Advanced Transition Metal Chemistry – Molecular Orbital Theory
Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 17
Ligand Field Theory (LFT)

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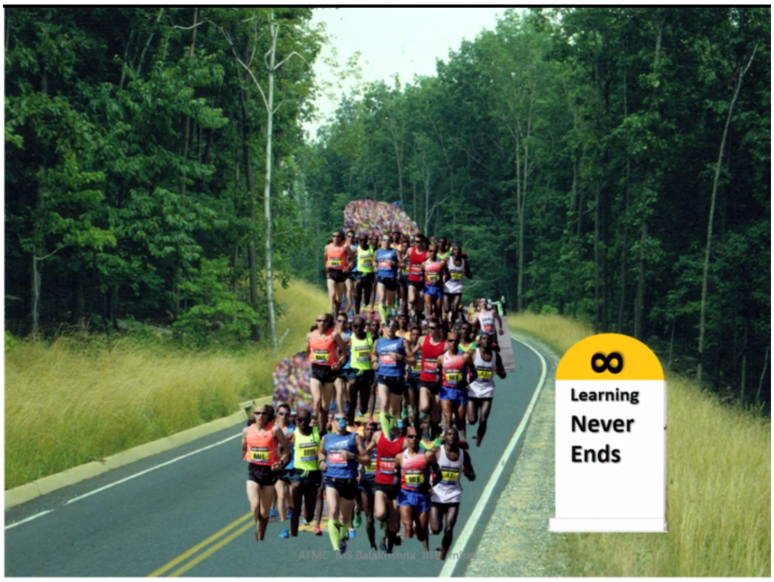

Hello everyone. In our day-to-day life, we get an opportunity to learn many things from both living and non-living objects. And if you have keen observation, you can learn lot of things. And also if we learn something good that we can pass it on to others that means irrespective of our age, irrespective of our profession, we have a lot to learn every day and hence I say learning never ends.

So, with this let us continue learning chemistry, especially chemistry of transition elements. So, today's focus will be on ligand field theory. And until last lecture, I was discussing about crystal field theory and its utility in understanding coordination chemistry and why people switched to ligand field theory, let us try to understand.

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CFT + MOT =LFT

To accommodate and account for both ionic and covalent characters in Metal—Ligand bonds, LFT was introduced. It is a combination of best parts of Valence Bond Theory, Crystal Field Theory and Mulliken's Molecular Orbital Theory.

To accommodate and account for both ionic and covalent characteristic in metal-ligand bonds, ligand field theory was introduced and it is a combination of best part of valence bond theory, crystal field theory and Mulliken's molecular orbital theory. So, let us try to conclude crystal field theory and its advantages and considering let us try to understand crystal field theory's simplicity and how it differs from ligand field theory and what is ligand field theory.

Crystal field theory of course is a simplest model for explaining the structures and properties of transition metal complexes. The theory emphasizes mainly on simple electrostatic interaction between the metal ion and the ligands and considering ligands as point charges, although some of assumptions made are inaccurate. It is still very simple to understand and also useful because of its effectiveness in using molecular symmetry.

It describes the properties of metal complexes such as colour, magnetism, geometry and relative stability of complexes having different type of ligands quite accurately. However, ligand field theory is more advanced and it is originated from molecular orbital theory. It is more complex compared to crystal field theory, but it is more accurate and ligand field theory will explain many questions accurately that crystal field theory may not.

From this context, and it is very appropriate to bring in ligand field theory concept, instead of crystal field theory, to understand or for better understanding of coordination compounds and their properties. Ligand field theory very effectively uses molecular orbital theory in coordination chemistry by giving importance to the effect of donor atoms that is the ligands on the energy of *d*-orbitals in the metal complexes.

Same thing we observed in case of crystal field theory also, the direction of approach of ligands how they influence the energy of d orbitals. The influence of ligands on the d electrons on a metal can be analysed from ligand field theory point of view, in two ways; electron-electron repulsion and of course this is due to the lone pairs from ligands when they start approaching the metal ion and bonding interactions between the metal and donor atoms.

The combined effect increases the energy of the d-electrons which in turn depend on the nature of ligand field and the geometry conferred by them at the metal centre. From crystal field theory, we know that in an octahedral field, e_g orbitals that is d_{z^2} and $d_{x^2-y^2}$ interact strongly whereas t_{2g} orbitals does not interact so strongly but rather weakly. Therefore, these two orbitals, that is d_{z^2} and $d_{x^2-y^2}$ along with the ligand orbitals form new bonding and antibonding orbitals.

