this potential energy term, this potential energy term due to inter-electron repulsion.

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Helium Atom (consists of a nucleus and two electron)

- Then, Hamiltonian operator is sum of Hamiltonian operator of two individual particles, i.e.

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

$$\hat{H}_1 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_o r_1}$$

$$\hat{H}_2 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_o r_2}$$

So in this case, when we ignore the inter-electron repulsion, we can express Hamiltonian operator as a sum of Hamiltonian operator of two individual electrons. So we can just write Hamiltonian is equal to Hamiltonian for 1 plus Hamiltonian of 2 and for 1 we can write the Hamiltonian as minus H cross square by 2me del 1 square minus Ze square by 4 Pi epsilon knot r1 and similarly for second electron we can write the Hamiltonian and now overall Hamiltonian operator is sum of Hamiltonian operator of two electrons.

So approximate wave function in this case will be product of two wave functions Psi 1 and Psi 2 and Schrodinger wave equation can be divided into two separated equation given by H1 Psi 1 is equal to E1 Psi 1 and H2 Psi 2 is equal to E2 Psi 2. In this case, the energy of the system will be the sum of energies of the two the electrons. So energy obtained using this equation plus energy obtained using this equation, so E will be the sum of E1 plus E2.

So if we take the approximate wave function and obtained eigen function of H1 operator plus H2 operator, what we will get is 2 E1s. So eigen value obtained will be equal to 2 multiplied by

energy of 1s orbital of is He plus okay 1 is orbital of He plus, remember here Z is equal to 2, so it will be 8 times minus 13.6 electron volt. If you remember when we calculated the energy of the different odd bits of hydrogen atom, what we got is minus 13.6 into Z square by n square electron volts. So energy of nth orbital of hydrogen atom or hydrogen like atom will be given by this equation.

So if I calculate this for helium atom, Z will be equal to 2. So what we will get is minus 13.6 into 4 divided by n square and if I take n is equal to 1 then we will get this 8 multiplied by minus 13.6 electron volt. So this is your eigen value for helium atom and this is equal to minus 108.8 electron volt. So till now we have calculated energy ignoring the repulsion between two electrons. Now we will calculate the repulsion energy of two electrons and that can be given by this formula. So this is your potential energy due to repulsing between two electrons.

So Psi star into this multiplied by Psi and then dv1 and dv2. If I integrate this, what we are going to get is 34 electron volt. So repulsion energy of two electrons can we calculated using this method. Now we have already calculated energy which does not include the repulsion energy between two electrons and now we have calculated repulsion energy between two electrons so what we are going to do is we are going to add it up to get the total energy.

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And when we add it up what we will get is minus 74.8 electron volt and this is quite close to exact value of energy, which is minus 79.0 electron volt. So this is the first method to calculate the approximate energy of helium atom.

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There are other methods reported, one of them is variation method. In the variation method, what we do is we take what is known as a wave function which we think that this can be a suitable wave function and then we try to get the energy. Here what was done is you consider effective nuclear charge Z dash less than Z as one electronic screen other than the average energy will be

given as this value. So here I am not going to discuss it in detail about variation theorem since it involves higher, you know higher hypothesis of quantum physics and if you want you can go to NPTEL lectures on quantum and look how to calculate e dash.

But here we start with a wave function which is known as trial wave function and then you try to calculate the energy, calculate the energy. Here what we generally do is in place of Z we take Z dash, Z dash and that will give you E dash and Z dash basically replaces your Z which is your nuclear charge and this Z dash is called effective nuclear charge. When you do that and you saw the integral, what you will be able to give is this equation. So E dash is equal to Z dash is square minus 27 by 8 Z dash multiplied by E square by 4 Pi epsilon knot a knot. Now question is how to get this Z dash?

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So you have to choose Z dash to give the lowest energy by minimizing E dash with respect to Z dash and when we differentiate that the equation which I have given in the previous slide you will get dE dash by dZ dash is equal to 2Z dash minus 27 by 8 e square by 4 Pi epsilon knot a knot. If you do that, you can get the value of Z dash. This put is equal to 0 and you can get Z dash minima and that is equal to 27 by 16. And now you can put this value into the previous equation.

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Here this equation put the value of Z dash.

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What you will get is the value of E dash which is around minus 77.5 electron volts. So this is the second method by which you can calculate the energy of different orbitals of helium atom.

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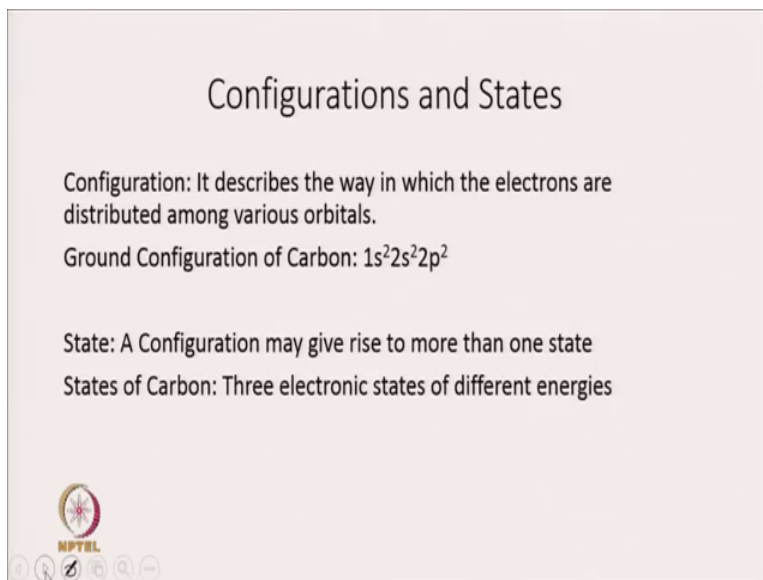
Helium Atom (consists of a nucleus and two electron):First order Perturbation correction

