Concepts of Chemistry for Engineering

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Lecture 14

Molecular Orbital Theory 2: Diatomic Molecules

In this lecture, we are going to complete our discussion of molecular orbital theory of H_2^+ dihydrogen cation.

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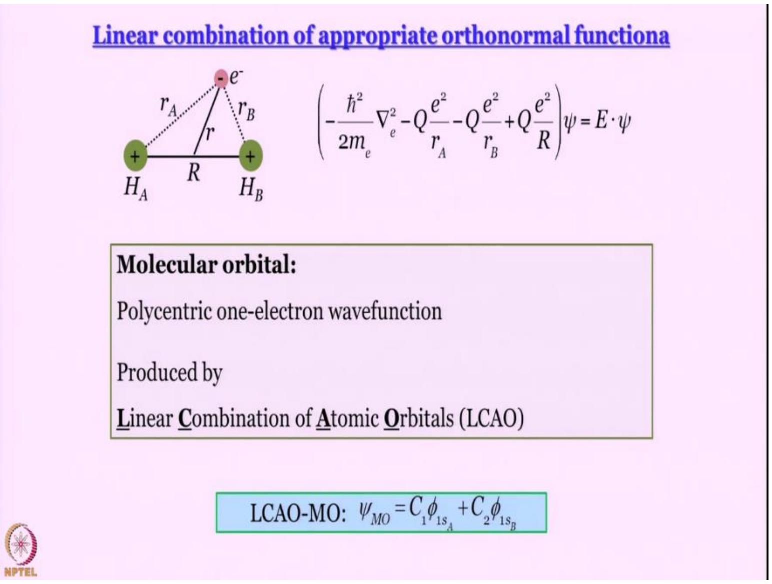

Linear combination of appropriate orthonormal functiona

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

Molecular orbital:

Polycentric one-electron wavefunction

Produced by

Linear Combination of Atomic Orbitals (LCAO)

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

So far, we have written down the Hamiltonian. And the reason why you are working with H_2^+ as we have said several times already is that, it is a unique case of a 1 electron molecule. So, here we have $-\frac{\hbar^2}{2m_e}$, there is a kinetic energy term of this lone electron. $-Q\frac{e^2}{r_A} - Q\frac{e^2}{r_B}$, these are the potential energy terms for the attraction of this electron by the 2 nuclei. And, where capital R is the inter-nuclear separation is the term in the Hamiltonian operator for inter nuclear repulsion.

So, we have formulated Schrodinger equation this way. And we have said that, we are going to construct the molecular orbital, not by solving Schrodinger equation directly even though it is possible, we are going to construct it by a, rather unique technique by taking a linear combination of atomic orbitals.

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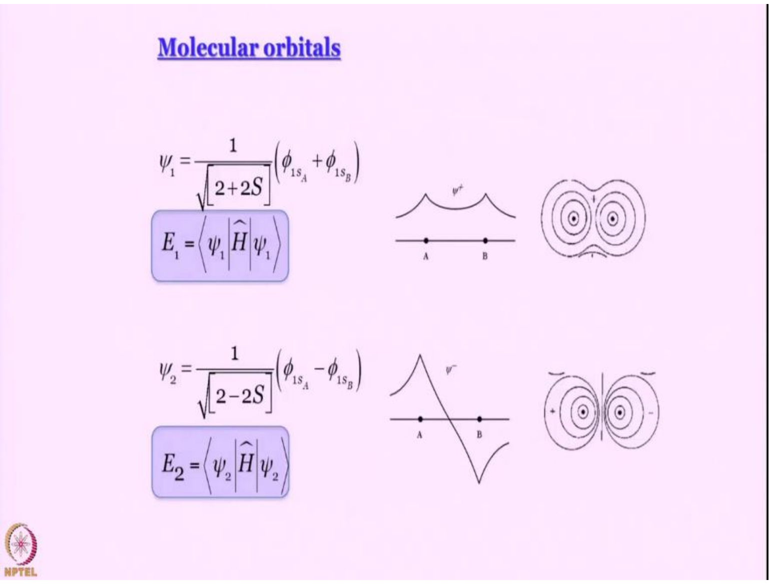

Molecular orbitals

$$\psi_1 = \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$$

$$\boxed{E_1 = \left\langle \psi_1 \middle| \hat{H} \middle| \psi_1 \right\rangle}$$

$$\psi_2 = \frac{1}{\sqrt{[2-2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$$

$$\boxed{E_2 = \left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle}$$

And when we do that, this is where we are, we made a little bit of progress identified a something called an overlap integral, integral $1s_A$ $1s_B$ overall space. And we have got two wave functions, $\psi_1 = \frac{1}{\sqrt{(2+2S)}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$ and $\psi_2 = \frac{1}{\sqrt{(2-2S)}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$. We have plotted the electron distribution, these are the contour diagrams, and these are the profiles that you take through this two.

And from these, we have said that it is quite obvious that in this case, in the upper case, that is where you have a buildup of electron density between the 2 nuclei, that is going to lead to stabilization. And here you have a depletion of electron density, if you take square of this, between A and B that is going to, that is going to contribute to increased inter nuclear repulsion. So, this will be a higher energetic state.

So, this here is called bonding situation, bonding lowers energy. And this here is called anti-bonding situation, anti-bonding orbital. Why because there is an increase in energy compared to isolated atoms. If there was no change in energy, we would have called it nonbonding orbital.

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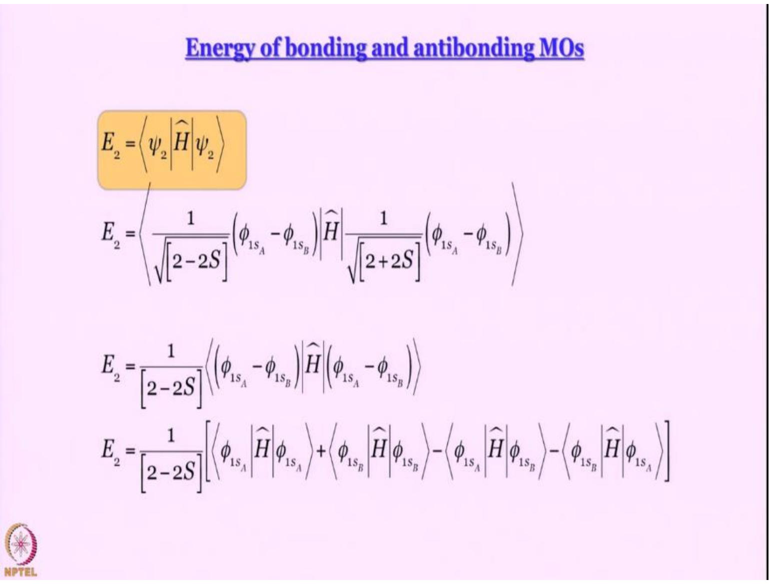


