Quantum Chemistry of Atoms and Molecules
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Lecture-62
Molecular Orbital Theory for Homonuclear Diatomic Molecules

We have defined molecular orbitals as you remember an orbital is a 1 electron wave function. So molecular orbital would be the wave function of a molecule with 1 electron and the simple 1 electron molecule that we have discussed so far is H 2 + now what do we do with this orbitals. Of course we do not want to talk about H 2 + and then go home we want to talk about H 2 and other more complicated molecules do not we.

So today we are going to learn how to use this molecular orbitals to understand the bonding of homonuclear diatomic molecules.

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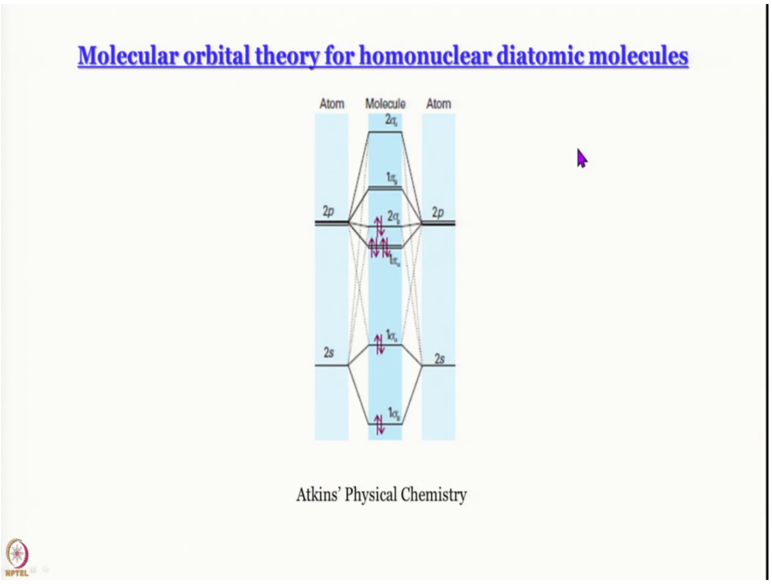

Molecular orbital theory for homonuclear diatomic molecules

Atkins' Physical Chemistry

We will discuss hydrogen at hydrogen molecule dihydrogen and then we will quickly go through well helium 2 does it form will answer question and then we will go through the second row homonuclear dynamic molecules in this class.

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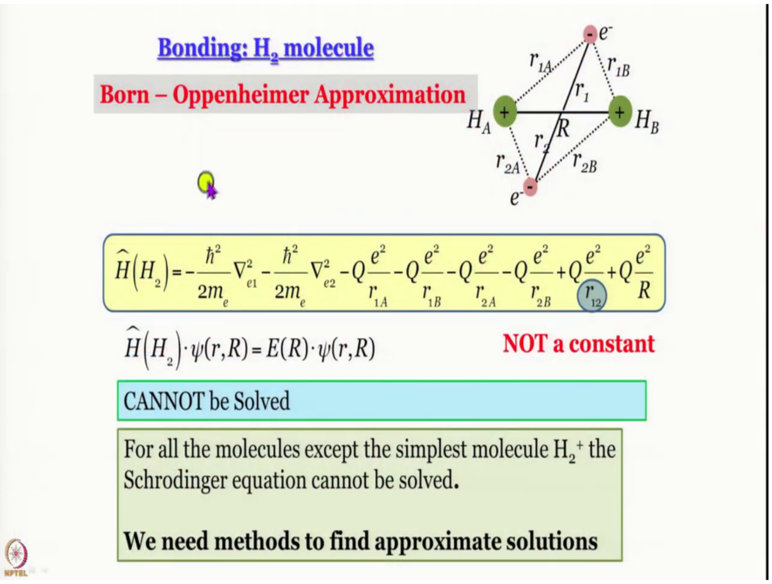

Bonding: H_2 molecule

Born – Oppenheimer Approximation

$$\hat{H}(H_2) = -\frac{\hbar^2}{2m_e}\nabla^2_{e1} - \frac{\hbar^2}{2m_e}\nabla^2_{e2} - Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} - Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

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

NOT a constant

CANNOT be Solved

For all the molecules except the simplest molecule H_2^+ the Schrodinger equation cannot be solved.

We need methods to find approximate solutions

So just to remind you for H 2 molecule the first system that we want to talk today under bond Born-Oppenheimer approximation we have already written that this big expression for the Hamiltonian simplifies somewhat because well sorry I did not realize I do not have the because here this R is a constant that is what we take. So for every value of r we have to work out these this Schrodinger equation using this Hamiltonian if possible.

And the complicating factor is that r 1 2 is not a constant so the moment you have 2 electrons it cannot be solved. So we have learnt how to use linear combination of atomic orbitals to generate these molecular orbitals you might remember that we can generate any wave function by taking an appropriate linear combination and things become simple if we take linear combination of an orthonormal set functions belonging to an orthonormal set that is the general case.

The special case we are using now is we are using this orthonormal set of atomic wave function. Linear combination of atomic orbitals by them we generate the molecular orbitals and of course we can use variation theorem and minimize energy that will be the upper bound of the energy that we can hope to get. And then we fill in the electrons.

