

**Quantum Chemistry of Atoms and Molecules**  
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**Lecture-61**  
**Molecular Orbital Theory for H<sub>2</sub><sup>+</sup>**

We have discussed the valence bond theoretical approach for the hydrogen molecule. Then we are gone on to discuss hybridization which gives access to polyatomic molecules and their shapes. Once again, let me remind you that hybridization is invoked to explain the shape. It is not the cause. Methane is tetrahedral it will not because it uses SP<sup>3</sup> hybrid orbitals, but because of VSEPR. You need a species hybridization to describe the system that is all.

Now that being done. It is time for us to move over to Molecular orbital theory. We have already given you a very, very small executive summary of a comparison between valence bond theory Molecular Orbital Theory.

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[Valence Bond and Molecular Orbital Approaches](#)

**Valence Bond Theory**

- Extension of Lewis electron dot model
- Overlap of atomic orbitals and sharing of electron pairs
- Works fine for many systems
- Limited to two center two electron bonds

**Delocalization:** Resonance

- Cannot describe excited states

**Molecular Orbital Theory**

- Electron(s) moving in the joint field of nuclei
- Set up the Hamiltonian: Exactly solvable for H<sub>2</sub><sup>+</sup> but not for more complex molecules
- Molecular orbitals: Linear combination of Atomic Orbitals (*LCAO*)
- Can handle delocalization, excited states. **A general theory**
- A bit too general at times (*ionic structure for H<sub>2</sub><sup>+</sup>, for example*)



The advantage of Molecular orbital theory over valence bond theory is that delocalization can be handled very easily it is a general theory and excited states are accessible without any hassle. Problem is and this is something that will encounter not today. But in the next class we are going

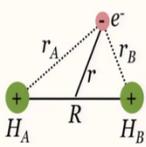
to see that sometimes it becomes a little to general it over does things. Ion structure of H2 for example is over emphasized in a molecular orbital treatment.

But never the less EMOT is the most popular way of handling electronic structure at this level at least later on you might want to go a little further, but this is really the beginning. So we need to discuss and understand molecular orbital theory most of the application of quantum chemistry quantum mechanics in chemistry involves molecular orbital calculations. Ok, you can use different levels as a different issue or together. Ok, but then when we do that let us not forget our definition of orbitals.

An orbital is a one electron system. So when we talk about molecular orbital what we mean is a one electron wave function for a molecular system they cannot be any other electron. So what is the simplest molecule that has only one electron and that therefore cannot be handled by VBT in the first place.

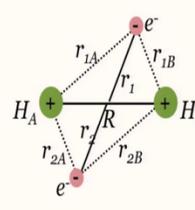
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**Bonding:  $H_2^+$  and  $H_2$  molecules**



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

$$-Q\frac{e^2}{r_A} - Q\frac{e^2}{r_B} + Q\frac{e^2}{R}$$



$$\hat{H}(H_2) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2$$

$$- \frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2$$

$$-Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} - \left[ Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}} \right]$$

$$+ Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

That molecule will be H2 + and already few classes ago a few years ago, we have shown you the Hamiltonian for H2 + as well as H2 there more terms as you go from hydrogen atom with H2 + to H2 the number of terms keeps increasing as the number of as well the different, different interactions comment.

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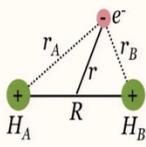
**Born-Oppenheimer approximation**

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

ignore
Constant for given R

Nuclei are STATIONARY with respect to electrons

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

$$\hat{H}(H_2^+) \cdot \psi(r, R) = E(R) \cdot \psi(r, R)$$


Albeit difficult, can be solved using elliptical polar co-ordinates

Now what you are going to do this we are going to use are good old Born-Oppenheimer approximation and say that the nucleus stationary with respect to electrons so we are going to hold this R inter nuclear separation to be constant for the calculation and we are going to royally ignore the kinetic energy term for 2 nu 3 so the Hamiltonian am going to use really is  $-\hbar^2 \nabla_e^2 - Q e^2 / r_A - Q e^2 / r_B + Q e^2 / R$ .

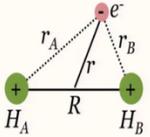
I am not using atomic unit here we should be equally comfortable with both so for a change let me use this. In the next discussion we have Huckel approximation perhaps we used the atomic unit once again, this is a Hamiltonian and it is a 1 electron system the difference is that unlike hydrogen atom it is not a central field problem. There are two nuclei right 2 4 Psi so you cannot use spherical polar coordinates anymore.

You can use spherical polar coordinates and you can actually solve accelerated exact solution for Schrodinger equation for H2 + but we will not do it. It has been done and the published literature it is there in some textbooks that you find that there in exotic textbook, you would not find them in the textbook that we use Macquarie or Pillar or even Sabo. There is no need you must have put in much of trouble and put electric polar coordinates and get some solution you cannot use them.