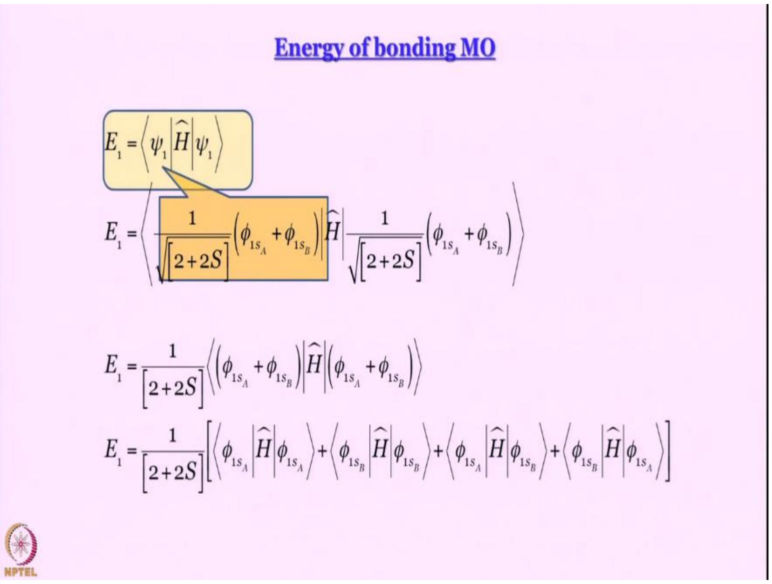
Energy of bonding and antibonding MOs

$$E_2 = \left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle$$

$$E_2 = \left\langle \frac{1}{\sqrt{[2-2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right) \middle| \hat{H} \middle| \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right) \right\rangle$$

$$E_2 = \frac{1}{[2-2S]}\left\langle \left(\phi_{1s_A} - \phi_{1s_B}\right) \middle| \hat{H} \middle| \left(\phi_{1s_A} - \phi_{1s_B}\right) \right\rangle$$

$$E_2 = \frac{1}{[2-2S]}\left[\left\langle \phi_{1s_A} \middle| \hat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \hat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_A} \middle| \hat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_B} \middle| \hat{H} \middle| \phi_{1s_A} \right\rangle\right]$$



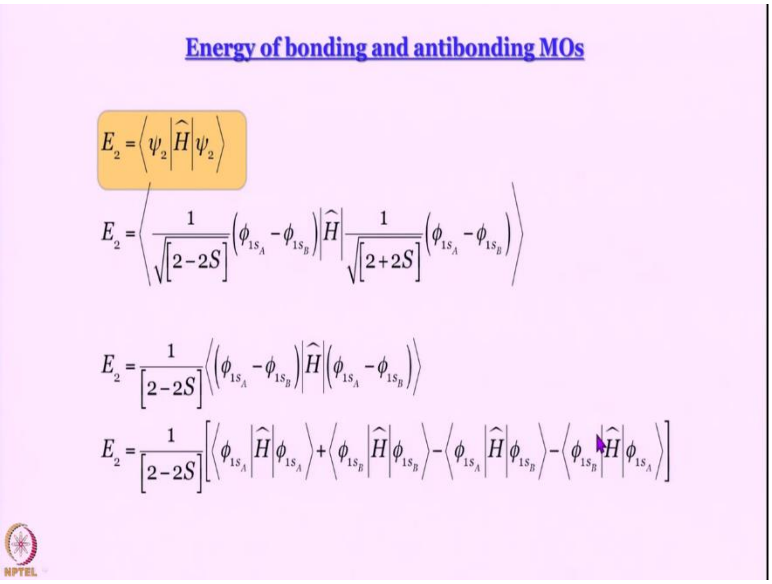
Energy of bonding MO

$$E_1 = \left\langle \psi_1 \middle| \hat{H} \middle| \psi_1 \right\rangle$$

$$E_1 = \left\langle \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right) \middle| \hat{H} \middle| \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right) \right\rangle$$

$$E_1 = \frac{1}{[2+2S]}\left\langle \left(\phi_{1s_A} + \phi_{1s_B}\right) \middle| \hat{H} \middle| \left(\phi_{1s_A} + \phi_{1s_B}\right) \right\rangle$$

$$E_1 = \frac{1}{[2+2S]}\left[\left\langle \phi_{1s_A} \middle| \hat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \hat{H} \middle| \phi_{1s_B} \right\rangle + \left\langle \phi_{1s_A} \middle| \hat{H} \middle| \phi_{1s_B} \right\rangle + \left\langle \phi_{1s_B} \middle| \hat{H} \middle| \phi_{1s_A} \right\rangle\right]$$



Energy of bonding and antibonding MOs

$$\boxed{E_2 = \left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle}$$

$$E_2 = \left\langle \frac{1}{\sqrt{[2-2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right) \middle| \hat{H} \middle| \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right) \right\rangle$$

$$E_2 = \frac{1}{[2-2S]}\left\langle \left(\phi_{1s_A} - \phi_{1s_B}\right) \middle| \hat{H} \middle| \left(\phi_{1s_A} - \phi_{1s_B}\right) \right\rangle$$

$$E_2 = \frac{1}{[2-2S]}\left[\left\langle \phi_{1s_A} \middle| \hat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \hat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_A} \middle| H \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_B} \middle| \hat{H} \middle| \phi_{1s_A} \right\rangle\right]$$

So, let me write the expression like this, $E_1 = \langle \psi_1 | \hat{H} | \psi_1 \rangle$. So, if you expand this, and again, the way to do this is, once I write this, please stop the video, do the expansion yourself, it is elementary. And then when you reach a point where you get some strange looking quantities, then you should turn the video back on.

So, this is what we have, we have replaced ψ_1 by $\frac{1}{\sqrt{(2+2S)}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$ in the bra vector as well as the ket vector. Of course, I can take the constants out and I will get $\frac{1}{2+2S}$. So that is sorted. Inside, we have this wave function, $\hat{H}$ wave function integrated over all space. Expand it, you are going to get four terms $\frac{1}{(2+2S)}\left[\langle \phi_{1s_A} | \hat{H} | \phi_{1s_A} \rangle + \langle \phi_{1s_B} | \hat{H} | \phi_{1s_B} \rangle - \langle \phi_{1s_A} | \hat{H} | \phi_{1s_B} \rangle - \langle \phi_{1s_B} | \hat{H} | \phi_{1s_A} \rangle\right]$. And now, we have to expand these terms and write them in some way that we can understand. Similarly, we can write an expression for E_2. The only difference between E_1 and E_2 is that for the last two terms, in E_2 the signs are negative, whereas the signs are positive for all terms for E_1, that is the only difference, terms are actually all the same.

