Lecture – 35
Excited States of Many Electron Atoms

We have talked about ground states of many electron atoms helium and lithium to be more precise. Now we talk about the excited states. Why is it that we must talk about excited states? First of all, let us not forget that one of the beginnings of quantum mechanics is in spectroscopy and spectroscopy involves transitions between ground and excited states. Secondly, well may be not secondly another way of saying it is that all the color that we see all around us.

We live in a colorful world. All the color that we see is because of transitions involving ground and excited states. Finally, it is not only color, but lot of reactions that take place. The very fact that we see is something that involves excited state. Photosynthesis something that we are all familiar with involves excited state processes. So, it is not sufficient to restrict our discussion to ground states, we must understand excited states as well.

Of course building descriptions for excited states is much more complicated than ground states, but what we achieve to what we try to do in this course our goals are not very, very high. We will able to do it and get an idea of what exactly is done and on a lighter note we often do things better when we are excited same holds for atoms and molecules. Many times they do things better whatever they are supposed to do when they are excited by absorbing light. So, that leads to all the photochemistry around us. Let us not neglect excited states let us learn how to study that.

(Refer Slide Time: 02:14)

Spin Orbitals and their linear combinations

Two electron system (electron labels: 1 and 2): **four** spin functions

Which witch is which?

✔ $\alpha(1)\alpha(2)$ ✔ $\beta(1)\beta(2)$ $\alpha(1)\beta(2)$ ± $\beta(1)\alpha(2)$

1 and 2: **indistinguishable**   **Linear combination**

Exchange Operator
$$\Psi(1,2) = \pm\Psi(2,1)$$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$
Symmetric

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$
Anti-symmetric

But before going there what we have learned so far is about spin orbital. Spin orbital let me for once define a spin orbital because I do not think I have said it so far. A spin orbital is one electron wavefunction incorporating the spin part that is as simple as that not rocket science, but it is important to not forget in an orbital is for the N + 1th time of one electron wavefunction.

A spin orbital in addition to having the spatial coordinates for the electron wavefunction also has the spin part. So, for two electron systems we have learned that we can have a 4 spin function alpha 1, alpha 2, beta 1, beta 2, but we cannot have alpha 1 beta 2 and beta 1, alpha 2 by themselves because we cannot distinguish between electron number 1 and electron number 2.

So, we cannot say for sure that it is electron number 1 and not electron number 2 that has alpha spin we cannot say for sure that it is electron number 2 and not electron number 1 that has beta spin. So, the best we can do is we can take linear combinations and while taking linear combinations there is no reason why we should stick only to plus. A linear combination connecting the 2 terms by a minus sign is equally acceptable so we have to take that as well.

And we have said that if you use exchange operator just interchange the labels then the wavefunction with plus is symmetric with respect to exchange, the wavefunction with minus is anti-symmetric with respect to exchange.

(Refer Slide Time: 04:00)

6th Postulate of Quantum Mechanics

The complete wavefunction of a system of identical fermions (e.g. electrons) must be anti-symmetric with respect to interchange of all their coordinates (spatial and spin) of any two particles

$$\Psi(1,2) = -\Psi(2,1)$$

He atom wavefunction:

$$\psi_{He} = \psi_{1s}(1) \cdot \psi_{1s}(2) \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

What if the two electrons in **1s** orbital had same spin?

$$\psi_{He} = \psi_{1s}(1) \cdot \psi_{1s}(2)\, \alpha(1)\alpha(2)$$

$$\Psi(1,2) = +\Psi(2,1) \quad \textbf{NOT ALLOWED}$$

Pauli exclusion principle

The reason why we worry about whether the functions are symmetric or anti-symmetric with respect to exchange is Pauli principle or 6th postulate of quantum mechanics which says that for fermions like electrons the complete wavefunction of the system must be anti-symmetric with respect to exchange. So psi of 1 and 2 must be equal to – psi 2, 1. If you interchange the labels 1 and 2 the wavefunction must change sign.

So what we are saying then is that if the 2 electrons in 1s orbital has same spin then we would end up getting the functions psi s1, psi s2, psi 1 s1, psi 1 s2 multiplied by alpha 1, alpha 2 which gives us psi 1, 2 would be equal to psi 2, 1 is not allowed. So that is what leads to Pauli Exclusion Principle.

