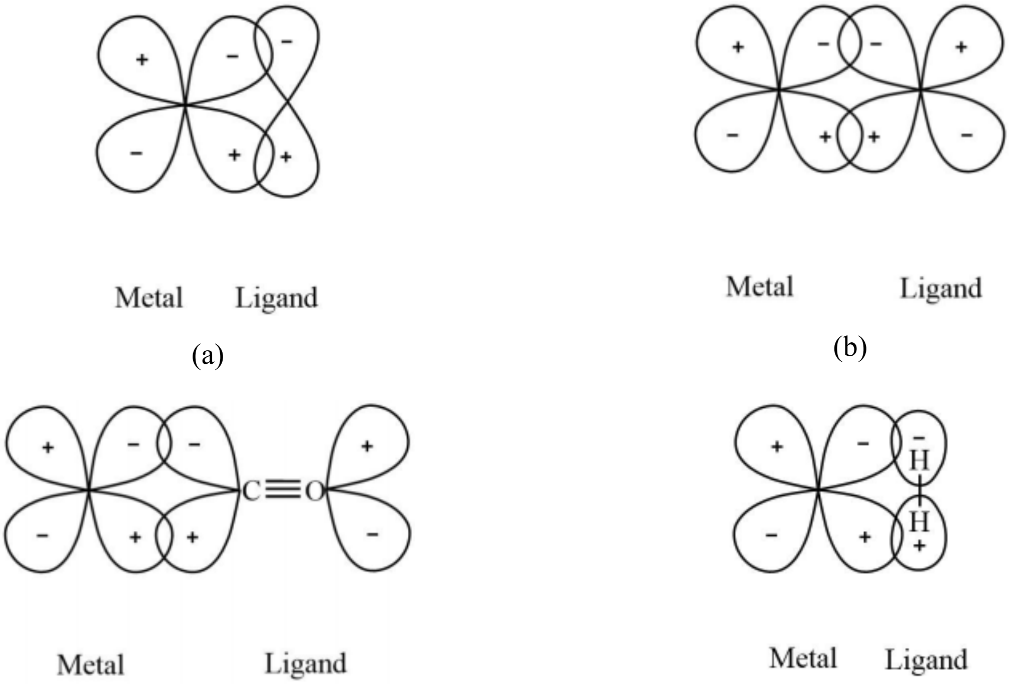
❖ π-Bonding and Molecular Orbital Theory

We have already studied the metal-ligand σ-overlap in the framework of molecular orbitals theory. Furthermore, this theory is also very useful for providing a rational explanation for the π-bonding in different metal-complex geometries. The basic approach remains the same except the fact that the orbital overlap in this situation is not along the internuclear axis but is sidewise in nature. The symmetry criteria governing these overlaps are absolutely clear but the extant up to which the overlap for different ligands takes place is still a matter of debate. In other words, the matching of metal and ligands orbital symmetry is not sufficient to assure the formation of π-bond as there are also some other factors (like size and energy) that signify the extent of overlap. It is quite possible that two orbital sets with the same symmetry may not be able to form molecular orbital due to a large difference in their energies.

There are four different types of metal-ligand interaction which can be resulted from the sidewise overlap of the orbitals.



(a)

(b)

(c)

(d)

Figure 15. The sidewise overlap (π-bonding) of the *d*-orbital metal with different types of ligands orbital (a) d_π-p_π, (b) d_π-d_π, (c) d_π-π^*, (d) d_π-σ^*.

Electron density can be transferred from filled ligand orbital to the empty d-orbital of the metal center, or from the filled d-orbital of the metal to the empty orbital of the ligand.

Table 4. Different types of π-bonding and the compatibility of various ligands.

Type	Explanation	Examples of the ligands involved
d_π-p_π	Transfer of electron density from filled *p*-orbital of the ligand to the empty *d*-orbital of the metal.	RS^-, RO^-, O^{2-}, F^-, Cl^-, Br^-, I^-, R_2N^-
d_π-d_π	Transfer of electron density from filled *d*-orbital of the metal to the empty *d*-orbital of the ligand.	R_2S, R_3P, R_3As
d_π-π^*	Transfer of electron density from filled *d*-orbital of the metal to the empty π^*-orbital of the ligand.	CN^-, CO, RNC, N_2, NO_2, ethylene, pyridine
d_π-σ^*	Transfer of electron density from filled *d*-orbital of the metal to the empty σ^*-orbital of the ligand.	R_3P, H_2, alkanes

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It can be seen from the above table that some ligands belong to more than one category and hence can use more than one type orbitals for π-bonding. However, it is observed that the contribution from one type of orbitals dominates the other in many cases. For instance, R_3P can accept *d*-electron density from metal in its empty *d*-orbital, or in the antibonding σ^* which is also greater in magnitude. Similarly, I^- also has the ability to donate electron from its filled *p*-orbital, or to accept electron density in its low lying empty *d*-orbitals.

