❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes

The crystal field theory fails to explain many physical properties of the transition metal complexes because it does not consider the interaction between the metal and ligand orbitals. The molecular orbital theory can be very well applied to transition metal complexes to rationalize the covalent as well as the ionic character in the metal-ligand bond. A transition metal ion has nine valence atomic orbitals which are consisted of five nd, three $(n+1)p$, and one $(n+1)s$ orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The molecular orbital theory is highly dependent on the geometry of the complex and can successfully be used for describing octahedral complexes, tetrahedral and square-planar complexes. The main features of molecular orbital theory for metal complexes are as follows:

1. The atomic orbital of the metal center and of surrounding ligands combine to form new orbitals, known as molecular orbitals.

2. The number of molecular orbitals formed is the same as that of the number of atomic orbitals combined.

3. The additive overlap results in the bonding molecular orbital while the subtractive overlap results in the antibonding overlap.

4. The energy of bonding molecular orbitals is lower than their nonbonding counterparts while the energy of antibonding molecular orbitals is higher than that of nonbonding orbitals.

5. The energy of nonbonding orbitals remains the same.

6. The ionic character of the covalent bond arises from the difference in the energy of combining orbitals.

7. If the energy of a molecular orbital is comparable to an atomic orbital, it will not be very much different in nature from atomic orbital.

The polarity of the bond can be explained by considering the overlap of two atomic orbitals of different energies. Suppose ϕ_A and ϕ_B are two atomic orbitals of atoms A and B, respectively. These two atomic orbitals have one electron in each of them and combine to form one bonding (σ) and one antibonding (σ^*) molecular orbital. After the formation of molecular orbitals, both electrons occupy σ-orbital. Now, if the energy of σ-orbital is closer to ϕ_A, it will have more ϕ_A character and hence the electron density of both of the electrons will be concentrated more on atom A than B. Similarly if the energy of σ-orbital is closer to ϕ_B, it will have more ϕ_B character and the electron density of both of the electrons will be concentrated more on atom B than A. This same explanation holds for the ionic character in metal-ligand bond.

The main concern here is that the total number of the molecular orbitals formed as a result of bonding and antibonding interactions is quite large; and therefore, many complications related to the understanding of symmetry-energy may arise, all of which needs a very sophisticated treatment of chemical bonding. Hence, without a comprehensive knowledge of the chemical applications of group theory, it is quite difficult to explain the whole concept. However, a primitive explanation for the σ-bonding in transition metal complexes of different geometry can still be given.

> ➢ *Octahedral Complexes*

In octahedral complexes, the molecular orbitals created by the coordination of metal center can be seen as resulting from the donation of two electrons by each of six σ-donor ligands to the *d*-orbitals on the metal. The metal orbitals taking part in this type of bonding are *nd*, $(n+1)p$ and $(n+1)s$. It should be noted down that not all *nd*-orbitals but only d_z^2 and $d_{x^2-y^2}$ orbitals are capable of participating in the σ-overlap. The d_{xy}, d_{xz} and d_{yz} orbitals remain non-bonding orbitals. The ligands approach the metal center along the *x*, *y* and *z*-axes in such a way that their σ-symmetry orbitals form bonding and anti-bonding combinations with metal's *s*, p_x, p_y, p_z, d_z^2 and $d_{x^2-y^2}$ orbitals. A total of six bonding and six anti-bonding molecular orbitals formed. The symmetry designations of different metal orbitals taking part in octahedral overlap are:

d_z^2, $d_{x^2-y^2}$	–	e_g
s	–	a_{1g}
p_x, p_y, p_z	–	t_{1u}
d_{xy}, d_{xz}, d_{yz}	–	t_{2g}

The exact nature of the Mulliken symbols, like e_g or a_{1g}, etc., can be understood only after the core level understanding of group theory. However, it still can be noted that *a*, *e* and *t* represents singly, doubly and triply degenerate orbitals, respectively. The subscripts *g* and *u* represent gerade and ungerade nature of the orbitals. An orbital is said to be gerade if it has the same sign in all opposite directions from the center. These are also said to be having the centre of symmetry. On the other hand, an orbital is said to be ungerade if it has the opposite sign in all the opposite directions from the center. These are also said to be lacking the centre of symmetry.

The symmetry adapted linear combinations of atomic orbitals (SALCs) for metal-ligand direct overlap can be obtained just by resolving the reducible representation based on the bond vectors along the axis of σ-overlap. As there are total six bond vectors for the metal-ligand σ-bonding, hexa-dimensional reducible representation will be obtained. As the six ligands in an octahedral complex approach the central metal ion along the three Cartesian axes (two along *x*-axis, two along *y*-axis and two along *z*-axis), the six σ-basis bond vectors must also be selected along *x*, *y* and *z*-axis.
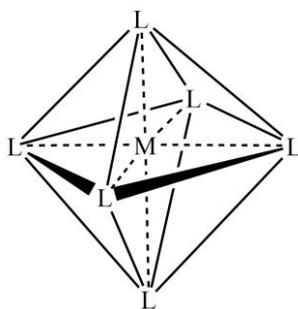
Figure 3. Continued on the next page…

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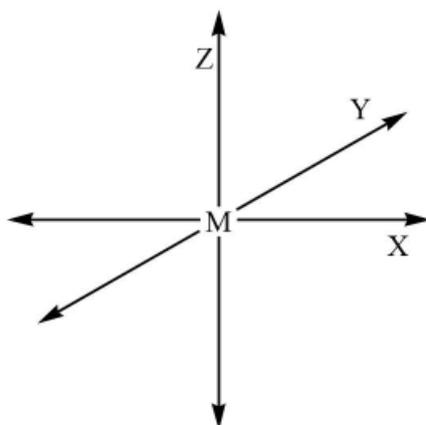
Figure 3. The octahedral coordination and corresponding σ-basis set for ligand orbitals in octahedral complexes.