You do not know what to do when you bring in one more electron and talk about H<sub>2</sub> which is the smallest real molecule. So, the thing is that it is better to start using approximation right away since you cannot avoid it one step down the line.

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**Linear combination of appropriate orthonormal functions**



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

**Molecular orbital:**  
 Polycentric one-electron wavefunction  
 Produced by  
Linear Combination of Atomical Orbital (LCAO)

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

Approximations that were going to use something we have learned while talking about the variation method. Remember we are said that since in any case the variation method allows us to change parameters and try and minimize energy with respect to these parameters. How does it matter? What kind of functions we use you might remember that elephant on the opening slide of a couple of the lectures that we had had some time ago those elephants were drawn using some mathematical function.

So any wave function, whatever is a real wave function? Even though we do not want to do it exactly we can use some of Gaussian, Lorentzian, exponential, polynomial sum and products of these functions and we can actually simulate the actual and the correct shape when there is good enough. So if you take an appropriate set of orthonormal functions orthonormality using an orthonormal set brings in some advantages as we have learned in a discussion of how many electron atoms.

And here the biggest advantage that you already have is a set of relevant orthonormal functions at your disposal and they are the atomic orbitals. So what you do this, we generate the molecular

orbitals by linear combination of atomic orbitals is a first approximation of course later on atomic orbitals and not used molecular orbitals are used by using just what I said product and sums of different types of functions but for this course we will stick to linear combination of atomic orbitals because it give us nice insight of what is going on and it can give us fairly good estimates of energy.

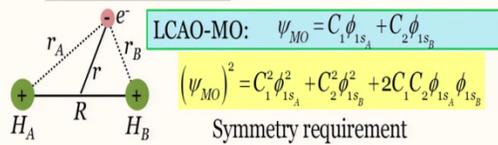
So LCAO as it is called is what is used. For  $H_2$  + the only atomic orbitals that we need to consider are the one is orbital's because where is electron? Electron will be the lowest energy state and is an energy gap between 1s and 2s, so this is something where implicitly we have used and important principle that going to come back and get use many times in a discussion that principle is that only orbitals of appropriate energies are going to participate in the linear combination.

And later on we are going to say only orbitals that have the correct symmetry will participate in a linear combination. Correct symmetry and comparable energies without that they do not participate in this linear combination little bit of different energies is ok but here reference should be is and 2s. So we cannot it make no sense in bring it into 2s you might get little bit of improvement if you do, but at all level in this course is good with this.

So LCAO-MO we use is  $C_1 1s_A C_2 1s_B$  and I hope this reminds you of wave function we had in the valence bond approach. There are also we used 2s orbitals, but the difference there was that we started with field orbitals that we started with  $\Phi 1s_A$  multiplied by  $\Phi 1s_B$  than to that we added  $\Phi 1s_B$   $\Phi 1s_A$  and then we proceeded. Here we do not bother about the electron to start with we are more interested in constructing the wave function and then will feel in the electron when it is appropriate time.

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## Molecular Orbitals



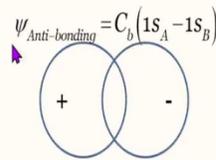
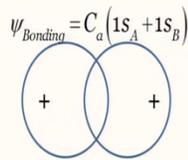
Symmetry requirement

$$C_1^2 = C_2^2 \Rightarrow C_1 = \pm C_2$$

$$C_1 = C_2 = C_a$$

$$C_1 = -C_2 = C_b$$

$$\psi_1 = C_a(\phi_{1s_A} + \phi_{1s_B}) = C_a(1s_A + 1s_B) \quad \psi_2 = C_b(\phi_{1s_A} - \phi_{1s_B}) = C_b(1s_A - 1s_B)$$



Let us work with this molecule orbital to start with  $C_1 1s_A + C_2 1s_B$  take square of that this will give you probability density that is  $C_1^2 \phi_{1s_A}^2 + C_2^2 \phi_{1s_B}^2 + 2C_1 C_2 \phi_{1s_A} \phi_{1s_B}$  now there is there any reason why in these two terms  $C_1^2$  going to be different from  $C_2^2$  where we use exactly similar argument for a valence bond theory also there is no reason why any of these two orbital make a different contribution.

