Concepts of Chemistry for Engineering
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Lecture No. 15
Molecular orbital theory 3: Homo-diatomic molecules-I

Having discussed H_2^+ this, now it is time for us to put in another electron and talk about the dihydrogen molecule.

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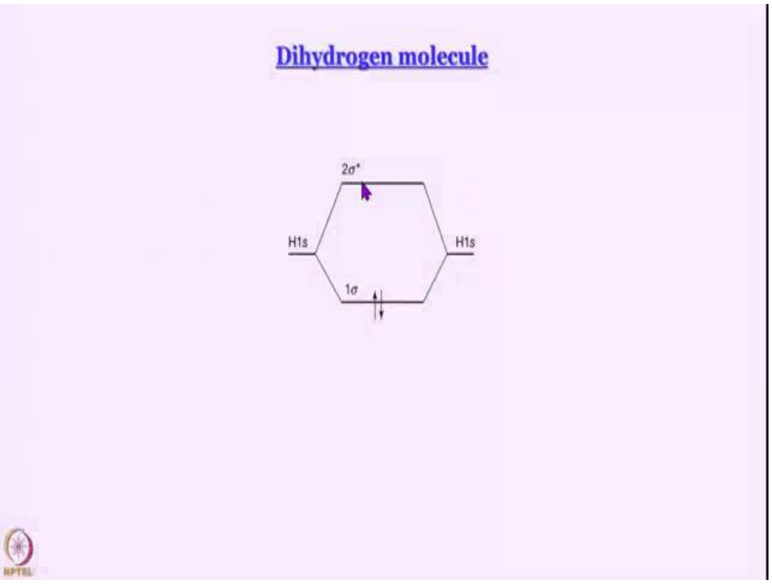

Dihydrogen molecule

And what you see here is an energy diagram, which I suspect all of us have seen earlier.

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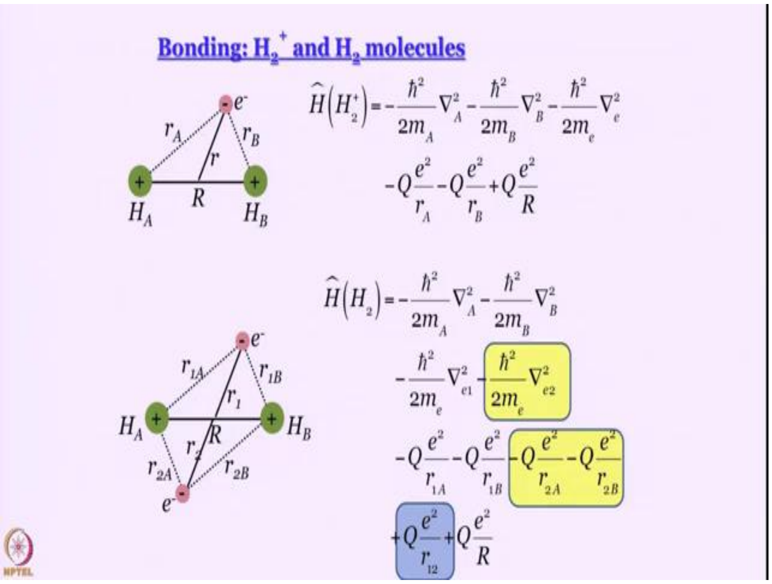

Bonding: H_2^+ and H_2 molecules

$$\hat{H}(H_2^+) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_A} - Q\frac{e^2}{r_B} + Q\frac{e^2}{R}$$

$$\hat{H}(H_2) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \boxed{\frac{\hbar^2}{2m_e}\nabla_{e2}^2} - Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} \boxed{-Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}}} \boxed{+Q\frac{e^2}{r_{12}}} + Q\frac{e^2}{R}$$

But just to remind ourselves, this is what we discussed already. We wrote down the Hamiltonian for the H_2^+ and there are already so many terms. When we introduce another electron, we have, we are going to get more terms here. First of all, the second electron is going to be attracted by nucleus A, by nucleus B and the two electrons are also going to repel each other.

So, these are the terms that come in. And one thing that I forgot to say just now is that we will also have a kinetic energy term for the second electron. So, you understand, it is impossible to solve this equation directly. You cannot solve it analytically. So, how do we go about building a quantum mechanical description of something as simple as a neutral dihydrogen molecule which has two electrons? This is how.

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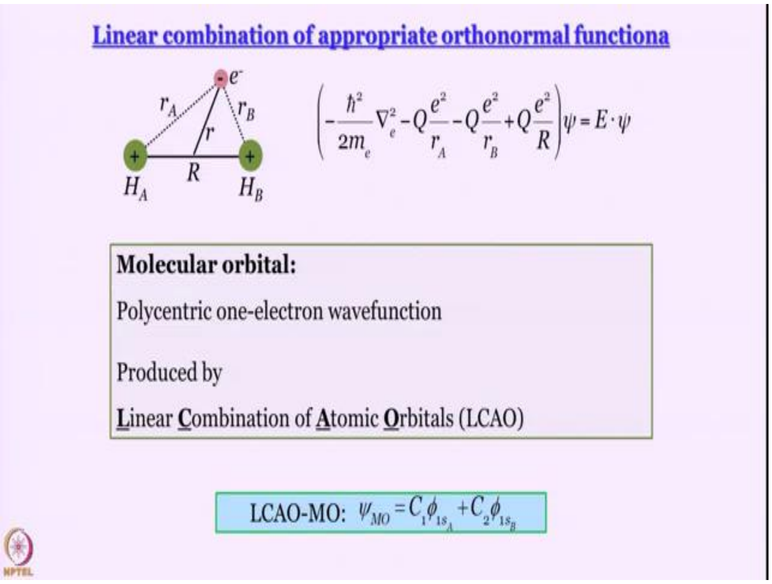

Linear combination of appropriate orthonormal functiona

$$\left(-\frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_A} - Q\frac{e^2}{r_B} + Q\frac{e^2}{R}\right)\psi = E\cdot\psi$$

Molecular orbital:

Polycentric one-electron wavefunction

Produced by

Linear **C**ombination of **A**tomic **O**rbitals (LCAO)

LCAO-MO: $\psi_{MO} = C_1\phi_{1s_A} + C_2\phi_{1s_B}$

We have already discussed that even for the cation, H_2^+, where in principle, we could have solved the Schrodinger equation using elliptical polar coordinates. We did not do that. Rather, we constructed the wave function by taking a linear combination of atomic orbitals. So, the wave functions are already there. What we will do, and this, incidentally, is the same strategy that is followed for many-electron atoms. There the same atomic orbitals that one obtains from a solution of the Schrodinger equation for the hydrogen atom is used with some modification for many-electron atoms. We will do the same thing for molecules here.