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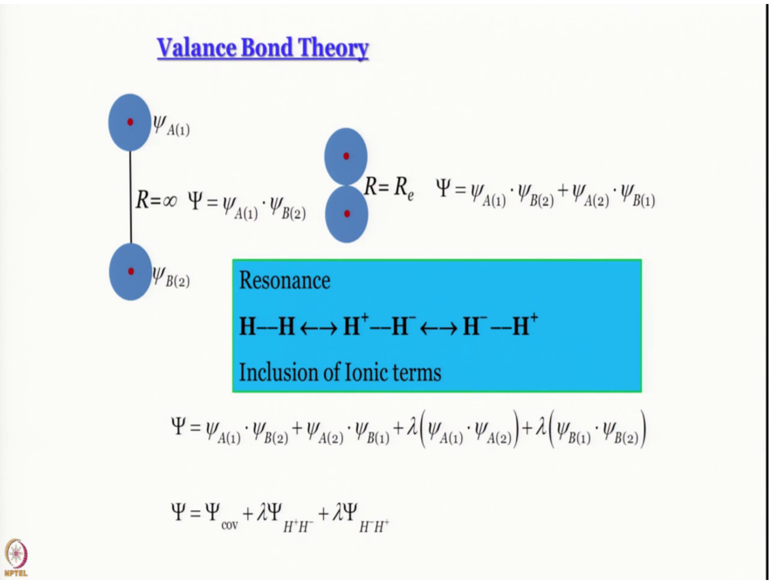

Valance Bond Theory

$\psi_{A(1)}$

$R=\infty \quad \Psi=\psi_{A(1)}\cdot\psi_{B(2)}$

$\psi_{B(2)}$

$R=R_e \quad \Psi=\psi_{A(1)}\cdot\psi_{B(2)}+\psi_{A(2)}\cdot\psi_{B(1)}$

Resonance

$H{-}H \longleftrightarrow H^{+}{-}H^{-} \longleftrightarrow H^{-}{-}H^{+}$

Inclusion of Ionic terms

$$\Psi=\psi_{A(1)}\cdot\psi_{B(2)}+\psi_{A(2)}\cdot\psi_{B(1)}+\lambda\left(\psi_{A(1)}\cdot\psi_{A(2)}\right)+\lambda\left(\psi_{B(1)}\cdot\psi_{B(2)}\right)$$

$$\Psi=\Psi_{cov}+\lambda\Psi_{H^{+}H^{-}}+\lambda\Psi_{H^{-}H^{+}}$$

That is the strategy for molecules real molecules beyond H2 +. Now we have already discussed valence bond theory and in valence bond theory what we said is that you do not have to restrict yourself to covalent bond you can also include ionic terms by considering this kind of resonance and realizing that these ionic terms have to be scaled down their contribution cannot be too much. Because in H 2 you do not really expect it to be H + and H - to a very great extent.

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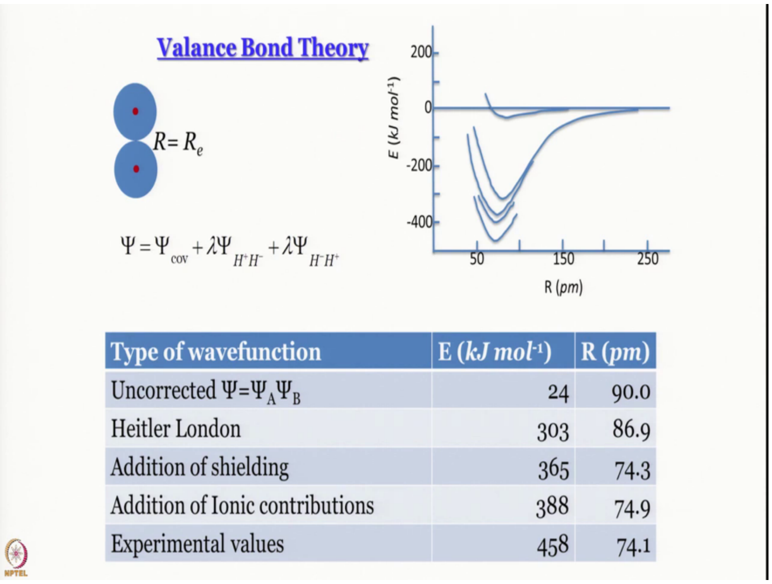

Valance Bond Theory

$R=R_e$

$$\Psi=\Psi_{cov}+\lambda\Psi_{H^{+}H^{-}}+\lambda\Psi_{H^{-}H^{+}}$$

Type of wavefunction	E (kJ mol⁻¹)	R (pm)
Uncorrected $\Psi=\Psi_A\Psi_B$	24	90.0
Heitler London	303	86.9
Addition of shielding	365	74.3
Addition of Ionic contributions	388	74.9
Experimental values	458	74.1

But it is not as if it makes no contribution as we have discussed as we keep on correcting the wave function even addition of ionic contributions takes the energy down from 365 kilo joule per mole to 388 kilo joule per mole whereas the experimentally observed value is 458 kilo joule per mole which is as good as it gets. So this ionic terms please remember can be brought in as an afterthought in valence bond theory by bring adding an appropriate term with that is appropriately scaled down. As we will see in molecular orbital theory it arises naturally is it good or is that bad? Well perhaps is good as well as bad but let us wait for it to come.

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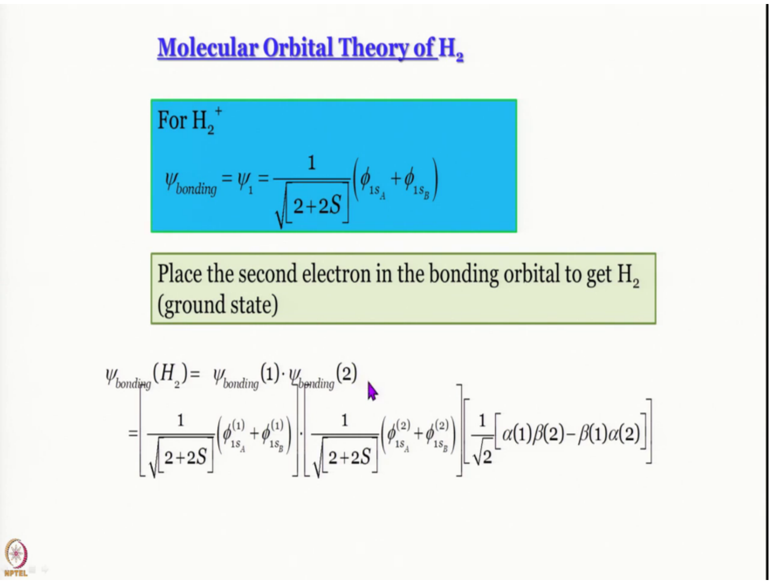

