Symmetry and Group Theory
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Lecture -44
Symmetry and Chemical Bonding

So, in the previous lecture we have learnt how to use projection operator to estimate the symmetry adapted linear combinations, out of a given set of atomic orbitals. So, now that we know how to construct SALCs. Now let us see how do we use these SALCs to develop the wave functions to describe the chemical bonding. So, before we actually do that, let us have a slight refresher on what is chemical bonding and all.

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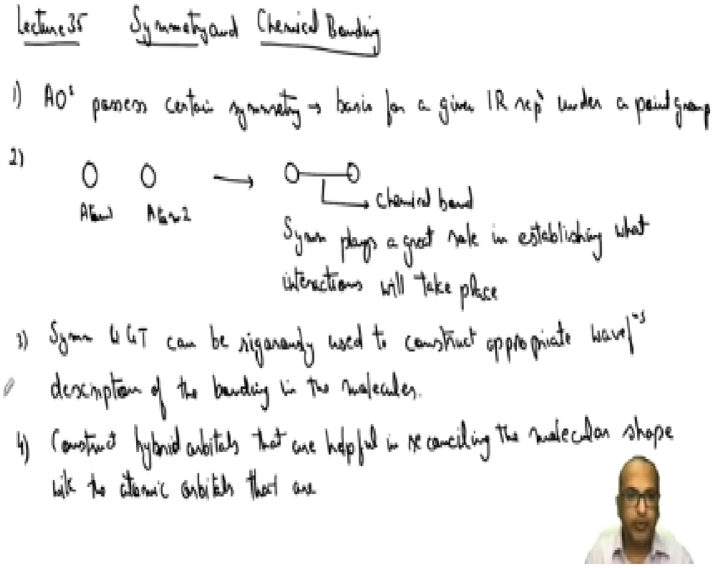
Lecture 35 Symmetry and Chemical Bonding

1) AO's possess certain symmetry → basis for a given IR rep^n under a point group

2)

Symm plays a great role in establishing what interactions will take place

3) Symm & GT can be rigorously used to construct appropriate wavef^{ns} description of the bonding in the molecules.

4) Construct hybrid orbitals that are helpful in reconciling the molecular shape w.r.t. the atomic orbitals that are

So, let us start with lecture 35, and we will be trying to understand the relation between symmetry and chemical bonding. So, we are well aware of that atomic orbitals possess certain symmetry, that is they can form bases for a given irreducible representation IR representation, under a point group. Now point group will be dependent on the molecular shape, so also when we know that if two atoms so this is let us say this is atom 1 and this is atom 2.

When two atoms are combining to form a chemical bond and this is my chemical bond. So, symmetry plays a great role here, we will see how in establishing what interactions will take place and what will not. So, we will see how symmetry comes into this picture but symmetry has a great role in forming the chemical bonds. So, this is what we already know, I am not telling anything new this is all we already know.

So, what we will be going to use is that symmetry and group theory can be rigorously used to construct appropriate wave functional description of the bonding in the molecules. So, this we are going to see how to do that and what else we can do? Using this theory, we can use construct hybrid orbitals that are helpful in reconciling the molecular shape, for example, why CH4 is tetrahedral.

And so on, so we will see that. So hybrid orbitals will be constructed with the atomic orbitals for example, 1s and 3p orbitals combined to give hybrid 4 SP3 hybrid orbitals that are oriented along the tetrahedral geometry in carbon CH4 hybrid orbitals that are available for bonding.

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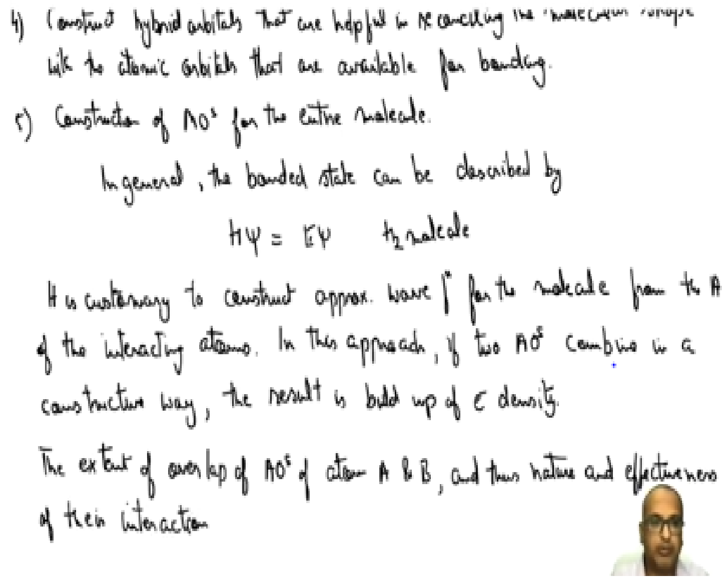

4) Construct hybrid orbitals that are helpful in reconciling the molecular shape with the atomic orbitals that are available for bonding.