$$E_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0$$

$$\hat{H}^1 = \frac{1}{r_{12}}$$

$$E_n^1 = \frac{5}{8} Z E_h$$

$$E_0 = E_0^0 + E_0^1 = -4E_h + \frac{5}{8} Z E_h = -74.8 \ eV$$

Now there is another method which is known as Perturbation correction. So what it does is, it first calculates assuming that there is no repulsion between electrons and now repulsion between electrons is considered as your perturbation. And you can calculate the energy due to this perturbation by using this formula. So if you saw this integral, what you are going to get is your what is known as first order perturbation. And here you see this as your potential energy, this is written atomic it means that what we have done is we have removed your the constant terms.

And if you plug in here and then integrate this, what you are going to get is En1, what you are going to get is En1 which is the first order perturbation correction for the helium atom and that is equal to 5 by 8 Z Eh where this Eh is your hartree energy for hartree energy. Okay, so your energy is E knot is equal to E knot, knot which is obtained neglecting the repulsion part plus this which is your perturbation and if you add this you will get minus 74.8 electron volt. So these are the 3 different methods in which you can calculate the energy of orbitals associated with helium atom. Now once we saw that, what we are going to look at is multi electron system.

So without going into detail of mathematics, what I am going to tell you is qualitative analysis now. An important effect of electron repulsion is to remove the degeneracy of 2s, 2p orbital 3s, 3p, 3d which are degenerate in hydrogen atom. So if you look at hydrogen atom, your energy is dependent on n value. So 2s, 2p has same energy whereas 3s, 3p and 3d has same energy.

But when you take multi-electron system this degeneracy is going to be removed. So 2s, 2p is going to have different energy. Similarly 3s, 3p and 3d are going to have different energy. So if you see here 1s, 2s, 3s now here 2s and 2p have different energy, 3s and 3p have different energy, 3s, 3p and 3d have different energy. So here your energy is not only dependent on n but it is also dependent on L value and that is the effect of electronic repulsion. So for multi-electron system we need to understand two different concepts. One is called configuration and another is a states.

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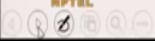
Configuration describe the way in which the electrons are distributed among various orbitals. For example, if I take the case of carbon, 1s orbital has two electron, 2s orbital two electron where as 2p orbital has two electrons. So this is known as configuration but each state is different, a configuration may give rise to more than one state, more than one state. For example 1 s2, 2 s2, 2 p2 can give you more than one state of carbon. And what generally we get is three electronic states of different energy.

I have talked about in case of, in case of at one electron system, I talked about how to get the how to get the electronic state during my previous lecture. And this I am going to talk about how to get the electronic state of multi-electron system.

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So first I will discuss about non-equivalent electrons and we will look for what are the states for atoms which have non-equivalent electrons. So what I mean by non-equivalent electron? Non-equivalent electrons are those that have different values of either n or l. For example, 3 p1, 3 d1.

So here one electron has l value of 1 whereas the another electron has l value of 2. So they have a different value of l and thus these two electrons are not equivalent. Now take the case of 3 p1, 4 p1 all the l value of the two electrons are same but n value is not same. For one electron n value is 3 and for another electron n value is 4 and so these are known as non-equivalent electrons. And getting states of non-equivalent electrons is not that difficult.

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So let us think about excited state of carbon or silicon, they have electronic configuration p1 d1, so for carbon it is 2 p1, 3 d1 and for silicon it is 3 p1 d1. So first we need to find out l that is what we discussed in the last lecture. So this is your electronic configuration of excited state of carbon. So one electron is in p levels, so l1 is equal to 1 and one electron is in d levels so l2 is 2 and so l is going to be from l1 plus l2 to l1 minus l2 and 1 plus 2, 3 to 1 minus 2 mod if you take mod of this is equal to1. So 3, 2, 1 so there are 3 value of l, capital (L) which is possible and magnitude of this L will be 12 half H cross 6 half H cross and 2 half H cross.

This is for this one, this is for this one and this is for this one, H cross l, l plus 1 so 3 into 4. So this is your H cross into root 12. When l is equal to 3, l is equal to 3. Similarly you can calculate for other value of l. So this is L-L coupling, so this is a small l and L coupling.

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Now let us go and look at the states. Once we calculated the l value now we can level the different states and the way we discussed last time l is equal to 0 corresponds to s, l is equal to 1 corresponds to p, l is equal to 2 corresponds to a state d, l is equal to 3 corresponds to a state f and we showed you last time that we have for carbon and silicon l is equal to 3, l is equal to 2, l is equal to 1, so we have F state, D state and P state. So both carbon and silicon is going to have F state, D state and P state.

The coupling between the spin momenta is referred as *ss* coupling.

$$S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2|$$

The labels for the terms indicate the value of S by having 2S+1 as a pre-superscripts to the S, P, D,.... labels. The value of 2S+1 is known as multiplicity.

Since 2S+1= 1 & 3, the excited configuration of C and Si give 1P, 3P, 1D, 3D, 1F, 3F terms.

Now let us see, S-S coupling, so again s will be from s1 plus s2 to s1 minus s2. If we take two electrons, so 2 p1,3d1 system, right? So let us see 2, 2 p1, 3 d1 system. So s is going to be your half one electron, half for another electron. So coupling will give you 2 state, S is equal to 0, S equal to 1. So level 4 terms indicate the value of S by having 2S plus 1 as pre-superscript to SPD that is what we discussed last time also, 2s plus 1 is known as multiplicity. So now see, what will the 2s plus 1? 2S plus 1 will be equal to 1 if S equal to 0 and it will be equal to 3 if S equal to 1 and so the excited configuration of carbon ion give 1P, 3P, 1D, 3D, 1F, 3F and these all are superscript so please do it. So it will be like a super script. Okay sorry for this but it will be pre-superscript. It will be before F but as a superscript.