The generally accepted explanation for the π-bonding in transition metal complexes of different geometry can be given as:

➢ *π-Bonding in Octahedral Complexes*

The π-bonding in octahedral complexes can happen in two ways; one through ligand *p*-orbitals that are not being used in σ bonding and other via π or π^* molecular orbitals present on the ligand. 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 symmetry adapted linear combinations of atomic orbitals (SALCs) for metal-ligand sidewise overlap can be obtained just by resolving the reducible representation based on the displacement vectors perpendicular to the axis of σ overlap. As each of the six ligands has two basis-vectors for π-symmetry, there are twelve in total.

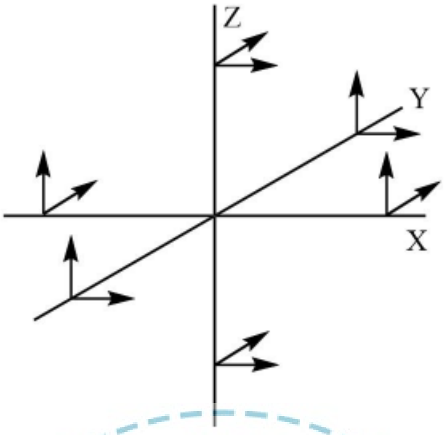

Figure 16. The π-basis set for ligand orbitals in octahedral complexes.

The symmetry adapted linear combinations of these fall into four triply degenerate irreducible representations labeled as t_{1g}, t_{2g}, t_{1u} and t_{2u}. The symmetry designations of different metal orbitals taking part in octahedral overlap are:

Table 5. Reducible representation based on perpendicular 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	12	0	0	0	–4	0	0	0	0	0	$t_{1g} + t_{2g} + t_{1u} + t_{2u}$

Two of these aforementioned sets are of t_{2g} and t_{1u} symmetry. The d_{xy}, d_{xz} and d_{yz} orbitals set on the metal also have t_{2g} symmetry, and therefore the π-bonds formed between a central metal and six ligands also have it as these π-bonds are just formed by the overlap of two sets of orbitals with t_{2g} symmetry. Similarly, the p_x, p_y and p_z-orbital set of the metal has t_{1u} symmetry which resembles with the symmetry of ligands SALCs. Therefore, these same-symmetry (t_{1u}) sets from metal and ligand may also interact to create bonding and antibonding molecular orbitals. However, the participation of t_{1u} set of the metal in π-overlap is highly disliked because the orbitals corresponding to this set are already being used in stronger σ-bonding and any deviation from this state is bound to destabilize the complex.

Hence, the SALC sets of t_{1g}, t_{2u} and also t_{1u} remain nonbonding. The pictorial representation of different SALC-orbitals in octahedral complexes, capable of π-overlap with metal orbitals, can be given as:

1. If four perpendicular *p*-orbitals of four ligands approaching along *x* and *y*-axis are pointing their lobes towards metal's d_{xy}-orbital in a sidewise manner, then the composite orbital becomes:

$$\varphi_1 = \pi_1 - \pi_2 + \pi_3 - \pi_4 \tag{7}$$

The pictorial representation is given below.

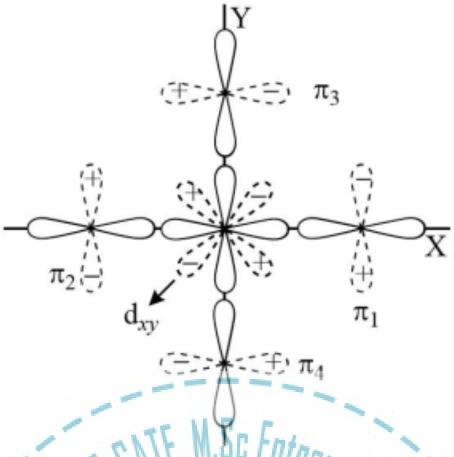

Figure 17. The combination of ligand orbitals overlapping with d_{xy}-orbital of the metal centre.

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2. If four perpendicular p-orbitals of four ligands approaching along y and z-axis and are pointing their lobes towards metal's d_{yz}-orbital in a sidewise manner, then the composite orbital becomes:

$$\varphi_2 = \pi_3 - \pi_4 + \pi_5 - \pi_6 \tag{8}$$

The pictorial representation is given below.

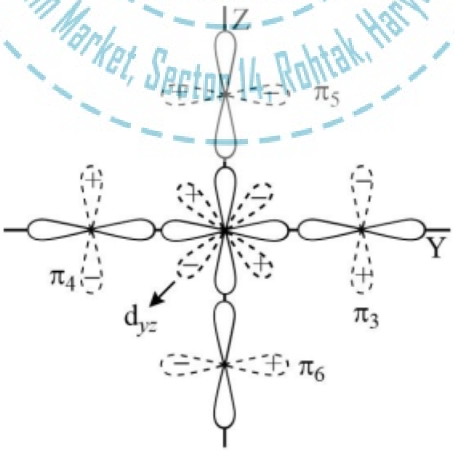

Figure 18. The combination of ligand orbitals overlapping with d_{yz}-orbital of the metal center.

3. If four perpendicular p-orbitals of four ligands approaching along x and z-axis are pointing their lobes towards metal's d_{xz}-orbital in a sidewise manner, then the composite orbital becomes:

$$\varphi_3 = \pi_1 - \pi_2 + \pi_5 - \pi_6 \qquad (9)$$

The pictorial representation is given below.