So, we are going to use the same molecular orbitals and as we bring in electrons, one thing that one needs to change eventually is the effective nuclear charge. So, in a very, very simple treatment, one needs to account for shielding and one can work out the energy. So, there are techniques for doing that. We will not get into that right now here. But what we are saying is that we will use the same LCAO molecular orbitals that we had obtained for H_2^+ even in the case of the dihydrogen molecule.

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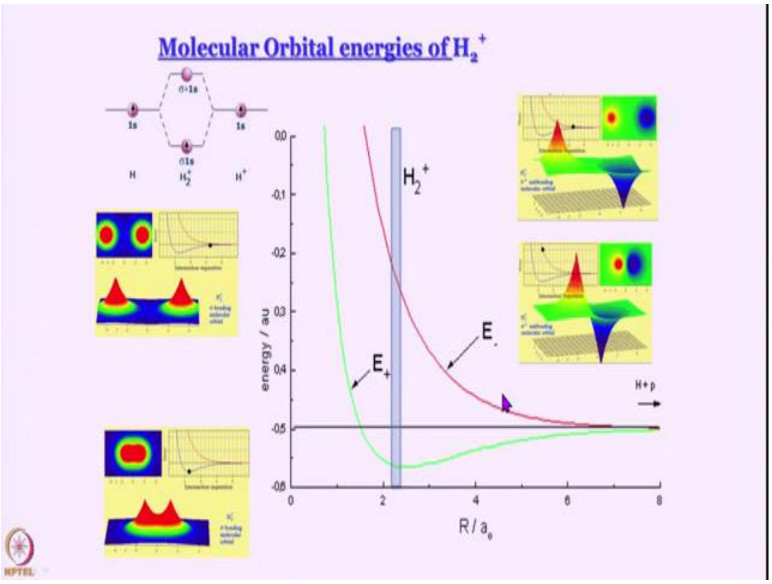

Molecular Orbital energies of H_2^+

And we are going to work with the same kind of energy level diagram, remember, the bonding molecular orbital has an energy that goes through a minimum and the internuclear separation where the minimum is obtained that is the equilibrium bond length. In the anti-bonding scenario, there is a monotonic increase as the internuclear separation keeps on decreasing. So, this here is the energy diagram for H_2^+.

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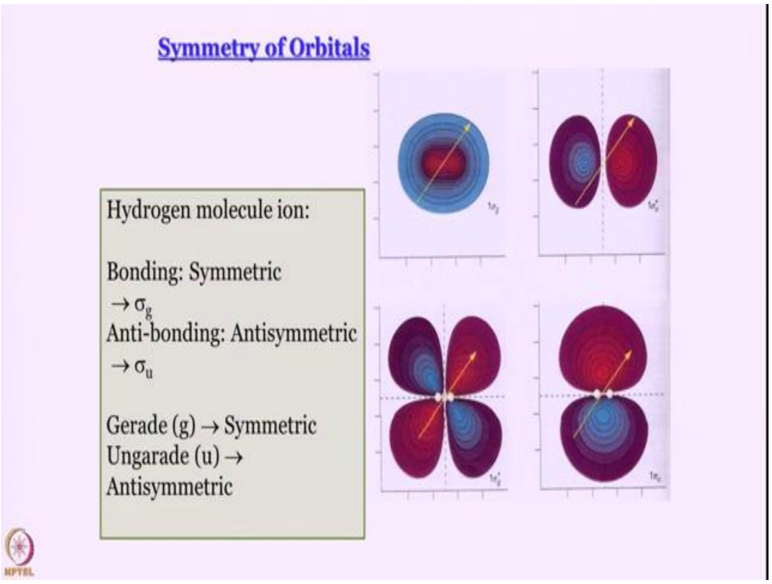

Symmetry of Orbitals

Hydrogen molecule ion:

Bonding: Symmetric
→ σ_g
Anti-bonding: Antisymmetric
→ σ_u

Gerade (g) → Symmetric
Ungarade (u) →
Antisymmetric

And another thing that we would better remember is the symmetries of the orbitals. If it is symmetric with respect to inversion, we call it gerade, we use a subscript g, if it is anti-symmetric, then we use ungerade u, and usually, for anti-bonding orbitals, we use the superscript *.

So, for σ orbitals, the bonding orbital, for σ orbital using s atoms, the ones that we have studied already, using σ orbitals, using s atomic orbitals that we have studied already, we get σ_g. Anti-bonding combination gives us σ_u^*. And in the case of π interaction, the bonding π orbital actually has ungerade symmetry and the anti-bonding orbital has gerade symmetry.

So, please do not think that bonding orbitals are necessarily gerade and anti-bonding orbitals are necessarily ungerade, they are not. And also we can use the subscripts g and u only for homonuclear diatomic molecules like H_2, like F_2, like N_2. If you want to talk about heteronuclear diatomic molecules, like say HCl or HF or HI, then you cannot use g and u anymore, because in any case, we are going to have an electron distribution that is not symmetric. We will talk about that later.