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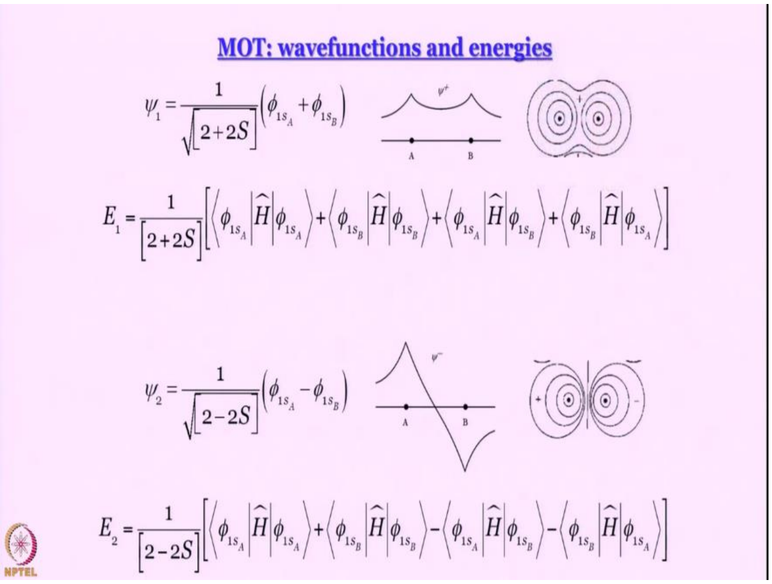

MOT: wavefunctions and energies

$$\psi_1 = \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$$

$$E_1 = \frac{1}{[2+2S]}\left[\left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle + \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle + \left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle + \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle\right]$$

$$\psi_2 = \frac{1}{\sqrt{[2-2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$$

$$E_2 = \frac{1}{[2-2S]}\left[\left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle + \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle - \left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle - \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle\right]$$

So, let us try to evaluate this one by one slowly. This is where we are right now, we have got the wave function, we have got an expression for the expectation values of energy for bonding as well as anti-bonding situation.

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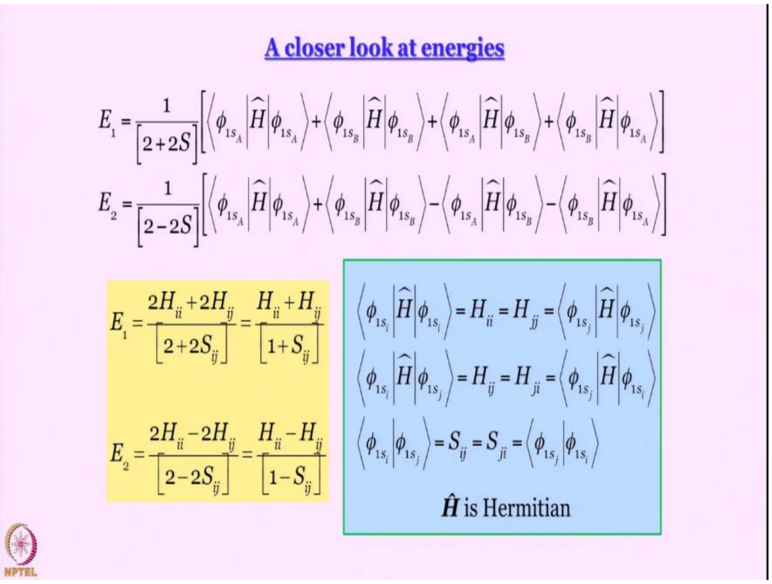

A closer look at energies

$$E_1 = \frac{1}{[2+2S]}\left[\left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle + \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle + \left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle + \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle\right]$$

$$E_2 = \frac{1}{[2-2S]}\left[\left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle + \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle - \left\langle \phi_{1s_A}\middle|\hat{H}\middle|\phi_{1s_B}\right\rangle - \left\langle \phi_{1s_B}\middle|\hat{H}\middle|\phi_{1s_A}\right\rangle\right]$$

$$E_1 = \frac{2H_{ii} + 2H_{ij}}{[2+2S_{ij}]} = \frac{H_{ii} + H_{ij}}{[1+S_{ij}]}$$

$$E_2 = \frac{2H_{ii} - 2H_{ij}}{[2-2S_{ij}]} = \frac{H_{ii} - H_{ij}}{[1-S_{ij}]}$$

$$\left\langle \phi_{1s_i}\middle|\hat{H}\middle|\phi_{1s_i}\right\rangle = H_{ii} = H_{jj} = \left\langle \phi_{1s_j}\middle|\hat{H}\middle|\phi_{1s_j}\right\rangle$$

$$\left\langle \phi_{1s_i}\middle|\hat{H}\middle|\phi_{1s_j}\right\rangle = H_{ij} = H_{ji} = \left\langle \phi_{1s_j}\middle|\hat{H}\middle|\phi_{1s_i}\right\rangle$$

$$\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle = S_{ij} = S_{ji} = \left\langle \phi_{1s_j}\middle|\phi_{1s_i}\right\rangle$$

$\hat{H}$ is Hermitian

Let us work with the energy of the bonding orbital and let us try to expand this a little bit. While doing that. Since we do not know what these integrals are, we are going to define them, we are going to give them some name, that is the best we can do at the moment. Because see, as I said, $1s_A$ is not really eigen function of $\hat{H}$.

So, you cannot just write E_0 and bring it out that is not going to work. So, what we say is whenever we have the same orbital before and after in the bra vector and ket vector, we call that integral H_{ii}, or H_{jj} both are actually the same. It does not matter because both are 1s orbitals.

When we have say $1s_A$ in the bra vector, and $1s_B$ in the ket vector or the other way around, we call it H_{ij}. Now, H_{ij} is equal to H_{ji} that comes from the property of the Hermitian operators, there is something called turnover rule, where if you have something like $\langle \phi_1 | \hat{H} | \phi_2 \rangle$, you might as well write $\langle \phi_2 | \hat{H} | \phi_1 \rangle$, does not matter, it is all the same. For this course, we are going to take it axiomatically.

And the last thing that we know already is the overlap integral, that in any case is very easy to understand. So, we are going to write the expression for energy in terms of these integrals now. What is the first one, $\langle \phi_{1s_A} | \hat{H} | \phi_{1s_A} \rangle$ that is H_{AA} or H_{11} or H_{ii} whatever we want to call it. What about the second one, that is also going to be H_{ii}. Because we have the same $1s_B$ in the bra vector and ket vector. The last two terms are going to be H_{ij} or H_{12} or H_{AB}, whatever we want to call it.

Because, there we have, if we have A in the bra vector, we have B in the ket vector, if we have B in the bra vector, we have A in the ket vector. So, this is what we get. 2 in the numerator and 2 in the denominator cancel each other, you are left with this expression $\frac{H_{ii}+H_{jj}}{[1+S_{ij}]}$. And I hope it is not very difficult to understand that for E_2, we will get more or less the same expression except for the fact that instead of plus sign, we are going to get minus sign.

Please work it out yourself and satisfy yourself then there is a case. What is the next task at hand, we should try to evaluate H_{ii} and H_{ij}, we should try to simplify their expressions in terms of some things that we know.