Molecular Orbital Theory of H_2

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)

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

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

Now see so for molecular orbital theory of hydrogen now we have moved on we want to use molecular orbitals that we generated in H 2 + and we want to describe dihydrogen H 2 using those same molecular orbitals. Well we might have to correct for shielding and all that is fine but assuming all that has been done and assuming that variation method has been used to minimize energy. The kind of expression we get is this your psi bonding would be 1 divided by root over 2 + 2s and I am sure you remember what 2 what s is? Is the overlap integral 1 by root over 2 + 2s is the normalization constant of the plus combination phi 1s a + phi 1s b this is our bonding orbital.

And we know what the antibonding orbital is as well but for hydrogen both the electrons would go into the bonding orbitals because like atomic orbitals molecular orbitals can also accommodate 2 electrons. So we will place the second electron in the bonding orbital then what is the wave function that I am going to get. So, psi bonding of dihydrogen is going to be something like psi bonding occupied by 1 multiplied by psi bonding occupied by 2.

Of course we are going to expand this expression and see what we get but well here it is without much I do. Do you agree with me that this thing that we have written this wave function it is symmetric with respect to exchange I hope you have not forgotten what we had learnt in while discussing many electron atoms. The total wave function which is a product of spatial part and spin part that wave function for a fermion like electron has to be anti symmetric with respect to exchange.

So what we have here is that we have a symmetric spatial part right you can just open it up we are going to show you the result of opening outs very, very simple. So since this spatial part is symmetric it is not very difficult to understand that the spin part is going to be anti symmetric alpha 1 beta 2 minus beta 1 alpha 2. So, what we learned right away is that the ground state of dihydrogen according to molecular orbital theory is a singlet state remember the spin wave function is a unique 1 in triplet.

You have 3 wave functions alpha alpha beta beta alpha beta plus beta alpha but alpha beta minus beta alpha is a unique wave function standalone wave function by itself and that is what gives a singular state singlet means there is only 1 state with that energy. And I hope you also recognize that this is the same result that we got in valence bond theory as well. In valence bond theory also we had worked out that the ground state of dihydrogen is going to be singlet remember the ground state when energy went to a minimum it was an associative state whereas the triplet state that we got from valence bond theory turned out to be a dissociative state it would never form.

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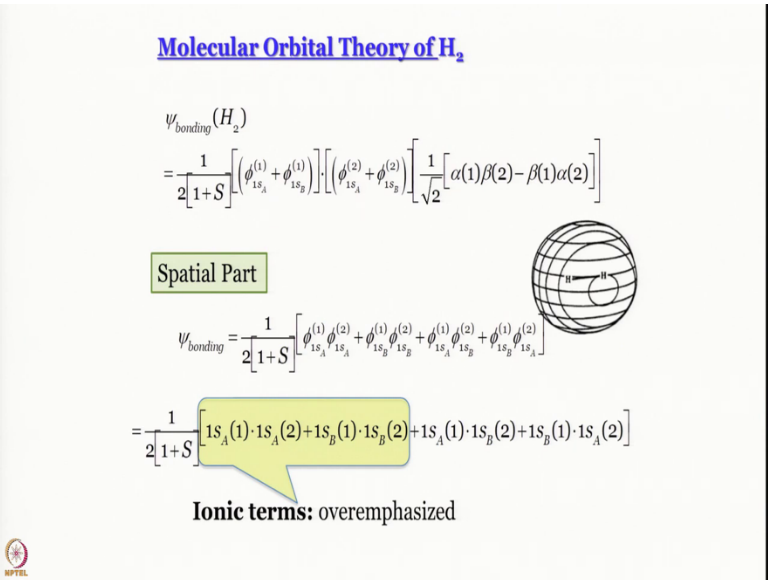

Molecular Orbital Theory of H_2

$$\psi_{bonding}(H_2)$$
$$=\frac{1}{2[1+S]}\left[\left(\phi^{(1)}_{1s_A}+\phi^{(1)}_{1s_B}\right)\right]\cdot\left[\left(\phi^{(2)}_{1s_A}+\phi^{(2)}_{1s_B}\right)\right]\left[\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\right]$$

Spatial Part

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

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

Ionic terms: overemphasized

So with that we can go ahead and complete our discussion let us expand the spatial part this is what we get and once again I am going fast because after all that we have learnt in this course all this is child's play for you. One thing that I want to highlight is this as usual we have written instead of phi s and all that we have done 1 s a 1 one a 2 etcetera. See just look at the first 2 well look at all the terms 1 by 1 start with the last last 1 is 1 is B 1 one is A 2 what does that mean?

Electron number 1 is in atom B electron number 2 is in atom A so exchange has taken place. Second last term the third term is 1S A 1 1 S B 2 electron number 1 in atom A electron number 2 in atom B. Now look at the first 2 terms 1S A 1 1S A 2 1S B 1 1S B 2 what do they stand for they stand for the situation where both the electrons number 1 and 2 reside on atom A or both the electrons reside on atom B so what kind of situation is that H plus H minus.

The atom which has both the electrons that would be H minus at that instance and the atom which has no electron now would be H plus and I mean it would there be resonance between all these forms. So these are the ionic terms and as you see right away so good thing what is the good thing about molecular body theory so far ionic terms have materialized by themselves we did not have to think that they would be there and we did not have to invoke them.