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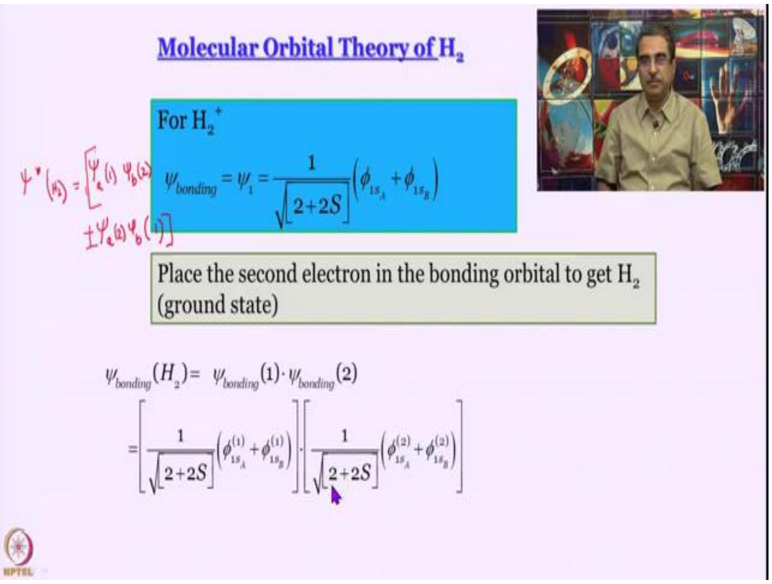

Molecular Orbital Theory of H_2

$\psi^{+}(H_2) = [\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)]$

For H_2^+

$$\psi_{bonding} = \psi_1 = \frac{1}{\sqrt{2+2S}}\left(\phi_{1S_A} + \phi_{1S_B}\right)$$

Place the second electron in the bonding orbital to get H_2 (ground state)

$$\psi_{bonding}(H_2) = \psi_{bonding}(1)\cdot\psi_{bonding}(2)$$

$$= \left[\frac{1}{\sqrt{2+2S}}\left(\phi_{1S_A}^{(1)} + \phi_{1S_B}^{(1)}\right)\right]\cdot\left[\frac{1}{\sqrt{2+2S}}\left(\phi_{1S_A}^{(2)} + \phi_{1S_B}^{(2)}\right)\right]$$

But coming back to the agenda of this lecture, we are trying to build a molecular orbital theoretical description of dihydrogen molecule. So, use the same orbital, same molecule orbital that we get for H_2^+. We do have some changes in the forms of the wave functions here. But for now, in this course, we are not going to discuss it.

So, all we have to do is that we place the second electron in the bonding MO. I think we are all familiar with the Pauli exclusion principle, as the in the form that we, most of us would have studied says that, in an atom, two electrons cannot have all four quantum numbers the same. It was down to the fact that each atomic orbital can accommodate at most two electrons.

Something similar folds, even though actually it is more complicated, but for now it is enough if you understand that like atomic orbitals, each molecular orbital can also accommodate no more than two electrons. So, we will place the second electron in the bonding orbital itself. And that is how we will obtain the ground state of the hydrogen molecule.

So, how do I construct the wave function now, I write like this. 1 and 2 are the labels for the electrons. What this product means is that electron number 1 is in the bonding orbital, electron number 2 is also in the bonding orbital, so ground state. What would happen if I want to draw, want to write the wave function for an excited state? I would write like this. And I am going to write in a little compact form here, ψ anti-bonding, I will just write $\psi^*_{H_2}$ excited state or rather I can write $\psi^*_{H_2}$ that is going to be, I will write, I will keep this a for later. ψ_a (1).ψ_b (2). But see that is not going to be enough.

Why is that not going to be enough, because who has told us that it is electron number 1 and not electron number 2 that is in the anti-bonding orbital. Electrons are indistinguishable. We are going to touch upon this again a little later, but electrons are indistinguishable. So, you cannot neglect the other term either, which is $\psi_a(2).\psi_b(1)$. Remember here ψ_a is the anti-bonding molecular orbital and ψ_b is the bonding molecular orbital.

So, you have to take linear combinations of the two and right away you see that I generate two different wave functions for the excited state, two different kinds of excited state. What is the application? Let us see. We discuss that a little later. I have actually not prepared slides for it, but maybe we can.

But now, one thing that is related here is when you write like this and this is the $\psi_{bonding}$ (H_2) . Well, $\psi_{bonding}$ (H_2) means the wave function, the spatial wave function for the molecule as a whole, $\psi_{bonding}$(1). $\psi_{bonding}$(2). Here these $\psi_{bonding}$ these mean actually molecular orbitals. It would have perhaps been better to write ψ_+ or something, but anyway that is how we have written it what to do. This is your spatial part. And you can easily open it out and you are going to get a constant of 1 by 2+2s. And inside the bracket, you are going to get four terms. We will come to that also.

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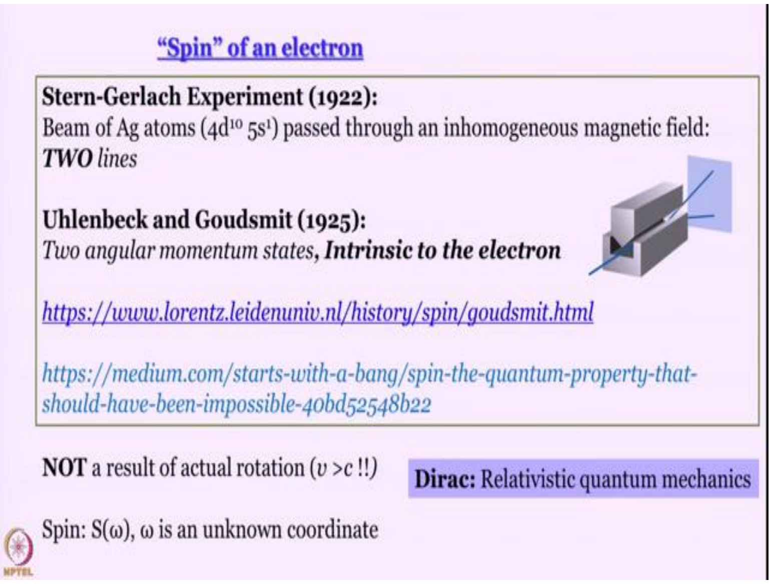

"Spin" of an electron

Stern-Gerlach Experiment (1922):
Beam of Ag atoms ($4d^{10}$ $5s^1$) passed through an inhomogeneous magnetic field: ***TWO** lines*

Uhlenbeck and Goudsmit (1925):
*Two angular momentum states, **Intrinsic to the electron***

https://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html

https://medium.com/starts-with-a-bang/spin-the-quantum-property-that-should-have-been-impossible-40bd52548b22

NOT a result of actual rotation ($v > c$!!)