(Refer Slide Time: 04:59)

Many Electron Atoms: Determinantal Wavefunctions

$$\psi = \frac{1}{\sqrt{N!}}
\begin{vmatrix}
\phi_1(1)\alpha(1) & \phi_1(1)\beta(1)\dots & \phi_m(1)\beta(1) \\
\phi_1(2)\alpha(2) & \phi_1(2)\beta(2)\dots & \phi_m(2)\beta(2) \\
\vdots & \ddots & \vdots \\
\phi_1(n)\alpha(n) & \phi_1(n)\beta(n)\cdots & \phi_m(n)\beta(n)
\end{vmatrix}$$

Slater determinant

$$\psi(Li) = \frac{1}{\sqrt{3!}}
\begin{vmatrix}
1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\
1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\
1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3)
\end{vmatrix}$$

If any two rows/columns are **same**, then the determinant becomes **zero**.
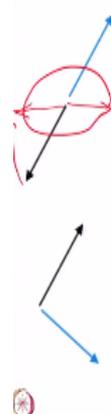⇒no two electrons occupy the same spin orbital.
Pauli Exclusion Principle

And we have sort of taken this idea forward a little more by looking at Slater determinants of bigger atoms as well. This is where we stopped in the last module.

(Refer Slide Time: 05:14)

Helium Atom: Excited States

If the second electron is in the *2s* orbital then it could have the same spin or the opposite spin.

He excited state $1s^1.2s^1$

$$\frac{1}{\sqrt{2}}\left[1s(1)\cdot 2s(2)+1s(2)\cdot 2s(1)\right]\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\frac{1}{\sqrt{2}} \quad (S=0; M_S=0)$$

He excited state $1s^1.2s^1$

$$\frac{1}{\sqrt{2}}\left[1s(1)\cdot 2s(2)-1s(2)\cdot 2s(1)\right]\left\{\begin{array}{ll} \alpha(1)\alpha(2) & (S=1; M_S=1) \\ \left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]\frac{1}{\sqrt{2}} & (S=1; M_S=0) \\ \beta(1)\beta(2) & (S=1; M_S=-1) \end{array}\right.$$

Now, let us talk about the excited states of helium. So, let us start with an electron configuration. What is a state? A state at least as a first approximation is determined by the electron configuration. So, we are going to have some excited state corresponding to say 1s 1, 2s 1 configuration. As we will see a particular configuration can give rise to different states that we will see in a moment, but let us start.

How do I write a wavefunction for a state with electron configuration 1s 1, 2s 1 I can write 1s then 1 in brackets multiplied by 2s 2 in brackets. The problem is what this implies once again is that it is electron number 1 in 1s orbital. Electron number 2 in 2s orbital and not vice-versa. Who has told you that this is going to be the case? As I said earlier electron numbers 1 and 2 are indistinguishable, 1 and 2 are labels that we are using to formulate the mathematical problem.

So, if we just write 1s 1, 2s 2 then our description would be incomplete. We must write 1s 2, 2s 1 as well and then as we have done in the earlier scenario we have to take plus and minus combinations of these two wavefunction. So, since we cannot say which, which is; which again this is becoming a cliche we have to consider this. This wavefunction with a plus sign and also this wavefunction with a minus sign.

So right away you see that corresponding to a single electron configuration for helium excited state 1s 1, 2s 1 I have generated 2 wavefunctions only while considering the spatial part. I have not even talked about spin yet only by spatial part I have constructed 2 wavefunction and it is not very difficult to see that the first one is symmetric and the second one is anti-symmetric. Now knowing Pauli principle our job should be simple.

We know that the total wavefunction has to be anti-symmetric. Now see a symmetric function multiplied by another symmetric function gives you a symmetric function and anti-symmetric function multiplied by an anti-symmetric function gives you a symmetric function. A symmetric function multiplied by an anti-symmetric function or vice-versa gives you an anti-symmetric function.

So now see in order to ensure that the total wavefunction is anti-symmetric the symmetric spatial part must be multiplied by an anti-symmetric spin part. Now you might remember what the spin wavefunctions are for a 2 electron system. Remember, we had said you can write alpha 1, alpha 2 or you can write beta 1, beta 2. You can write 1 / root 2 alpha 1, beta 2 + beta 1, alpha 2 and you can write 1 / root 2 alpha 1, beta 2 – beta 1, alpha 2.