What is the bad thing MOT has actually overdone it where is that lambda remember the lambda scaling factor that we used in valence bond theory and we said that this lambda has a small value. So ionic terms have a small contribution as might be expected that lambda is not here. So MOT is a general theory that well gets us the ionic terms that is great the problem is it over does it once in class I said that it in its enthusiasm to be very general molecular orbital theory over does it.

And the problem was somewhat somebody quoted me and wrote this in the exam so when we are correcting everybody else correcting the scripts had a good laugh at my expense because the student had written according to professor Anindya Datta molecular orbital theory in its enthusiasm to be too general sometimes overdoes things. So then I realized that I have also perhaps overdone I have been too enthusiastic so I do not say that joke anymore but well I have right now anyway pj is a part MOT as you see over emphasizes the ionic terms so that is the problem.

So when you get MOT results you need to keep an eye on them right sometimes you might get a little extra that is not really correct.

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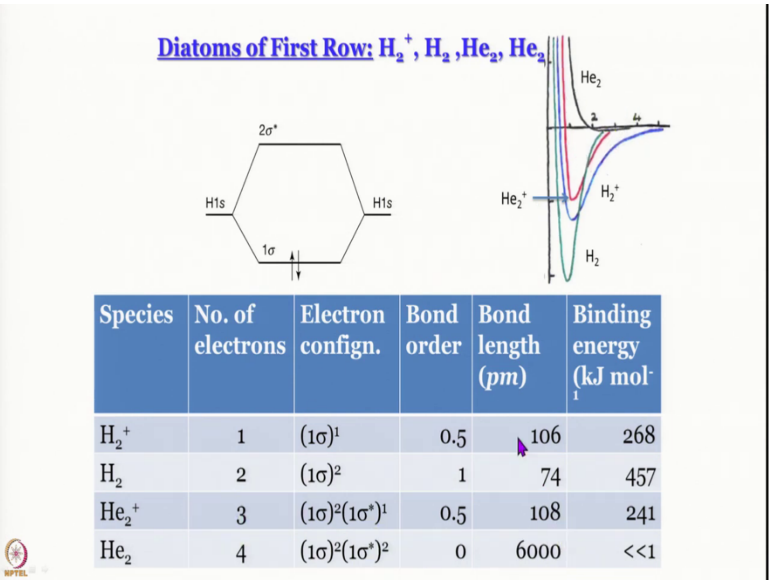

Diatoms of First Row: H_2^+, H_2, He_2, He_2

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

So now we know this well constant probability surfaces of bonding orbital antibonding orbital for H 2 both the electrons reside here and this would be the energy level diagram, excellent. Now if you fill in the electrons and make it say H e 2 + H e 2 then what happens. Let us have a look at the numbers and these are all calculated using variation method. So H 2 + has a bond order of 0.5

that is not very difficult to understand we know what bond order means bond length is 106 picometer binding energy kilo in kilo joule per mole is 268.

H 2 boundary is 1 because 2 electrons are there in the bonding orbital no electron in the anti bonding orbital bond length is 74 which is not very far apart far away from the reality binding energy turns out to be 457 kilo joule per mole. H e 2 + bond order is again 0.5 very similar to H 2 + but bond length is well more or less same 108 but a little longer right 108 is a little longer than 106. So bond length for H e 2 + is a little longer little more than that of H 2 + also if you look at binding energy that is a little more well what am I saying its actually minus right so H e 2 + is not as stable as H 2 + it is more unstable than H 2 + of course both of them are more unstable than H 2 there is a best case scenario.

But the point is that He 2 + and H 2 + both have same bond order but energies are not same H 2 + actually has a little more stability than H e 2 + why because in H 2 + you just have 1 electron. In the bonding orbital in H e 2 + you have 2 electrons here and 1 electron here and if you remember the picture that we had shown in the last lecture this energy difference between the isolated atom and antibonding orbital is a little more than the energy difference between the bonding orbital and the atomic orbitals at equilibrium bond length.

So H e 2 + is less stable than H 2 + and what about H e 2 well bond order is 0 you do not even expect it to form right mind but if you look at this graph there is something is not it. There is a little shallow trough all these are much bigger truss H 2 is the deepest followed by H 2 + followed by H e 2 +. H e 2 has a minimum for a bigger inter nuclear separation much bigger much larger 6000 picometer but there is a minimum right binding energy is very small much much less than 1 kilo joule per mole but it is there it is not 0 where has that come from?

That has come from inter molecular interactions you might have studied van Der Waals interactions and all even separate molecules that are not bonded to each other when they come close to each other they can induce dipole moments in each other right. So this induced dipole induced dipole interaction is what you see as a as the factor that causes a little bit of stabilization at very large inter nuclear separation of 6000 picometer for H e 2 so that is first row.

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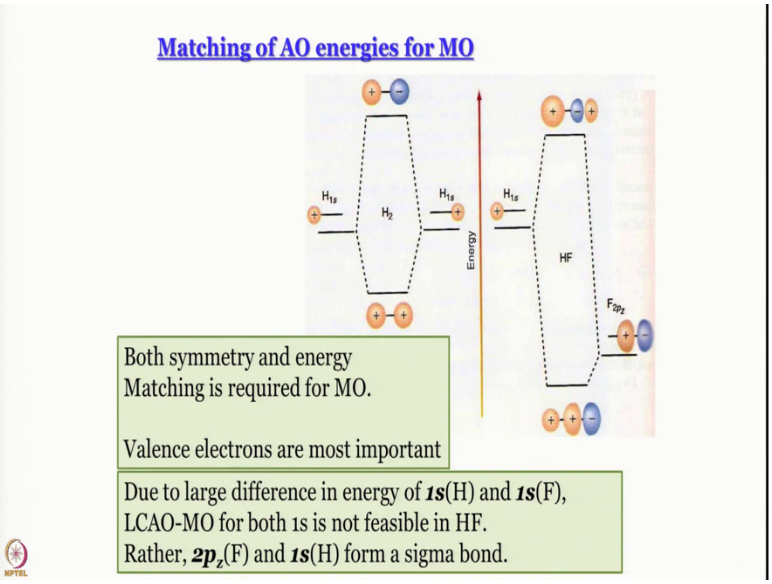

Matching of AO energies for MO

Both symmetry and energy Matching is required for MO.