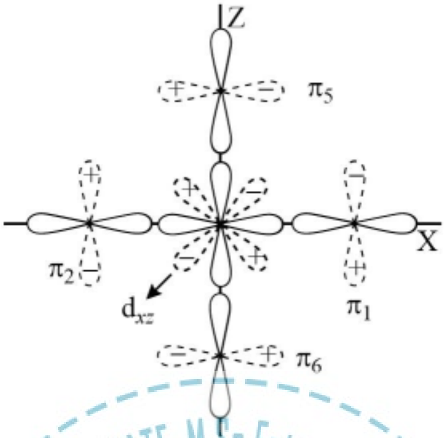

Figure 19. The combination of ligand orbitals overlapping with d_{xz}-orbital of the metal center.

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Molecular orbitals and the effect of π-bonding on crystal field splitting can be categorized in three ways as follows:

1. When ligand π-orbitals are filled and are of lower energy: The one form of coordinative π-bonding is ligand-to-metal bonding. This situation arises when the t_{2g}-symmetry p or π-orbitals on the ligands are filled and are low in energy. They combine with the d_{xy}, d_{xz} and d_{yz} orbitals on the metal and donate electrons to the resulting π-symmetry bonding orbital between them and the metal.

The metal-ligand bond is somewhat strengthened by this interaction, but the complementary anti-bonding molecular orbital from metal-ligand overlap is not higher in energy than the antibonding molecular orbital from the σ-bonding. The molecular orbital of t_{2g}^* are greater in energy than nonbonding sets of t_{1g}, t_{2u} and t_{1u}. On the other hand, the bonding molecular orbitals of t_{2g} are lower in energy than that of nonbonding SALCs of the ligands.

Therefore, when 36 electrons (12×2 from π-bonding and 6×2 from σ-bonding) from ligands are filled in the molecular orbitals, they will completely saturate the a_{1g}-bonding, t_{1u}-bonding, e_g-bonding, t_{2g}-bonding and the nonbonding sets of t_{1g}, t_{2u} and t_{1u}. The electron previously filled in d-orbital of the free metal ion can now be considered as distributed between t_{2g}^* and e_g^*. Hence, the crystal field splitting Δ_o decreases when ligand to metal bonding takes place.

The overall molecular orbital energy level diagram for this type of π-bonding in octahedral complexes can be shown as:

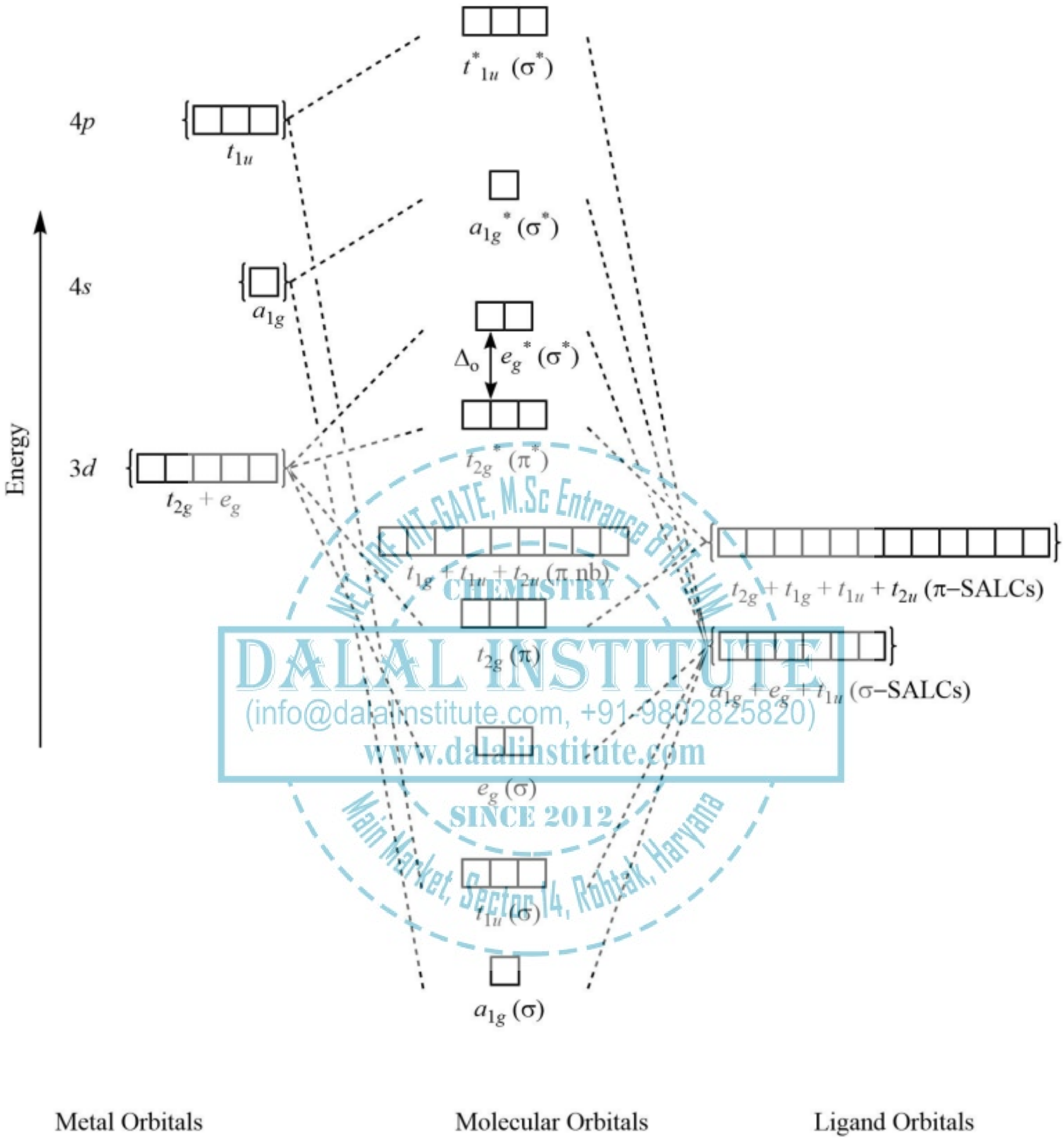
t^*_{1u} (σ^*)
4p
t_{1u}
a_{1g}^* (σ^*)
4s
a_{1g}
Δ_o
e_g^* (σ^*)
Energy
3d
$t_{2g} + e_g$
t_{2g}^* (π^*)
$t_{1g} + t_{1u} + t_{2u}$ (π nb)
$t_{2g} + t_{1g} + t_{1u} + t_{2u}$ (π–SALCs)
t_{2g} (π)
$a_{1g} + e_g + t_{1u}$ (σ–SALCs)
e_g (σ)
t_{1u} (σ)
a_{1g} (σ)
Metal Orbitals
Molecular Orbitals
Ligand Orbitals