Dirac: Relativistic quantum mechanics

Spin: S(ω), ω is an unknown coordinate

But before that, it is not enough, for a two electron system, it is not enough to talk only about the spatial part of the wave function. We have to take care of something else. Once again, we have heard about this quantity is a spin of an electron. The original spin of electron goes back to almost 100 years ago, where Stern and Gerlach performed this experiment in which they passed a beam of silver atoms through an inhomogeneous magnetic field. And then they obtained two lines. So, what was going on there?

To explain this, and that was the formative phase of quantum mechanics. So, Goudsmit, the way Goudsmit puts his story and that story can we actually read here and a more neutral account can be read in the second link here. So, Goudsmit and Uhlenbeck they sort of collaborated and they figured that the only way to explain these doublets, Goudsmit had this fascination for doublets, the only way they found, they could explain this kind of a doublet structure is by considering what they call the fourth degree of freedom for the electron.

And that fourth degree of freedom is the spin quantum number. n,l,m we have studied. From these experiments, it was understood that you need a fourth degree of freedom, a fourth quantum number, and Goudsmit actually thought that it is because of electrons that are spinning about their own axis, because see this is the time when old quantum theory is at its prime and new quantum theory is just about taking over.

So, they thought of extending the classical analog a little further. We know the Earth rotates about its axis and also revolves around the sun. So, they thought that maybe electron spins a little bit. And immediately this was, and they proposed, published a paper. Immediately it met with severe criticism of a lot of people like Pauli and Uhlenbeck himself was very, very uncomfortable.

So, because it was quite obvious by doing very back of the envelope kind of calculation that the kind of energies we are talking about, if it is due to spin of an electron, then the electron has to spin with a velocity that is more than the speed of light. Speed of the electron, linear speed of the electron has to be more than the speed of light, which is not going to happen.

Only later, when Dirac formulated his relativistic quantum mechanics, when I say later, I do not mean 20 years, 30 years later, but later than the first report. When Dirac combined his relativity theory with quantum mechanics in a more rigorous fashion, see relativity and quantum mechanics never diverged from each other. Even Sommerfeld's modification of Bohr theory was a relativistic correction. But it was still part of old quantum theory.

Dirac, using these four particular matrices, could bring in relativity and quantum mechanics in a much more rigorous fashion. And it was established that it is essential in that kind of treatment to consider something that some angular momentum which is beyond n,l,m, so this angular momentum is associated with something called spin for historic reasons, nothing else, but it is important to understand that it is not really arising out of a spinning electron. It is a spin with respect to some unknown coordinate s omega.

Does that sound very mysterious, enigmatic to the point of being unbelievable? If it sounds like that, you are not the only one who has felt that way. Anybody and everybody who is exposed to this for the first time would better feel this way. If somebody just accepts this, then that means that person is not thinking. It is a very disturbing thought. And to be honest, if you want to understand what exactly spin is you need to study an advanced quantum mechanics course, not with us chemists, but with physicists.

So, for now, we will take it axiomatically that there is an additional angular momentum associated with something called spin with the understanding that this pain is not really what we can think of the electron spinning like this. However, this angular momentum is such that you can do all the mathematics associated with it.

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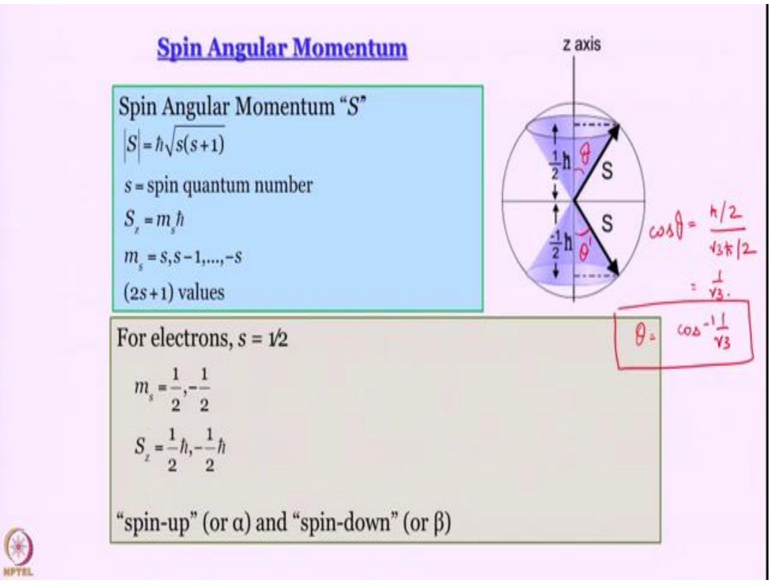

Spin Angular Momentum

Spin Angular Momentum "S"

$|S| = \hbar\sqrt{s(s+1)}$

s = spin quantum number

$S_z = m_s\hbar$

$m_s = s, s-1, \ldots, -s$

$(2s+1)$ values

For electrons, $s = 1/2$

$m_s = \frac{1}{2}, -\frac{1}{2}$

$S_z = \frac{1}{2}\hbar, -\frac{1}{2}\hbar$

"spin-up" (or α) and "spin-down" (or β)

$\cos\theta = \frac{\hbar/2}{\sqrt{3}\hbar/2} = \frac{1}{\sqrt{3}}$

$\boxed{\theta = \cos^{-1}\frac{1}{\sqrt{3}}}$

You can write the magnitude of the angular momentum "S" $|S| = \hbar\sqrt{s(s+1)}$ where s is the spin quantum number. Does that ring a bell? The expression is similar to the expression for the orbital angular momentum. When we did n l m, the Φ dependent part of Schrodinger equation hydrogen atom we obtained the magnitude of the angular momentum to be $L = \hbar\sqrt{l(l+1)}$, a very similar expression.