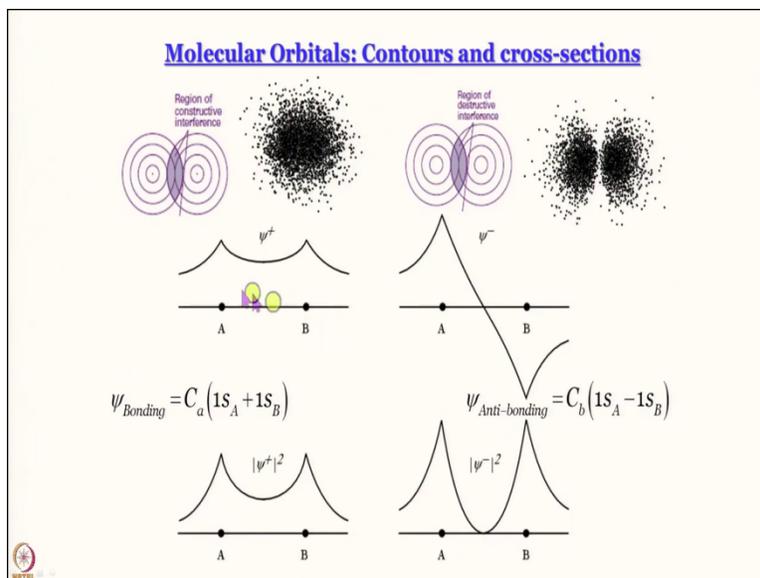
So it makes sense to say that  $C_1^2 = C_2^2$  +  $C_1 = \pm C_2$  so that we can write when  $C_1^2 = C_2^2$  when  $C_1 = C_2$  we write  $C_1 = C_2$  is equal to  $C_a$  and when  $C_1 = -C_2$  then we equate to  $C_b$  of course it is a bad choice will; should say actually is a bad choice because it is better to write  $b$  here and here for reasons you see very soon. What is a wave function and the first wave function.

Where we use linear combination with plus sign is  $C_a$  multiplied by  $\phi_{1s_A} + \phi_{1s_B}$  so in the subsequent discussion most of the time we have not written  $\phi$ , a simple written  $1s_A + 1s_B$  what about  $\psi_2$ ?  $\psi_2$  would be  $C_b$  into  $1s_A - 1s_B$  and I think most of you would know already that plus combination is a bonding orbital minus combination is the anti-bonding orbital why bonding and anti-bonding we will come to it in its time.

But now this is what we have, generally we like to draw pictures instead of writing algebraic expressions and this is the picture that we like to draw. We draw 2 circles for the  $2s$  orbital and

we would put two plus signs to denote and that the combination is plus and for anti-bonding we could put the minus sign in one of them to denote that the combination is minus.

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In fact, it is better for us since we know about contour diagrams and all we can look at the contours understand better. These are the overlapping contour of A and B orbitals here the only difference is that you put in the plus and minus sign and you can draw this Psi square like this as dots we remember we put a dot wherever they some probability so we can generate the diagram of Psi Psi star Psi square it will be like this note here, here there we will be a node right because in this region there is going to be a destructive interference.

If look at the profiles take a cross section of this orbital you get to peaks for Psi cross the bonding orbital. Here however 1s orbital point's up other one is orbital point's down. This is plus and this is minus remember so you are going to get a node 0 crossing point exactly between the two nuclei and if you take this Psi square then Psi square looks like a circus tent. In case of the bonding orbital and it looks like 2 circus tents right beside each other for the anti-bonding orbital.

So generally what the argument that is given in many textbooks even though it is not it is little bit un waiting argument that there is a buildup of electron density because Psi square is more Psi square dr will be more here. Buildup electron density will have 2 nuclei and that is why the

electrons or shields the two nuclei from each other and act as a cement for them. Here actually, there is a decrease in electron cloud if you just use 2 s orbitals it was no bonding at all. Then the picture would have been something like this and I will draw normalized picture.

It would have been something like this. So, in this region you have this much of electron density more than what you have for the anti-bonding orbital. So generally even in 11 and 12 books. This is the explanation that is given will not worry about the explanation for the moment just go ahead and see how it turns out.

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**Normalization**

$$1 = \langle \psi_1 | \psi_1 \rangle = C_a^2 \langle \phi_{1s_A} + \phi_{1s_B} | \phi_{1s_A} + \phi_{1s_B} \rangle$$

$$1 = C_a^2 \left[ \langle \phi_{1s_A} | \phi_{1s_A} \rangle + \langle \phi_{1s_B} | \phi_{1s_B} \rangle + \langle \phi_{1s_A} | \phi_{1s_B} \rangle + \langle \phi_{1s_B} | \phi_{1s_A} \rangle \right]$$