The symmetry adapted linear combinations of these fall into three irreducible representations labeled as a_{1g}, e_g, and t_{1u}. The symmetry designations of different ligand orbitals taking part in octahedral overlap are:

Table 1. Reducible representation based on bond vectors in the octahedral geometry.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Irreducible components
Γ_π	6	0	0	2	2	0	0	0	4	2	$a_{1g} + e_g + t_{1u}$

The metal-orbital sets of a_{1g}, e_g and t_{1u} symmetry participate in σ-bonding by interacting with the same symmetry SALCs sets to produce σ-bonding and antibonding molecular orbitals. However, the triply degenerate t_{2g} orbitals set on the metal remains nonbonding as there no ligand orbitals of this symmetry. The exact nature of the "symmetry adapted linear combination of atomic orbitals" or simply SALCs is quite complex and is beyond the scope of this volume but still we can simply give a superficial explanation for these ligand orbitals. The pictorial representation of various SALC orbitals in octahedral complexes, capable of σ-overlap with metal orbitals, can be given as:

1. If the six atomic orbitals of six ligands are pointing their positive lobes towards metal's *s*-orbital, then the composite orbital becomes:

$$\varphi_1 = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 \tag{1}$$

The pictorial representation is given below.
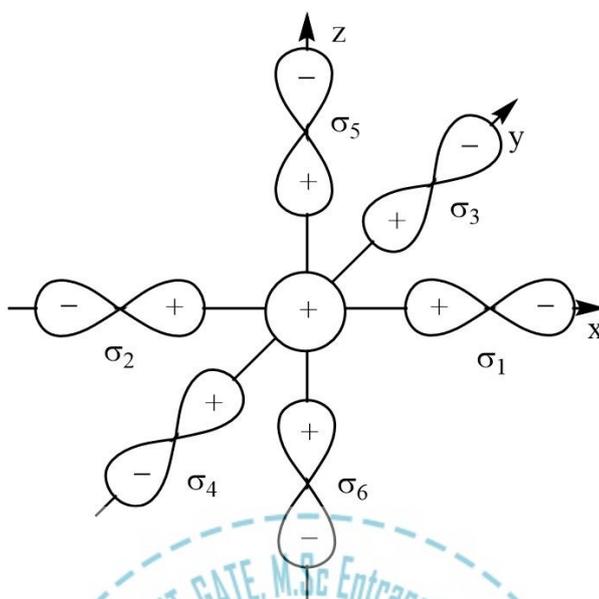
Figure 4. The combination of ligand orbitals overlapping with s-orbital of the metal center.

2. The p_x-orbital of metal center can overlap with ligands atomic orbital approaching along the x-axis. Hence, the composite orbital becomes:

$$\varphi_2 = \sigma_1 - \sigma_2 \tag{2}$$

The pictorial representation is given below.
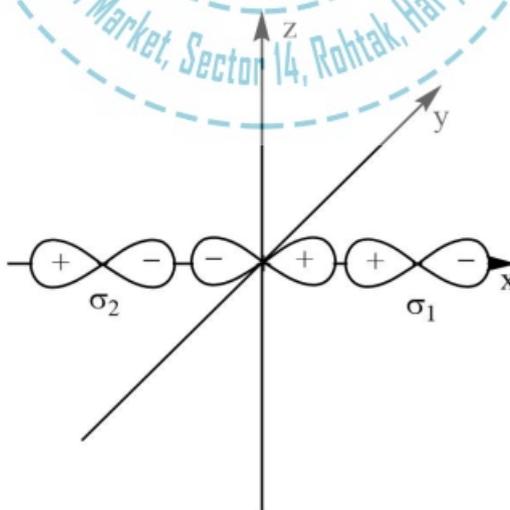
Figure 5. The combination of ligand orbitals overlapping with p_x-orbital of the metal center.

3. The p_y-orbital of metal center can overlap with ligands atomic orbital approaching along y-axis. Hence, the composite orbital becomes:

$$\varphi_3 = \sigma_3 - \sigma_4 \tag{3}$$

The pictorial representation is given below.
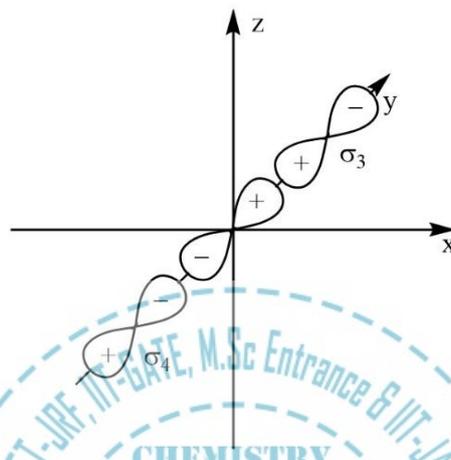
Figure 6. The combination of ligand orbitals overlapping with p_y-orbital of the metal center.