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$$J = L+S, L+S-1, \ldots, |L-S|$$

If L>S, J can take 2S+1 value

If L<S, J can take 2L+1 values
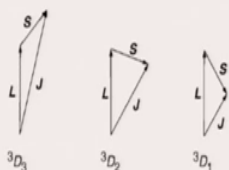
Now we have calculated l, we have calculated s, now we will look at L-S coupling. and this also I have discussed in last class. So J is going to have value between L plus S to L minus S with the mod sign. If L is greater than S then J can take 2S plus 1 value and if L less than S, then J can take 2L plus 1 value.

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L-S coupling in ^3D term

$= 2S+1$

S=1, L=2

L>S...........J=3, 2 or 1

$^3D_3$ $^3D_2$ $^3D_1$

Now let us think about L-S coupling in 3-D term. So for 3D, S will be equal to 1 because this is equal to 2S plus 1 and so S is equal to 1 for 3D and L is equal to 2 for D. What does this mean? Is L is greater than S, L is greater than S and so you are going to have, so let us see here.

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$$J = L + S, L + S - 1, \ldots, |L - S|$$

If L>S, J can take 2S+1 value

If L<S, J can take 2L+1 values
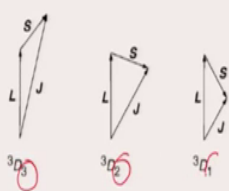
If L is greater than S then J can take 2S plus 1 value, right.

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L-S coupling in ^3D term

$= 2S+1$

S=1, L=2

L>S..............J=3, 2 or 1 $2 \times 1 + 1 = 3$

So 2S plus 1 is 2 into 1 plus 1 is equal to 3 value and 3 value will be J3, 2, 1. 3, 2, 1 and this value will come in the term as subscript as subscript 3, 2, 1 (3, 2, 1).

So total number of states for carbon or silicon of configuration p1d1 will be your 1 p1, 3 p1,3 p0, 3 p1 ,3 p2, 1 d2, 3 d1, 3 d2, 3 d3, 1 f3, 3 f2, 3f3 and 3 f4 that is what all combination of states will exist for carbon or silicon configuration. This is the excited state remember, it is not the ground state it is not p2 configuration. It is p1 d1, it is excited state of carbon or silica. So they are going to have these many energy levels.

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Non-equivalent electrons	
Configuration	Terms
s^1s^1	$^{1,3}S$
s^1p^1	$^{1,3}P$
s^1d^1	$^{1,3}D$
s^1f^1	$^{1,3}F$
p^1p^1	$^{1,3}S, ^{1,3}P, ^{1,3}D$
p^1d^1	$^{1,3}P, ^{1,3}D, ^{1,3}F$
p^1f^1	$^{1,3}D, ^{1,3}F, ^{1,3}G$
d^1d^1	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G$
d^1f^1	$^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G, ^{1,3}H$
f^1f^1	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G, ^{1,3}H, ^{1,3}I$

So you can go and practice a bit on these configurations and their terms are given here. So one electron in S another electron in other S orbital then you will get 1S 3S and that is written as 1, 3S so these are the different terms for different configurations. So for s1 d1 you have 1 3D, s1 f1, 13F, so these things you can practice it. (Now) it is not that difficult just you need to understand the concept.

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Equivalent electron

C $1s^2 2s^2 2p^2$

$n=2$ and $l=1$ for both electrons and as per Pauli's exclusion principle two electrons have different values of either m_l or m_s.

It should be noted that the indistinguishability of the electrons has been taken into account when deciding about different states so that, for example, the combination $(m_l)_1 = (m_l)_2 = 1, (m_s)_1 = -1/2, (m_s)_2 = 1/2$ cannot be included in addition to $(m_l)_1 = (m_l)_2 = 1, (m_s)_1 = 1/2, (m_s)_2 = -1/2$, which is obtained from the first by electron exchange.

Now we will go to equivalent electrons. Equivalent electrons are a bit different because we have to take care of Pauli exclusion principle and Hund's multiplicity rule. So let us see the with one

example what do we mean by equivalent electron? So let us look at the ground state of carbon. Now we are looking at ground state of carbon, not the excited state. So in the ground state of carbon, there are two electrons in level P or level 2P. These electrons have same value of n and same value of l, so these electrons have same value of n and same value of l and so they are equivalent electrons.

So n is equal 2, l is equal to 1 for both electrons and as per Pauli exclusion principle two electrons have different value of either ml or ms. They are not going to have (you know) same value of everything. Also it should be noted that the indistinguishability of the electrons has been taken into account when deciding about the different states. For example, combination ml 1 is equal to ml 2 is equal to 1, ms1 is equal to minus half, (ns) ms 2 is equal to half cannot be included in addition to ml 1 is equal to 1 and ms1 is equal to half, ms 2 is equal to minus half which is obtained from the first electron exchange.

So what I mean is if there are two electrons and this is p orbitals, so one is like this and other is like this, another cannot be like this and this is first Pauli exclusion principle. Now the second is thing which you need to remember that it can be like this but writing this is down, this is up, this is not going to help. Thus violates your indistinguishability of two electrons, so these two are not different.