The difference is that l depends on which energy state the electron is in, in the hydrogen atom. What do I mean? L depends on n. N is what determines the energy state. So, if n equal to 1, l can be only 0, if n is equal to 5, then l can be 0, 1, 2, 3, 4, so on and so forth. So, that is what it is. However, take any electron, it has only one spin quantum number and that is half.

So, perhaps this is where some of us should object because we studied in 11th, 12th a electron can have a spin quantum number of plus half and minus half. My submission here is that that thing that we studied in the name of spin perhaps is not really spin quantum number it is m_s. Remember the magnetic quantum number that we studied n,l,m. Here this is an analogue of m. Since it is about, it is something to do with spin, we call it m_s, the magnetic quantum number associated with spin.

And that gives us an idea about the z component of the spin angular momentum, maddening, is not it. We are saying that the spin is about some imaginary coordinate, not about x, y, z, not about unknown, nothing. Yet, in real space, in Cartesian space, we can draw an arrow that can give us an idea of not only the magnitude of the angular momentum associated with spin, but also its orientation.

Why, because it is also associated with the magnetic quantum number m_s, which like the magnetic quantum number we have encountered earlier, can go from +s to -s. So, 2s+1 values would be there. Now, for all electrons in the universe spin quantum number is half. So, how many different values of m_s would be there, 2 (1/2)+1 that is 2. What are those two values, +1/2 and -1/2? What do they designate? They designate the z component of spin angular momentum that would be $\hbar$ multiplied by m_s.

So, for an electron, any electron, whether it is bound to an atom or whether it is free, you have two different kinds of z components of angular momentum is $\hbar$(1/2), -$\hbar$ (1/2). And since the length is specified h$\sqrt{s(s+1)}$ and the z component is also specified, this angle θ is specified as well. What is θ going to be? Well, that is not very difficult to figure out I think, cos(θ)is going to be, well, I am just working with this θ. You can obtain this $\theta'$by just subtracting the same value of θ from 180 degrees.

So, cos θ, what is cos $\theta=\frac{\hbar/2}{\sqrt{3}\hbar/2}$. $\sqrt{s(s+1)}$, remember, so that we are left with 1 by root 3. So, what is θ, $\theta=\cos^{-1}\frac{1}{\sqrt{3}}$. You figure out how much it is. I will not tell you. And when you figure it out, think whether you have encountered this quantity somewhere else or not. So, space quantization is there for the angular momentum associated with spin. Even though spin is not spin, spin is not an electron spinning about its own axis.

Very often, for the sake of understanding, you would see people discussing things in perspective of electron spinning, please remember that all that matters is angular momentum. We cannot really say that electron is spinning about this axis. So, this is what we have discussed. Only one more thing to say, the two wave functions associated with spin up or spin down that is Eigenvalues of $\hbar$(1/2), -$\hbar$ (1/2), they are α and β.

Can you write them out in some functional form like you did for hydrogen atom wave functions? No, you cannot. Because they are functions of Ω and we do not even know what Ω is. We just call them α and β and that is what we work with.

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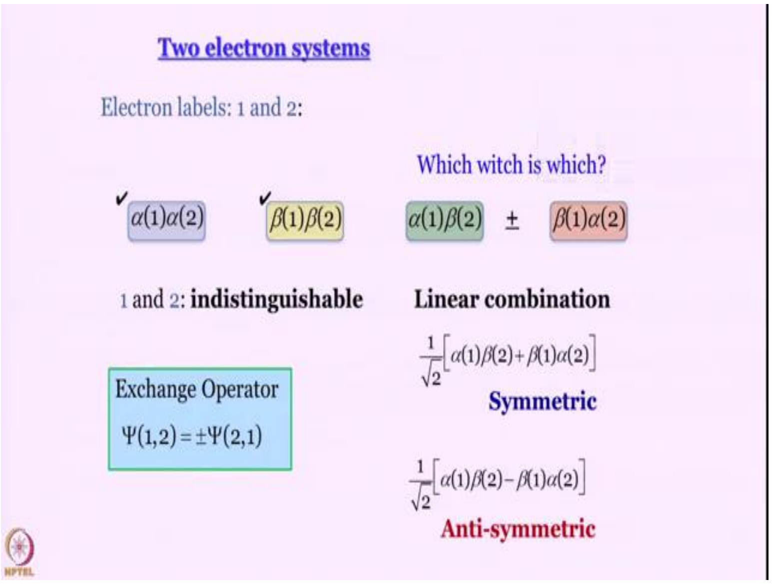

Two electron systems

Electron labels: 1 and 2:

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

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

Symmetric

Exchange Operator

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

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

Anti-symmetric

Why are you saying all this, because we are dealing with a two electron system. And in two electron system, we have used these electron labels 1 and 2. So, suppose both the electrons have up spin and this is experimentally determinable, then the spin wave function would be α (1), α (2), no problem with that. Similarly, both electrons have down spin wave function would be β (1), β (2). The problem arise is when you have a situation where one electron has up spin, one electron has down spin. What is the wave function?

Well, α (1), β (2) that can be a wave function. Who has told us that it is not β (1) α (2). So, this is the same situation that we encountered a few minutes ago when we tried to talk about the spatial part of the excited state of the dihydrogen molecule. See, electrons do not wear jerseys. They do not have a number one or number two branded on them. They do not even know that I am number 1 and you are number 2. They are indistinguishable. You cannot distinguish between the two.

So, while it is experimentally determinable that the two electrons have opposite spins, it is impossible to tell whether it is electron number 1 or electron number 2 which is up spin or down spin. So, when you have the situation of post spins, then you must take a linear combination. You cannot tell which is which. So, you have to take a linear combination.

While taking linear combination, plus and minus both are equally valid. And of course, you need some kind of a normalization constant. So, you get $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$, $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$. So, you see four different wave functions are possible for a two-electron system.