5) Construction of MO's for the entire molecule.

In general, the bonded state can be described by

$$H\psi = E\psi \quad H_2 \text{ molecule}$$

It is customary to construct approx. wave f^n for the molecule from the AO's of the interacting atoms. In this approach, if two AO's combine in a constructive way, the result is build up of e density.

The extent of overlap of AO's of atom A & B, and thus nature and effectiveness of their interaction

So, we will also see construction of, that will come later but not in this lecture, construction of molecular orbitals for the entire molecule. So, in general we know that so again this is just a refresher, I am sure you all know this, in general, the bonded state can be described by the famous Schrodinger equation it is H phi equal to E phi where we all know this H is the Hamiltonian Psi the state function.

And the eigen function and E is the energy of that particular state. So, now we can solve this equation for simple molecules like H2 but typically it is not easy and straightforward to solve, to first set up it correctly, for more complex molecules. And then solving is another step, which is not possible for because it is very very difficult to invoke all sorts of interactions in a molecule so typically what is done is, it is, I will write, it is customary to construct approximate wave functions for the molecule from the atomic orbitals. So, we use the given atomic orbitals and we construct the molecular orbitals from those and from the atomic orbitals of the interacting atoms you can say. So, what happens, in this approach if two atomic orbitals combine in a constructive way we can say that the result is buildup of electron density.

So, atomic orbitals are described by wave functions, so wave functions have positive phases and negative phases. If two positive phases are going to interact there would be a, it is like simple addition of waves. So, there would be an enhancement of electron density in that area if two opposite phases of atomic orbitals will interact then there would be a loss of electron density and the corresponding interaction is called as bonding and anti bonding.

And if there is no change in electron density upon combination of atomic orbitals, then it is called as non-bonding interaction. So, we will see that how it works out. So, the extent of let us the extent of a overlap of atomic orbitals of let us say atom A and B, so nature and effectiveness will depend on the extent of overlap, and thus we can say nature and effectiveness or the strength we can say of their interaction is given by Slater overlap integral.

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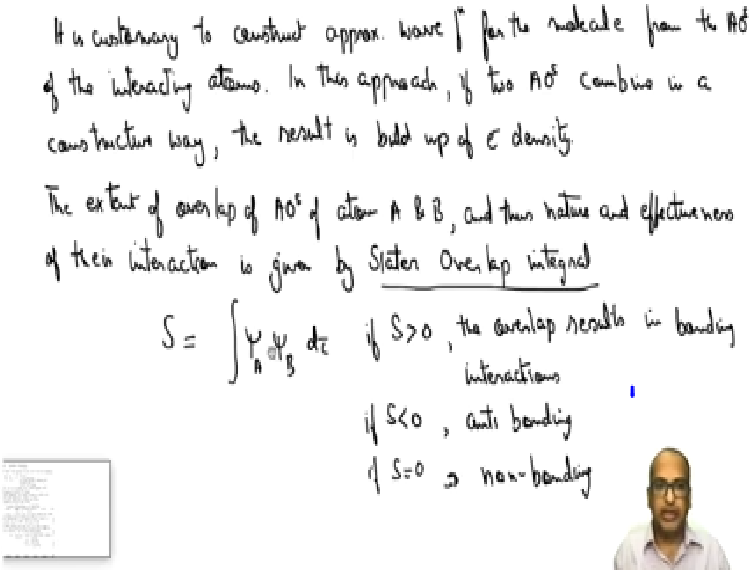

It is customary to construct approx. wave f^n for the molecule from the AO^s of the interacting atoms. In this approach, if two AO^s combine in a constructive way, the result is build up of e density.

The extent of overlap of AO^s of atom A & B, and thus nature and effectiveness of their interaction is given by Slater Overlap integral

$$S = \int \psi_A \psi_B \, d\tau$$

if $S > 0$, the overlap results in bonding interactions

if $S < 0$, anti bonding

if $S = 0$ ⇒ non-bonding

So, what is Slater overlap integral? It is defined as S then the integration of psi A, where psi A is the wave function describing the atomic orbital, of atom A and psi B and over d tau. Of course, there is going to be boundary conditions and all so now we can say that if S is positive then the overlap results in bonding interactions which is again characterized by buildup of electron density.

If S is negative, it is anti-bonding interaction and if S is equal to 0 it is possible, then it is non-bonding interaction.