I S

$$1 = C_a^2 [2 + 2S]$$

$$C_a = \frac{1}{\sqrt{2 + 2S}}$$

Similarly

$$C_b = \frac{1}{\sqrt{2 - 2S}}$$

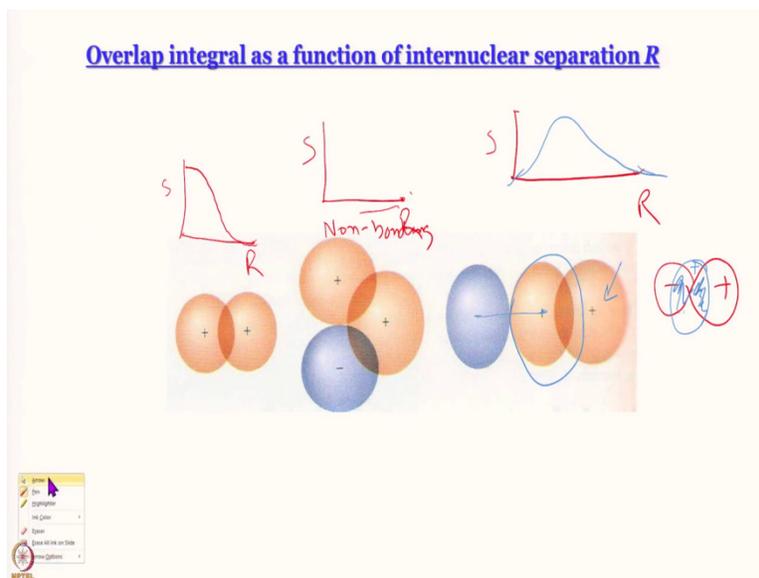
**S : Overlap Integral**

To start with let us normalized wave function we know that this is what we usually like to do first. So, integral Psi 1 squared dr in this case will be equal to will it be dr? It will be dr1 and dr2 there are that double integral again that will be equal to 1 so you write this I am going very first here because this is more or less what we have done in the valence bond theory approach as well. You expand this you get four terms and look at the four terms they are familiar.

Integral Phi 1s A and Phi 1s A B rA is equal to 1 because 1s A is normalized. Same is true for 1sB. And what is this integral 1s A 1s B V d tau integral 1s B 1s A d tau you might remember from all valence one discussion that these are overlap integral. Remember overlap integral these are simply overlap integrals so what do you have? You have 1 equal to see C a square multiplied by 2 + 2 S so C a turns out to be 1 by root 2 + 2S.

Similarly you can find the expression for  $C_b$  that is equal to  $1/\sqrt{2}$  -  $2S$  I am going at breakneck speed because it is so simple, please work this out yourself then only to understand fully.

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Now you might remember that overlap integral is actually a function of inter nuclear separation we have done at least one of this can we have done in fact for that were given expression and we had shown you the plot is not very difficult to see that when this two orbitals are infinitely far away overlap integral is of course 0 it comes closer, overlap will go up up and finally will be something like this. What about this? It is a very curious case overlap integral when this  $R$  is equal to infinity of course 0.

Now even in this case what is your overlap? Is it 0 or it is something else? Yeah do not forget what overlap integral is you have do point by point multiplication of the two wave functions in  $x$ . And so this is really an example of non bonding interactions. Here when you have Sigma interaction between an s and p orbital then what will the overlap integral will be 0 here. And then when I bring this close together say this is your p orbital minus plus change colour and this is your s orbital plus now what happens?

Is it 1, is it 0 what is it? For this part is going to be plus for this part it will be minus and the magnitude same so it is going to be 0 at R is equal to 0, 0 at R is equal to infinity somewhere in the middle it will be at peak, where will it be peak? It will peak in the situation where this s orbital is here. That is where it is going peak. So for internuclear separation here to; let us say here. So in tutorial we have some problems in which you have to work this out. I think you might have done it already in assignment.

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**MOT so far**

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

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

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

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

This is what we have; we have their expressions for the bonding and anti-bonding orbitals that is great and now our job is to find the expression for energy expectation value of energy by using these wave functions for bonding and anti-bonding orbitals. We will call the energy of the bonding orbital  $E_1$  MO  $E_1$  and will call the energy of the anti-bonding MO  $E_2$ . It is perfectly ok to call the MO's orbitals they are all orbitals, but I prefer to call them MO's because you are also using atomic orbital and by now you have become used to referring atomic orbitals as just orbitals.

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### Energy of bonding MO

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

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

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

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



Now, let us see what the expression for energy of bonding MO would be and once again, I am going fast because this is now cake walk for us. What is the integral? First thing to do is plug in the value of Psi 1 and take out the product of the normalization constant this is what we get E 1 is 1 by 2 + 2S multiplied by in bra vector we have Phi 1s A + Phi 1s B. In the ket vector we have H hat 1s A + 1s B of course you should expand and you will get 4 terms. And the 4 terms I hope do not look absolutely unfamiliar to us. For E 2 integral remain the same only in these two cases plus becomes minus there is no other difference.