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Figure 20. The generation of π and σ-molecular orbitals in octahedral complexes.

2. When ligand π-orbitals are empty and are of higher energy: The second important form of π-bonding in coordination complexes is metal-to-ligand π bonding, also called π-backbonding. It occurs when the LUMOs (lowest unoccupied molecular orbitals) of the ligand are anti-bonding π^*-orbitals and are high in energy. The ligands end up with electrons in their π^* molecular orbital, so the corresponding π-bond within the ligand weakens. The complementary anti-bonding molecular orbital from metal-ligand overlap is higher in energy than both, the first antibonding molecular orbital from the σ-bonding (e_g^*), and the nonbonding sets of t_{1g}, t_{2u} and t_{1u}. On the other hand, the bonding molecular orbitals of t_{2g} are higher in energy than all σ bonding molecular orbitals. The overall molecular orbital energy level diagram for this type of π-bonding in octahedral complexes can be shown as:

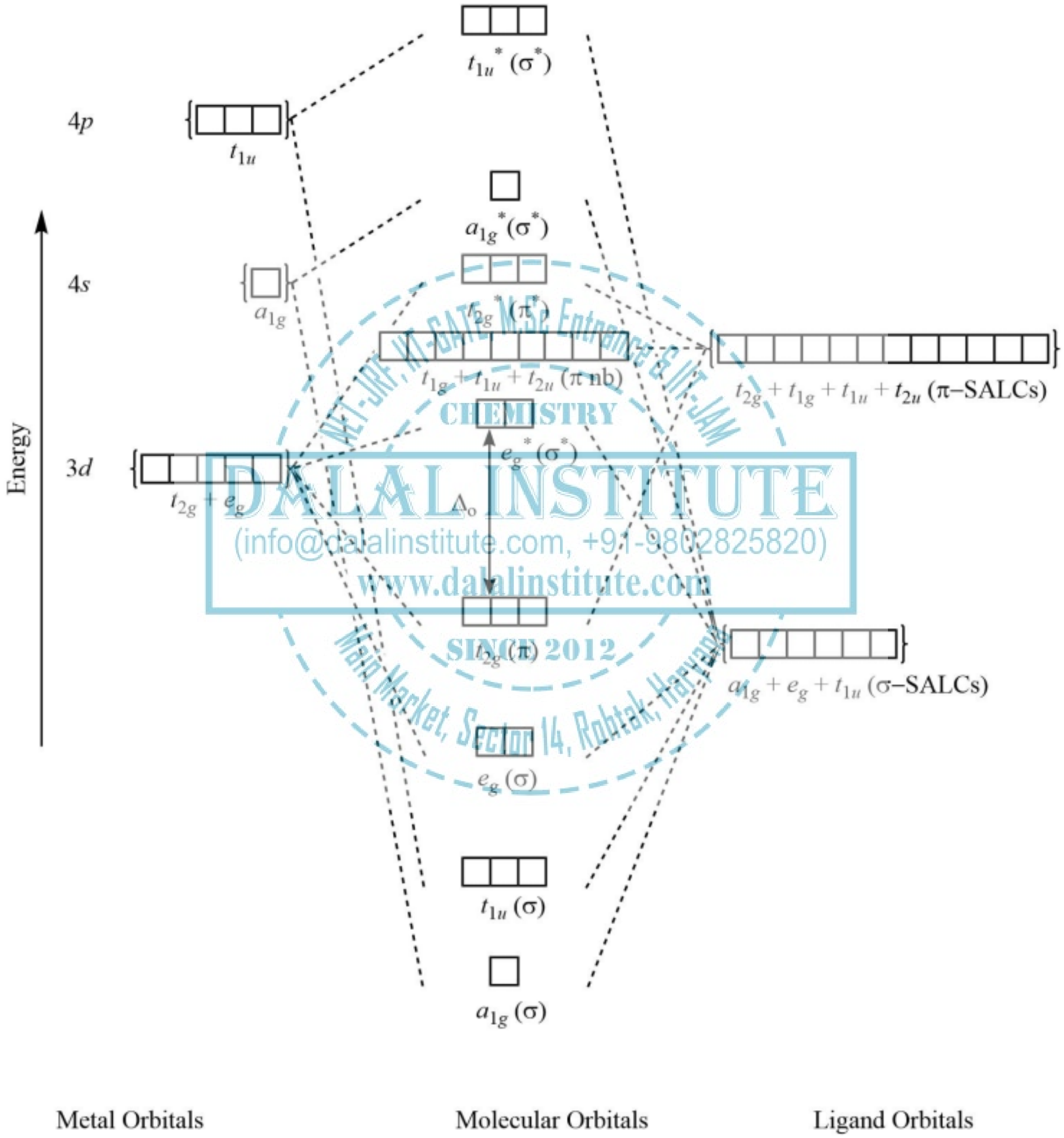
t_{1u}^* (σ^*)
4p
t_{1u}
a_{1g}^*(σ^*)
4s
a_{1g}
t_{2g}^*(π^*)
$t_{1g} + t_{1u} + t_{2u}$ (π nb)
$t_{2g} + t_{1g} + t_{1u} + t_{2u}$ (π–SALCs)
Energy
3d
e_g^* (σ^*)
$t_{2g} + e_g$
Δ_o
t_{2g} (π)
$a_{1g} + e_g + t_{1u}$ (σ–SALCs)
e_g (σ)
t_{1u} (σ)
a_{1g} (σ)
Metal Orbitals
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Figure 21. The generation of π and σ-molecular orbitals in octahedral complexes.

Therefore, when twelve electrons (12×0 from π-bonding and 6×2 from σ-bonding) from ligands are filled in the molecular orbitals, they will completely saturate the a_{1g}-bonding, t_{1u}-bonding and e_g-bonding. The electron previously filled in *d*-orbital of the free metal ion can now be considered as distributed between t_{2g} and e_g^*. Hence, the crystal field splitting Δ_o increases and the bond between the ligand and the metal strengthens when metal to ligand bonding takes place.

3. When ligand π-orbitals are empty as well as filled: There are many ligands, like I^-, which have both filled *p*-orbitals as well as vacant d-orbitals of π symmetry. In these cases, the prediction of crystal field splitting energy is quite difficult as the two effects counterbalance each other to different extents for different ligands. The six bonding MOs which are formed are actually filled by the electrons coming from the ligands, and electrons from the *d*-orbitals of the metal ion occupy the nonbonding and, sometimes, antibonding molecular orbitals. The energy difference between the latter two types of MOs is called Δ_o and is determined by the nature of the π-interaction between the ligand orbitals with the *d*-orbitals on the central atom. As described above, π-donor ligands lead to a small Δ_o and are called weak- or low-field ligands, whereas π-acceptor ligands lead to a large value of Δ_o and are called strong or high-field ligands. Ligands that are neither π-donor nor π-acceptor give a value of Δ_o somewhere in-between.