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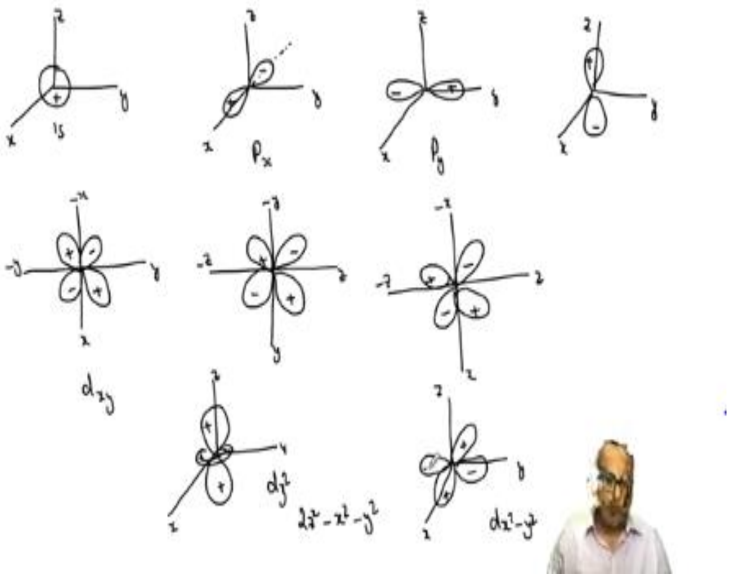

So, now to understand this, let us actually take draw the balloon diagrams of these orbitals which will help us understand how this works out. How the bonding and anti-bonding and non-bonding interactions work out? So, let me just draw first the balloon representations, the first is the S orbital so S orbital is typically drawn like a sphere. Let us call this as and then it will have a positive phase all together all through it will be positive phase.

So, remember that this is a wave function to the wave functions will have plus phase, and minus phase. Then we have let us say px, py, pz orbitals. So, this is my x, y and z and then I will call it as plus and minus this is px. So, I will write it as px, similarly I can have py, balloon diagram for py, so then you will have x, y, z. So, in some books you will see that the positive and negative phases of these lobes are different colours basically.

So, you will see that positive is shown in dark face, dark color or negative in shown in dark colour; or either way or in some books you will see just the plus and minus because these are basically just the phase of this wave functions. So, similarly for pz, we have x, y, z, you will have plus and minus, while we are doing this let us also quickly draw for just to remember for all 5 d orbitals. So, for x, y, minus x, minus y so I am drawing, this so z is coming out of the plane of the board.

So, I am not drawing z axis here, so the lobes are going to be in between the axis and this is positive this is positive negative negative. So, this is dxy then you have yz so we can have y, z, like this minus y, minus z, and again this will be in between. So, it is very easy to see that which lobe will be positive the positive side of the two axis, if these are multiplying this will give you positive sign the two negative sides if they are multiplying they will give you a positive sign.

One negative and one positive this will give you negative because the multiplication is negative and then so on. So, this is just a simple thumb rule, this applies for everything so here positive side of x axis, will be positive negative side of x axis will be negative. And so on so forth, so also draw it for x, z, minus x, minus z again this will be minus and now let us also draw for the rest of the two d orbitals.

Which will be the dz square and then there is a ring of negative phase over here like this. So, you have negative here and positive, positive here this is called as dz square. And the actual functional form if you want to write in terms of Cartesian coordinates; you can also write it as 2 z square minus x square minus y square. So, for the calculation purposes it is taken like this. I mean it is taken in the complete form. This is x, y, z and for x, y, z the last one is dx square minus y square which will be along the axis.

Now this will be x will be positive y will be negative because we have y square is negative x square is positive so now that we know how this works;

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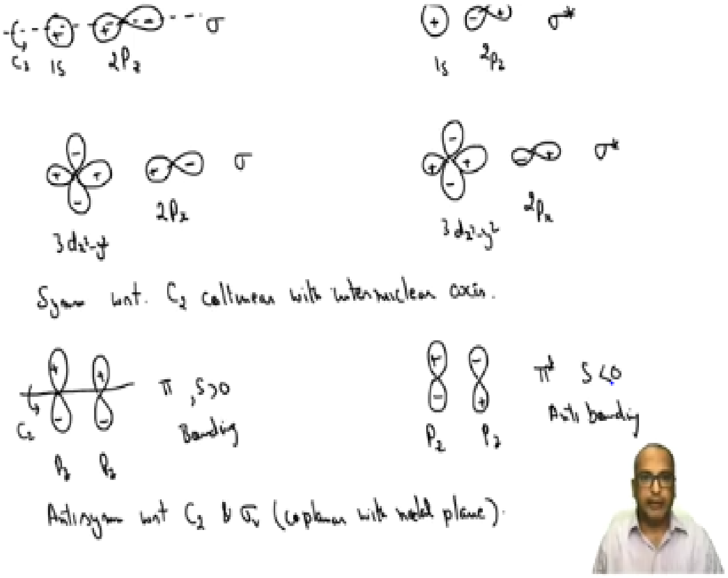

Symm wrt. C_2 collinear with internuclear axis.