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### A closer look at energies

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

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

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

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

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

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

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

$\hat{H}$  is Hermitian



Ok now let us take a closer look at these energies. Do we know this integrals have we encountered integrals like this integral Phi SA H hat Phi SA+ Phi 1 SA H hat Phi 1SA integral

Psi I H Psi I what is it, is not it H ii integral Phi 1SB H hat Phi 1 SB again there is H ii we call it H jj but they are same it does not matter. Integral Phi 1SA H hat Phi 1 SB what is that? That is a H ij and integral Phi 1SB H hat Phi 1SA is S ji but then Si and Sj are equal because if you remember H hat is hermitian and so we can use turnover rule.

So this are familiar integrals for us we might as well write E 1 in terms of a H ii Hij and for now will write S ij and whenever we are bored of writing ij we are go back to S does not matter. So E 1 turns out to be H ii and H ij divided by 1 + S ij you might as well write H 11 + H 12 does not matter perhaps it is better to write H 11 + H 12. What about E 2? Remember the only difference was that the last two turns had minus negative coefficient negative signs you plug that in you get E 2 to be H ii – H ij divided by 1 – S ij both become minus.

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The integral  $H_{ii}$

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

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

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

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

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

So, now to go further we need to evaluate H ii will need to evaluate S ij you already know what S ij we already know what S ij is. In fact we know what H ii and H ij are as well as we are just revising. So, this is your Hamiltonian this time not in atomic units –h cross by 2m e del square - Q r square by r i you can recognize these two terms constitute one electron wave function -Q square by r j + Q square by R this is your this is for the potential energy for attraction between electron and nucleus.

Sorry, but this  $Q^2$  by  $R$  is for internuclear repulsion nucleus-nucleus repulsion so we club these two together and we are going to write Hamiltonian of one electron. So now our Hamiltonian has three terms. So  $H_{ii}$  is integral  $\phi_{1s_i}$  left multiplying Hamiltonian operator  $\phi_{1s_i}$  so will write like this same expressions no harm done  $H_{ii}$  some of these 3 terms.

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**The integral  $H_{ii}$**

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

Constant at fixed internuclear distance

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

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

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

$\langle \phi_{1s_i} | \phi_{1s_i} \rangle = 1$

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

$J \Rightarrow$  Coulomb Integral

Now look at this  $1/R$  is a constant at a fixed internuclear distance we are working under the ambit of Born Oppenheimer approximation here I might digress little bit and I might say that the Born-Oppenheimer approximation does not hold in all cases but that comes under the beyond approximation theory that is a little more complicated phenomenon. For our purpose Born-Oppenheimer approximation is actually very good approximation we can work without its ambit without losing generality.

So this is a constant at fixed inter nuclear distance fine, we can bring it out. So, we can write like this integral  $\phi_{1s_i}$   $H_{1e}$   $\phi_{1s_i}$  will come back to this  $+Q^2$  integral  $\phi_{1s_i}$   $\phi_{1s_i}$   $- Q^2$  integral  $\phi_{1s_i}$   $1/r_j$   $\phi_{1s_i}$  again I hope that these terms do not look unfamiliar to you because first of all  $\phi_{1s_i}$   $\phi_{1s_i}$  integral of that. What is that? it is simple 1 normalised.

Integral of  $\phi_{1s_i}$  into  $1/r_j$  into  $\phi_{1s_i}$  what is that? Is I hope you remember that it is the coulomb integral  $J$  remember coulomb integral? Coulomb denotes the electrostatic interaction

we have work this out when we talked about the dihydrogen molecule in your valence bond theory. And I hope it is not very difficult to see that integral  $\langle \phi_{1s_i} | \hat{H} | \phi_{1s_j} \rangle$  that will be the expectation value of energy of 1s orbital.

It does not matter whether I use A or B. This 1s orbital still the same, energy of 1s orbital is  $+Q$  square by  $R - Qe$  square into  $j$ .

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**The integral  $H_{ij}$**

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

Constant

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

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

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

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

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

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

$K \Rightarrow$  Exchange Integral Resonance Integral

Now that is evaluate the integral  $H_{ij}$  it is not enough to evaluate  $H_{ii}$  right I want energy finally. So,  $H_{ij}$  similarly we can proceed and we can again use this on  $1$  by  $R$  to be a constant  $H_{ij}$  will be first of all, this is the value of energy for 1s orbital. Then  $Q$  square by  $R$  as we know that this what is this integral of  $1$   $S_i$   $1$   $S_j$  what is that going to be that is going to be  $S$  right overlapping integral and not be  $1$  and this integral  $-Q$  square integral  $\langle \phi_{1s_i} | \frac{1}{r_j} | \phi_{1s_j} \rangle$  what is that?