The other three orbitals that are present on metal centre that are d_{xy}, d_{yz} and d_{xz} that is t_{2g} will remain as nonbonding with almost unchanged energy. Of course, these assumptions we made in crystal field theory as well. And then let us consider octahedral complexes. In octahedral complexes, the electrons of the ligand occupy all 6 bonding molecular orbitals, whereas any electron from the metal cation occupy the nonbonding or antibonding orbitals.

Nonbonding means it is t_{2g} or sometimes antibonding means it is e_g, especially when the metal ions have more than 6 electrons in their d orbitals. The separation between t_{2g} and e_g orbital is designated as the orbital ligand field parameter Δ_o similar to what we call it as crystal field stabilization energy. So, ligands whose orbitals interact strongly with the metal orbitals are called strong field ligands, for such ligands the orbital splitting is little larger.

In contrast, ligands whose orbitals interact only weakly with the metal orbitals are called weak field ligands, for such ligands the orbital splitting is very small. So, that means still the concept of weak field ligand, strong field ligand is continued in ligand field theory. The other comparisons between various d configurations and strong and weak ligands are very similar to what we come across in crystal field theory.

When we talk about ligand field theory, it proposes two types of bonds known as sigma bonds and pi-bonds for coordination compounds similar to what we see in organic chemistry or main group chemistry with the aid of valence bond theory. The sigma bonds are symmetrical about the axis of the bond, whereas pi-bonds are unsymmetrical with regard to the bond axes that we should remember.

And of course, the same concept we use in valence bond theory also while explaining organic molecules. Again, in coordination compounds pi-bonding may result from donation of electrons from ligands. For example, halogens or oxygen atoms to empty d-orbitals of the metal atoms, especially in case of early metals in their high oxidation states where all the d orbitals are empty.

And they are halophilic and oxophilic in nature or electrons from d-orbitals of the metal to appropriate empty orbitals of the ligand as in the case of metal carbonyl such as chromium hexacarbonyl, iron pentacarbonyl or nickel tetracarbonyl and other carbonyl compounds or carbonyl clusters. In the chromate ion if you consider $[CrO_4]^{2-}$ the oxygen atoms donate electrons to the chromium ion, which is in +6 oxidation state having no electrons at all in the d-orbitals.

In case of carbonyl and phosphine complexes, electrons from the metal orbitals especially t_{2g} may be donated to empty pi-star (π^*) orbitals in case of carbon monoxide or sigma-star (σ^*) orbitals in case of phosphines, this is also known as back bonding and such ligands are called back bonding ligands pi-donor or pi-acceptor ligands. So, now with this information about ligand field theory and how slightly modified concept it uses from crystal field theory can be understood.

And using this theme, let us try to do the classification of ligands. I shall tell you, of course, I will be discussing the classification of ligands by donor atoms after a couple of lectures, but now for convenience with the help of ligand field theory, let us try to understand whatever the ligands we have at our disposal can be classified for simplicity and for better understanding to make coordination chemistry much simpler than what it looks like.

And I was telling you the main drawback of crystal field theory is it does not identify the system where metal is neutral and ligands are neutral. In that case what happens; metal, if it is neutral, it can also generate a dipole. And of course, neutral ligands can always generate a dipole because of electronegativity difference between the donor atom and the peripheral atoms. In that case what happens?

When the metal ligand bond takes place that could be like dipole-dipole interaction. According to crystal field theory, if you give emphasis for electrostatic attraction. In that case, it would be dipole-dipole interaction as we see in case of nickel tetracarbonyl or chromium hexacarbonyl or other carbonyl complexes, but crystal field theory does not explain about the nature of the bond having fully covalent property.

So, that means in order to introduce both covalent and ionic character, ligand field theory came into existence and based on this theme, let us try to classify whatever the ligands we come across into broadly three categories.