Valence electrons are most important

Due to large difference in energy of *1s*(H) and *1s*(F), LCAO-MO for both 1s is not feasible in HF. Rather, $2p_z$(F) and *1s*(H) form a sigma bond.

For second row when we go there we are not going to discuss this in too much of detail because again we have been studying this since we were in class 11 or class 12, one thing that we need to remember and I think we have used this term earlier but now we bring it back it is important that symmetry and energy both are matched symmetry and energy of the atomic orbitals would have to match in order for them to participate in the linear combination which gives rise to the molecular orbital and we work with valence electrons.

What are we saying here this is H 2 we have discussed already there 1s and 1s of course at the same energy and they have given you the picture we have discussed. If you talk about HF and will come back to it what happens is for as z increases stability of the orbitals increases also they go down in energy. So 1s orbital of fluorine is much lower in energy than once orbital of hydrogen their energies are not compatible they do not in do not form bond they do not participate in the linear combination for forming molecular orbitals.

However the energy that is close that also there is a difference right and we will talk about the implication of this difference in the next lecture but the 1 that is closest is F 2 p. So it is F 2 p that participates in linear combination with hydrogen atom 1s orbital to form the bonding and antibonding orbitals even then 1 needs to consider in a symmetry as well. See let us say this is my 1s orbital from hydrogen. So let us say this is z axis approach of direction of approach this is p z since color is free let me use colors.

This is p y the there is no meaning of this larger lobe of p y it is just my poor artistic scales and this is p x pointing towards us. We can make this a little fat and going away from us this is p x. Now see p x p y and p z all have the same energy do not they, however only p z is in the right disposition to give you sigma interaction with hydrogen or I will even say bonding interaction with hydrogen 1s orbital yeah because this is plus oh I think I chose white as color that is why it is a problem so this is plus this is minus let us say this is plus.

What about p x or p y this is 1s lets say this is plus and p x of p y would be like this + minus that would be non bonding is not it. So p x and p y would actually remain so if I draw this p x and p y here they would remain as non bonding orbitals this is the meaning of non bonding orbitals. Orbitals which have either in improper energy or improper symmetry to participate in bonding and antibonding interactions they remain non bonding orbitals and they remain property of 1 particular atom.

And p z forms these sigma and sigma star orbitals that will talk about later. So energies have to be close symmetries have to be compatible then only orbitals or 2 different atoms are going to participate in the linear combination and give rise to MO. This is the most important it might sound to be very simple but it is important nevertheless we better understand.

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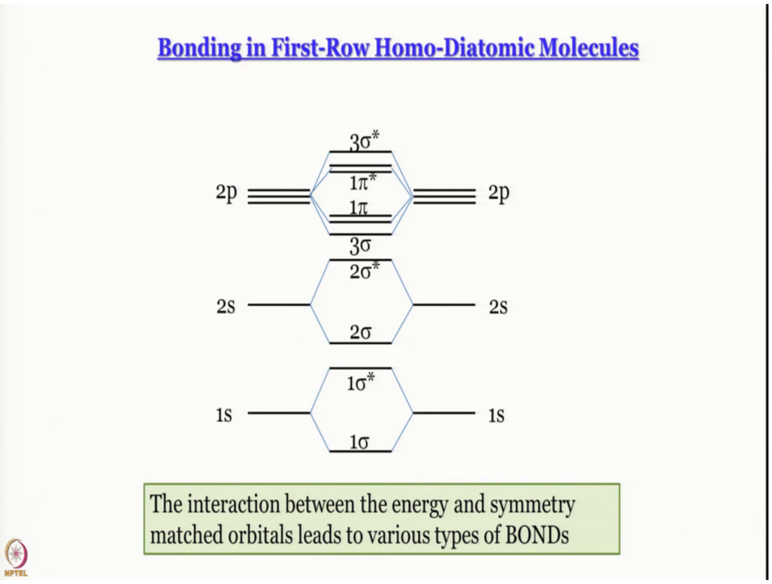

Bonding in First-Row Homo-Diatomic Molecules

The interaction between the energy and symmetry matched orbitals leads to various types of BONDs

It now with that background we can try to develop an energy scheme for second row homo diatomic molecules and this is what the scheme would be see in multi electron atoms right. So 2s and 2p would not have the same energy here in hydrogen atom 2s and 2pb all have the same energy you might remember the energy expression has nothing in l its N all the way. So here what will happen 1s and 1s the close in energy and symmetries are same.

So you get 1s 1 sigma 1 sigma star well this 1, 2 these are just sequence in increasing order of energy there are different ways of writing the names of these orbitals I have used this convention. Then 2s and 2s give you 2 sigma 2 sigma star 2p z 2p z 3 sigma 3 sigma star and then 2p y 2p z in this case they will not remain anti bonding sorry they will not remain non bonding because this 1 has 2p x 2p y this 1 also has 2p x 2p y right. So they are going to form pi orbital pi MO's like this. This is 1 pi MO this is 1 pi MO.