4. The p_z-orbital of metal center can overlap with ligands atomic orbital approaching along z-axis. Hence, the composite orbital becomes:

$$\varphi_4 = \sigma_5 - \sigma_6 \tag{4}$$

The pictorial representation is given below.
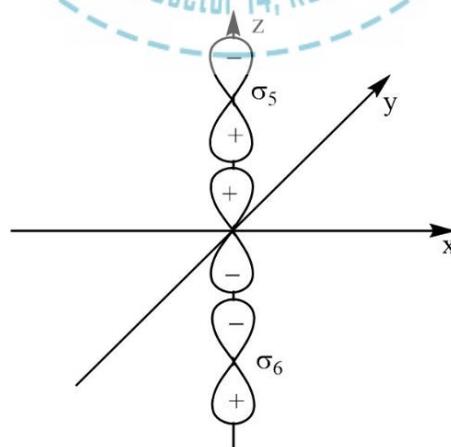
Figure 7. The combination of ligand orbitals overlapping with p_z-orbital of the metal center.

5. The $d_{x^2-y^2}$ orbital of metal center can overlap with ligands atomic orbital approaching along x and y-axis. Hence, the composite orbital becomes:

$$\varphi_5 = \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 \tag{5}$$

The pictorial representation is given below.
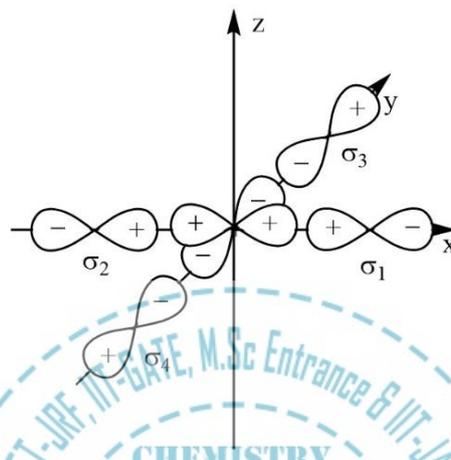
Figure 8. The combination of ligand orbitals overlapping with $d_{x^2-y^2}$ orbital of the metal center.

6. The d_{z^2} orbital of metal center can overlap with ligands atomic orbital approaching along x, y and z-axis. Hence, the composite orbital becomes:

$$\varphi_6 = \sigma_5 + \sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 \tag{6}$$

The pictorial representation is given below.
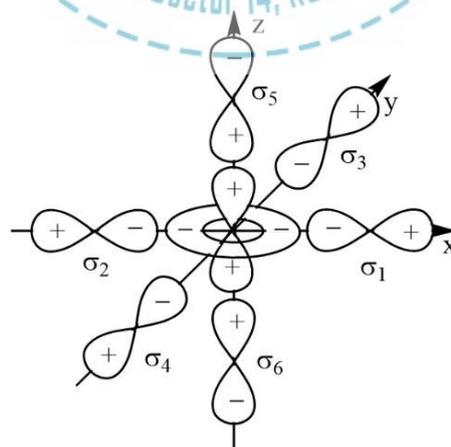
Figure 9. The combination of ligand orbitals overlapping with d_{z^2} orbital of the metal center.

The overall molecular orbital energy level diagram for σ-bonding in octahedral complexes can be shown as:

Metal Orbitals   Molecular Orbitals   Ligand Orbitals
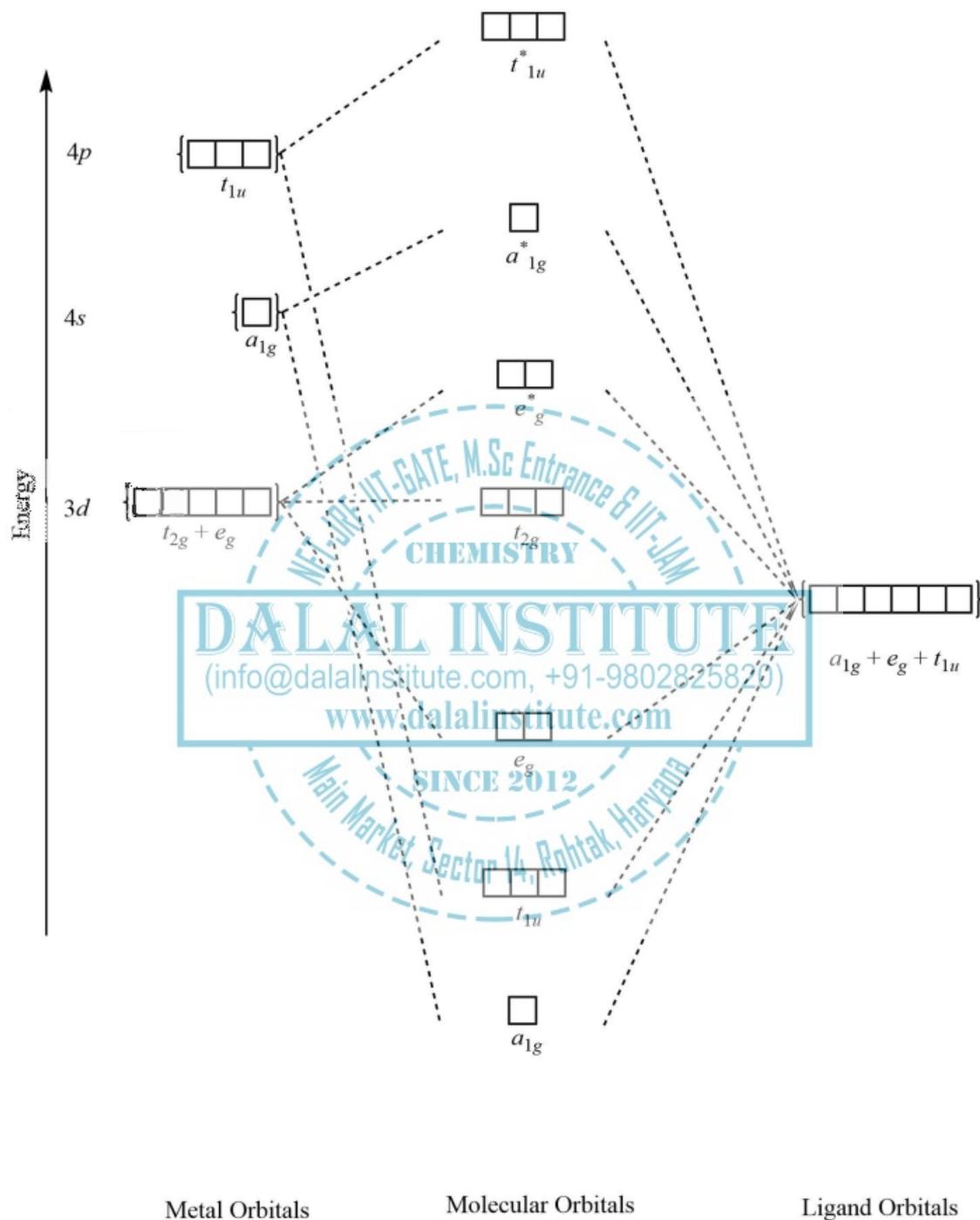
Figure 10. The formation of σ-molecular orbitals (bonding, antibonding and non-bonding) in octahedral complexes of transition metals.

The φ_1 composite orbital of a_{1g} symmetry interacts with a_{1g} orbital set of metal ions and produces one bonding (a_{1g}) and one antibonding molecular orbital (a^*_{1g}). The φ_2, φ_3 and φ_4 composite orbital set of t_{1u} symmetry interacts with t_{1u} orbital set of metal ions and produces triply-degenerate bonding (t_{1u}) and triply-degenerate antibonding molecular orbital (t^*_{1u}) set. The φ_5 and φ_6 composite orbital set of e_g symmetry interacts with e_g orbital set of metal ions and produces doubly-degenerate bonding (e_g) and doubly-degenerate antibonding molecular orbital (e^*_g) set. The t_{2g} orbital set of the metal center remains non-bonding in nature. The electron-filling in various orbitals is done in accordance with the Aufbau principle, Hund's rule and Pauli exclusion principle.

Some typical explanations in the view of MO-theory are:

i) Spin only magnetic moments: Just like crystal field theory, MO-theory can also be used to rationalize the spin only magnetic moments of different transition metal complexes. For instance, 5.9 B.M. magnetic moment of $[Mn(H_2O)_6]^{2+}$ is generated when seventeen electrons (five from Mn^{2+} and twelve electrons from six aquo ligands) are filled in different molecular orbitals. Twelve out of seventeen electrons occupy six bonding molecular orbitals of a_{1g}, t_{1u} and e_g. Three out of the remaining five electrons are filled in nonbonding t_{2g} and the last two electrons occupy e^*_g giving a total of five unpaired electrons.

ii) 18- electron rule: It is a well-known fact that metal carbonyls and many other complexes follow 18-electron rule quite well. This is also analyzed in terms of effective atomic number which suggests that a total of 18-electrons in the valence shell generally makes overall electron-count to resemble a noble gas core. However, a strong basis for this rule can found in molecular orbital theory. Six bonding molecular orbitals can accommodate a total of 12 electrons and only six electrons can be filled in the non-bonding t_{2g}. Any extra electron is bound to occupy the antibonding e^*_g orbital and hence affects the stability.

iii) The splitting of d-orbital: According to crystal field theory, the splitting, Δ_o of d-orbital in t_{2g} and e_g is produced by the difference in the Coulombic repulsion experienced various metal orbitals. However, the molecular orbital theory sees the splitting of d-orbital as a result of the interaction of metal orbitals with ligand orbitals and labels it as splitting between nonbonding t_{2g} and antibonding e^*_g.