We know that also right. So, the first term is  $E_{1s}$  into  $S$  let me work that out? I think I made a careless statement just few minutes ago. I working this out, what is it  $\hat{H}_{1e}$  operating on  $\phi_{1s_j}$  use me  $E_{1s}$ . So if I write it in bracket notation we have in bra vector  $\phi_{1s_i}$  What will I get this becomes  $E_{1s}$  multiplied by  $\phi_{1s_j}$  of course? So take this and plug it in and moreover you take this  $E_{1s}$  out you are left with  $E_{1s}$  multiplied by integral  $\langle \phi_{1s_i} | \phi_{1s_j} \rangle$  that is your  $S$ .

E 1S S next one will be just Q e square by R multiplied by S same S is there. When you look at the third integral it is K is not it exchange integral or I did not tell you this name earlier is also called resonance integral because here you are considering 1Si and 1Sj in the same integral so exchange. So please remember that will come back later, but listed like this -Q e square into K and remember that there K is a purely quantum mechanical concept. There is absolutely no classical counterpart for K.

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**Energies of bonding and antibonding MOs**

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

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

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

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

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

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

Variation method for upper bound to energy

Fine we know H ii and we know H ij we of course S ij it is equal to S so I have written S ij is equal to S here. Now let me login the values of H ii this is H ii hope you recognize E 1S + I have taken Q e square common Q e square multiplied by 1 by R -J and H ij is E 1S + Q e square multiplied by S by R -K. So E 1 will then be equal to if I now collect the coefficients of E 1S Q square by R and -Q e square. So, what will be the coefficient of E 1S E 1S into 1 + S is not it one from here S from here.

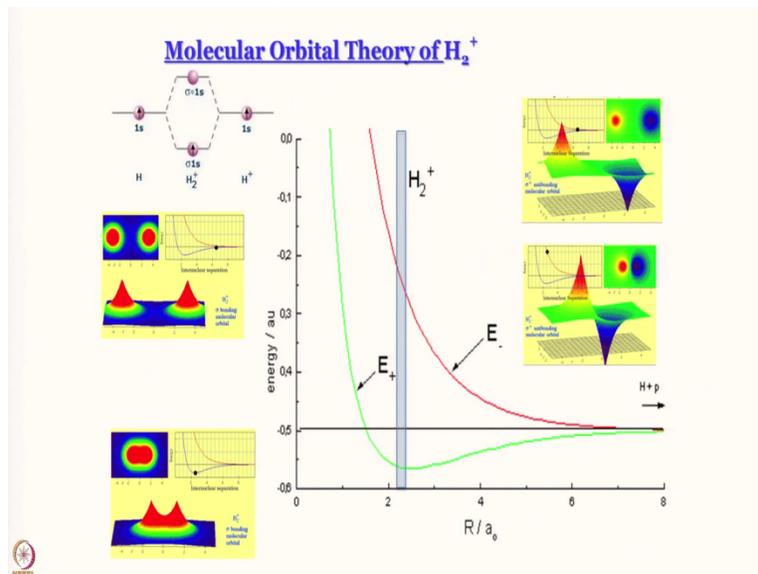
What will be the coefficient of Q e square by R? So 1 from here and S from here so 1 by S -Q square What will be the coefficient take minus outside from this term you get J this term you get K; -Q e square multiplied by J + K that is E 1, E 1 then turns out to be just simplified divide throughout by 1 + S you get E 1S + Q e square by R - Q e Square multiplied by J + K by 1 + S. Similarly we work out an expression for E 2 and that turns out to be E 1S + Q e square by R - Q square into J - K divided by 1 - S.

So see  $E_{1S} + Q e^2 / R$  what is that? There is simply energy of 1S orbital plus the nucleus-nucleus repulsion term  $Q e^2 / R$  is the potential energy for a nucleus-nucleus repulsion. So, this is the energy that we get if there is nothing is happening this basically destabilization this  $Q e^2 / R$  is  $R$ . So, when you bring in the  $Q e^2 / R$  into  $J + K$  divided by  $1 + S$  or  $-Q e^2 / R$  into  $J - K$  divided by  $1 - S$  this third term decides whether you get net stabilization or net destabilization.

So that depends on the integrals and remember we are constructing this integrals using 1s orbital to start with but that obviously not give me very good result. So what is done is as we discussed hydrogen type of hydrogen like orbitals STO's GTO's. In 1S orbital expression that  $Z$  is kept as variation of parameters, here are also two nuclei, right. You do not have a second electron yet but that  $Z$  instead of  $Z$  you write zeta variational parameter.

So, that is varied and it also vary  $N$ . Using variation method you can find the upper bound for the energy that is how you find the expression for  $E_1$  and  $E_2$  for given values of  $R$ . Another thing to remember is that  $J K S$ , these are also integrals that depend on the value of  $R$ .