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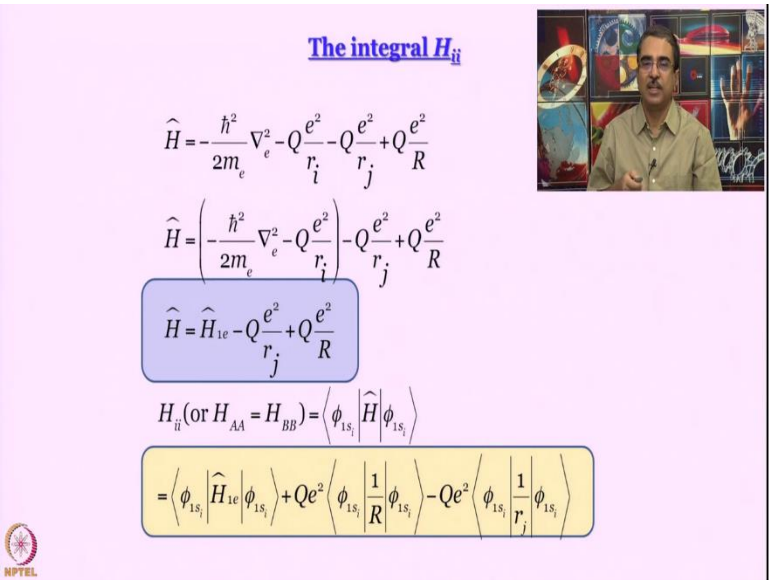

The integral H_{ii}

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_i} - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}$$

$$\hat{H} = \left(-\frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_i}\right) - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}$$

$$\hat{H} = \hat{H}_{1e} - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}$$

$$H_{ii}(\text{or } H_{AA} = H_{BB}) = \left\langle \phi_{1s_i} \middle| \hat{H} \middle| \phi_{1s_i} \right\rangle$$

$$= \left\langle \phi_{1s_i} \middle| \hat{H}_{1e} \middle| \phi_{1s_i} \right\rangle + Qe^2 \left\langle \phi_{1s_i} \middle| \frac{1}{R} \middle| \phi_{1s_i} \right\rangle - Qe^2 \left\langle \phi_{1s_i} \middle| \frac{1}{r_j} \middle| \phi_{1s_i} \right\rangle$$

So let us do that. To evaluate it, we will write down the expression for the Hamiltonian. Now, when I do that, I can take these first two terms in bracket, isn't it essentially a 1 electron Hamiltonian? So, we are going to write it as $\widehat{H}_{1e}$

So, now our Hamiltonian $\widehat{H} = \widehat{H}_{1e} - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}$ And remember by Born Oppenheimer approximation, this last term is essentially a constant. So, this is what it is.

So, $H_{ii} = \langle \phi_{1s_i} | \widehat{H} | \phi_{1s_i} \rangle$, we are going to put this expression for the Hamiltonian in the expression for H_{ii} and obviously, we will get 3 terms in that case, we will get a sum of 3 integrals, these are what they are.

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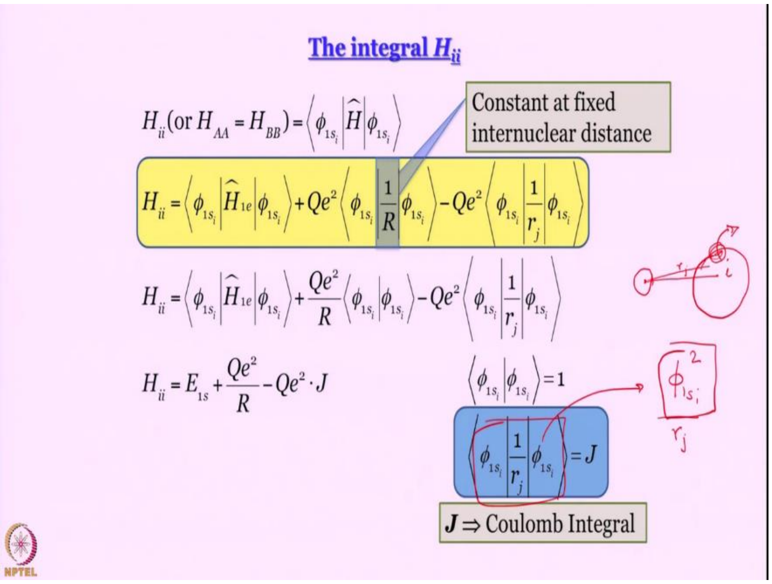

The integral H_{ii}

$$H_{ii}(\text{or } H_{AA}=H_{BB})=\left\langle \phi_{1s_i}\middle|\hat{H}\middle|\phi_{1s_i}\right\rangle$$

Constant at fixed internuclear distance

$$H_{ii}=\left\langle \phi_{1s_i}\middle|\hat{H}_{1e}\middle|\phi_{1s_i}\right\rangle+Qe^2\left\langle \phi_{1s_i}\middle|\frac{1}{R}\middle|\phi_{1s_i}\right\rangle-Qe^2\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_i}\right\rangle$$

$$H_{ii}=\left\langle \phi_{1s_i}\middle|\hat{H}_{1e}\middle|\phi_{1s_i}\right\rangle+\frac{Qe^2}{R}\left\langle \phi_{1s_i}\middle|\phi_{1s_i}\right\rangle-Qe^2\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_i}\right\rangle$$

$$H_{ii}=E_{1s}+\frac{Qe^2}{R}-Qe^2\cdot J$$

$$\left\langle \phi_{1s_i}\middle|\phi_{1s_i}\right\rangle=1$$

$$\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_i}\right\rangle=J$$

$J \Rightarrow$ Coulomb Integral

Let me just write it like this, it will need some space to write more things as well. H_{ii} turns out to be $< \phi_{1s_i}$ here instead of A and B, I am just writing i and j more general coefficient, more general notations. $\langle \phi_{1s_i}|\widehat{H_{1e}}|\phi_{1s_i}\rangle$, now this is something nice. Remember, this ϕ_{1s_i} is 1s orbital and what is the 1 electron Hamiltonian. Now, the 1s orbital is going to be an eigenfunction of 1 electron Hamiltonian. So, energy of 1s orbital is actually going to come out, so this first one is very simple to work out.

What about the second one, what about the third one, we will see. Even in the second one you can see that $\frac{1}{R}$ is constant, so that can come out. Third one that is more interesting. So, this is how we write it now. First, we take this constant out it becomes $Q\frac{e^2}{R}\left\langle \phi_{1s_i}\middle|\phi_{1s_i}\right\rangle$. Now, we know that that is equal to 1, we are working with normalized S orbitals, that is great.

Now, what we do not know is the third one, first one I already said, I do not know I have not written it yet. But it will come also. In the first one I think you will understand what will happen, energy of 1S orbital is going to come out inside you are going to be left with $\left\langle \phi_{1s_i}\middle|\phi_{1s_i}\right\rangle$ which is going to be 1 and so this will simply become, the first term will simply become energy of 1S orbital. Second term is $Q\frac{e^2}{S}$.