Wait now these 3 wavefunctions are symmetric with respect to exchange. This known wavefunction is anti-symmetric with respect to exchange and here the spatial part is symmetric. So, in order to have an anti-symmetric total wavefunction it is imperative that the spin part has to be anti-symmetric. So the only choice we have for this spatial part is this alpha 1, beta 2 – beta 1, alpha 2 function.

This is called S = 0 MS = 0 state we will come to that shortly, but before that let us see what happens for this spatial part where there is a minus sign. This itself is anti-symmetric. So, we have to multiply it by one of the symmetric functions, we can multiply it by alpha 1, beta 1 what am I saying.

We can multiply it by alpha 1, alpha 2 or beta 1, beta 2 or alpha 1, beta 2 + beta 1, alpha 2 multiplied by 1 / root 2 all these 3 functions can be multiplied. So what do you do? What do you get? From the symmetric spatial part, we generate a single wave function. From the anti-symmetric part, however, since we have 3 symmetric spin parts. I will generate 3

wavefunctions by multiplying this single spatial part by one of the 3 different symmetric spin parts of the wavefunction.

And then this is going to be called the collection is called S = 1 the first one is called S = 1, MS = 1 state. Second one is S = 1 well capital S = 1 capital MS = 0 state. Third one is called capital S = 1 capital MS = - 1 state. What does all this mean? Well, before saying what all this means. Let us have a look and let us see whether it rings a bell. I have 2 quantum numbers A = 0, B = 0.

Then the next one is A = 1 and for A = 1, B = 0 and + - 1. Have you encountered the situation somewhere? Of course we have. Remember, J and M rigid rotor, remember L and M hydrogen atom same thing when L = 0 ML has to be equal to 0. When L = 1, ML can be 0 + 1 or -1. So, same thing is there. So, what this capital S stands for really is a total angular momentum and capital MS stands the Z components of this total angular momentum.

Once again this is a quantum mechanical phenomenon completely. However, as I told you it is strange, but it is true that when you talk about spins you can actually get most of the things done by using a very simple classical vector model where you just draw the angular momentum as an arrow of appropriate length. So, how do I depict this S = 0 state? Well, first of all I draw this arrow up spin.

Now remember the angle, the angle is same for all electrons. Now, when electron number 1 has alpha spin, electron number 2 has beta spin and vice-versa we have to look at individual term. So how do I depict this individual first tem when electron number 1 has up spin, electron number 2 has down spin and in order to get S = 0. S you can think is a vector sum of the angular momentum of the 2 spins.

So, these two have to be disposed along a straight line. Yes, so what I am saying is that if this is angular momentum vector for electron number 1 this is the angular momentum vector for electron number 2. Do not forget that their 5 values are not defined. In the classical picture they are assumed to be precision like this. I do not like to confuse students by invoking this precision business too much, but if you understand better.

Well, I am saying is that it is both the up spin and the down spin of electron numbers 1 and 2 are actually delocalized over all possible values of phi, but then delocalize in a correlated manner it is important to understand. Suppose, you could freeze and measure you would always find that the difference in phi between the angular momentum vector of 1 and angular momentum vector of 2 is 180 degrees.

Suppose, I for this situation I take projections on the x, y plane. Do not forget where the x, y plane is. It was something like this. This circle is in the x, y plane. Suppose, I draw up a perpendicular, I draw a projection of the spin angular momentum of electron number 1 and I draw projection of spin angular momentum of electron number 2. This 2 projections are going to opposite in direction in the x, y plane that is what it means they cancel each other.

So, of course if you take Z components then also one is up, one is down they will cancel anyway that is why $S = 0$ and if $S = 0$ what is MS? MS is also equal to 0 because if the length of the arrow that you get by vectors only 0 what will the Z component be? It has to be 0 and nothing else. Next, let us look at this $S = 1$ business. Here, the vector model is something like this. $S = 1$ means what? It means that the total length has to be 1.

We have to add up so the first one alpha 1, alpha 2 is like this. Beta 1, beta 2 is like this. What would be the Z component of this case? You added 2 remember this length is root 3 / 2 and the Z component is + 1 / 2. This length is root 3 / 2 Z component is + 1 / 2, 1 / 2 + 1 / 2 what do you get? You get + 1. Of course you might ask if this is root 3 / 2 this is root 3 / 2 we just add them you get root 3 and not 1 so that problem is actually there.