Now, we will introduce something and that is the exchange operators. Exchange operator means you just interchange the labels. Instead of 1, you write 2, instead of 2 you write 1. You see if I interchange the labels what happens? Well, first of all, even before going there, $\alpha(1)$, $\alpha(2)$, if I interchange labels, will the wave function change, no, it would not, $\beta(1)$, $\beta(2)$, same. $\alpha(1)$, $\beta(2)$ would actually have changed. $\alpha(1)$, $\beta(2)$ would have become $\alpha(2)\ \beta(1)$, but it is not a valid wave function anyway.

If you take the linear combination, the first one, the plus combination, there if I interchange 1 and 2 then what do I get, $[\alpha(2)\beta(1)+\beta(2)\alpha(1)]$. It is the same thing. So, $[\alpha(1)\ \alpha(2)\ \beta(1)\ \beta(2)+\alpha(1)\ \beta(2)+\beta(1)\ \alpha(2)]$ are all symmetric with respect to exchange. Whereas the last wave function is such that if you interchange 1 and 2 what will happen is you get $\alpha(2)\beta(1)-\beta(2)\alpha(1)$ which is minus of the original wave function.

So, the last one, the minus combination is actually anti-symmetric with respect to invert exchange. Why are you talking about this? What is there? How does it matter if they are indistinguishable? And how does it matter if some wave function is symmetric and some are not?

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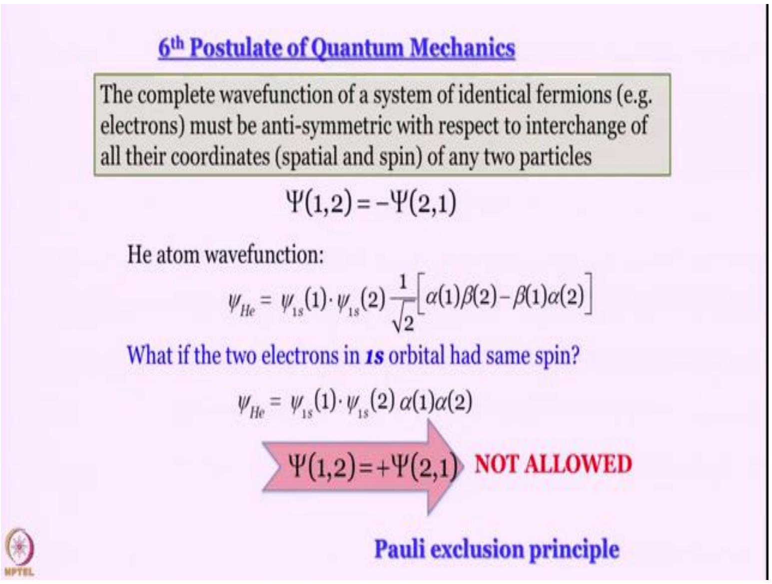

6th Postulate of Quantum Mechanics

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?

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

$$\Psi(1,2) = +\Psi(2,1)$$ NOT ALLOWED

Pauli exclusion principle

It matters because of sixth postulate of quantum mechanics, which also goes by the name Pauli principle, not Pauli Exclusion Principle. Pauli Exclusion Principle follows from here. Pauli principle, it essentially says that the complete wave function of a system of identical fermions must be anti-symmetric. What are fermions? Fermions are fundamental particles with half integral spins. So, electron is a fermion. What are bosons? Bosons are fundamental particles with integral spins. Well, photons, for example, are actually bosons.

And I hope you know that bosons are named after an Indian scientist professor S.N. Bose. And professor Bose is very well known because of his Bose-Einstein statistics that he had formulated along with Einstein. I encourage you to read how this Bose-Einstein statistics began. It began from a simple curiosity. Bose just wanted to derive Planck's law in a very different, in a different way. And this is correct, because Bose himself has gone on record several times saying it that his only intention was to derive Planck's law in a different manner. He was very good at derivation.

But that was the beginning of Bose statistics, Bose-Einstein statistics, which led to things like Bose condensation and paved the way for things like superconductivity. Let that be the story for another day. And many engineers, as well as basic scientists, would be interested in those. But for now, we just need to know the definition. Fermions are particles with half-integral spins, bosons are particles with integral spins. Electrons are fermions.

And the postulate or Pauli principle says that for identical fermions, the total wave function, complete wave function that means spatial part into spin part must change sign if the labels are exchanged. And this is nicely demonstrated if you try to write down the helium atom wave function ground state. In helium atom, what do we have? We have two electrons in the 1s orbital. So, is something like this, $\psi_{1s}(1)$, $\psi_{1s}(2)$, very similar to our hydrogen molecule wave function, is not it?

Now, that has to, well, that spatial part of helium atom wave function as you see is symmetric, it does not matter, if you exchange one and two you get the same wave function. So, in order for the complete wave function to be anti-symmetric, the only option is to multiply it by the only anti-symmetric wave function, anti-symmetric spin wave function we have at our disposal $\alpha\beta - \beta\alpha$. So, this is what it is.

What happens if two electrons in 1s orbital had the same spin, I will write $\alpha(1)\alpha(2)$, spatial part is well defined. This is symmetric. So, that is not allowed by sixth postulate of quantum mechanics and that is what leads to Pauli Exclusion Principle which says that, in the form that we have studied, it says that in an orbital the two electrons must have different spins.

Actually Pauli Exclusion Principle is more general than that and it says that for a system of two fermions in a quantum mechanical system, you are going to get a situation where the complete wave function must be anti-symmetric. That is what it is.