No, just $Q\frac{e^2}{R}$, no capital S. Third term is $-Qe^2\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_i}\right\rangle$. What is this, this is called an integral J, the name is Coulomb integral. When you say Coulomb, what do you think? Which field of physics would you think of if I took the name of Coulomb, electrostatics.

So, this Coulomb integral has got to do with electrostatics as well. See, what do I have in the numerator, I have $1s^2$, ϕ_{1s}^2 , what is ϕ_{1s}^2 remember, that is the energy density right. So, inside the integral I essentially have ϕ_{1s}^2 I will write i also and here it is $\frac{\phi_{1s_i}^2}{r_j}$. So, if I draw it like this, this is the 1s orbital I am talking about if this is i, and the distance I am talking about is this r_j.

So, what is this, if I just multiplied by electronic charge that gives me charge of this electron cloud. This square is essentially your probability density, probability density multiplied by charge gives you charge density. So, in the numerator, if you just want to play by e, which is just a constant, that is a measure of, that is your charge density. So, we have a charge density at a separation of r_j from the second nucleus.

So, this essentially then gives me well one term gives me, for a particular value of r_j the potential for electrostatic attraction between the second nucleus and the electron cloud around the first nucleus. Similar treatment is encountered, if you want to talk about say, electrolyte solutions, electrolyte solutions, what we do is we take say a positive ion, cation and we take the ionic atmosphere to be a delocalized negative charge to keep charge balance.

So, similar treatment is there as well, you consider the electrostatic attraction between this point positive charge and this negatively charged cloud, ionic atmosphere, same thing here. And you are integrating overall space. So, that will give you the total potential energy for electrostatic attraction between 1 nucleus and the electron charge cloud, electron cloud on the, near the other nucleus. So, it has a physical meaning. J => Coulomb integral talks about an electrostatic interaction.

So, let us write the expression for H_{ii} now, the first term is E_{1S} as we said, second time is $Q\frac{e^2}{R}$, third time is $-Qe^2.j$. We have got H_{ii} already. Why do we want H_{ii}, because H_{ii} appears in the expression for energies E_1 and E_2.

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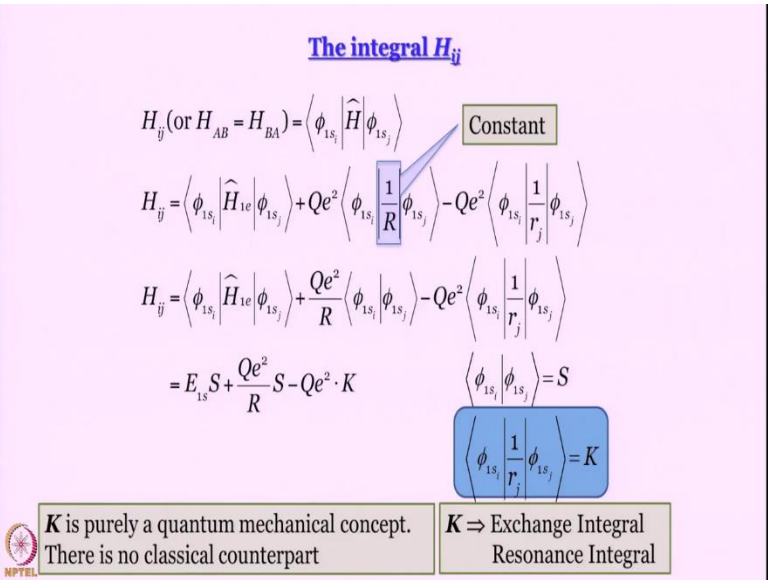

The integral H_{ij}

$$H_{ij}(\text{or } H_{AB}=H_{BA})=\left\langle \phi_{1s_i}\middle|\hat{H}\middle|\phi_{1s_j}\right\rangle$$

Constant

$$H_{ij}=\left\langle \phi_{1s_i}\middle|\hat{H}_{1e}\middle|\phi_{1s_j}\right\rangle+Qe^2\left\langle \phi_{1s_i}\middle|\boxed{\frac{1}{R}}\middle|\phi_{1s_j}\right\rangle-Qe^2\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_j}\right\rangle$$

$$H_{ij}=\left\langle \phi_{1s_i}\middle|\hat{H}_{1e}\middle|\phi_{1s_j}\right\rangle+\frac{Qe^2}{R}\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle-Qe^2\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_j}\right\rangle$$

$$=E_{1s}S+\frac{Qe^2}{R}S-Qe^2\cdot K$$

$$\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle=S$$

$$\left\langle \phi_{1s_i}\middle|\frac{1}{r_j}\middle|\phi_{1s_j}\right\rangle=K$$

K is purely a quantum mechanical concept.
There is no classical counterpart

K ⇒ Exchange Integral
Resonance Integral

What is the next integral H_{ij}, H_{ij} is a little more interesting. Why, because unlike H_{ii}, you have 1s orbital in the bra vector, different s orbital in the ket vector. And you might as well start guessing what, which quantity, which integral we are going to encounter in a similar like, in a situation like this. So, this is your H_{ij}. Again, the first one there is no problem, we still get energy of 1s orbital. Second one once again your $\frac{1}{R}$ is a constant it comes out, but when $\frac{1}{R}$ goes out, what do you have inside the integral, $\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle$.

I hope by now we all recognize this integral, this integral is simply the overlap integral, S_{ij} as we are putting it here more often, we just call it capital S. So, what is H_{ij}, first term we have no problem. I do not know why I have written it in so many steps. Anyway, second term is $Q\frac{e^2}{R}\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle$, third term is this integral, which is, which looks somewhat similar to the Coulomb integral but not exactly the same. We have 1s orbital in the bra vector, we have another s orbital in the ket vector. Remember here r_j is not a constant.

So, how you evaluate these integrals we will come to that. But let us write this expression. The first one what happens is you take the energy of 1s orbital out, no problem with that. But inside you are going to have $\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle$ that is again your overlap integral. So first one will be energy of

1s orbital multiplied by overlap integral that is the difference between H_{ii} and H_{ij}. Second one also is $\frac{Qe^2}{R}S$, overlap integral shows up in H_{ij}, it did not show up in H_{ii} or H_{ij}.

Now, in the third term again, we have an integral, which at the moment, we do not know what to do with, we will give it a name. It is, since the earlier integral was called j, we go alphabetically, and we call this $K=\left\langle \phi_{1s_i} \middle| \frac{1}{r_j} \middle| \phi_{1s_j} \right\rangle$. And there are textbooks in which they try to make sense of it. But I do not think it is a good idea. This is a purely quantum mechanical quantity, it is called an exchange integral or resonance in detail. So, this is what your expression is, it is very important to understand there is a purely quantum mechanical concept there is no classic analog.