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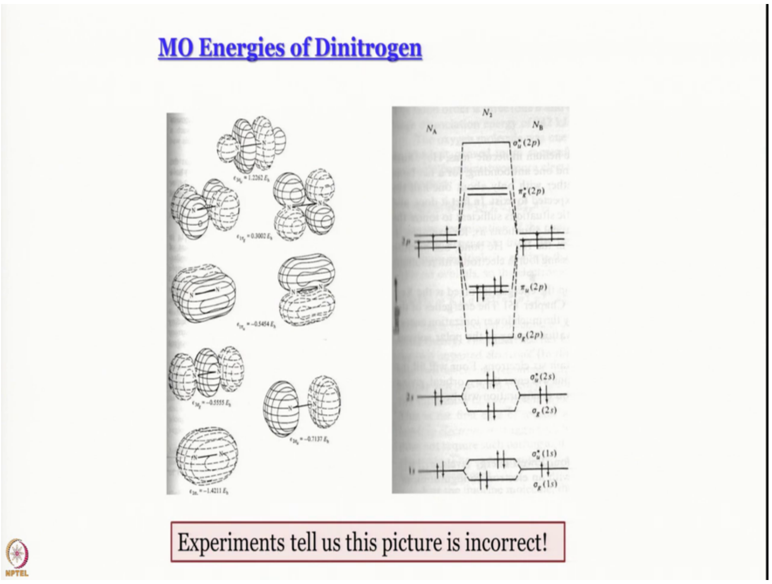

MO Energies of Dinitrogen

Experiments tell us this picture is incorrect!

Now next thing to do is to fill in the electrons when we do that if you take this scheme that we have done already sorry for the quality of these figures they are xerox from I think Hughes's inorganic chemistry book but I think you understand what I am trying to say. So if you use this scheme and fill in the electrons for dinitrogen how many electrons are there in nitrogen 2 4 5 6 7 right and then you start distributioning them 7 into 14 electrons 2 4 6 8 10 12 14.

So what we see is that the homo highest occupied molecule orbital would be a pi orbital but if that is the case then nitrogen should have been very reactive. Remember alkenes are prone to addition reaction right remember bromine water test for unsaturation you have alkene or alkyne you add bromine water it gets decolorized why? Because bromine adds and gives you dibromo derivative if nitrogen indeed had pi orbitals as the highest occupied molecular orbitals then they would participate in addition reaction.

Fortunately that is not the case because you remember what is the percentage of nitrogen in our atmosphere in air? That is by far the biggest component if it was very reactive then everything would have rusted everything would have perhaps caught fire everything would have reacted away with nitrogen and we will have a world or universe full of nitrides fortunately that is not the case nitrogen is inert and it does not undergo addition reactions. That means this model that we have constructed is not right we need a different model.

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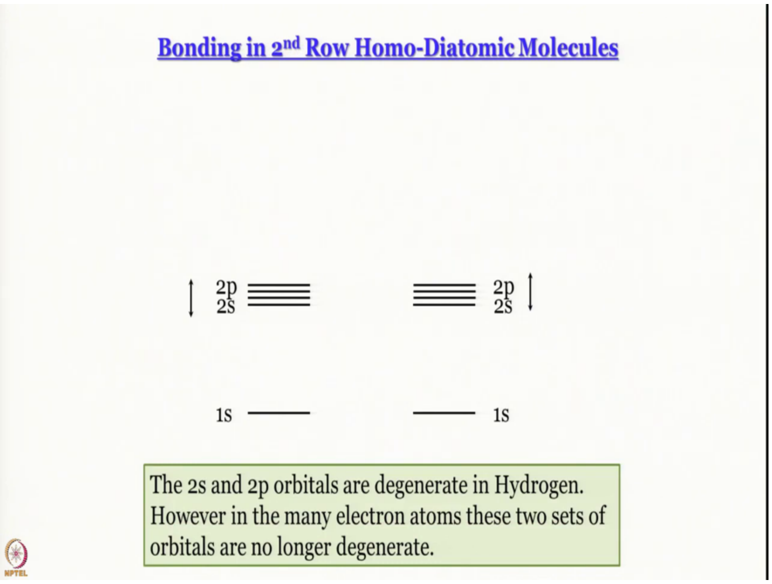

Bonding in 2^{nd} Row Homo-Diatomic Molecules

The 2s and 2p orbitals are degenerate in Hydrogen. However in the many electron atoms these two sets of orbitals are no longer degenerate.

And this different model is built keeping in mind that not all atoms or not all elements in the second row have to behave in the same way. So we start from the situation of hydrogen. So in hydrogen 2s and 2p orbitals are degenerate right. Now when in in a many electron atom we said they are different but then is it of 0 1 situation or is it gradual is it that for hydrogen you have this 2s and 2p orbitals that are of same energy and all of a sudden you go to second row and they become different in energy from the beginning or is it that it is graded?

That for the lighter elements for second row do we still have s and p close to energy and since their energies are close can they mix to form hybrid orbitals and then as the atomic number increases does this energy difference between 2s and 2p become more prominent and does the model that we have proposed earlier become applicable let us see.