Antisymm wrt C_2 & σ_v (coplanar with nodal plane).

Let us try to see different bonding interactions. So bonding, where S will be greater than zero. And then let us also look at the corresponding anti bonding where S is less than zero. Now let us say that our interaction is between 1S and 2Pz, so positive side positive side negative side this is 2P z this would be called as sigma, and if my S is interacting from the other side you have negative positive 2Pz, 1S, this would be called as sigma star.

You must have seen that in when you describe the bonding pictures, so bonding formation bonding interaction anti bonding interaction. So, now let us also see let us say if you have dx square minus y square and 2Px. So, dx square minus y square, will look like this where we have positive side that is x, and negative side that is y. So, this is dx square minus y square and you have 2Px.

So, this will be sigma because now there is a buildup of electron density over here when you combine these two orbitals these two lobes over here whereas if you do it the other way around this will be anti bonding, plus plus, minus minus and you have negative positive; So, this will be sigma star 2Px 3dx square minus y square so similarly so these are sigma and sigma star these type of interactions are basically, we can say that these are symmetric with respect to, I can write it here symmetric with respect to C2 collinear with the internuclear axis, nuclear axis. So, that is if you pass an axis through this is my internuclear axis and you do a C2 operation this will be symmetric. So, sigma sigma star interactions are symmetric with respect to C2 which is collinear with internuclear axis. Now let us look at the pi pi star interactions;

So, pi pi star interactions will be sideways interaction of these lobes. So, for example, if I have Pz interacting with Pz and I have positive phase interacting with positive phase negative interacting with negative then this would be called as pi interaction. Again, the S will be greater than 0 here because this is bonding interaction. And now if you have, I can write here S greater than 0 or bonding this will lead to pi bond this will lead to sigma bond.

Now if you have opposite phases of the two orbitals interacting then you have positive negative, negative positive this will be called as pi star, S will be less than zero this will be anti bonding. So, now if we see this if we now run as C2 through this will be antisymmetric that is the character under C2 operation will give you a negative sign; negative 1 with respect to C2, and if we say sigma v which is coplanar with the nodal plane.

So, if you draw C2 versus sigma v this C2 and sigma v the sigma v will be coplanar with nodal plane and this will be antisymmetric. So, that is the character under these two symmetry operations will be minus 1, so we know what is antisymmetric and what is symmetric with respect to a given symmetry operation?

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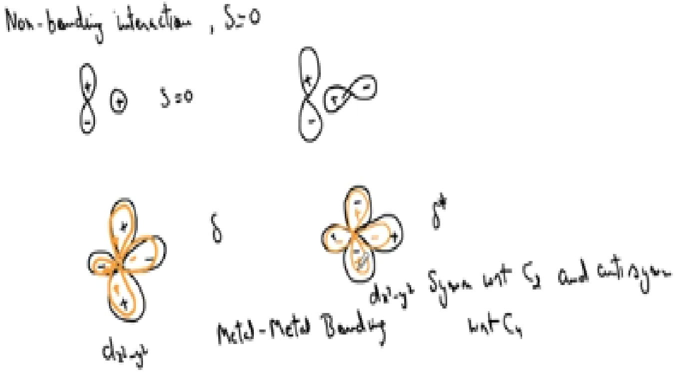

Now let us also look at nonbonding interaction, for which S will be equal to zero. So, this is just again a balloon representation example, so let us say if I have P orbital oriented like this and S orbital oriented like this. So, this will be positive positive and positive negative so there is no change in electron density. So, this will give you S equal to zero or non-bonding interaction. Similarly, you can also have between two P orbitals like in this way.

So, here also it is positive positive and positive negative interaction, which will cancel out each other and this will be called as nonbonding interaction. Let us also consider d orbitals overlapping for interacting with the orbitals, this is mostly seen in case of metal-metal complexes. Let us say if we have sorry for the bad drawing so let us see if this is my d orbital and on top of that I have another d orbital with same lobes something like this.

Now those will also have same signs then this will be called as delta and if you have opposite signs negative negative, positive positive, and you have instead of positive here you will now have negative of black, positive of black, positive and negative; So, this will be called as delta star interaction. So, these are typically seen in metal-metal bonding. So and these are symmetric with respect to C2 and anti-symmetric with respect to C4.

So, and the C2 is basically collinear with the z axis, z axis is coming out of the plane of the board so for example, this one is dx square minus y square, dx square minus y square interacting with the same thing; We can also have d xy interacting with dxy and so on. So, this gives you a brief introduction of what is chemical bonding, in next lecture we will take up different theories.

For example, valence bond theory and molecular orbital MO theory. So, we will see how symmetry and group theory rules and symmetry adapted linear combinations can be used to describe the wave functions in case of both of these theories. That is all for today so see you next class thank you.