The magnitude of Δ_o determines the electronic structure of d^4-d^7 metal ions., The nonbonding and antibonding MOs in types of metals complexes can be filled in two ways; the first one in which maximum possible electrons are put in the nonbonding orbitals before the antibonding filling, and second one in which maximum possible unpaired electrons are put in. The first case is labeled as low-spin, while the second is labeled as high-spin complexes. A small Δ_o can be outranked by the energetic stabilization from avoiding the electron pairing, leading to the spin-free case. On the other hand, if Δ_o is large, the spin-pairing energy would become negligible in comparison and a spin-paired state arises. An empirically-obtained list of various ligands which are arranged by the magnitude of splitting Δ they produce is called as the spectrochemical series. It can be seen that the low-field ligands are all π-donors (such as I^-), the high field ligands are π-acceptors (such as CN^- and CO), and ligands such as H_2O and NH_3, which are neither, are in the middle.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO^{3-} < N^{3-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN <$ py (pyridine) $< NH_3 <$ en (ethylenediamine) $<$ bipy (2,2'-bipyridine) $<$ phen (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- < CO$

It is also worthy to note that the electrons transfer from metal *d*-orbital to the antibonding molecular orbitals of carbonyl and its analogs is actually partial in nature. The electron-transfer increases metal-carbon bond strength but weakens the carbon–oxygen bond. The increased M–CO bond strength is obvious in the increases of vibrational frequencies for the metal–carbon bond and usually lie outside the range of normal IR spectrophotometers. Moreover, the bond length of M–CO bond is also shortened. The decreased bond strength of C–O bond is obvious from the decreasing wavenumber of ν_{CO} bands. The high stabilization which results from metal-to-ligand bonding (back-bonding) is caused by the relaxation of the negative charge from the metal center. This permits the metal ion to accept the σ-donation more effectively. The combination of ligand-to-metal σ-bonding and metal-to-ligand π-bonding is a synergic effect, as each enhances the other.