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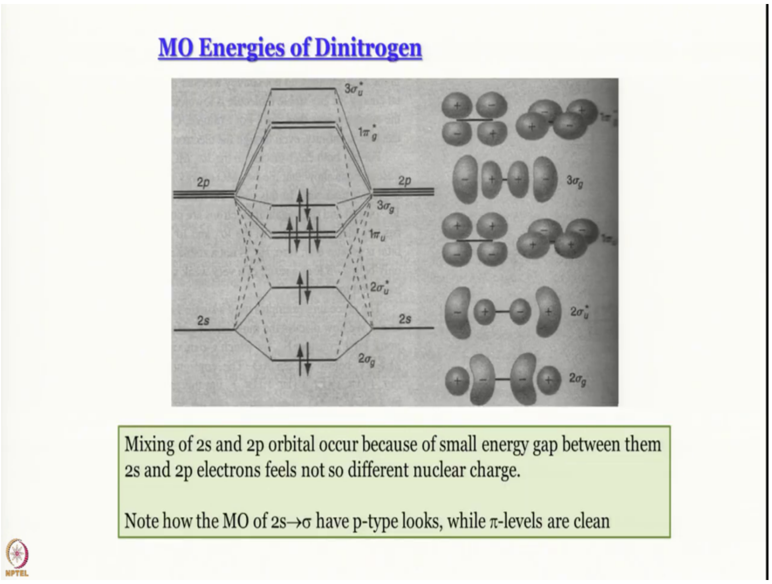

MO Energies of Dinitrogen

Mixing of 2s and 2p orbital occur because of small energy gap between them 2s and 2p electrons feels not so different nuclear charge.

Note how the MO of 2s→σ have p-type looks, while π-levels are clean

So, for dinitrogen if we invoke this model where we have sp mixing again this picture is from Hughes's and I am not discussing too much in detail because I am sure all of you have seen this in case of any doubt feel free to contact us we the TA's are there or I will help you out. So when we consider sp mixing then the energy level changes you have a will come to this well you remember we talked about g and u last in the last class.

We have this bonding gerade symmetric to inversion orbital followed by antibonding but look at the lines here this antibonding orbital has contribution from not only this 2s not only this 2s of nitrogen but also 1 of the 2p's 2p z 1 of the 2p's here right 2p z. So this these lines are drawn to indicate that s p mixing has taken place and when that happens energy levels do not follow that pattern that we had shown you earlier.

What happens is this sigma bond this sigma orbital which you would expect to be lower than the pi orbital comes above in energy. So now homo that we get is actually a sigma orbital which would not undergo addition reaction that is what makes dinitrogen so unreactive and that is why 1 of the pioneers or perhaps the pioneer of modern chemistry in india Acharya Profula Chandra Rai he became famous because he could make dinitrogen react with mercury to get a nitride of mercury.

In later time this claim has been disputed and another eminent researcher also from India had said that PC Rai was wrong it is not mercuric not nitrite of mercury but then yet another group got together and using x ray crystallography showed that he was right after all it is nitrite. So the reason why there was so much of fascination about formation of this nitrite with mercury is that nitrogen is so unreactive because the homo is sigma.

So these modified energy schemes considering sp mixing nicely describe the situation for dye nitrogen ok.

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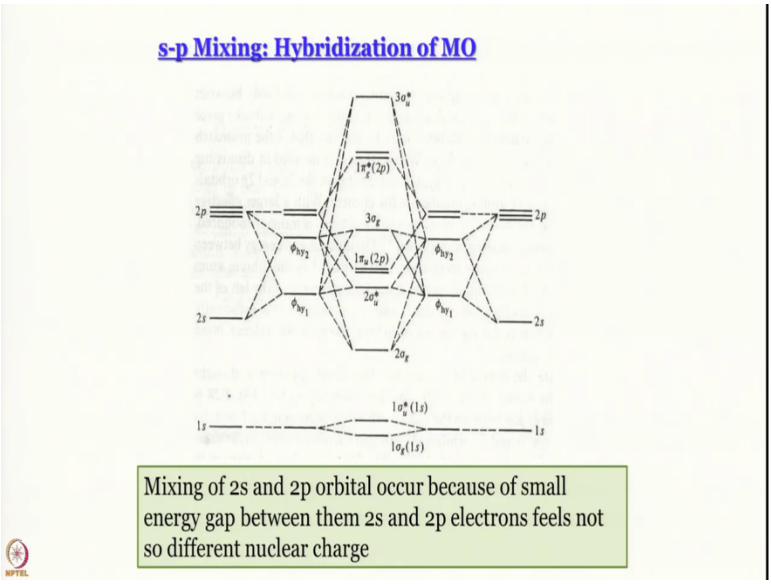

s-p Mixing: Hybridization of MO

Mixing of 2s and 2p orbital occur because of small energy gap between them 2s and 2p electrons feels not so different nuclear charge

So what we are saying is that for small energy gap between 2s and 2p that is for smaller z values in the second row there will be mixing and the scheme that you have is like this as a B.Sc student I used to be fascinated by this diagram even before I read this, this is again from Hughes book it looks like a lunar or by orbiter lunar lander well I forgot the name right now lunar module used by the first lunar expedition it looks something like that right.

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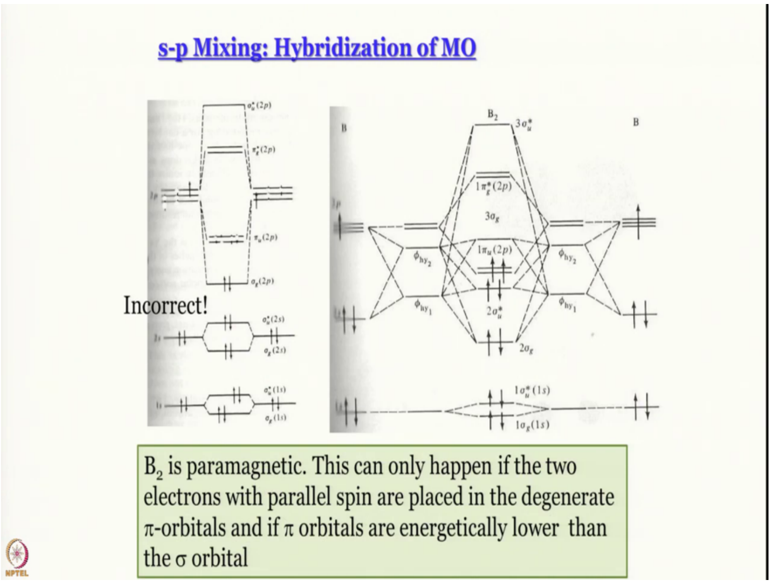

s-p Mixing: Hybridization of MO

B_2 is paramagnetic. This can only happen if the two electrons with parallel spin are placed in the degenerate π-orbitals and if π orbitals are energetically lower than the σ orbital

So this is the scheme that is proposed involving sp mixing now does it work only for nitrogen or for other things as well now I will go this quickly B 2 is known to be paramagnetic and that would only happen if you have energetic's like this. See if this sigma orbital would have been lower then that would be homo and the electrons would be paired. Actually paramagnetism indicates that the electrons are unfair which can only happen if the homo is a set of 2 degenerate orbitals that is pi orbitals.