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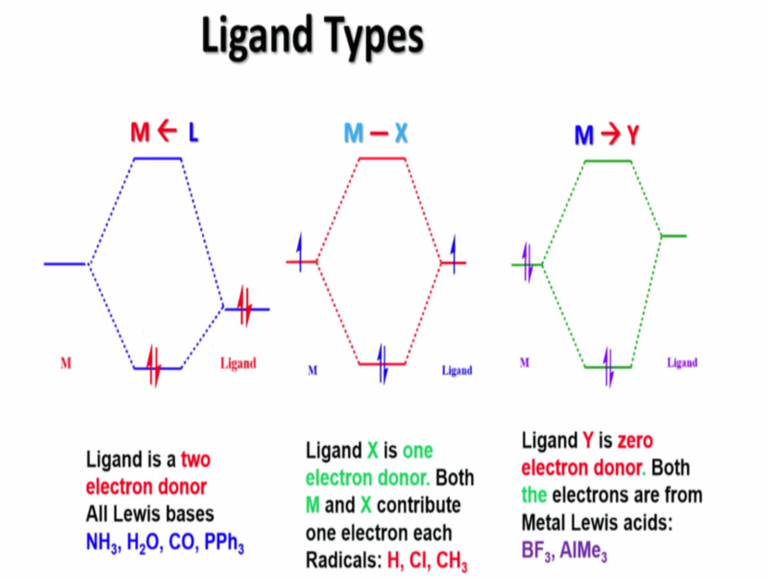

Ligand Types

M ← L

M − X

M → Y

Ligand is a two electron donor
All Lewis bases
NH_3, H_2O, CO, PPh_3

Ligand X is one electron donor. Both M and X contribute one electron each
Radicals: H, Cl, CH_3

Ligand Y is zero electron donor. Both the electrons are from Metal Lewis acids:
BF_3, $AlMe_3$

So that, I shall show you on this slide. The most common one is, ligands comes with a pair of electrons that can be readily donated to the metal. So, here ligand is a two electron donor and all Lewis bases considered as this type of ligands; ammonia, water, carbon monoxide and triphenylphosphine And then what happens here you can see ligand is one electron donor, both metal and X is a ligand here, contribute one electron each, so that radical such as H, Cl and CH_3 are considered as these type of ligands.

And in the last one metal has sufficient electrons and acts as a Lewis base and that interacts with the ligand which is not Lewis base but Lewis acid, in that case ligand Y is zero electron donor, both the electrons are from metal, they are called Lewis acids and examples are BF_3 and $AlMe_3$. And again, this type of system, we can further classify into three categories.

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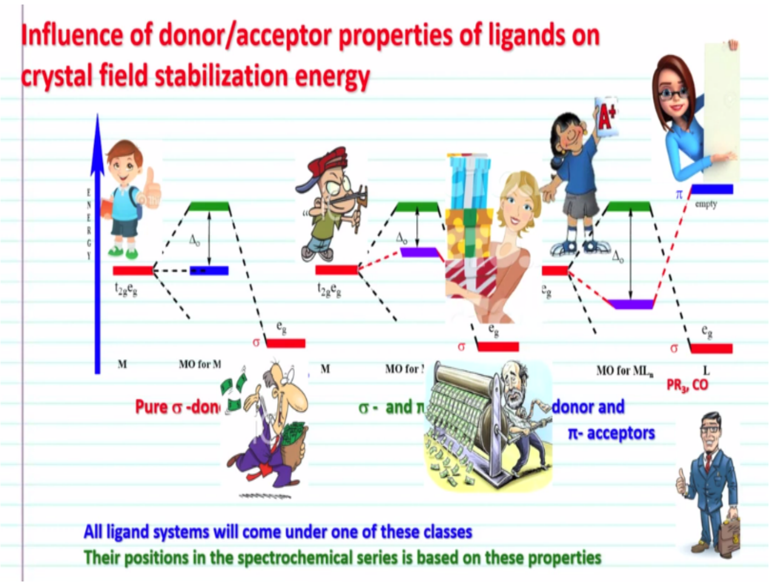
Influence of donor/acceptor properties of ligands on crystal field stabilization energy

All ligand systems will come under one of these classes

Their positions in the spectrochemical series is based on these properties

And by considering both the donor and acceptor properties of ligands, as I mentioned in case of chromate or carbonyl complexes, and how this donor and acceptor properties of ligands influence the crystal field stabilization energy, let us look into it from these diagrams. You can see here, we have the metal. The metal orbital energy somewhere here and the ligand is a pure sigma-donor here and the energy is relatively low, here, compared to this one.