iv) High spin – low spin complexes: Just like in the case of crystal field theory, the magnitude of Δ_o decides the multiplicity nature of the complexes. If the separation between nonbonding t_{2g} and antibonding e^*_g is pretty large, the electrons prefer to pair up with the electrons already present in nonbonding t_{2g} and the complex becomes low-spin. On the other side, If the separation between nonbonding t_{2g} and antibonding e^*_g is small, the electrons prefer to occupy antibonding e^*_g and the complex becomes high-spin. For example, in $[Co(NH_3)_6]^{3+}$, the magnitude of Δ_o is very large and the configuration becomes t_{2g}^6, e^{*0}_g. Furthermore, the comparatively lower stability and weaker metal-ligand bond in high spin complexes may be attributed to the presence of electrons in a molecular orbital of antibonding nature.

v) Jahn-Teller distortions: The concept of molecular orbital theory can also be used to rationalize the z-out or z-in distortion of the octahedral metal complexes. For example, octahedral complexes of Cu^{2+} ion have been known to undergo Jahn-Teller distortion due to d^9 configuration. According to molecular orbital theory, the electronic configuration octahedral complexes of Cu^{2+} will be t_{2g}^6, e^{*3}_g. Now, as the energy of e_g^* molecular

orbital is close to the pure atomic orbitals of metal ion, $e_g{}^*$ would resemble more to the metal orbitals than the ligand's. Therefore, we can approximate $e_g{}^*$ to pure $d_{x^2-y^2}$ and d_{z^2}. Now if the configuration is $(d_{x^2-y^2})^1 (d_{z^2})^2$, higher antibonding electron density along z-axis would result in a weaker bond and an elongation of bonds would take place along z-axis, giving a z-out distortion. On the other hand, if the configuration is $(d_{x^2-y^2})^2 (d_{z^2})^1$, higher antibonding electron density along x and y-axis would result in a weaker bond and an elongation would take place along x and y-axis, giving a z-in distortion.

vi) Variation of ionic radii: Experimental values of ionic radii of central metal ions in bivalent salts of first transition series were very well explained by the crystal field theory. The same can be done in the frame of molecular orbital theory. The decrease in ionic radii, when one moves from Ca^{2+} to V^{2+}, may be attributed to the increasing magnitude of effective nuclear charge while the filling of valence electrons takes place in nonbonding t_{2g}. However, after V^{2+}, the fourth electron in Cr^{2+} is filled in antibonding e^* and this effect makes the metal-ligand bond to increase, which in turn results in an increment in effective ionic radius. This trend continues up to Mn^{2+}, but as we move from Fe^{2+} to Ni^{2+}, the electron filling again goes to nonbonding t_{2g} and thus thereby decreases the ionic radii. The ninth and tenth electron in Cu^{2+} and Zn^{2+} are filled in antibonding e^* and therefore, the effective ionic radius increases again. The whole situation creates two minima in effective ionic radii, one for V^{2+} and other for Ni^{2+}.

It is worth to note down that the more sophisticated rationalization of the MO-diagram for octahedral complexes can be given in the terms of molecular symmetry combined with detailed quantum mechanics involved. In general practice, six symmetry-adapted linear combinations (SALCs) of atomic orbitals, corresponding to the irreducible components of the bond-vector based reducible representation, are created. The irreducible representations that these SALCs span to are a_{1g}, t_{1u} and e_g. The metal also has six valence orbitals that span the same irreducible representations (s-orbital is labeled as a_{1g}, a set of three p-orbitals is labeled t_{1u}, and the d_{z^2} and $d_{x^2-y^2}$ orbitals are labeled e_g). The six σ-bonding molecular orbitals result from the combinations of ligand SALC's with metal orbitals of the same symmetry.

➢ *Tetrahedral Complexes*

In tetrahedral complexes, the molecular orbitals created by the coordination profile can be seen as resulting from the donation of one electron pair by each of four σ-donor ligands to the d-orbitals on the transition metal. The visualization of the composite orbital of a tetrahedral complex in the molecular orbital framework is quite difficult because of the absence of the centre of symmetry. However, the symmetry designations of different metal orbitals taking part in this type of overlap can still be given as:

s	–	a_1
p_x, p_y, p_z	–	t_2
d_{xy}, d_{xz}, d_{yz}	–	t_2
$d_{z^2}, d_{x^2-y^2}$	–	e