So this model of sp mixing nicely explains not only nitrogen but also behavior of other molecules that would have appeared to be anomalous with smaller z. There are many where there will be no problem at all. I actually wanted to show you a very recent paper on B 2 unfortunately I forgot it if I remember maybe in 1 of the next classes I will slash it but actually the moment is gone I should have shown it now.

There is a paper published on this as recently as 3 weeks ago in 1 of the most reputed journals of chemistry this is from Indian association for the cultivation of science professor Devashi Gosh and professor Ankonpal have done some fantastic work on this homonuclear diatomic molecular vital theory I am saying this to indicate that it is not as if we are studying something that was worked out many, many years ago it was.

But it continues to remain relevant and enchanting we will come back to this when we talk about carbon monoxide as well all right.

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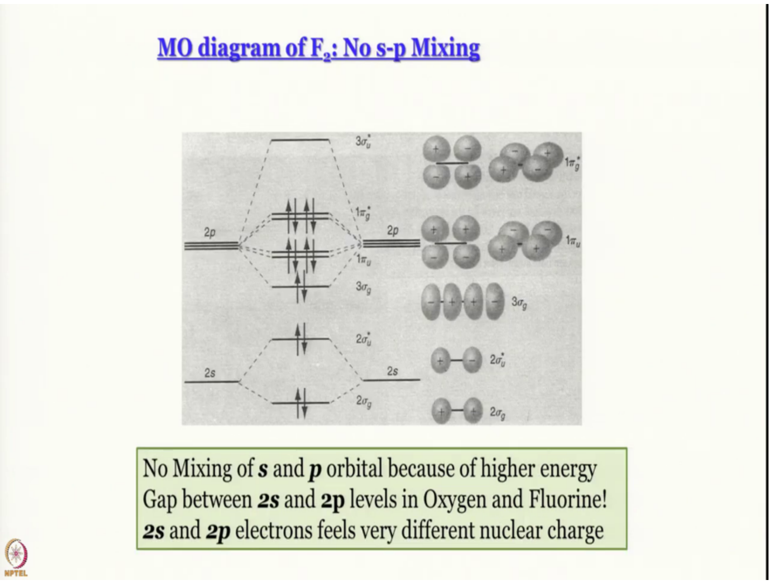
MO diagram of F_2: No s-p Mixing

No Mixing of ***s*** and ***p*** orbital because of higher energy Gap between ***2s*** and **2p** levels in Oxygen and Fluorine! ***2s*** and ***2p*** electrons feels very different nuclear charge

For F 2 there is no sp mixing and that is what we see experimentally so the energy scheme that is to be used is the other one.

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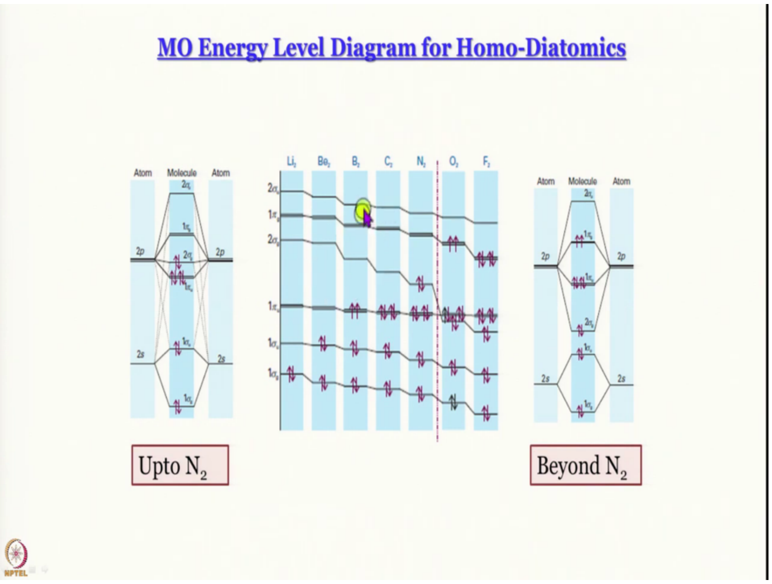
MO Energy Level Diagram for Homo-Diatomics

Upto N_2

Beyond N_2

So, what we see is that if you go from lithium 2 to f 2 it appears that first of all this energy lowering will be there but this relative change in the relative ordering of energy of the sigma and pi orbital appears to take place between nitrogen and oxygen. If you ask me why my honest answer will be I do not know we are not saying that we know why it happens; we just saying that the sp mixing model works nicely up to nitrogen dinitrogen and it is not manifested beyond dinitrogen that is all.

Oxygen for example yeah oxygen is paramagnetic right. So these are things that get explained by this interchange of sp mixing model to know sp mixing model between dinitrogen and dioxygen. So, that is all we wanted to discuss for homo nuclear diatomics in the next class we will discuss very briefly heteronuclear diatomics and then again briefly we will talk about polyatomic molecules. And we will see how symmetry plays a very important role in bonding of polyatomic molecules and what we say is going to be only the tip of the iceberg.