Table 7.3 Derivation of terms arising from two equivalent p electrons

Quantum number	Values
$(m_\ell)_1$	1 1 1 1 1 1 1 1 1 0 0 0 0 0 −1
$(m_\ell)_2$	1 0 0 0 0 −1 −1 −1 −1 0 −1 −1 −1 −1 −1
$(m_s)_1$	½ ½ ½ −½ −½ ½ ½ −½ −½ ½ ½ ½ −½ −½ ½
$(m_s)_2$	−½ ½ −½ ½ −½ ½ −½ ½ −½ −½ ½ −½ ½ −½ −½
$M_L = \sum_i (m_\ell)_i$	2 1 1 1 1 0 0 0 0 0 −1 −1 −1 −1 −2
$M_s = \sum_i (m_s)_i$	0 1 0 0 −1 1 0 0 −1 0 1 0 0 −1 0

Pairs of values of M_L and M_S can be rearranged as follows:

M_L	2 1 0 −1 −2	1 0 −1	1 0 −1	1 0 −1	0
M_S	0 0 0 0 0	1 1 1	0 0 0	0 −1 −1 −1	0
	^1D		^3P		^1S

So now we are going to write the different combination of quantum number for these two electrons and then we are trying to find out the terms. Now let us see here, the first is we started with 1, 1 it means that suppose you have a P orbital okay, this is 1, 0 minus 1 so two electron in this one okay two electron in this one. Only one combination is feasible and that is 1, 1 half minus half. You cannot have this combination, cannot have this combination, you cannot have, you cannot write like this, this down, this up. This I already discussed and that is why there is only one combination.

Similarly, if you look at when I put a 0, 0 then there is only one combination minus 1, 1 then there is one combination. So if ml 1 and ml 2 are equal there is only one combination possible. Now let us check if I take the ml 1 is equal to 1 and ml 2 is equal to 0, ml2 is equal to 0. Now there are 4 possibilities, what are the 4 possibilities? Both can be up, one is up, another is down, this is down, this is up and both are down. These all 4 possibility exists, so we have written all the possibilities. Now similarly if I take 1, minus 1 then I have 4 possibilities and if I take 0, minus 1 there is 4 possibilities.

So we have looked at every case, so 1 1 and 1 0, (1) minus 1, this is 0, (what) 0 I did not take 0 1 because 0 1 is here, 1 0 and 0 1 so these four already we have taken into account, so we do not need 0 1 and similarly 0 minus 1 we do not need because those two are similar. So you have this

combination of terms. Now what we will do is this is the different combination of ml and ms value possible for two electrons.

Now what we are going to do is calculate the L value and S value, L value and S value for each combination. If you do that you will get L is equal to 2, S equal to 0, L is equal to 1, S is equal to 1, 1 0 1 0 so this you will get, once you do that, now try to arise this. So first look at 2 0 is here so this is 2 0 then you see 1 0, 1 1 0 I took then 0 0, 1 0 0 I took minus 1 0, minus 1 0 is here and minus 2 0, so 5 combinations will give you one data is 5 combinations is going to give you one data.

Now go and look at this 1 1, so where is 1 1? You have 1 1 then 0 1, so this is 0 1 and minus 1, 1 this is minus 1, 1, 1 0 this is 1 0, 0 0 so this is 0 0, minus 1, 0, minus 1 0, 1 minus 1, 1 minus 1 and 0 minus 1, 0 minus 1 and minus 1 minus 1this one, this corresponds to 3p level and 0 0 corresponds to 1s. So this is the way to get the terms for your equivalent electrons, transfer equivalent electrons. You have to write all the combination of ml and ms, L or S

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Just you need to keep in mind that you cannot repeat it or you cannot violate your Pauli exclusion rule and you must take into account indistinguishability of the electrons. Once you do that then it is easy to get the terms for different transfer equivalent electrons. So now see this, we looked at p1d1 and p2 configuration, p1d1 corresponds to non-equivalent electron and p2 corresponds to equivalent p electrons.

It is interesting to note that of the ^1S, ^3S, ^1P, ^3P, ^1D and ^3D terms which arise from two non-equivalent p-electrons, as in the $1s^22s^22p^13p^1$ configuration of the carbon atom, only ^1S, ^3P and ^1D are allowed for two equivalent electrons: the Pauli exclusion principle forbids the other three.

Rule for derivation of term symbol for non-equivalent symbol: *a vacancy in a sub-shell behaves like an electron*. For example, the ground configurations of C ($1s^22s^22p^2$) and O ($1s^22s^22p^4$): ^1S, ^3P, ^1D give rise same terms as do the excited configuration of C ($1s^22s^22p^13d^1$) and Ne ($1s^22s^22p^53d^1$): $^{1,3}P$, $^{1,3}D$, $^{1,3}F$.

What is interesting to note that the terms which arise from two non-equivalent p electrons as in case of 1 s2, 2 s2, 2 p1, 3p1 or 3 d1 for carbon atom so this 3 p1 okay, we saw 2 p1, 3 p1. Only one is 3p and 1d are allowed for two equivalent electrons. So what happens to other three?

They are basically forbidden by Pauli exclusion principle, they are basically for forbidden by Pauli, Pauli exclusion principle. Now rule for derivation of terms symbol for non-equivalent electron that if vacancy in a sub-shell behave like an electron. So this is a very important role, what it does is if suppose you have a p4 electron then you can look at the terms arising from p2 electron and that simplify (approx), simplify the complicated combination of 4 non-equivalent electrons, 4 equivalent electrons, terms (arise), terms when you are writing term for 4 equivalent electrons it will list to several different combination.

And so it is easy for you to go and write different combination for p2 and your term symbol is going to be same for p2 and p4. So a vacancy and sub-shell in a sub-shell behaves like an electron for example, ground configuration of carbon 1 s2, 2 s2, 2 p2 and oxygen give rise to same terms. I do the excited configuration of carbon 2 p1 d1 and neon 2p, 5 3d1. So this is important simplification when writing for different terms.