And they when they interact, this is the magnitude of crystal field stabilization energy here. That means we are interacting metal with low energy sigma-orbitals, low energy sigma orbitals that are filled, to be precise that metal is interacting with filled low energy sigma orbitals of the ligands, in this case this is the magnitude here. Example, you can consider pure sigma donors, ammonia and water. Let us look into the second case here.

So, in this case, we have these ligands which have low energy filled sigma-orbitals and low energy filled pi-orbitals. If you consider halides such as chloride, bromide, iodide; they have s^2p^6 electronic configuration and 8 electrons are there and that means completely filled valence shell. When they interact with metal, they come up with low energy filled sigma orbitals and low energy filled pi orbitals. In this case what happens?

Because of their interaction, what happens, CFSE decreases relatively compared to what we see in the first case. You can see a drop in the magnitude of CFSE. That means we can know, between them which one is relatively stable and which one is relatively less stable. Now, the third case is we have filled low energy sigma-orbitals and empty high energy pi-orbitals. When such ligands are coming to establish a bond with metal this is what happens here.

The magnitude of CFSE increases. That means any ligand that is sigma donor and pi acceptor having low energy filled sigma orbitals and high energy empty pi orbitals, so they stabilize complex to a greater extent and hence they are called as stronger ligands because CFSE is larger. So, this is how you can classify the ligands and this is how you can tell why a particular ligand is called as weak ligand, why a particular ligand is called as strong ligand.

Crystal field theory classifies ligands according to spectrochemical series and also gives authenticity through electronic spectra showing the relative crystal field stabilization energy and shows why one ligand is weaker, another ligand is stronger, but the explanation lies here. If I say why chloride is a weaker ligand compared to water, we should not say CFSE, CFSE is the authenticity, it gives evidence but it does not explain why.

In order to explain why a ligand is weaker compared to other one, we have to classify according to these three categories and we have to see where exactly the given ligand falls. It has to fall into one of these categories. If it falls here, we can explain yes it has a low energy filled sigma orbitals and high energy empty pi orbitals. As a result, what happens? This is what happens to the CFSE, in the same way we can explain.

So, this explanation gives precise meaning to the position of ligands in the spectrochemical series. So, this is pure sigma donor and they are pure sigma donors and pi donors, and they are called sigma donor and pi acceptors, and examples I have already given here. All ligand systems will come under one of these classes. Their positions in the spectrochemical series is based on these properties.

And if somebody asks why a ligand is weaker, you should not tell because CFSE is an evidence through electronic spectral means, but it does not tell you why. So, this will give you a satisfactory answer for why these ligands have these kinds of different properties. And of course, on a lighter note, we can also compare into something that we are observing day-to-day life. For example, here is a person who earns enough money to take care of his family.

When he has school going student, what happens he takes care and he gives him enough money for his school and all those things without any problem and the student becomes good and he learns properly and he achieves what he wants. This is in case of pure sigma donor ligands. And then here, father is business minded. He earns lots of money, you can see it is almost like minting money and then what happens?

He does not have much time to worry about his son or daughter, and when he goes to school, he will be giving whatever the money he asked, double so that he should not bother him. On the other hand, since he has lots of money, mother also gives lots of gifts, in that case what happens? He does not show any interest because he has lots of money to spend, and as a result he becomes something like this.

This is what happens to metal complexes having sigma donor and pi donor, they are very reactive and labile. That is the reason when you take anhydrous metal halide and keep it and see tomorrow (next day), what happens? It appears like wet because what happens, the atmospheric moisture steadily replaces and it forms hexaaqua compound, that means, very unstable. On the other hand, he is very intelligent person and he knows how much money has to be given including his fees and pocket money whatever and he gives.

But mother is even more clever. She thinks that father has given more money to the student and she takes little money from him for future, and as a result what happens, the student understands the value of money and he puts all his time for studies and the student becomes A+, that means very stable. So, everyone should be like sigma donor and pi acceptor ligands so that they can achieve whatever they want without any problem.

And examples in this case are all kind of tertiary phosphines, carbon monoxide, olefins and heterocyclic carbons and all those things. Of course, I shall discuss and give a relative comparison of all sigma donor and pi acceptor ligands at later stage.