So, to say that when this electron is here, that is charged cloud interacting with the other nucleus and then when they change places, that gives extra energy all this is trying to extrapolate the classical logic too much into the quantum world, you cannot do it beyond an extent. So, please understand that it is a purely quantum mechanical concept, nobody knows to be honest, any classical analog for this, so let us not even try.

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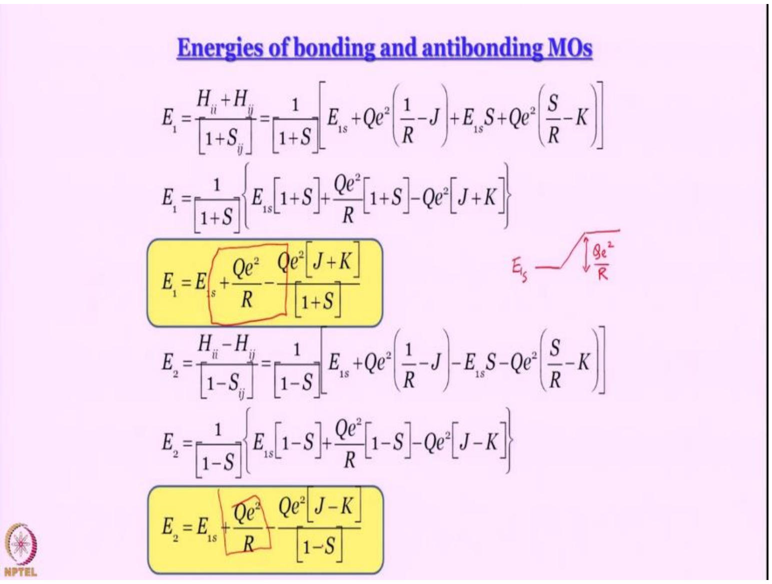

Energies of bonding and antibonding MOs

$$E_1 = \frac{H_{ii}+H_{ij}}{\left[1+S_{ij}\right]} = \frac{1}{\left[1+S\right]}\left[E_{1s}+Qe^2\left(\frac{1}{R}-J\right)+E_{1s}S+Qe^2\left(\frac{S}{R}-K\right)\right]$$

$$E_1 = \frac{1}{\left[1+S\right]}\left\{E_{1s}\left[1+S\right]+\frac{Qe^2}{R}\left[1+S\right]-Qe^2\left[J+K\right]\right\}$$

$$\boxed{E_1 = E_{1s}+\boxed{\frac{Qe^2}{R}}-\frac{Qe^2\left[J+K\right]}{\left[1+S\right]}}$$

$$E_2 = \frac{H_{ii}-H_{ij}}{\left[1-S_{ij}\right]} = \frac{1}{\left[1-S\right]}\left[E_{1s}+Qe^2\left(\frac{1}{R}-J\right)-E_{1s}S-Qe^2\left(\frac{S}{R}-K\right)\right]$$

$$E_2 = \frac{1}{\left[1-S\right]}\left\{E_{1s}\left[1-S\right]+\frac{Qe^2}{R}\left[1-S\right]-Qe^2\left[J-K\right]\right\}$$

$$\boxed{E_2 = E_{1s}+\boxed{\frac{Qe^2}{R}}-\frac{Qe^2\left[J-K\right]}{\left[1-S\right]}}$$

So, we have the expression for H_{ij}, we have the expression for H_{ii}, what will I do, we will now just put the expressions in the expressions for E_1 and E_2. And here I am going to go fast because it is so easy. I will just put everything in if you want to please pause and do it yourself, please do it yourself, then you will understand this is the expression for E_1, this is the expression for E_2.

Now, look at the expression, what do we get, E_{1S} is the energy of an isolated 1s orbital, what is $\frac{Qe^2}{R}$, you see this $+\frac{Qe^2}{R}$ appears in both E_1 and E_2. So, that is essentially the inter nuclear repulsion between a and b. So, no matter what you do that inter nuclear repulsion term will be there and depending on capital R it will be large or small. If it is very far away capital R is large, the second term will be close to 0. If it is very close to each other, it will be very large, but it is going to increase.

So, if I just consider the two terms, the first two terms then I can draw like this, this here is the energy of the 1s orbitals, both of these energies would increase to some value and this is going to be how much, this difference will be $\frac{Qe^2}{R}$ as you understand that this extent of destabilization is going to change depending on what is the value of R. Now, we have something interesting, the third term has a negative sign in both the cases but here in the numerator, we have J + K and in the denominator also we have 1+ S, here in the numerator we have J - K and in the denominator we have 1 - S.

Now J, K, S these are integrals, we have already shown how S varies and S is definitely something that depends strongly on capital R. J and K can be evaluated not analytically, but numerically, meaning for different values of capital R, you can just put in all the values and by brute force you can calculate what will, what will that integral be by doing summation it is not very difficult to do if you know a little bit of computer programming, this is where computer programming comes in big time in chemistry.

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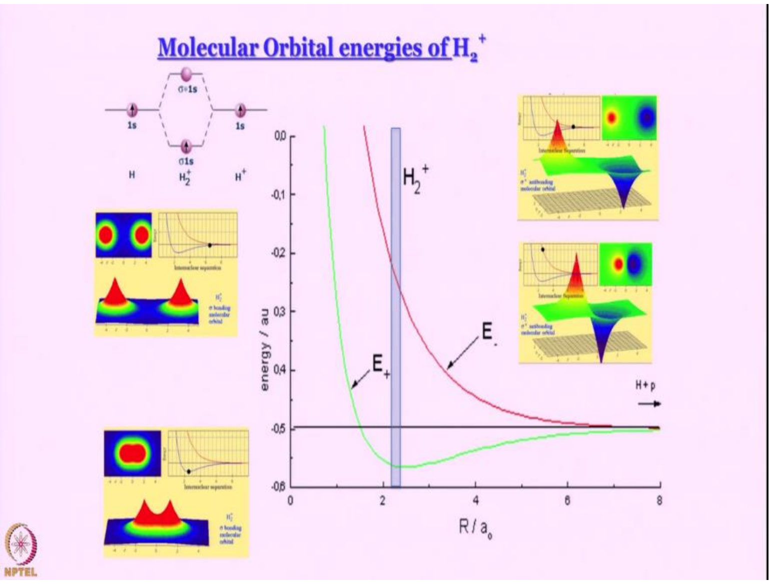

Molecular Orbital energies of H_2^+

So, this is what you get. For E_+ or E_1, you have a function that goes through a minimum. This is the energy remember of the bonding orbital, and here this is the energy of the antibonding orbital, which increases monotonically when you, when you decrease capital R from infinity to a very small value. This position or internuclear distance, where you get an energy minimum for E_1 that is the inter nuclear bond distance. And you can look at these insets, so here this is a situation where the two nuclei are very far apart from each other, see what the energy is and you can work out what S is.