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Equivalent electrons	
Configuration	Terms[a]
p^2	$^1S, ^3P, ^1D$
p^3	$^4S, ^2P, ^2D$
d^2	$^1S, ^3P, ^1D, ^3F, ^1G$
d^3	$^2P, ^4P, ^2D(2), ^2F,$
	$^4F, ^2G, ^2H$
d^4	$^1S(2), ^3P(2), ^1D(2),$
	$^3D, ^5D, ^1F, ^3F(2),$
	$^1G(2), ^3G, ^3H, ^1I$
d^5	$^2S, ^6S, ^2P, ^4P, ^2D(3),$
	$^4D, ^2F(2), ^4F, ^2G(2),$
	$^4G, ^2H, ^2I$

So p2 is your 1S 3P 1D, p3 is 4S 2P 2D so these are the different terms for different, different type of equivalent electrons and you can practice one of them to see whether you understood or not.

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Ground State

Of the terms arising from equivalent electrons those with the highest multiplicity lie lowest in energy.

C $1s^2 2s^2 2p^2$
O $1s^2 2s^2 2p^4$ } $^1S, ^3P, ^1D$

Among these ^3P term is lowest in energy.

Now we know what are the terms which, which is which comes due to your electron-electron repulsion. But now we need to know what? Which one is of lowest energy without calculating lowest energy or which energy state is the ground state, which energy state is the ground state? So of the terms arising from equivalent electrons, those with highest multiplicity lie lowest in the

energy. So this is the rule which you need to remember that the term with highest multiplicity is going to be lowest in energy.

For example, carbon oxygen, you saw that it will give rise to 3 different term, one is 3p 1d, among this 3p term is lowest in energy, because this has highest multiplicity. Whereas other two terms has lower multiplicity then 3p.

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d^2 $^1S, {}^3P, {}^1D, {}^3F, {}^1G$

Of these, lowest is that with the highest value of L

^3F is the lowest in energy.

But sometimes what will happen that if there are two terms with the same multiplicity. So although they have a higher multiplicity but there are two terms. For example in this case, if we take d2 configuration, you have two terms 3P and 3F which has the same multiplicity. Although they are higher than other terms but two of them are equal or two of them have equal multiplicity.

In that case, lowest is the one with the highest value of L. So if you compare between 3P and 3F the term with highest value of L is 3F and so 3F is the lowest in energy, 3F is lowest in the energy. So first criteria is look for multiplicity and the second criteria a look for the value of L and in both thing what we are looking for is the maximum value of multiplicity, maximum value of L. Okay so till now we did not discuss about spin orbit coupling, we looked at the terms based on electron repulsion based on electronic repulsion.

Now comes the spin orbit coupling, we have discussed it in the hydrogen atom (())(38:58) now again we are going to discuss it for equivalent electrons.

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The splitting of a turn by spin orbit interaction in proportional to J value and J value we know, what is J value? J comes from this is J is basically total angular momentum which is sum of orbital angular momentum plus spin angular momentum. So Ej minus Ej minus 1 is Ej so it is proportional to value of J.

Here Ej the energy corresponding to J and a multiplet results. So spin orbit coupling gives rise to splitting of the peak or multiplet results. If A is positive then component with smallest value of J lies lowest in the energy, so this is very important. So if they split some will be of higher energy, some will be of the lower energy but if value of A is positive then J the term with the smallest J value will be lowest in energy and in that case multiplet is said to be normal. But if A is negative then multiplet inverted and in that case, the energy will be just apposite.

Okay so there are two further rules for ground terms which tell us whether a multiplet arising from equivalent electrons is normal or inverted. Normal multiplets arise from equivalent electrons when partially filled orbital is less than half filled. Inverted multiplets arises from equivalent electrons when a partially filled orbital is more than half filled.

Let us take this case of titanium, so it has 3d2, 4s2, d2 corresponds to 1S, 3P, 1D, 3F, 1G these are the terms and 3F is lowest in the energy you see these two have 3P and 3F both have same multiplicity and they have highest multiplicity. So they are going to be lowest in energy in

between two F has highest value of L and so it is going to be the ground state and again 3F will give you, so 3F means S equal to 1 and L is equal to 0, 1, 2, 3 here S is equal to 3, L is equal to 3. L is equal to 3 and S is equal to 1 so it is going to have value from 4 to J value from 4 to 2, so 4, 3, 2 and the lowest value of J is 2 and so ground state is going to be 3F2 since D is less than half filled, D less than half filled.

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Now take this case, carbon-oxygen they give 3 different terms, this one has highest multiplicity and so this is going to be ground state, okay, 3P is going to be ground state for both carbon and oxygen. Now 3 for 3P your S is equal to1 and L is equal to 1, S is equal to 1 and L is equal to 1. So it is going to have J value 2, 1, 0 so it is going to have j value 2, 1, 0. Now look here, now here the difference, for carbon the 3 P0 will be the ground state because the carbon molecule, your P orbital is less than half filled but for oxygen it is going to be different, for oxygen 3 P2 is going to be the ground state. Since the P orbital is more than half filled, more than half filled. And so carbon will give you normal multiplet whereas oxygen will give you inverted multiplet, so please keep that thing in mind.

Now we will discuss about a spectra of alkali metal. All alkali metal has one valence electron in outer ns orbital, n is 2 for lithium, n is equal to 3 for sodium, n is equal to potassium and so on. Considering only orbital changes involving this valence electron, the behavior of electron resembles that of hydrogen atom, hydrogen atom. What is the reason? Reason is that core of alkali metal has net positive charge, net positive charge, nucleus charge has plus Ze charge and filled orbitals has Z minus 1 charge, (charge) please change this charge.