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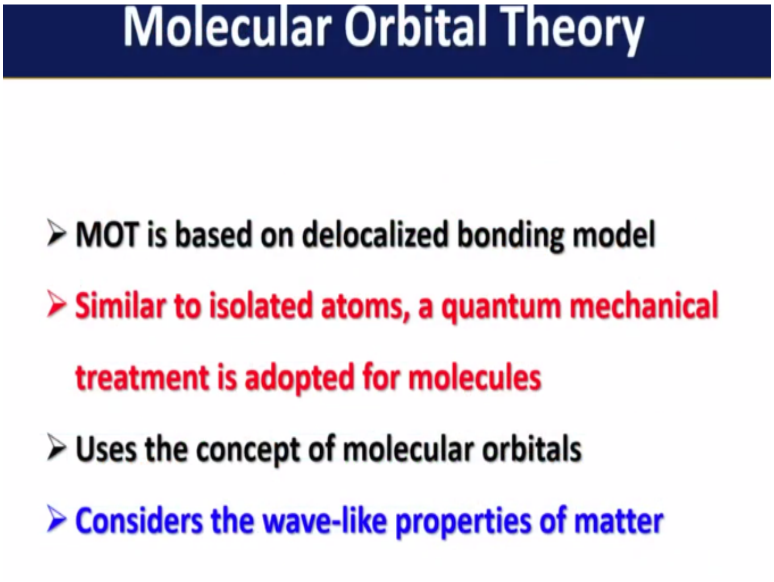

Molecular Orbital Theory

- MOT is based on delocalized bonding model
- Similar to isolated atoms, a quantum mechanical treatment is adopted for molecules
- Uses the concept of molecular orbitals
- Considers the wave-like properties of matter

Now, let us come to molecular orbital theory. As I mentioned, ligand field theory has embedded best parts of valence bond theory, crystal field theory, and Mullikan’s molecular orbital theory. So, before I introduce ligand field theory, I want to make you familiar with molecular orbital theory so that understanding ligand field theory would be very easy. For that one I have given some points here.

Molecular orbital theory is based on delocalized bonding model, unlike valence bond theory. And similar to isolated atoms, a quantum mechanical treatment is adopted for molecules and uses the concept of molecular orbitals. Considers the wave like properties of matter.

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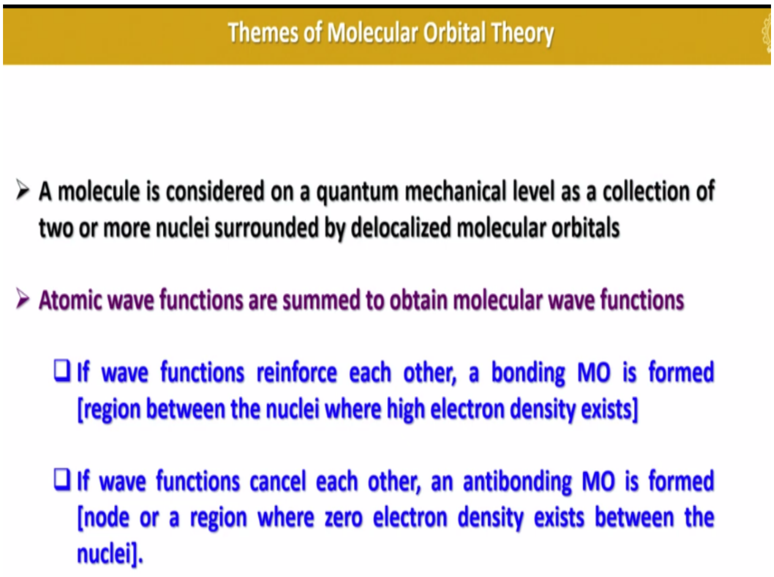

Themes of Molecular Orbital Theory

- A molecule is considered on a quantum mechanical level as a collection of two or more nuclei surrounded by delocalized molecular orbitals
- Atomic wave functions are summed to obtain molecular wave functions
  - ❑ If wave functions reinforce each other, a bonding MO is formed [region between the nuclei where high electron density exists]
  - ❑ If wave functions cancel each other, an antibonding MO is formed [node or a region where zero electron density exists between the nuclei].

A molecule is considered on a quantum mechanical level, as a collection of two or more nuclei surrounded by delocalized molecular orbitals over the surface of two nuclei. Atomic wave functions are summed to obtain molecular wave functions. If wave functions reinforce each other, a bonding molecular orbital is generated or formed and it is nothing but the region between the nuclei where high electron density exists. On the other hand, if wave functions cancel each other, an antibonding molecular orbital is formed, that means a node or region where zero electron density exists, between the nuclei.