When they are at internuclear this separation, this is what the wavefunction would look like, very strong reinforcement. And in case of the minus combination of the orbitals, this is the situation when they are very far away, it is still 0. When they are very close, say when they are at this equilibrium bond length. Now we have this destructive interference between the two wave functions and energy goes up to this value.

And another point to note is that at equilibrium bond length stabilization of the bonding orbital is actually less in magnitude compared to the destabilization of the antibonding orbital, you can explain this qualitatively by talking about buildup of electron density and depletion of electron density between the two nuclei but only qualitatively. So, these are the energies of H_2^+.

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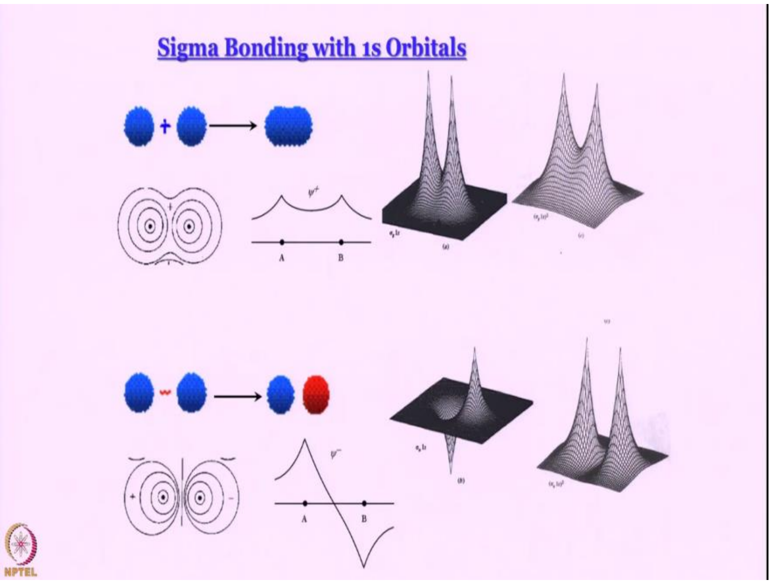

Sigma Bonding with 1s Orbitals

Now, the way we proceed, now is that we can just fill in electrons if we have more electrons here, that is how you handle H_2 and other diatomic molecules, homonuclear diatomic molecules. But before that, this is an executive summary of what we have learned so far.

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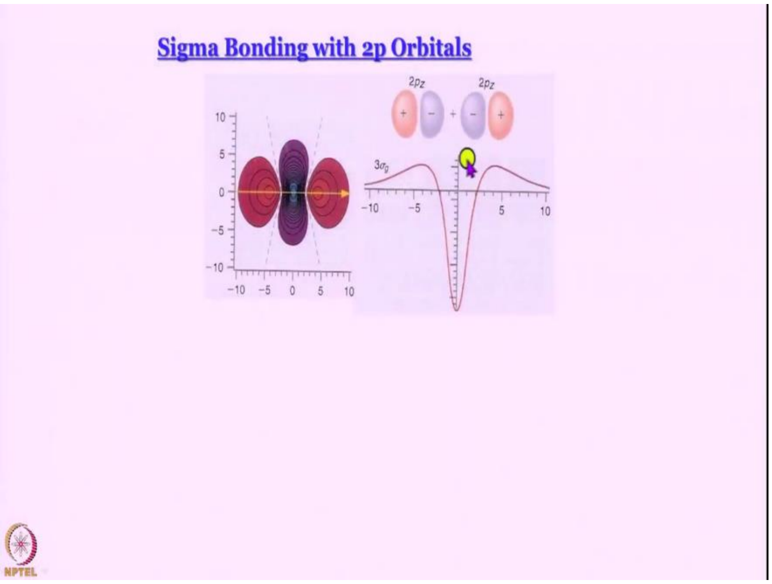

Sigma Bonding with 2p Orbitals

And another thing that I want to say here is that, this is what happens when you talk about hydrogen, if you want to talk about homonuclear diatomics like C_2, N_2, O_2 and so on and so forth, you might need to, you will need to invoke the combination of not only 1s orbitals, but also 2s orbitals, 2p orbitals and so on and so forth, you can do it in exactly the same way and you can generate orbitals bonding and anti-bonding in this way.

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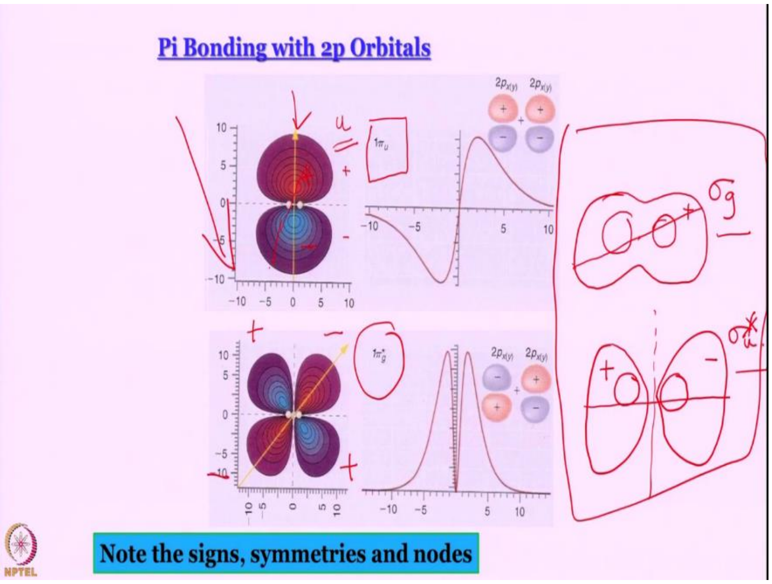
Pi Bonding with 2p Orbitals

Note the signs, symmetries and nodes

So, I am going very quickly through this because it is not all that difficult for you to figure out. One thing that I would like to point out is that symmetry of these orbitals is, actually they have a role to play later on in many different things. So, let us note the symmetry. And let us note the symmetry using this linear combination of p orbitals, when there is π- bonding side on overlap, this is the kind of contour diagram that you generate. See here we have plus sign and here we have minus sign, sign of wave function just right beside it plus and minus and here we have a node.

So, if you start from any point of the wave function, go through the center equal distance on the other side, you get a change in the sign of the wave function. So, this is called anti-symmetric with respect to inversion and the term for it is ungerade. So, these orbitals, these molecular orbitals come with the subscript u. So, this is called π_u orbital, you can neglect this 1 for now. Why π, because it is a π interaction. If I go back to the orbitals, that we have drawn molecular orbitals, what does this orbital look like when you combine this 1s and 1s for the bonding situation it is something like this.

The contour diagram would be something like this. Now, see it is plus everywhere, so if you go from 1 any point through the center equal distance to the other side, you get no inversion at all, no change in sign of a function. So, this is called a σ_g wave function, g for gerade, gerade and ungerade are German words. Well, gerade mean symmetric, ungerade means symmetric as far as we are concerned.