Thereby they so similar effect on the valence electron as the nucleus of hydrogen atom also has one electron in its outermost orbital, spectra of alkali metal can be excited in a discharge lamp containing a sample of the appropriate metal.

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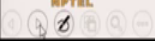

Spectra of Alkali metal

Emission Spectrum of Hydrogen atom shows only one series i.e. Balmer series, while in the visible region alkali metals show at least three.

The *selection rule* governing the excitation of electron to the higher orbital and also its falling back from an excited orbital are

Δn is unrestricted

$\Delta l = \pm 1$

These selection rules lead to the sharp, principal, diffuse and fundamental series if the promoted electron is in *s, p, d* and *f* orbital.

Now emission spectrum of hydrogen atom shows only one series, Balmer series in the visible region, we are talking in the visible region this shows only one series. While in the visible region alkali metals show at least 3 series. The selection rule is seen what we discussed for hydrogen atom at delta n is unrestricted and delta l is plus, minus 1. Selection rules, these selection rules lead to sharp, principle, diffuse and fundamental series. If the promoted electron is in s, p, d and f orbital respectively.

So if a promoted electron is an s then it leads to sharp series. If the promoted electron is in p then it leads to principal series, if a promoted electron is in d then it leads to diffuse, diffuse series and if the promoted electron is in f it is called your fundamental series.
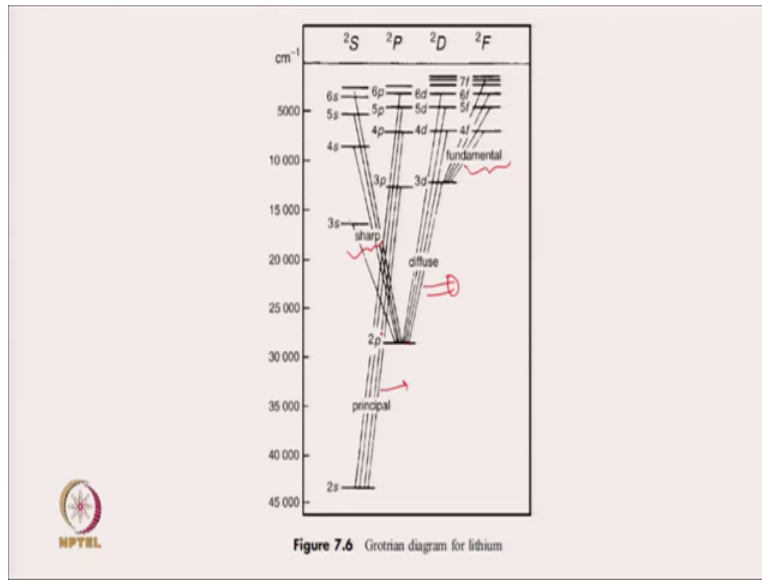
Figure 7.6 Grotrian diagram for lithium

So here is the example, this is the diagram for lithium atom you can see that from 2p it can go to 3s, it can go to 2p to all the s, all the s here of 2s term and 2p to all the d up to 2d term. And when promoted electron is in s for example this and this is called sharp series or here you see it is going from 2s to 2p, 3p, 4p, 5p, 6 p delta n is unrestricted you must remember that and so this is known as principle series. Now look at here p to d since it is going to d and so this is known as the diffuse series. Now from d to f, this is known as fundamental series. Now 2s to 3d is not allowed because delta l is plus 2 but delta l can be minus 1, so 2p to 3s is allowed. So this is your diagram for spectrum of the lithium.

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Figure 7.5 Four series in the emission spectrum of lithium
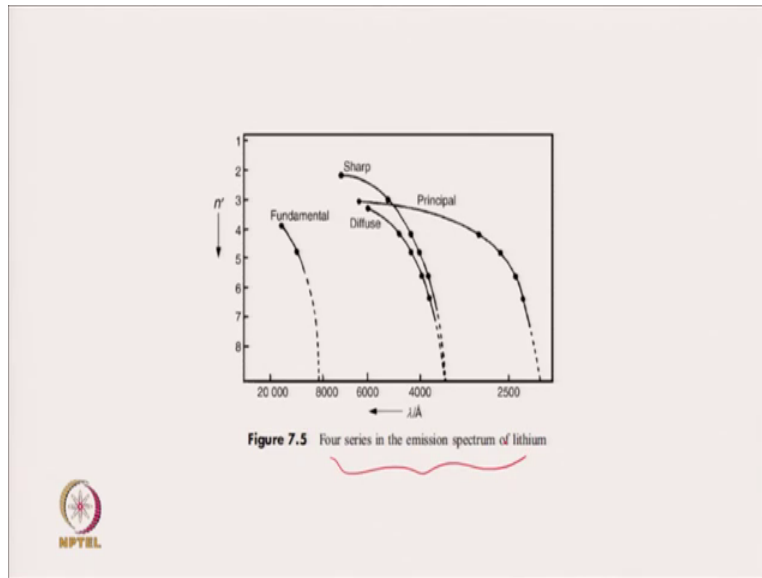
Now these are the 4 different series, this is the fundamental, this is your n-dash versus lambda. If n-dash increases then you see lambda is this side is increased, so this side is decrease. Okay so it is decreasing. So these is like diffuse, this is like sharp and this is like principle. so these are the 4 series in the emission spectrum of lithium.

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So lithium can have, you see, if you look at the lithium, what is the ground state? 1s to 2s 1 and that state is 2s half. When the excited electron goes to the P state then you have these two terms. It can go to D state that will lead to two different terms and if it goes to F state it can give you

two different terms. So this is about a one electron going from the ground state to excited state. Excited state can be S level, can be P level and can be D and F and this are the different your terms for different kind of excited state.

