Quantum Chemistry of Atoms and Molecules
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Lecture 34
He atom wavefunction

Actually I thought all these materials will be complete in one module, but as usual my estimate was not right. So we will just start from here, it is okay. So see, we are talking about helium atom wave function.

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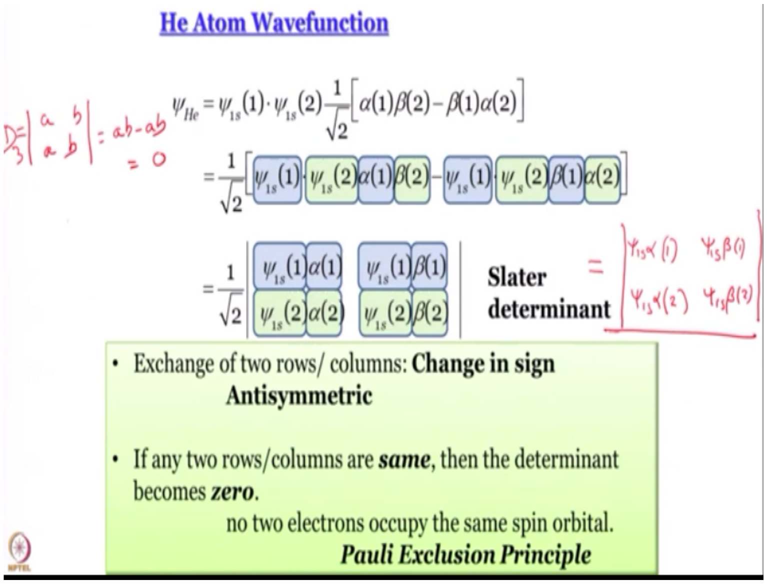

He Atom Wavefunction

$$D_3 = \begin{vmatrix} a & b \\ a & b \end{vmatrix} = ab - ab = 0$$

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

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

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(1)\beta(1) \\ \psi_{1s}(2)\alpha(2) & \psi_{1s}(2)\beta(2) \end{vmatrix}$$

Slater determinant $= \begin{vmatrix} \psi_{1s}\alpha(1) & \psi_{1s}\beta(1) \\ \psi_{1s}\alpha(2) & \psi_{1s}\beta(2) \end{vmatrix}$

- Exchange of two rows/ columns: **Change in sign**
  Antisymmetric
- If any two rows/columns are ***same***, then the determinant becomes ***zero***.
  no two electrons occupy the same spin orbital.
  Pauli Exclusion Principle

Many electron atom wave function and we have learnt this elegant way of writing the wave function in the form Slater determinant. Let us have a look at this slater determinant. Look at the first row. What is constant and what is varying? Electron number is constant, is not it? Psi 1s1 alpha 1 psi 1s1 beta 1. What has remained same is the electron number and what has changed, even psi 1 is the same. What has changed is from alpha we have gone to beta.

So if you look at the whole thing, what has really changed is your spin orbital. Similarly, in the second row, go from first column to the second one. Electron number remains 2, but from psi s2 alpha 2 psi 1s2 alpha 2, we go to psi 1s2 beta 2. So on going from left to right in Slater determinant, these spin orbital changes and the electron label remains the same and upon going from top to bottom, then what happens psi s.

Let us look at the first column now psi 1s1 alpha 1 psi 1s2 alpha 2. So psi 1s alpha that is your spin orbital. That has remained same when you went from top to bottom. What has changed is the electron label has changed from 1 to 2 and same here. So for the record, let me write that in many textbooks, Slater determinant is written in a slightly different way. It means the same, so you should not get confused, but very often the same thing would be written like this.

So you write psi 1s alpha and then write 1 psi 1s alpha, then write psi 1s alpha 2 and this one is psi 1s beta 1. This is psi 1s beta 2. This is another way of writing the same thing, matter of convention nothing else. Please do not get confused if you read a textbook that uses this kind of notation instead of this and you can see the mean exactly the same, but in one way the second way of writing is better, because here it is very clear psi 1s alpha psi 1s alpha.