The symmetry adapted linear combinations of atomic orbitals (SALCs) for metal-ligand direct overlap can be obtained just by resolving the reducible representation based on the bond vectors along the axis of σ-overlap. As there is a total of four bond vectors for the metal-ligand σ-bonding, the four-dimensional reducible representation will be obtained.
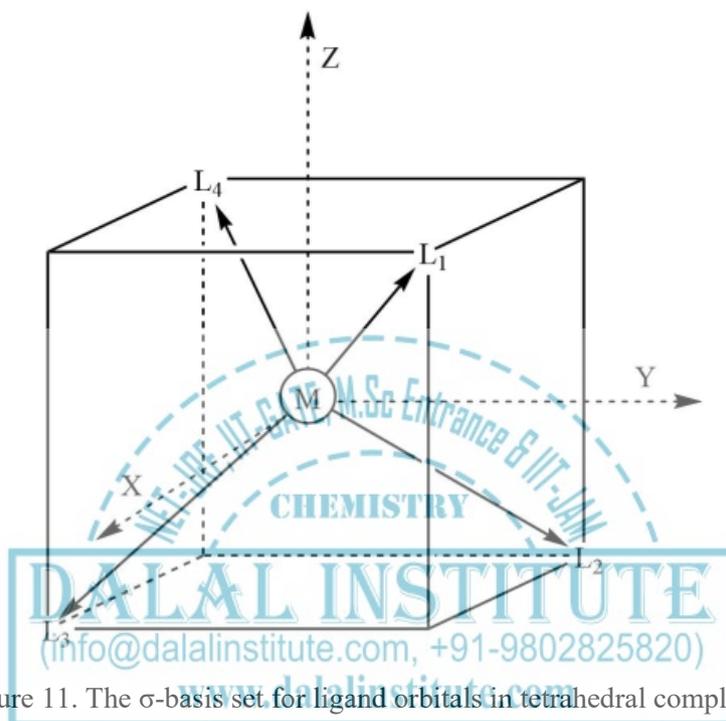
Figure 11. The σ-basis set for ligand orbitals in tetrahedral complexes.

The symmetry adapted linear combinations of these fall into two (one singly and one triply degenerate) irreducible representations labeled as a_1 and t_2. The symmetry designations of different ligand orbitals taking part in tetrahedral overlap are:

Table 2. Reducible representation based on perpendicular vectors in a tetrahedral geometry.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Irreducible components
Γ_π	4	1	0	0	2	$a_1 + t_2$

The d_{xy}, d_{xz} and d_{yz} orbitals set on the metal also have t_2-symmetry. Similarly, the p_x, p_y and p_z-orbital set of the metal also has t_2 symmetry which resembles with the symmetry of one of SALCs set on ligands. Therefore, these same-symmetry (t_2) sets from metal and ligand interact to create three bonding and antibonding molecular orbitals. Moreover, s-orbital on metal has a_1-symmetry and hence mix-up with one of ligand SALC with a_1-symmetry. This also results in one bonding and one antibonding molecular orbital. One metal-orbital set of a_1 symmetry and two sets of t_2 symmetry participate in σ-bonding while the doubly

degenerate *e*-symmetry set remains nonbonding. The overall molecular orbital energy level diagram for σ-bonding in tetrahedral complexes can be shown as:
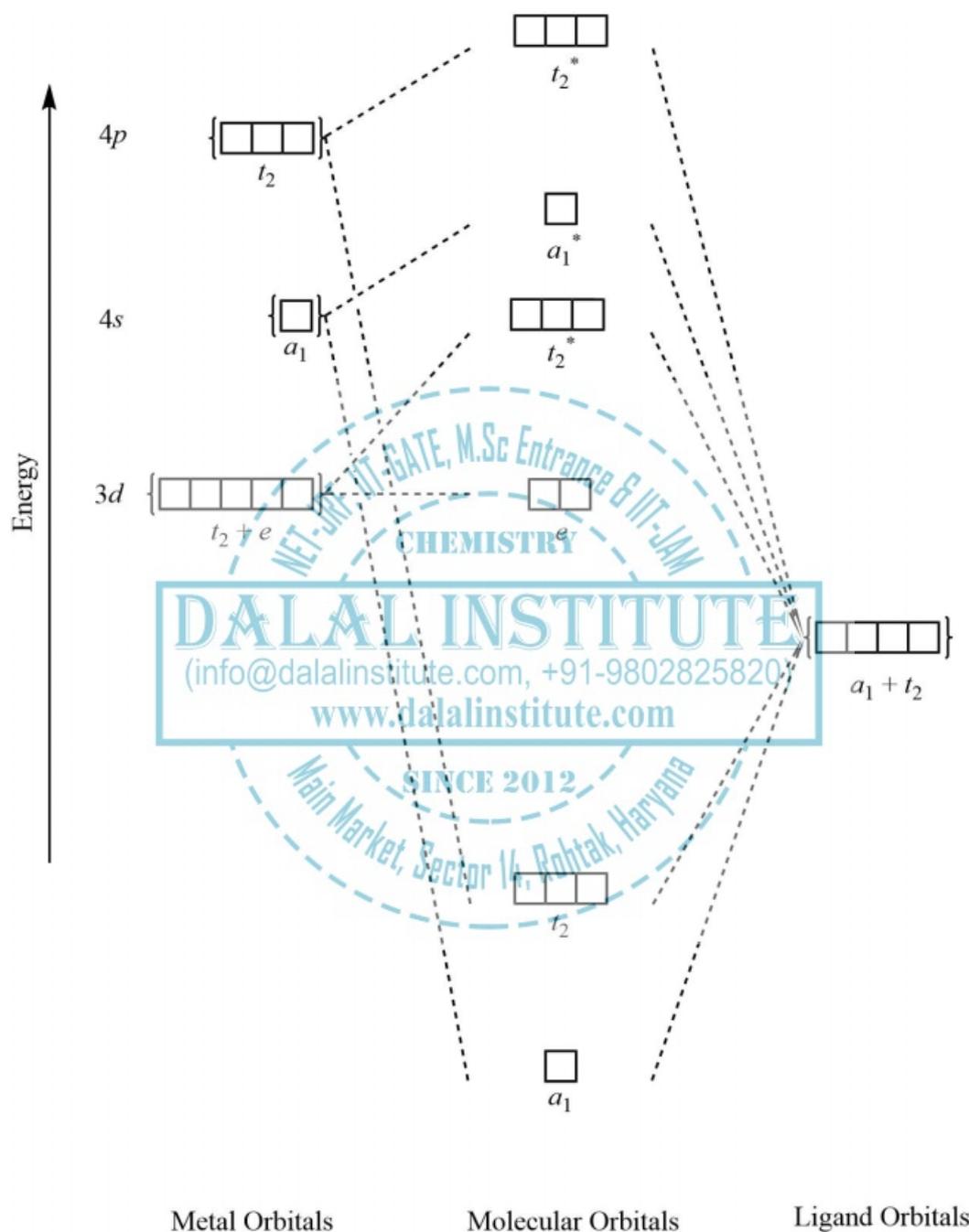
Figure 12. The formation of σ-molecular orbitals (bonding, antibonding and non-bonding) in tetrahedral complexes of transition metals.