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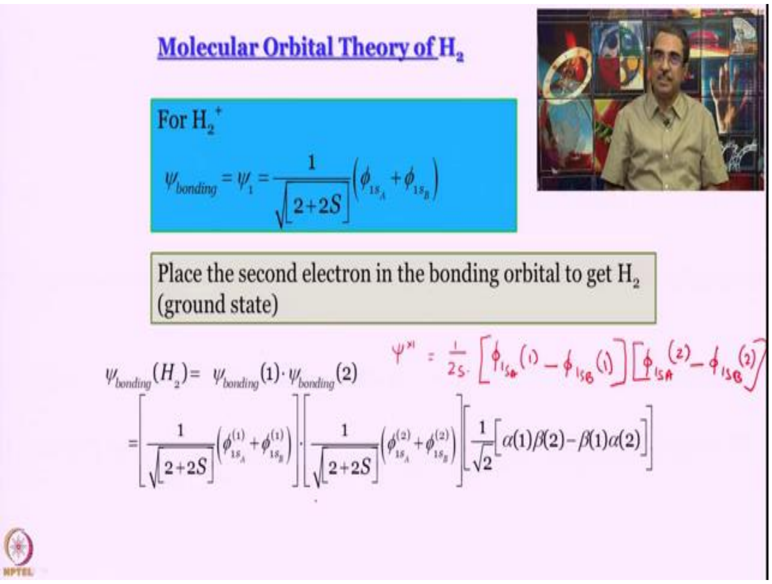

Molecular Orbital Theory of H_2

For H_2^+

$$\psi_{bonding} = \psi_1 = \frac{1}{\sqrt{2+2S}}\left(\phi_{1S_A} + \phi_{1S_B}\right)$$

Place the second electron in the bonding orbital to get H_2 (ground state)

$$\psi_{bonding}(H_2) = \psi_{bonding}(1) \cdot \psi_{bonding}(2)$$

$$= \left[\frac{1}{\sqrt{2+2S}}\left(\phi_{1S_A}^{(1)} + \phi_{1S_B}^{(1)}\right)\right] \cdot \left[\frac{1}{\sqrt{2+2S}}\left(\phi_{1S_A}^{(2)} + \phi_{1S_B}^{(2)}\right)\right]\left[\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\right]$$

$$\psi^{x1} = \frac{1}{2S}\left[\phi_{1sA}(1) - \phi_{1sB}(1)\right]\left[\phi_{1sA}^{(2)} - \phi_{1sB}^{(2)}\right]$$

Now, knowing that we will come back and plug this into molecular orbital theory, look at the ground state wave function of dihydrogen, of course, it is symmetric. So, of all these four spin wave functions that we have the only one that works like in helium atom is the one with the minus combination. So, this is the complete wave function of dihydrogen molecular, dihydrogen molecule. So, this is, is singlet. What would happen if I think of the excited state?

So, as we wrote, I will write something like this, ϕ (1) that has to be 1/2s multiplied by, what is the combination we use, we use a minus combination, is not it? So, [$\phi_{1sA}(1) - \phi_{1sB}(1)$, let us see letter number 1 is in the anti-bonding orbital, and electron number 2 is still in the ground state. Again, it will interchange actually. [$\phi_{1sA}(2) - \phi_{1sB}(2)$] and you can write it in different ways. You can expand and you will see that you have access to a singlet as well as triplet. This state is a singlet, because there is only one way function.

But if the spatial part of the wave function is symmetric, then you can multiply it by the anti-symmetric, if the spatial part is anti-symmetric, then you can multiply it by the symmetric wave functions. And there are three such possibilities $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, $\alpha(1)\beta(2) + \beta(1)\alpha(2)$, that is what takes you to the excited triplet state of dihydrogen. The ground state of the hydrogen molecule is definitely singlet.

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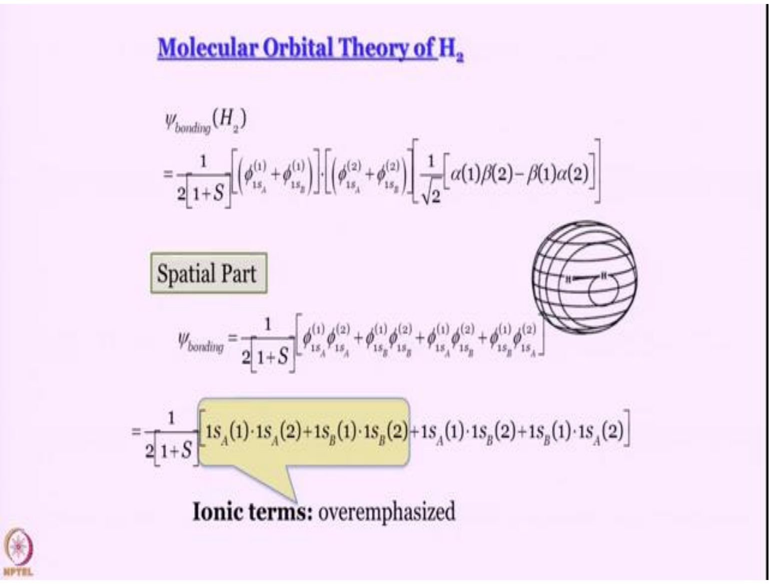

Molecular Orbital Theory of H_2

$$\psi_{bonding}(H_2)$$

$$= \frac{1}{2[1+S]}\left[\left(\phi_{1s_A}^{(1)} + \phi_{1s_B}^{(1)}\right)\right] \cdot \left[\left(\phi_{1s_A}^{(2)} + \phi_{1s_B}^{(2)}\right)\right]\left[\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\right]$$

Spatial Part

$$\psi_{bonding} = \frac{1}{2[1+S]}\left[\phi_{1s_A}^{(1)}\phi_{1s_A}^{(2)} + \phi_{1s_B}^{(1)}\phi_{1s_B}^{(2)} + \phi_{1s_A}^{(1)}\phi_{1s_B}^{(2)} + \phi_{1s_B}^{(1)}\phi_{1s_A}^{(2)}\right]$$

$$= \frac{1}{2[1+S]}\left[1s_A(1)\cdot 1s_A(2) + 1s_B(1)\cdot 1s_B(2) + 1s_A(1)\cdot 1s_B(2) + 1s_B(1)\cdot 1s_A(2)\right]$$

Ionic terms: overemphasized

Now, one last thing that we wanted to discuss our dihydrogen molecule is just forget the spin part for the moment, look at the spatial part, expand it. This is what you get. And I will write it in an another way. Instead of writing ϕ so many times, I will just write $1s_A$, $1s_B$, so on and so forth.