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Spectra of Sodium Atom

In the Sodium atoms: promotion of 3s valence electron to any np orbital with $n > 2$ results in pairs of $^2P_{1/2}$, $^2P_{3/2}$ states.

Labelling of these states with n gives $n^2P_{1/2}$ and $n^2P_{3/2}$.

n label is helpful for the states when only one electron is promoted and the unpromoted electrons are either in filled orbital or in a s orbital.

n label can be used for hydrogen atom, alkali metals, helium atoms and alkaline earth metals.

In other atoms, it is usual to precede the state symbols by the configuration of the electrons in unfilled orbitals. For example, the $2p3p\ ^1S_0$ state of carbon

So in the sodium atom, promotion of so now will talk about sodium atom. In a sodium atom promotion of 3s valence electron to any np orbital with n greater than 2 results in pair of these two states, this is the same like you know lithium. Similar kind of things can happen in case of the sodium. Labeling of these state with n gives you n2 P half and n2 P3 by 2. So suppose we are discussing about 3s to 4p then you write 4 here, 4 here if it is 3s to 5p then we can write 5 2p half and 5 2p3 by 2. N label is helpful for the state when only one electron is promoted and the unprompted electrons are either in filled orbital or in a s orbital.

N label can be used for hydrogen atom, alkali metal, helium atoms or alkaline earth metals. In other atoms it is usual to proceed the state symbols by configuration of the electrons in unfilled orbital.

For example, 2P 3P 1 s0 state of carbon is splitting between 3 2P half and 3 2P 3 by 2 states of sodium is 17.2 centimeter inverse and it reduces with increasing n so if you look at the splitting, the difference between 4 2P half and 4 2P 3 by 2 it will decrease.

So it will be 5.6 centimeter inverse, 2.5 centimeter inverse, 1.3 centimeter inverse for n is equal to 4, 5, 6 respectively. The splitting decreases rapidly with l as exemplified by the splitting of only 0.1 centimeter inverse for 3 2D 3 by 2 and 3 2D 5 by 2 states. So here splitting a very small compared to a splitting between 3 2P half and 3P 3 by 2 states. All these 2P, 2D multiplets are normal, the states with lowest J lying lowest in the energy.

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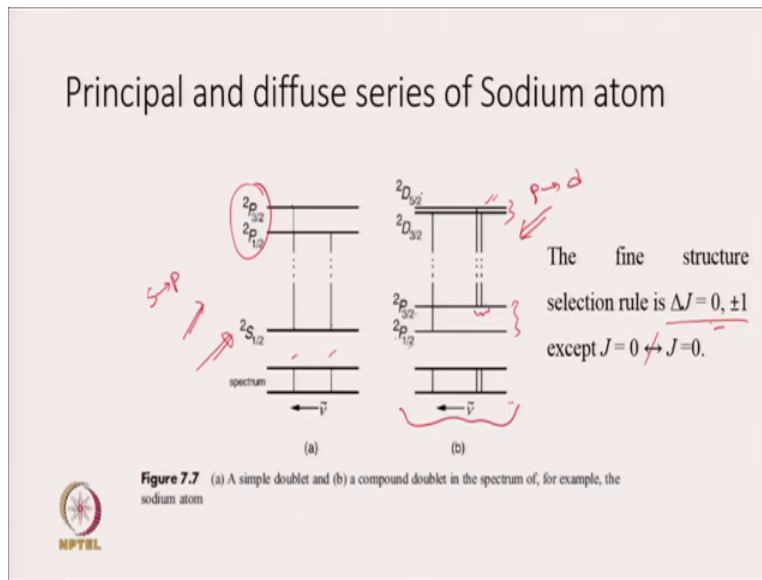
So here is the different series of sodium atom. So what we are looking at the, from S to P and P to D. So this is for S to p, so promoted electron is going to be in P or P to D. So promoted electron is going to be in D, since it is going to be in P so this one corresponds to principal series and this corresponds to your diffuse series. Selection rule is delta J is equals 0 plus minus 1 except J is equal to 0 to J is equal to 0 is not allowed. And you can see here 2S half we saw that 2S has only one term, whereas 2P has 3 terms due to spin orbit coupling the. So 2P half 2p 3 by2.

And so from here to here there is a possibility because delta J is 1 and here to here is a possibility because delta J is equal to 0. So this two are these two transitions satisfies selection rule okay and so you will get a simple doublet. Now look at from p to d, p is split into two different states and d splits into two different state. We see the difference between these two state is high compared to the difference between this states. So difference between 2p 3 by 2 and 2p half is higher comparison to difference between 2d 5 by 2 and 2d 3 by 2. So we are talking about difference in energy levels, energy of these two levels.

So now you see from here there is only one possibility of transition. So you are going from half to 3 by 2, so delta J is plus 1 but you cannot go from 2p half to 2d 5 by 2. Since delta J will be plus 2 which is not allowed but from here transition to both the D state is possible because you are going from 3 by 2 to 3 by 2 which corresponds to the delta J is equal to 0 and then you are

going from 3 by 2 to 5 by 2 where delta J is plus 1 and so there will be a kind of small doublet but here one thing you must notice is since this difference is very small so this two will be quite you know, almost merge into each other and that is why this is known as compound doublet.