> ➢ *Square Planar Complexes*

In square-planar complexes, the molecular orbitals created by coordination can be seen as resulting from the donation of two electrons by each of four σ-donor ligands to the *d*-orbitals on the metal. The metal orbitals taking part in this type of bonding are *nd*, $(n+1)p$ and $(n+1)s$. It should be noted down that not all *nd* or $(n+1)p$ orbitals but only d_z^2, $d_{x^2-y^2}$, p_x and p_y-orbitals are capable of participating in the σ-overlap. The d_{xy}, d_{xz}, d_{yz} and p_z-orbitals remain non-bonding orbitals. The symmetry designations of different metal orbitals taking part in square-planar overlap are:

s	—	a_{1g}
p_x, p_y	—	e_u
d_z^2	—	a_{1g}
$d_{x^2-y^2}$	—	b_{1g}
p_z	—	a_{2u}
d_{xy}	—	b_{2g}
d_{yz}, d_{xz}	—	e_g

The symmetry adapted linear combinations of ligand atomic orbitals (SALCs) for metal-ligand sidewise overlap in square planar complexes can be obtained just by resolving the reducible representation based on the bond vectors along to the axis of σ-overlap. As there are total four bond vectors for the metal-ligand σ-bonding, the four-dimensional reducible representation will be obtained.
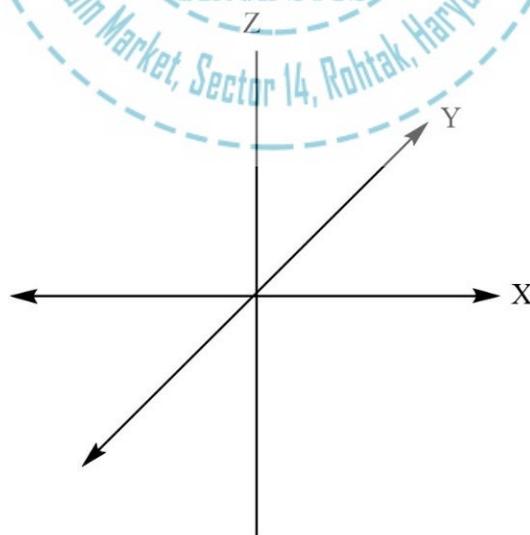
Figure 13. Continued on the next page…

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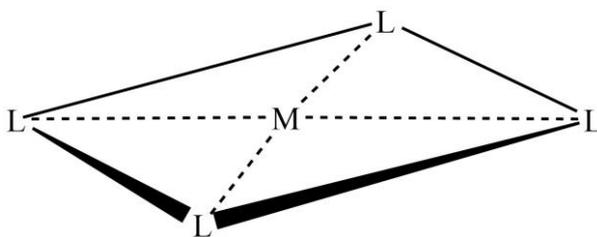
Figure 13. The σ-basis set for ligand orbitals and corresponding coordination in square-planar complexes of transition metals.

The symmetry adapted linear combinations of these fall into three irreducible representations labeled as a_{1g}, b_{1g} and e_u. The symmetry designations of different ligand SALC-orbitals taking part in square-planar overlap are:

Table 3. Reducible representation based on perpendicular vectors in square planar geometry.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Irreducible components
Γ_π	4	0	0	2	0	0	0	4	2	0	$a_{1g} + b_{1g} + e_u$

The irreducible components that these SALCs span to are a_{1g}, b_{1g} and e_u. The molecular orbitals of σ-bonding in square-planar complexes result from the mixing of ligand SALCs with metal orbitals of the same symmetry. Two metal-orbital sets of a_{1g} symmetry, one set of b_{1g} symmetry and one set on e_u symmetry participate in σ-bonding while the doubly degenerate e_g and singly degenerate b_{2g} sets remain nonbonding. This is quite logical because there are no ligand orbitals with these symmetry properties and hence no orbital overlap is possible. The ligands approach the metal center along the x and y-axes in such a way that their σ-symmetry orbitals form bonding and anti-bonding combinations with metal's s, p_x, p_y, d_z^2 and $d_{x^2-y^2}$ orbitals. Two a_{1g}-symmetry sets of metal orbitals (s and d_z^2) interact with the ligands SALC of the same symmetry and form three molecular orbitals. The b_{1g}-symmetry set of metal orbital ($d_{x^2-y^2}$) interact with the ligands SALC of same symmetry and form two molecular orbitals, one bonding and one of antibonding nature.