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➢ *π-Bonding in Tetrahedral Complexes*

The π-bonding in tetrahedral complexes can happen in two ways; one through ligand *p*-orbitals that are not being used in σ bonding and other via π or π^* molecular orbitals present on the ligand. The symmetry designations of different metal orbitals taking part in tetrahedral overlap are:

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 sidewise overlap can be obtained just by resolving the reducible representation based on the displacement vectors perpendicular to the axis of σ overlap. As each of the four ligands has two basis-vectors for π-symmetry, there are eight in total. Each pair of perpendicular vectors (p_x and p_y) is attached about its own *z*-axis so that all the *y*-vectors are parallel to the *xy*-plane of the tetrahedral complex.

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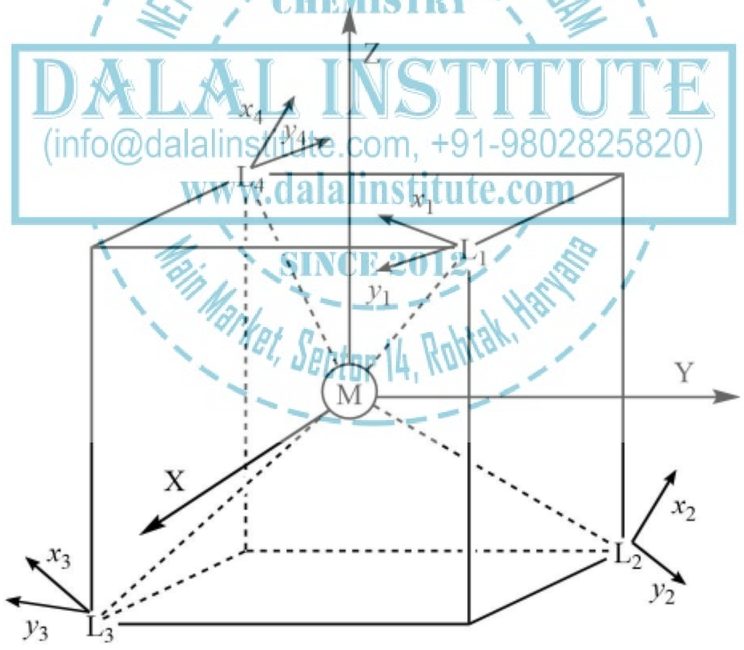

Figure 22. The π-basis set for ligand orbitals in tetrahedral complexes.

The symmetry adapted linear combinations of these fall into two doubly and on singly degenerate irreducible representations labeled as e, t_1 and t_2. The symmetry designations of different ligand orbitals taking part in tetrahedral overlap are:

Table 6. Reducible representation based on perpendicular vectors in the tetrahedral geometry.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Irreducible components
Γ_π	8	–1	0	0	0	$e + t_1 + t_2$

Two of these aforementioned sets are of *e* and t_2 symmetry. The $d_{x^2-y^2}$ and d_{z^2} orbitals set on the metal also have *e*-symmetry, and therefore the π-overlap between a central metal and four ligands is possible as far as the generation of molecular orbitals with *e*-symmetry is concerned.

Similarly, the p_x, p_y and p_z-orbital set of the metal 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 may also interact to create bonding and antibonding molecular orbitals. However, the π-overlap in tetrahedral complexes is not independent of the σ-bonding because the ligand SALCs and metals atomic orbital, of both types of *e* and t_2 symmetry, participate in σ as well as π-bonding.

Hence, when twenty-four electrons (8×2 from π-bonding and 4×2 from σ-bonding) from ligands are filled in the molecular orbitals, they will completely saturate the a_1 (σ), t_2 (σ), t_2 (π), *e* (π) and t_1 (π nb). The electron previously filled in *d*-orbital of the free metal ion can now be considered as distributed in e^* (π^*) and t_2^* (σ^*, π^*) which are predominantly $d_{x^2-y^2} = d_{z^2}$ and $d_{xz} = d_{yz} = d_{xy}$ in character, respectively.

Therefore, the pattern of crystal field splitting energy, provided by the molecular orbital theory, is the same as that of what it was given by crystal field theory. Moreover, the ligand to metal charge transfer spectral band can be considered as a result of the transition of an electron from nonbonding or bonding molecular orbitals to the antibonding molecular orbitals. These charge transfer peaks are very high in intensity they are spin as well as Laporte allowed in nature.

Tetrahedral complexes are almost always high-spin in nature because the energy separation between e^* (π^*) and t_2^* (σ^*, π^*) energy levels, Δ_t, is very small. That's why, during the filling of metal *d*-electrons, the promotion of electrons is always preferred over pairing. This is the same result as provided by the application of crystal field theory.