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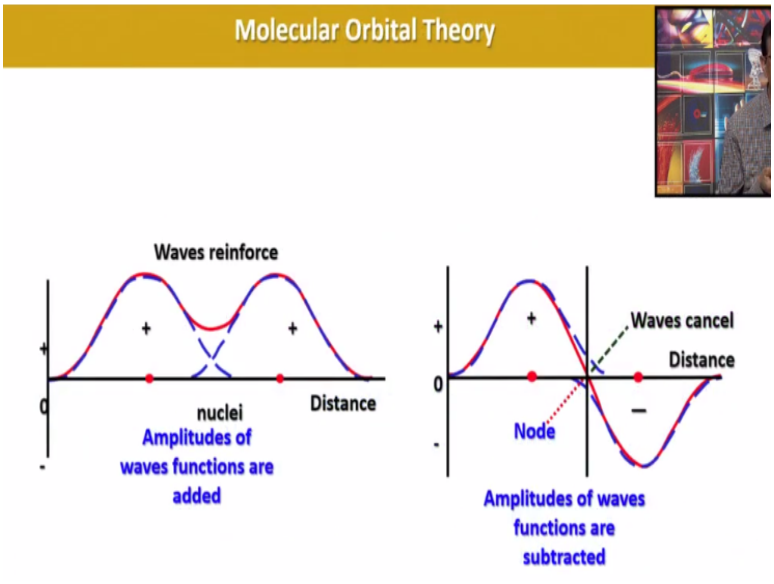

Molecular Orbital Theory

So, this is how you can represent: a summing up, and subtraction. So, here you can see, the electron density resides here, when the waves are reinforced, on the other hand when the amplitude of waves subtracted, so you can see a node between two electrons. This is called antibonding, and this is called bonding.

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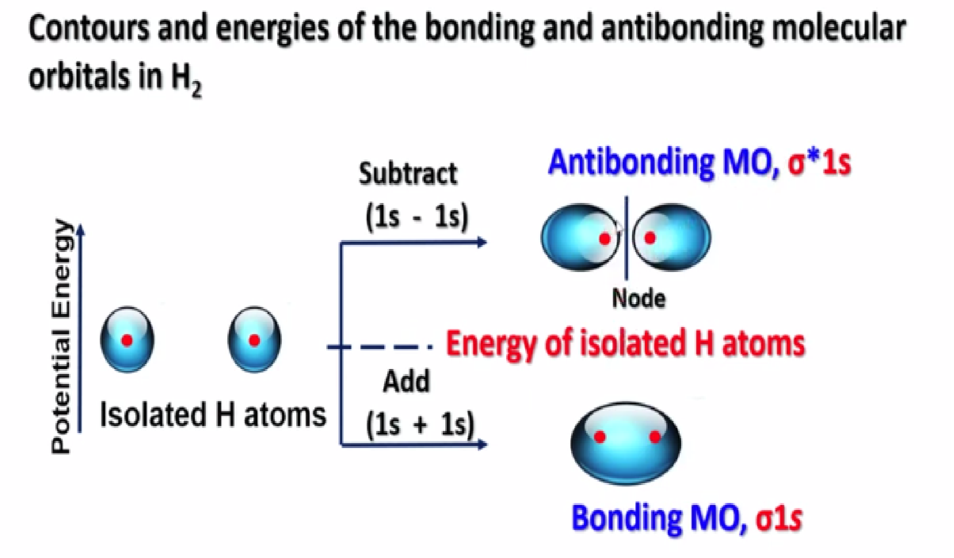

Contours and energies of the bonding and antibonding molecular orbitals in H_2

So, contours and energies of the bonding and antibonding molecular orbitals in H_2. I am going to show here. You can consider two isolated hydrogen atoms having one electron in their 1s orbitals. When they interact, as I mentioned, two levels are generated, one is due to subtracting and one is due to addition.

And energy of isolated atoms remains here. And now, the bonding molecular orbitals are generated, where you can see, two nuclei are there, in between electron density resides is called sigma (σ) 1s, and this is antibonding where we call it sigma star (σ*) 1s. All antibonding will be given the superscript star next to it. So, node is generated here which is called antibonding.