Similarly, e_u-symmetry set of metal orbitals (p_x, p_y) interacts with the ligands SALC of the same symmetry and form bonding and antibonding molecular orbital sets. A total of nine sets of molecular orbitals are formed in which electron filling has to occur. Furthermore, it should also be noted that bonding molecular orbitals are predominantly associated with ligands which can be attributed to the lower energy of ligand SALCs while the antibonding molecular orbitals are primarily associated with the metal center owing to the higher energy of its atomic orbitals. In other words, the simplistic approach can treat bonding molecular orbitals as ligand orbitals and antibonding molecular orbitals as metal orbitals.

The molecular orbital energy level diagram for σ-bonding in square-planar complexes can be shown as:
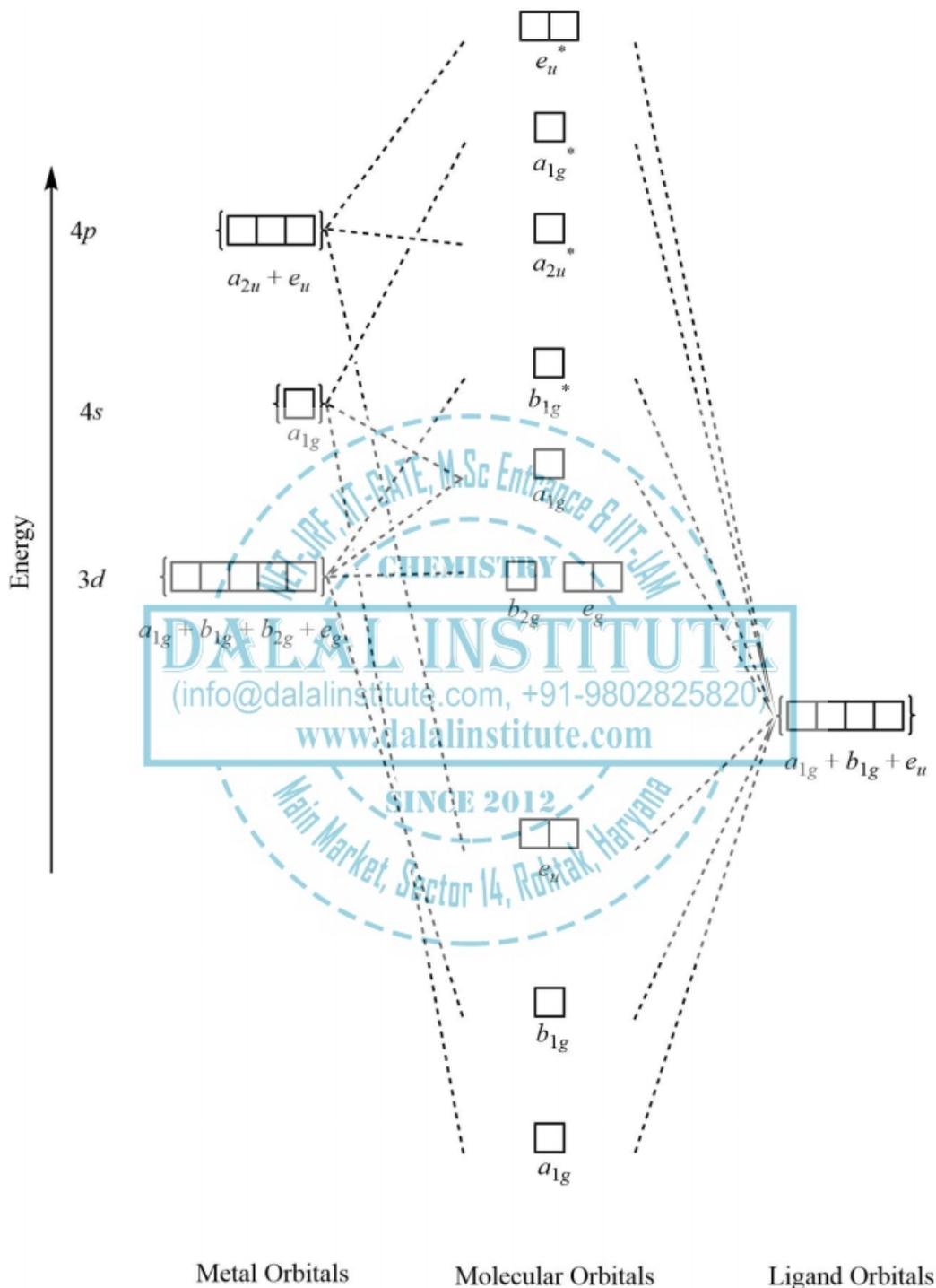
Figure 14. The generation of σ-molecular orbitals in square-planar complexes.

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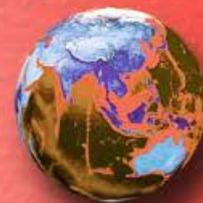
A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

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Table of Contents

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