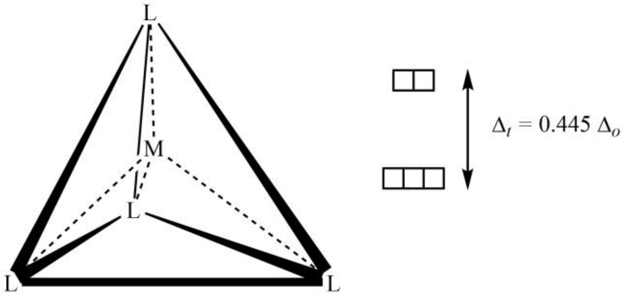

Figure 23. The crystal field splitting of *d*-subshell in tetrahedral complexes.

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The overall molecular orbital energy level diagram for this type of π-bonding in tetrahedral complexes can be shown as:

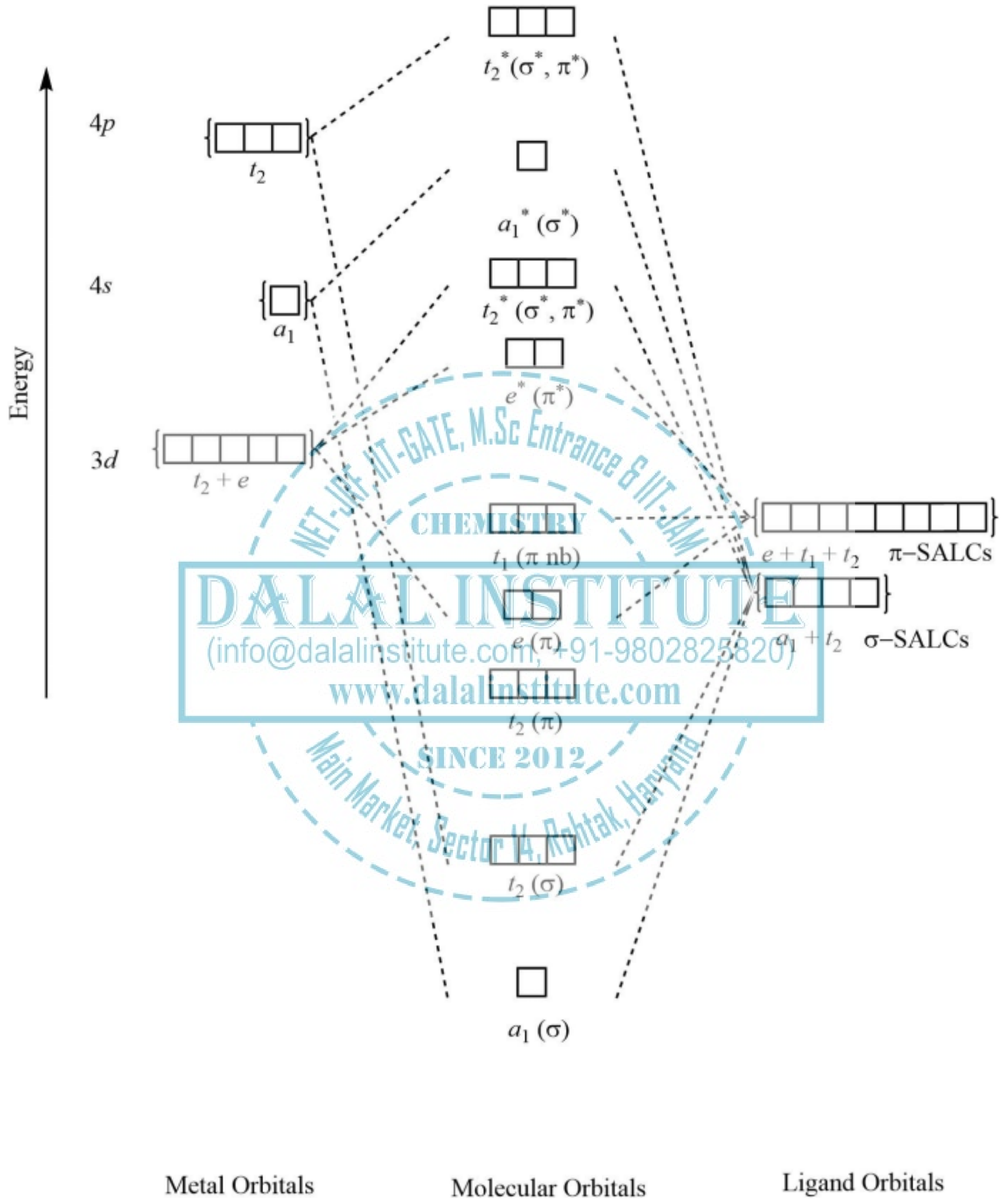
Energy
4p
t_2
4s
a_1
3d
$t_2 + e$
$t_2^*(\sigma^*, \pi^*)$
$a_1^*(\sigma^*)$
$t_2^*(\sigma^*, \pi^*)$
$e^*(\pi^*)$
$t_1(\pi$ nb)
$e(\pi)$
$t_2(\pi)$
$t_2(\sigma)$
$a_1(\sigma)$
$e + t_1 + t_2$ π–SALCs
$a_1 + t_2$ σ–SALCs
Metal Orbitals
Molecular Orbitals
Ligand Orbitals

Figure 23. The generation of π and σ-molecular orbitals in four-coordinated tetrahedral complexes of transition metals.