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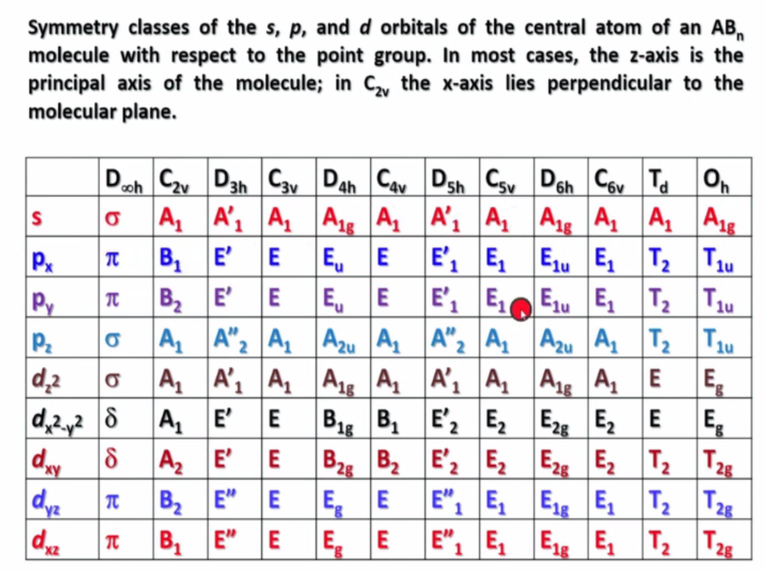

Symmetry classes of the *s*, *p*, and *d* orbitals of the central atom of an AB_n molecule with respect to the point group. In most cases, the z-axis is the principal axis of the molecule; in C_{2v} the x-axis lies perpendicular to the molecular plane.

	$D_{\infty h}$	C_{2v}	D_{3h}	C_{3v}	D_{4h}	C_{4v}	D_{5h}	C_{5v}	D_{6h}	C_{6v}	T_d	O_h
s	σ	A_1	A'_1	A_1	A_{1g}	A_1	A'_1	A_1	A_{1g}	A_1	A_1	A_{1g}
p_x	π	B_1	E'	E	E_u	E	E'_1	E_1	E_{1u}	E_1	T_2	T_{1u}
p_y	π	B_2	E'	E	E_u	E	E'_1	E_1	E_{1u}	E_1	T_2	T_{1u}
p_z	σ	A_1	A''_2	A_1	A_{2u}	A_1	A''_2	A_1	A_{2u}	A_1	T_2	T_{1u}
d_{z^2}	σ	A_1	A'_1	A_1	A_{1g}	A_1	A'_1	A_1	A_{1g}	A_1	E	E_g
$d_{x^2-y^2}$	δ	A_1	E'	E	B_{1g}	B_1	E'_2	E_2	E_{2g}	E_2	E	E_g
d_{xy}	δ	A_2	E'	E	B_{2g}	B_2	E'_2	E_2	E_{2g}	E_2	T_2	T_{2g}
d_{yz}	π	B_2	E''	E	E_g	E	E''_1	E_1	E_{1g}	E_1	T_2	T_{2g}
d_{xz}	π	B_1	E''	E	E_g	E	E''_1	E_1	E_{1g}	E_1	T_2	T_{2g}

And of course, this is very important. The symmetry classes of s, p and d orbitals of the central atom of an AB_n molecule with respect to the point group, in most cases the z axis is the principal axis of the molecule. So, whatever the molecules we are considering in coordination chemistry or in general, always we keep z as principal axis.

For example, if I ask you a question to write crystal field splitting diagram for a molecule, octahedral molecule or a square planar molecule kept along the x-axis, if your molecule is kept along the x-axis instead of z-axis then it will be yz plane. Then accordingly what happens the splitting varies. So, one should be able to understand these aspects. If you understand these aspects, you should be able to write crystal field diagrams, no matter which axis we are considering as principal axis.

So, nevertheless here we have considered z-axis as principal axis, and when you consider according to various point groups, what are the Mulliken's symbols, we are giving and what is the nature of bond we come across for various orbitals, have listed here. This is very good, very informative and there is no need to remember this one, just whenever you get time, go through this one to understand the terms we are using for different orbitals and for different point groups.