Same spin orbital you have changed from 1 to 2. Here also psi 1s beta psi 1s beta, you have only changed from 1 to 2 and go from left to write 1 is same, psi 1s alpha has become psi 1s beta. So maybe this is actually easier to read, but we are going to follow this convention for now. What is the advantage of writing the wave function all of a sudden in terms of a determinant. First of all, as we are going to say very soon, eventually when you talk about complex systems, atoms or molecules, you have to use computers.

Computational chemistry is a very, very big field nowadays, not nowadays and it has been very, very big field for several decades now, because you cannot do all these calculation by hand. You want to find energy, right now we are working within the ambit of orbital approximation. As you will see, there are ways to actually generate this wave functions without resorting to 1s 2s also. Then, you might want to relate them; that is a different issue. How do you do all that?

All that is done using computer and computer can work only when you give it the input in a very nice manner or if you let it provide the outputs in nice organized manner. That is why matrices determinants, these things come very handy, because they are essentially data arranged in array forms. That is one thing. Second thing, very elegantly something nice comes out.

If you go back to the properties of determinants in mathematics, those of us who has studied determinants in mathematics would know that if you exchange two rows or two columns, the determinant changes sign; not very difficult to understand, because determinant means if you write a, b, c, d, it is ad – bc, just interchange. It is going to change sign obviously. Let u say I am talking about this determinant a, b, c, d.

Forgive me for writing da, I am feeling lazy and do not want to erase da d are the same, minus bc. Now suppose, I just interchange the two rows, then what happens, write cd first row ab in the second row. What do you get, bc minus, since I have written da there I will write da. You see what happened. If you call this d1 and you call this d2, then obviously d2 = -d1. Satisfy yourself by interchanging the two columns that the same thing happens once again.

So exchange of two rows or two columns leads to change in sign of denominator. So what, which means that they are anti-symmetric; now we are talking. Remember our total wave function has to be anti-symmetric. So in any case, in whichever form we write, we are working with wave functions, but now by property of determinants, you are always going to get anti-symmetric functions. So you cannot make a mistake while writing.

By mistake, I write +1 here, the determinant will not be the same. We cannot write the determinant that way. So that is where, we will understand that we have made a mistake. So since the determinants change sign upon exchange of two rows or two columns, when you write the wave function in the determinant form you are assured that you have written an anti-symmetric wave function. You do not have to worry.

Another property is if any two rows. If any two rows are the same or two columns are the same, then the determinant becomes 0. Once again, since we have promised some of the students to do things from scratch by and large, we will do it. Here I have a matrix; I call them d1 d2 so determinants are not matrix or a determinant. I have this bad habit of referring to determinants as matrices. Please do not get confused.

As far as this part is concerned, we are only dealing with determinants. So if I say matrices, please correct yourself and understand that I am talking about determinant. Sometimes, I am sufficiently careless to use these terms, interchangeably, but you do not do it. So I call this determinant d3. What are we saying? We want to prove that if any 2 rows are the same or any 2 columns are the same, then the determinant is 0. So let us write 2 rows to be the same.

What do I get, ab – ab obviously that is equal to 0. So if 2 rows are the same or 2 columns are the same, you do the column, you would write a determinant with 2 identical columns and satisfy yourself that this holds, the determinant becomes 0. That leads to something very, very interesting and something that we are familiar with something that we have been using axiomatically all the time. So going there let me remind you where we started from.

We started from pauli principle or this 6 rule of quantum mechanics, 6 postulate of quantum mechanics, which said essentially that for fermions like electrons, the total wave function has to be anti-symmetric. Since it is anti-symmetric you can write in determinant form. Now since in a determinant if 2 rows are the same or 2 columns are the same that your determinant becomes 0, it is essential that no 2 electrons can occupy the same spin orbital.