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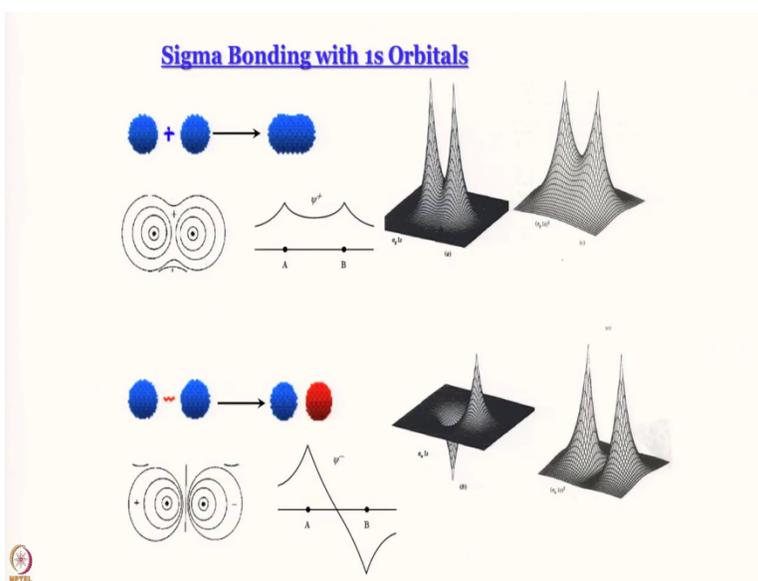


It is very strong dependence of the energies and this is what you get for  $E_+$  plus minimum it goes up for  $E_-$  minus it goes up all the way. So this is how the energy of an bonding orbital varies as

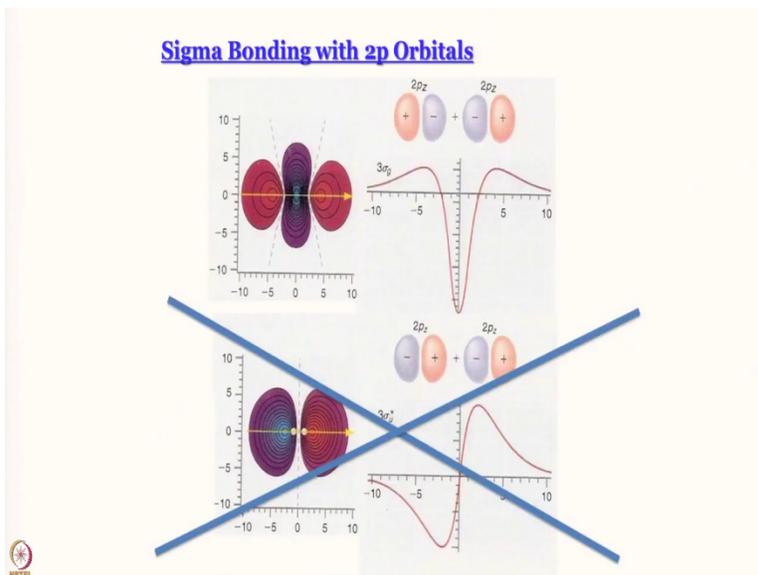
function of R this is how the energy of bonding orbital varies as of bonding and antibonding orbital, varies as a function of inter nuclear separation. At equilibrium bond length, you can see that stabilization the amount of stabilization that you have for the bonding orbital is actually less than the amount of the stabilization that you have in the antibonding orbital.

So if you have 1 electron in bonding orbital and 1 electron in antibonding orbital energy of the system will not be 0 it will be more than 0 and that is often explain by the hand waving arguments and using this kind of orbital picture.

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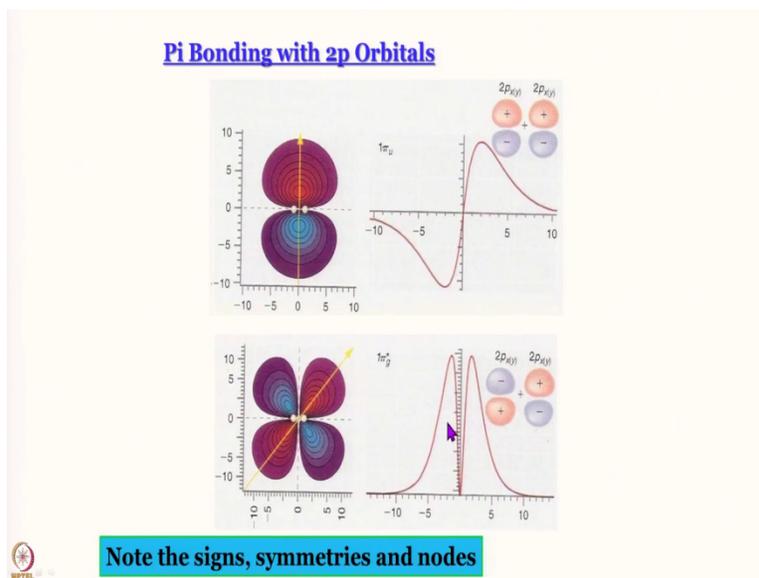