But do not forget this is a very qualitative classical picture, but Z component is easy to understand. Z component is definitely going to be 1. In this case, it is not difficult to see that Z component is going to be – 1. Now, if you draw like this then you will get some component along the X direction or whatever plane these two vectors are in. So S will still be equal to 1, but MS has to be 0 because the vector sum is going to along say X axis or Y axis or somewhere in the x, y plane Z component will be 0.

So this is roughly we have not really done the vector sum in very great detail, but roughly this is what the picture is this is why you call them capital $S = 0$, capital $S = 1$ and so on and so forth. We are going to come back to this later on in a little more detailed manner.

Helium Atom: Excited States

If the second electron is in the **2s** orbital then it could have the same spin or the opposite spin.

He excited state $1s^1.2s^1$ (**singlet**)

$$\frac{1}{\sqrt{2}}\left[1s(1)\cdot 2s(2)+1s(2)\cdot 2s(1)\right]\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\frac{1}{\sqrt{2}} \quad (S=0; M_S=0)$$

He excited state $1s^1.2s^1$ (triplet)

$$\frac{1}{\sqrt{2}}\left[1s(1)\cdot 2s(2)-1s(2)\cdot 2s(1)\right]\begin{cases} \alpha(1)\alpha(2) & (S=1; M_S=1) \\ \left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]\frac{1}{\sqrt{2}} & (S=1; M_S=0) \\ \beta(1)\beta(2) & (S=1; M_S=-1) \end{cases}$$

But for now we have without saying it learned a very, very important concept. See, when this spatial part is symmetric. As we said earlier the single anti-symmetric part has to be multiplied by it to get the total wavefunction. Since you get only one wavefunction for the spatial part this is called the singlet wavefunction. The state described by it is called the singlet state.

What about this? Here, the spatial part has minus sign fine, but you still have 1s, 2s orbital. Does it matter whether electron number 2 or electron number 1 is in orbital 1s or orbital 2s it does not. So this energy of this state where the sign here is minus is going to be exactly the same as the energy in this state. Unless, you want to consider the energies unless you consider that there is interaction between spin and all that, that is not there so we do not have to worry about that.

Just think of the spatial part, think of Schrödinger equation. We could solve Schrodinger equation. Here we have one electron in 1s, one electron in 2s orbital same thing here. Look at the configuration they are the same so energies are same. So energies of these things are same and then the energies of these 3 wavefunctions is definitely going to be the same because the sign here is different from what it is here.

Are you saying the energy of singlet and triplet are same? Actually no from whatever we have discussed so far maybe you think the answer is yes and from what I said, but one thing we have not mentioned so far is what is the effect of spin to be considered while talking about

energy. For that, let me remind you once again something that we have studied in high school.

Remember Hund's maximum multiplicity rule states that have a greater multiplicity have a lower energy everything else being the same. Here you see which one has greater multiplicity this one has greater multiplicity. You might have studied multiplicity as 2s + 1 and here the 2s + 1 this is the edge that you talk about the 2s + 1 in this case is 1, 2s + 1 in this case is 3 not very difficult to see this is what you have learned.

But what I am saying is that the singlet and triplet actually has got to do with the total number of wavefunctions associated with the states. For a singlet state where capital S = 0 you have only one single wavefunctions. For a triplet state where capital S = 1 MS varies you have 3 wavefunctions that is why it is called triplet and remember triplet has a lower energy because of Hund's rule it will suffice if we say that right now is actually little more complicated than that, but right now we do not have to get into it. So, we have learned this very important concept of singlet and triplet states and perhaps the stakes are understandings a little beyond this 2s + 1 business.

(Refer Slide Time: 21:24)

Now, let us try to write the wavefunctions and let us see whether we can use our old friend Slater determinant to write the wavefunction of the excited states. To start with, let us focus on one of the triplet wavefunction. I start with this because the answer is simple and since we are not doing it for the first time we know already that the answer is going to be simple. The answer here is going to be more difficult because you see that there are 2 terms.

So here I have 2 terms I am multiplying it by another factor with one term so I am going to get 2 terms here I will get 4. So let us start one by one 1s 1, 2s 2 – 1s 2, 2s 1 multiplied by alpha 1, alpha 2. We will have 4 terms sorry we will 2 terms each term will consist of 4 factors let us work out the first one. 1s 1, 2s 2 alpha 1, alpha 2. So, we can write it as a determinant.