What am I saying here? No 2 electrons can occupy the same spin orbital, so what is the meaning of 2 electrons occupying the same spin orbital. So it will be psi 1s alpha 1 and psi 1s alpha 2 at the same time and the other one will be psi 1s beta 1 and psi 1s beta 2 simultaneously. So you try and do that, you will get a 0 determinant. That is what needs to all be very familiar Pauli exclusion principle.

Pauli exclusion principle, what we might have learnt earlier excludes the possibility that in a particular atom, the 2 electrons can have all 4 quantum numbers at the same. If n, l, m are same at least ms has to be different. This is what we studied qualitatively. What we are saying now in a little more quantitative manner is that no 2 electrons can occupy the same spin orbital. If electron number 1 occupies psi 1s alpha spin orbital, then electron number 2 must necessarily occupy psi 1s beta.

Otherwise you get a 0 determinant, which means the wave function is 0. If wave function is 0, then probability density and therefore probability of finding the electron anywhere is 0 and then what are we talking about. So very beautifully, using this concept of Slater determinants, we arrive at Pauli exclusion principle. So that is one great thing, but I have made things, I have kept things very, very simple so far. We have only worked with helium. We have only worked with a 2-electron system.

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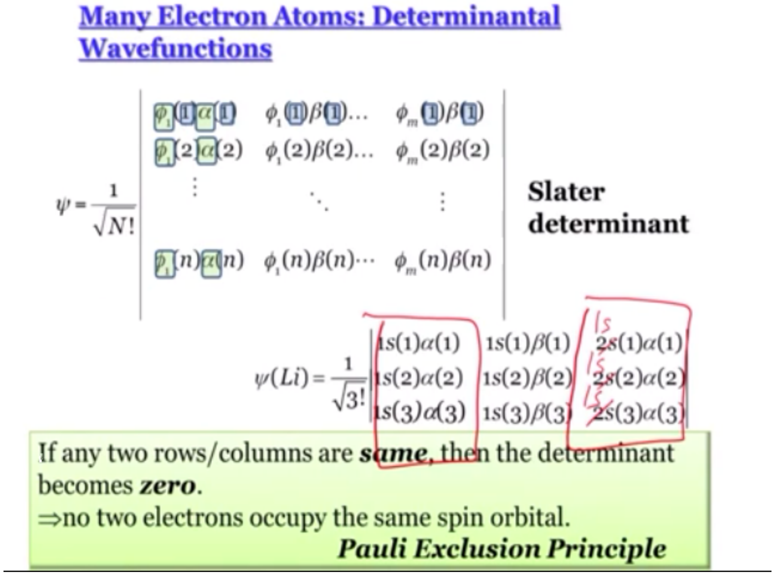

Many Electron Atoms: Determinantal Wavefunctions

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

Slater determinant

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

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

What happens if I want to include more electrons? For many electron atoms, you can write similar determinantal wave functions, which means you can write the wave functions as Slater determinant and here I have shown you one for an n electron atom. Let us see what the determinant would look like. Look at the first row. In the first row, we have kept, we label the same as usual and spin orbitals have changed from phi 1 alpha phi 1 beta.

Next one will be phi 2 alpha, next one will be phi 2 beta, so on and so forth. We were going to say something, what are we going to say. First of all two things, yes, now remember. First of all, why phi 1 alpha first, why not phi 1 beta? The answer is convention. We have to speak the same language. We do not want to create a tower of Babel where if you do not know what a tower of Babel is, just do a Google search. It is a beautiful biblical story that you can learn.

A tower of Babel essentially means where one does not understand the other person's language. So we must formulate things in such a way that you understand each other's language, so just convention. That is the need of convention. That is point number 1. That is why we write phi 1 alpha first and not phi 1 beta first. Point number 2, why is it that we keep the label constant while going from left to right in a row.

We might as well have kept label constant while going from top to bottom in a column. It is a determinant. Determinant will remain unchanged if we just transpose it. So why do not we do it? The answer once again is convention. See, Slater wrote it this way and Slater is a famous scientist after whom these determinants have been named. So until we become more famous than Slater and until the scientific community is agreeable to our convention over Slater's, we better follow Slater's convention.