Now, look at the first two terms. The first two terms tell you $1s_A$ has electron number 1, $1s_A$ itself has electron number 2. The second term tells you $1s_B$ has electron number 2, $1s_B$ itself has electron number 2. Third term tells you electron number 1 is in $1s_A$, electron number 2 is in $1s_B$. Fourth term tells you electron number 1 is in $1s_B$, electron number 2 is in $1s_A$.

So, the last two terms they tell you about the neutral dihydrogen molecule. What about the first two terms? There both the electrons are in the same atomic orbital, either $1s_A$ or $1s_B$. So, that represents the ionic terms. So, it takes into account that h+h- can also be there. But the problem is that it overemphasized these ionic terms. Of course, in dihydrogen molecule, you do not have too much of ionic form. But here it seems that the contribution of ionic and covalent forms are the same, which is a mistake.

So, this is a problem with the molecular orbital theory. The good thing is that it is a general theory. The bad thing is that it is too general a theory. So, sometimes it overdoes things you have to be careful.

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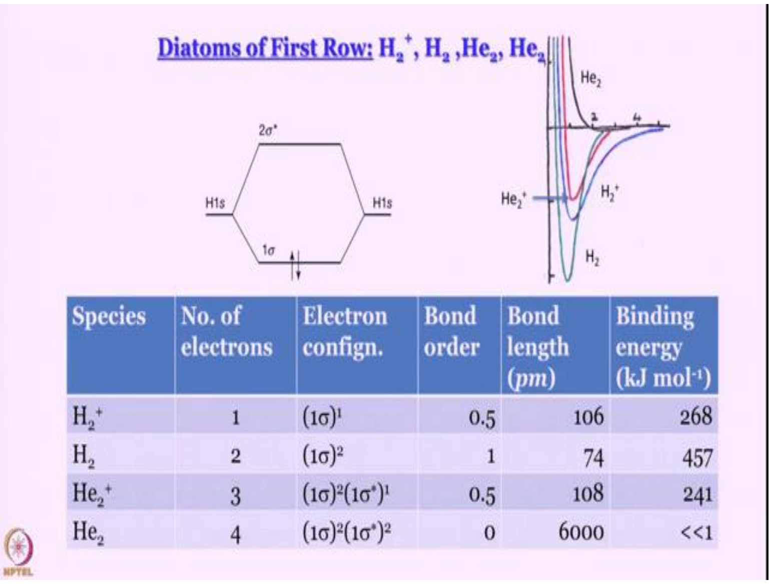

Diatoms of First Row: H_2^+, H_2 ,He_2, He_2

Species	No. of electrons	Electron confign.	Bond order	Bond length (pm)	Binding energy (kJ mol⁻¹)
H_2^+	1	$(1\sigma)^1$	0.5	106	268
H_2	2	$(1\sigma)^2$	1	74	457
He_2^+	3	$(1\sigma)^2(1\sigma^*)^1$	0.5	108	241
He_2	4	$(1\sigma)^2(1\sigma^*)^2$	0	6000	<<1

That being said, let us now fill in these different electrons and let us see what is the situation for different diatomic molecules based on H_2^+. So, H_2^+ we have discussed already. H_2 we have discussed already. What are the bond order? H_2^+ has a bond order of half, because you have only one electron in the lower energy molecular orbital, H_2 has a bond order of one. And look at the bond length. Bond length, experimentally determined bond length is 106 pm for H_2^+ only 74 pm for H_2. Why, the second electron actually effectively shields the first one from the nuclear charge. Well, rather the electrons shield the nuclei from each other that is why they can come a little closer and you see binding energy is so much more.

What happens in He_2^+? Bond order is the same as that of H_2^+, but bond length is a little longer, binding energy is a little lesser. Why, because now in addition to these two electrons you have an electron in the anti-bonding orbital, and destabilization of anti-bonding orbital at equilibrium bond length is actually a little more than the stabilization of the bonding molecular orbital that is why there is a problem.

And what about He_2^+? He_2^+ we already discussed. He_2, what about He2? In He_2, you have two electrons here in the bonding orbital, two electrons there in the anti-bonding orbital, bond order is 0. But energy is not 0. It is still a little less than 1 and actually, you get an energy minimum at a much longer distance of 6,000pm. Why is it that at 6,000pm we have this, so 1 nm is huge for an atom? Why is it that we have a minimum that is because of inter-atomic interaction? So, this is what we learn for the atoms of the first row.

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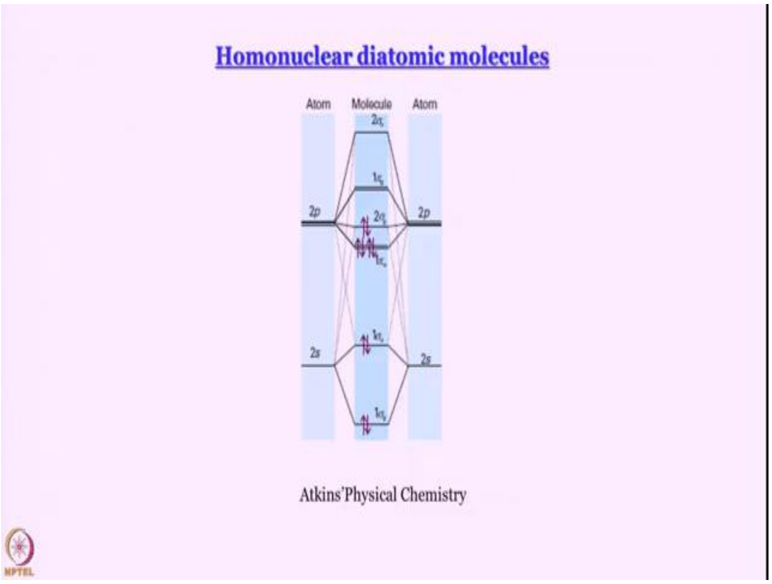
Homonuclear diatomic molecules

Atkins'Physical Chemistry

In the next lecture, we will talk about homonuclear diatomic molecules once again, but of the second row. That will be a shortest lecture.