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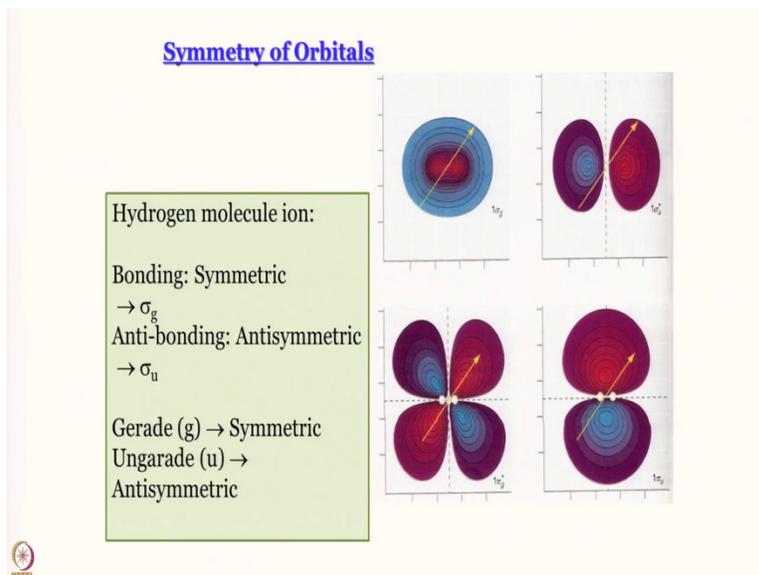
So you have already study sigma bonding with 1s orbital. I will leave it you to work out the the shapes of bonding and antibonding orbitals using 2p orbitals this is from one of the textbook forgotten which one but this one is wrong, please do not look at that.

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And this is what you get for PI bonding using 2P orbitals this side one the overlap.

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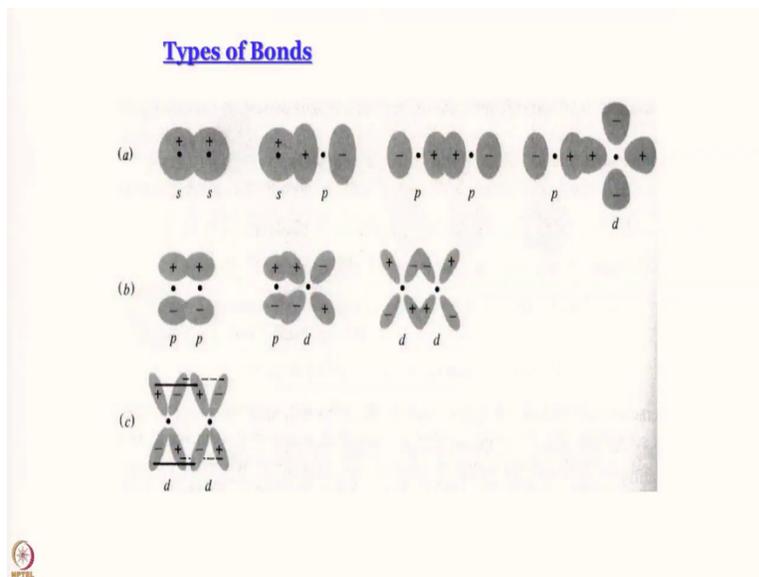


And one thing that you should remember or know or understand is that symmetry of orbitals is often used as very important parameters for the hydrogen molecule and for bonding orbitals it is symmetric with respect to inversion so it is called Sigma g, g for gerade. The antibonding orbital

is antisymmetric with respect to inversion that is called Sigma u, do not think that always bonding orbitals are gerade and antibonding orbitals are ungerade that is not the case.

If you look at the bonding Pi orbital used by side on overlap of 2P orbitals you see that this bonding orbital for Pi is ungerade and antibonding orbital is actually gerade ok. So we are going to use this nomenclature of MO's when we talk about actual molecules.

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And using this you already know what are the types of bonds. Bonds Sigma PI Delta these are examples of what kind of bonds are formed using different orbitals. Again I leave this to you as an assignment in case of any difficulty any question, please feel free to contact us or ask in the open session. This completes our discussion of H2 + little longish module sorry very fast but its repetition of what we done earlier and I am sure you will be able to handle it.

With this knowledge we next discuss H2 molecule we bring in another electron and use the same orbital perhaps with modification for things like shielding and we will see how that compares with earlier valence bond approach. And after that we are going on to homonuclear diatomic for second row then heteronuclear diatomic and polyatomic molecules. Finally we will talk about Pi molecular systems.