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Simple Doublet in the principal series of sodium atom

- Sodium D lines: series in sodium appears in the yellow region of the spectrum with components at 589.592 nm and 588.995 nm.
- The $3^2P_{1/2}$ and $3^2P_{3/2}$ excited states involved in the sodium D lines are the lowest energy excited states of the atom.
- Consequently, in a discharge in the vapour at a pressure that is sufficiently high for collisional deactivation of the excited states to occur readily, a majority of atoms find themselves in these states before emission of radiation takes place. Therefore, the D lines are prominent in emission, which explains the predominantly yellow colour of sodium discharge lamps.
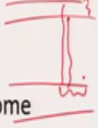
Sodium shows simple doublet in the principal series and that is well known sodium D lines. Series in sodium appears in the yellow region of the spectrum with components at 589.592 and 588.995 nanometers. These two excited state involved in sodium D lines are the lowest energy excited state of the atom. Consequently, in a discharge in the vapor at a pressure that is sufficiently high for collisional deactivations of excited state to occur (rapidly) readily a majority of atoms finds themselves in these state before emission of radiation takes place. Therefore D lines are quite prominent in emission, which explains the predominant yellow color of sodium a discharge lamps.

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Now let us talk about diffuse series of sodium atom. All members of a diffuse series consist of compound doublet as I have shown in the previous slide but the splitting of 2d 3 by 2 and 2d 5 by 2 state may be too small for the close pair of transition to be resolved. If you remember then I solved that these two are quite so since these two energy levels are quite close to each other, so this looks like a single p and so what you will see is kind of compound doublet rather than triplet. So it is for this reason, that set of 3 transitions has become known as compound doublet rather than a triplet.

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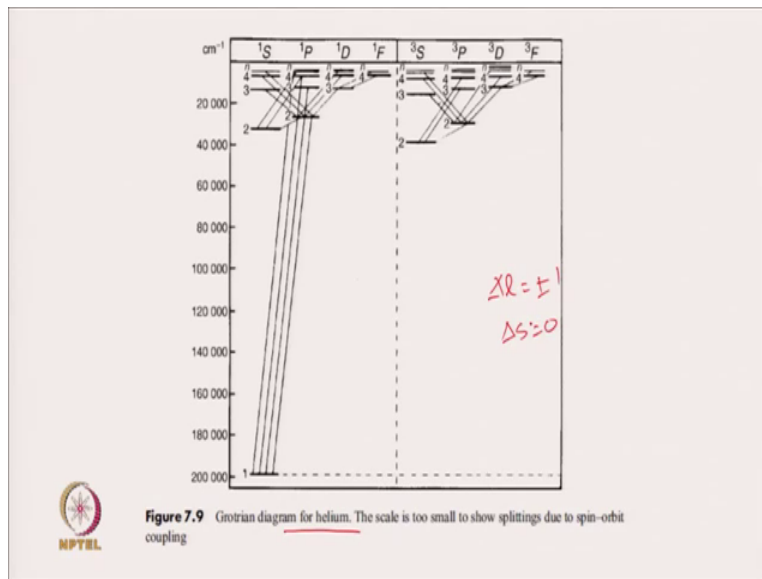Now selection rule for spectra of helium and alkaline earth metals. So selection rule for spectra for helium, alkaline earth metals are delta l is plus-minus 1 for promoted electron and delta s is equal to 0.

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Figure 7.9 Grotrian diagram for helium. The scale is too small to show splittings due to spin-orbit coupling

And so this is your, this what you known as Grotrain diagram for helium and this is your, you can see that delta l is plus-minus 1, delta n it can go anywhere, delta s would be 0 and so you have a different kind of spectra.
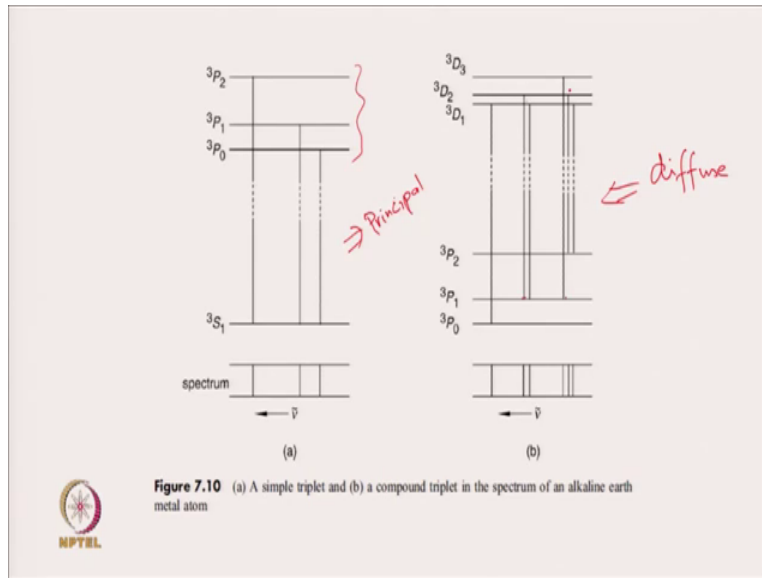
Figure 7.10 (a) A simple triplet and (b) a compound triplet in the spectrum of an alkaline earth metal atom

 Now this is alkaline earth metal again you see 3 s1 and now 3p is now you have 3p 0, 3 p1, 3p 2 and for p to d, so this is your, you can say this is principle and this is transition associated with the diffuse series, diffuse series and you can see that all 3 transition are possible because you are going from 0 plus-minus 1. Here there is only one possibility, from this place there is 2 transition possible and from this state there are 3 transition possible. So once you know the selection rule it is quite easy to know how many transitions are possible and that can tell you about how does the spectra of different metals look like.

So thank you very much for listening, I have taken a lot of material from this modern spectroscopy by Hollas and mathematical equations has been taken from Fundamentals of Molecular Spectroscopy by Banwell. So I will like to stop here and see you in the next class. Thank you very much.