For example, if you consider tetrahedral or octahedral, s orbital is spherically symmetrical and it forms sigma bonds and we say it is a_{1g}, so same thing is there. And the p orbitals p_x, p_y, p_z are degenerate, we call them with t_{1u} that you have seen or you are going to see. And then d_{z^2} and $d_{x^2-y^2}$ we call e_g that is what is here, and d_{xy}, d_{yz} and d_{xz} collectively called t_{2g}. So, these are the terms we are using.

And again in case of Td, because of lack of centre of symmetry, we removed the subscript "g" and that is what quoted here. We can see of course p-orbitals, some variation will be there. And if we take D_{4h} for square planar complexes, you can see whatever the most Mulliken symbols we are using, you will be coming across in ligand field theory as well as in molecular orbital theory. And then this is for octahedral, and this is for tetrahedral complex and this is for square planar.

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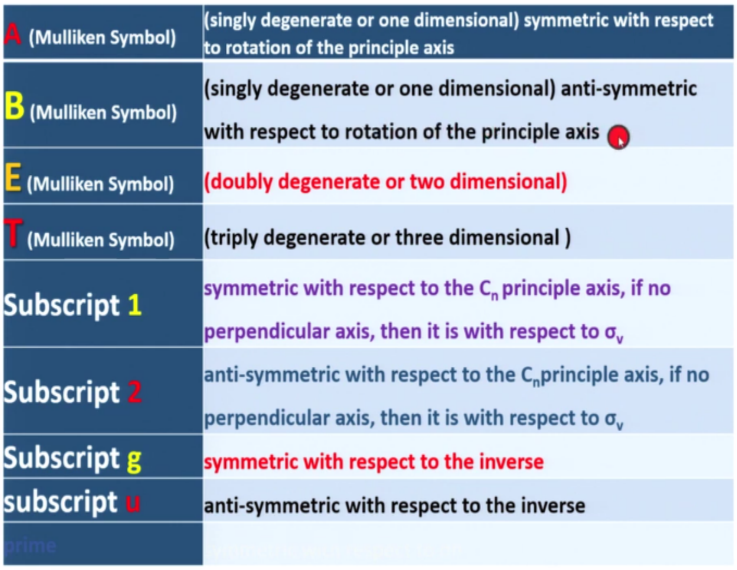

A (Mulliken Symbol)	(singly degenerate or one dimensional) symmetric with respect to rotation of the principle axis
B (Mulliken Symbol)	(singly degenerate or one dimensional) anti-symmetric with respect to rotation of the principle axis
E (Mulliken Symbol)	(doubly degenerate or two dimensional)
T (Mulliken Symbol)	(triply degenerate or three dimensional)
Subscript 1	symmetric with respect to the C_n principle axis, if no perpendicular axis, then it is with respect to σ_v
Subscript 2	anti-symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_v
Subscript g	symmetric with respect to the inverse
subscript u	anti-symmetric with respect to the inverse
prime	

And then I have just expanded what is that one. What is Mulliken symbol "A" means singly degenerate or one dimensional symmetric with respect to rotation of the principal axis. Because of its spherically symmetrical nature, it is symmetric with respect to the rotation with respect to any axis for that matter. And “B” singly degenerate or one dimensional antisymmetric with respect to rotation of the principal axis on what basis we have given.

For example, if you want to try to see a particular orbital and with respect to a geometry you can understand, whether the statement is true or not. And E means doubly degenerate or two dimensional, E_g we are using. So, “T” Mulliken symbol triply degenerate or three dimensional, so that we use in case of T_{2g}. And subscript 1 if you use like a A_{1g}, B_{1g} or B_{2g}; means symmetric with respect to the Cn principal axis, if no perpendicular axis then it is with respect to sigma σ_v.

In some molecules, we lack a perpendicular axis in that case we have to consider this one with respect to σ_v. And the subscript 2 means antisymmetric with respect to the principal axis, if no perpendicular axis then it is with respect to σ_v again. And g means symmetric with respect to the inverse, that means if you have centre of symmetry and subscript u antisymmetric with respect to the inverse.

So, this is the explanation for various superscript and subscript we come across for various Mulliken’s symbols. So, let me stop at this juncture and continue discussing molecular orbital theory to make you familiar with understanding for simple molecules and also a couple of very interesting main group compounds. And then I switch over to ligand field theory to explain the bonding in various transition metal complexes for various geometries. Until then have an excellent time reading chemistry.