That being said, there are textbooks, in which the opposite convention, transpose convention is used. Actually they are one and the same, but since we do not want to create a tower of Babel for the purpose of this course, let us write Slater determinants in this way. Upon going from left to right, the electron label remains the same in a row and the spin orbitals change going from lower energy to higher energy and upon going from top to bottom, the spin orbital remains the same.

Labels change from 1 to 2, to 3 and so on and so forth up to n. What is the last one here? This is phi m, why not phi n? Because remember each spin orbital, for any given orbital, I can generate 2 spin orbitals; one with alpha, one with beta. So m has to be less than n. So if m = n by 2, yes provided n is even. Understand what I am saying? Each so, phi 1 gives you 2 spin orbitals, phi 2 gives you 2 spin orbitals, phi 10 gives you 2 spin orbitals.

So up to phi 10, how many spin orbitals do we have? 20 and what will the value of m be, if n = 10? 10. Now what I am saying is that. Let me say that once again. I think I made a mistake. So let us say, I am working with a 10-electron system. So for 10-electron system, what will happen? You will have phi 1 alpha 1s and then next one will be phi 1 beta 1. Next we will have phi 2 alpha 1, next we will have phi 2 beta 1, then we will have phi 3 alpha 1.

Next we will have phi 3 beta 1 and so on and so forth. How far will we go? We have already accounted for 6 electrons when we went up to phi 3. So to account for 10 electrons, we have to go up to 5, m phi 5. So in this case, m = n by 2. What happens if n = 11, where will I stop? Phi 1 alpha 1, phi 1 beta 1, phi 2 alpha 1, phi 2 beta 1, phi 3 alpha 1, phi 3 beta 1, so on and so forth up to phi 5 alpha 1 phi 5 beta 1, so 10 electrons are accounted for, 1 is left.

Next one will be phi 61 alpha 1. So this m is going to be either n by 2 or n by 2 + 1 depending on whether n is even or odd. In the preceding couple of minutes, I might have said things that might have confused you a little bit, but you just do it yourself, it should not be difficult. It will not be difficult. So this is how we write Slater determinants. Let us show you one example for lithium, what will happen? How many electrons are there? 3.

You write like this 1s1 alpha 1 1s1 beta 1 2s1 alpha 1 then 1s2 alpha 2, so on and so forth. Finally, the third row is for electron number 3. Is this the complete wave function? This is something that I want you to take as homework. What I am asking is, this wave function I have written first of all is normalizeable. Secondly, is it complete or do I need some other term? I said that as a matter of convention I use alpha, but this beta is not equally probable.

How do I incorporate that, is there a need to incorporate that. These are things that I would like you to work out by yourselves, but to conclude this part of the discussion, this is what we have learnt that you can write it in determinantal form, any 2 rows or columns are same, then the determinant would become 0. Once again, I would like you to take this as homework. What I am saying is put electron number 3 in 1s orbital, then what happens.

Then this becomes electron number 3 in 1s orbital. So this 2s will be replaced by 1s everywhere. Then what happens? The first row and the third row, they become one and the same. What I am saying is the third electron, when I say electron number 3 that can be a little confusing for you, because you might think that I am talking about the label. I am not talking about the label. I am saying the third electron, in whichever way we have filled in, 123, 321, 213 whatever.

What I am saying is let us say that the third electron also goes to 1s. Then, this last column is going to become 1s1 alpha 1, 1s2 alpha 2, 1s3 alpha 3. Now what has happened? 1s1 alpha 1, 1s2 alpha 2, 1s3 alpha 3 is exactly the same as the first column. So the two columns are same. Therefore, the determinant is 0. So here we have shown that even for lithium, poly exclusion principle follows very nicely from this 6th postulate of quantum mechanics.

So we have learnt Slater determinant and we have learnt how to express the wave function of the ground state of helium and lithium using Slater determinants.

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Excited states of many electron atoms

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In the next module, we want to see whether we can extend this discussion to excited states of these atoms.