Now, what about the antibonding orbital for the H_2^+, there we take something like this, you have depletion. So, you have a node in between, this is the node. So, here the wavefunction is plus, here it is minus. Start from any point go through the center equal distance on the other side, you have inversion. So, this is called σ_u . Well, for now, let us say that this is σ, because it is σ interaction. And this one here is π, because you have π interaction, there is more to it, it comes from the symmetry notations we will not get into that in this course.

But this is what we get for σ interaction involving s orbitals, this is what we get for π interaction involving p orbitals. So, the bonding orbital here. So, for sigma interaction involving 1s orbitals the bonding orbital has gerade symmetry, the anti-bonding orbital has ungerade symmetry. For π bonding with p orbitals, the bonding orbital actually is ungerade and anti-bonding orbital, you see, this is plus, this is minus, this is plus, this is minus. So antibonding orbital is actually gerade π_g^*.

And another thing that we often do is that, for antibonding orbitals we put star (*). Different books use different notations, but this is the notation that is used most universally star for anti-bonding, and gerade and ungerade to indicate whether they are symmetric or anti-symmetric with respect to inversion.

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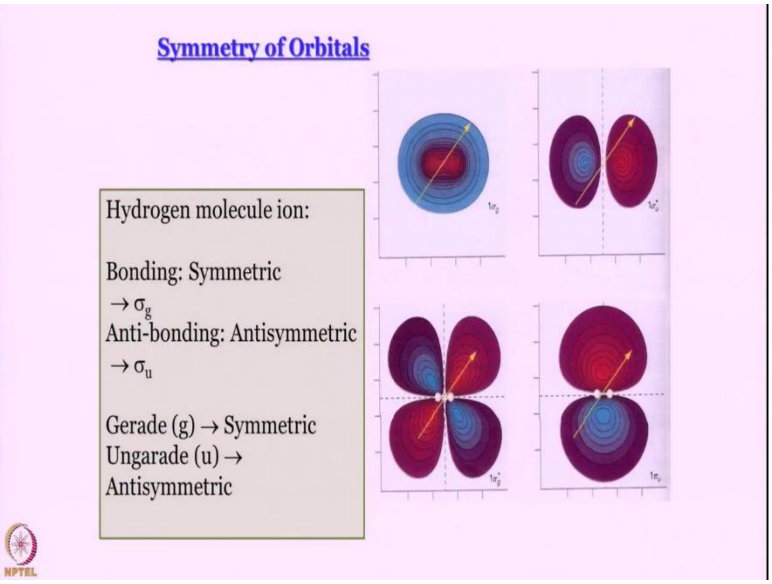

Symmetry of Orbitals

Hydrogen molecule ion:

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

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

So, this is, in a nutshell, the symmetry of orbitals that we just discussed.

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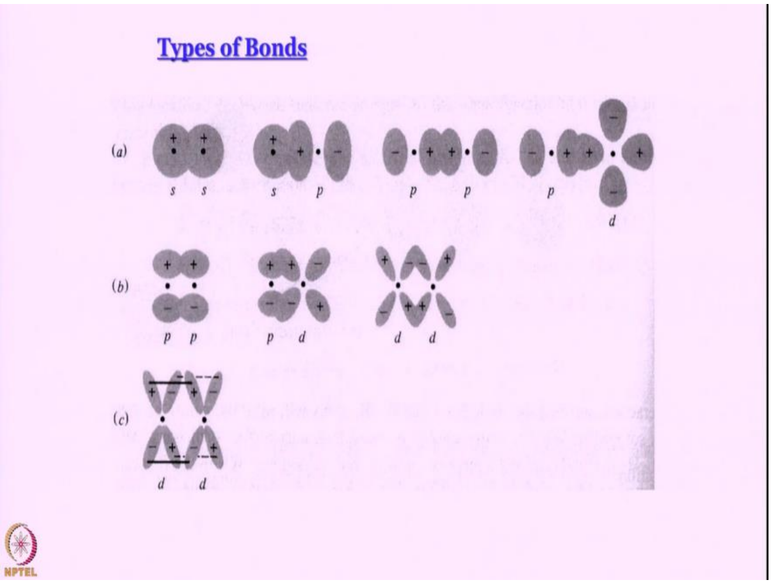

Types of Bonds

You can have different kinds of bonds, σ, π and δ. σ is head on, π is with p orbitals this is π, with d orbitals this is π. No, with d orbitals this is π, of course, I do not have enough fingers to show you the 2 lobes at the bottom as well for the orbitals, these are the 2 lobes at the top, this interaction is p interaction.

So once again, s orbitals, σ interaction, no π interaction possible. p orbitals, σ interaction, π interaction. d orbitals well, you can have σ interaction also. d orbitals you can have this kind of σ interaction or maybe I should show this kind of σ interaction, where is π interaction like this and this is δ interaction face on, head on, side on, face on. So, these are the different kinds of bonds.

We will not discuss the symmetries of orbitals and all these in this course, but it is a good exercise for the students to work out by themselves. Now, what we have done so far is that, we have generated the alphabet by which we can discuss homonuclear diatomics in terms of molecular orbital theory, we have generated the molecular orbitals using the single electron, 1 electron molecule, that is H_2^+.

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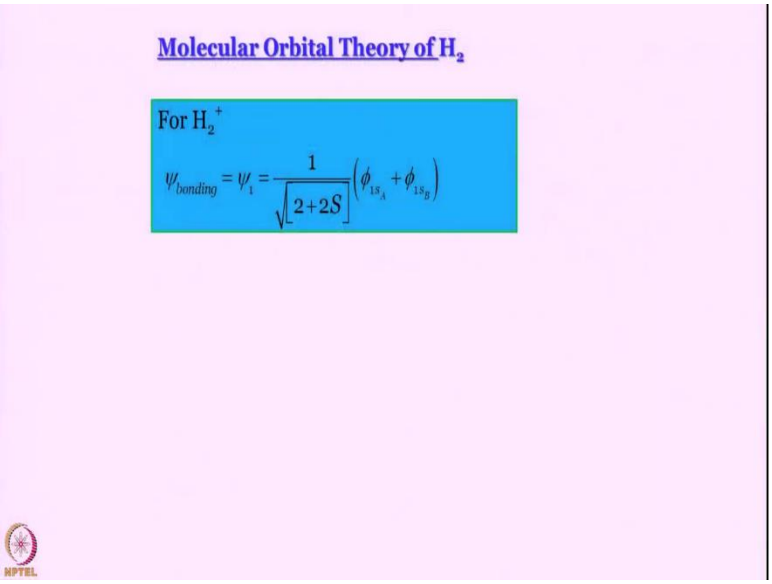

Molecular Orbital Theory of H_2

For H_2^+

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

Next, we are going to learn how we can fill in electrons into these same orbitals and how we can develop a molecular orbital theory of dihydrogen.