We will write it as a determinant and we will write it in such a way that the determinant we write is going to be Slater determinant. So what happens in Slater determinants? What changes when you go from left to right in a row what changes when you go from top to bottom in a column I hope you remember. In one case a label changes in one case a spin orbital changes.

So let me write what will be 1, 1 element be? The term I have is 1s 1, 2s 2, alpha 1, alpha 2 so we start with the lowest energy. So we will write 1s 1, alpha 1 here and in the diagonally opposite one we will write 2s 2 alpha 2. Since we are going diagonal your label as well as spin orbital both change. So this is what we will write 1s 1 alpha 1, 2s 2 alpha 2. What will I write here and what will I write here?

What changes when you go from left to right in Slater determinants, what changes when you go from top to bottom. When you go from top to bottom we write the same spin orbital change the label. When you go from left to right you change the spin orbital and keep the label. So this is the Slater determinantal form of the wavefunction for the 3, 1 state. State in which capital S = 3 and MS = 1.

Now I would like you to pause the video, work out the determinant for this one actually I do not want you to pause the video without pausing you should be able to tell me what the answer is. What would the answer be exactly the same treatment right instead of alpha we have to write beta. So the answer is similar determinant wherever there is alpha we write beta that is your psi 3 – 1 state.

Wavefunction for the state in which capital S is 3 so triplet and the Z component of the angular momentum, total angular momentum is -1. Second one, now we are going to have not 2, but 4 terms. So, we are going to have to write a sum of 2 determinants, but then in every

term we have we still have 4 factors. So I can still write 2 / 2 determinants. Let us see what we get if we try to write this as a sum or difference of 2 determinants.

Now I want you to pause the video really and see whether you can write it in such a way that you get a linear combination of 2 Slater determinants. Can you do it please? I hope you have done it. I hope you had stopped this video and you have done it and let us see if you have got the right answer this is the answer 1s 1 alpha 1, 2s 2 beta 2 – 1s 2 alpha 2, 2s 1 beta 1 + 1 / 2 into 1s 1 beta 1, 2s 1 alpha 1, 1s 2 beta 2, 2s 2 alpha 2.

Slater determinants right when you go from left to right you keep the label when you go from top to bottom you change the label. So this is what you get for the triplet state for the alpha, alpha, beta, beta functions you get Slater determinants. For the alpha, beta + beta, alpha function you get a sum of 2 Slater determinants.

(Refer Slide Time: 26:16)

To conclude this discussion let us see what we are going to write for the singlet wavefunction. As you see the singlet wavefunction is almost identical well almost identical is little oxymoronic. The singlet wavefunction is very, very similar to the S = 1, MS = 0 wavefunction. What is the difference? The difference is instead of plus here there we had a minus instead of minus here we had a plus that is all.

So, this will also be a linear combination of 2 determinants this is what it is going to be. Please workout yourself these things you can understand only when you practice by yourself. Now let us compare the wavefunction for the 1, 0 state to that of the 3, 0 state what do we

get? Why have I written 1, 0 it is actually 0, 0 sorry this is 0, 0 psi 0, 0 state and psi 3, 0 state. Same Slater determinants in the psi 0, 0 case your minus sign between them in psi 3, 0 case you have a plus sign between them that is what makes a difference.

(Refer Slide Time: 27:35)

Helium Atom: Excited States

Spin-orbital wavefunctions
are represented as
Slater determinants
or their **sums**

So what we have managed to learn is that we can write spin orbital wavefunction for multilateral atoms as Slater determinants or there it is better to say linear combinations and this is an extremely useful way of writing wavefunctions and it is also the starting point of more sophisticated treatment of multi electron systems. So, that is what we are going to discuss now and that is where we are going to enter the next phase of quantum mechanics.

Because all these interactions are going to make thing so complicated that we have to invoke approximations. So far we have used approximations, but they have been very, very simple ones. Next, we are going to talk about little more vigorous applications again vigorous application sound strange. We are going to talk about more systematic detailed thorough approximation methods that have commonly used in quantum mechanics.

We are going to talk about the variation method and we are going to discuss perturbation theory. Somewhere down the line if time permits, it fits in I really would like to talk a little more about angular momentum until then.