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➢ *π-Bonding in Square Planar Complexes*

The π-bonding in square planar complexes can be visualized in terms of the sidewise overlap of different kinds of orbitals on metal and ligands, having comparable energy and proper symmetry. 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 displacement vectors perpendicular to the axis of σ-overlap. As each of the four ligands has two basis-vectors for π-symmetry, there are eight in total.

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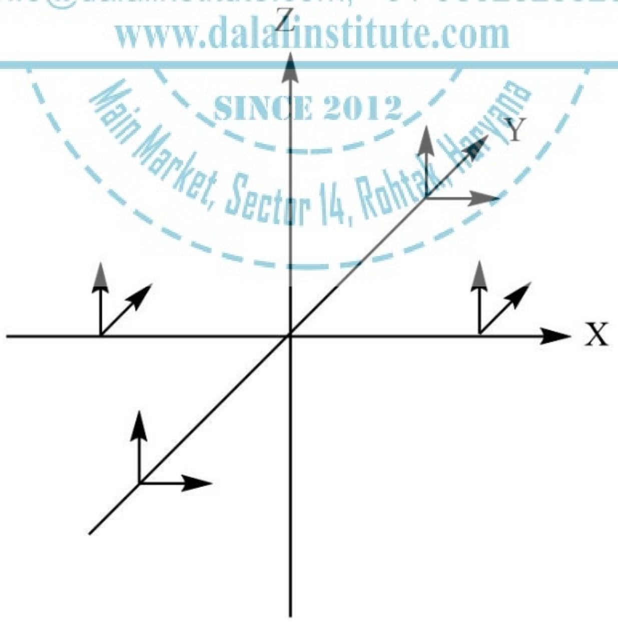

Figure 24. The complete π-basis set for ligand orbitals in square planar complexes of transition metal centers.

The symmetry adapted linear combinations of these fall into six irreducible representations labeled as a_{2g}, b_{2u}, e_u, a_{2u}, e_g and b_{2g}. The symmetry designations of different ligand SALC-orbitals taking part in square-planar overlap are:

Table 7. The complete reducible representation based on perpendicular vectors (usable in sidewise overlap) 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	8	0	0	–4	0	0	0	0	0	0	$a_{2g} + b_{2u} + e_u + e_g + b_{2g} + a_{2u}$.

Two of these aforementioned sets, with a_{2g} and b_{2u} symmetry, remain nonbonding and are localized on the ligands. This is quite logical because there are no metal orbitals with these symmetry properties and hence no orbital overlap is possible.

The metal orbitals of e_u-symmetry take part in σ as well as π-bonding. Now, as there are two sets of SLACs with e_u-symmetry, the number of molecular orbital sets formed with e_u-symmetry is also three. The lowest energy molecular orbitals set of e_u-symmetry is primarily of σ-bonding while the higher energy molecular orbitals set is mainly π-bonding in nature. The highest doubly degenerate molecular orbitals set of e_u-symmetry is of both σ^* and π^*-antibonding character.

The d_{yz} and d_{xz} orbitals set on the metal has e_g-symmetry, which resembles with the symmetry of one of SALCs set on ligands. Therefore, these same-symmetry (e_g) sets from metal and ligand also interact to create bonding and antibonding molecular orbitals. Furthermore, the b_{2g}-symmetry d_{xy} orbital and a_{2u}-symmetry p_z orbitals on the metal interacts with b_{2g}-symmetry and a_{2u}-symmetry SALC, respectively, to produce π-bonding and antibonding molecular orbitals.

Hence, when twenty-four electrons (8×2 from π-bonding and 4×2 from σ-bonding) from ligands are filled in the molecular orbitals, they will completely saturate the a_{1g} (σ), b_{1g} (σ), e_u (σ), b_{2g} (π), e_g (π), a_{2u} (π), e_u (π), a_{2g} (π nb) and b_{2u} (π nb). The electron previously filled in d-orbital of the free metal ion can now be considered as distributed in e_g^* (π^*), a_{1g} (σ^*), b_{2g}^* (π^*) and b_{1g}^* (σ^*) which are predominantly d_{xz}=d_{yz}, d_{z^2}, d_{xy} and $d_{x^2-y^2}$ in character, respectively. Hence, the pattern of crystal field splitting energy, provided by the molecular orbital theory, is the same as that of what it was given by crystal field theory. In other words, the formal electronic configuration of tetrahedral metal complexes is the same from both theories.

Moreover, the ligand to metal charge transfer spectral band can be considered as a result of the transition of an electron from nonbonding or bonding molecular orbitals to b_{1g}^* (σ^*). These charge transfer peaks are pretty high in intensity due to their spin and Laporte allowance.

The overall molecular orbital energy level diagram for the π-bonding in square-planar complexes can be shown as:

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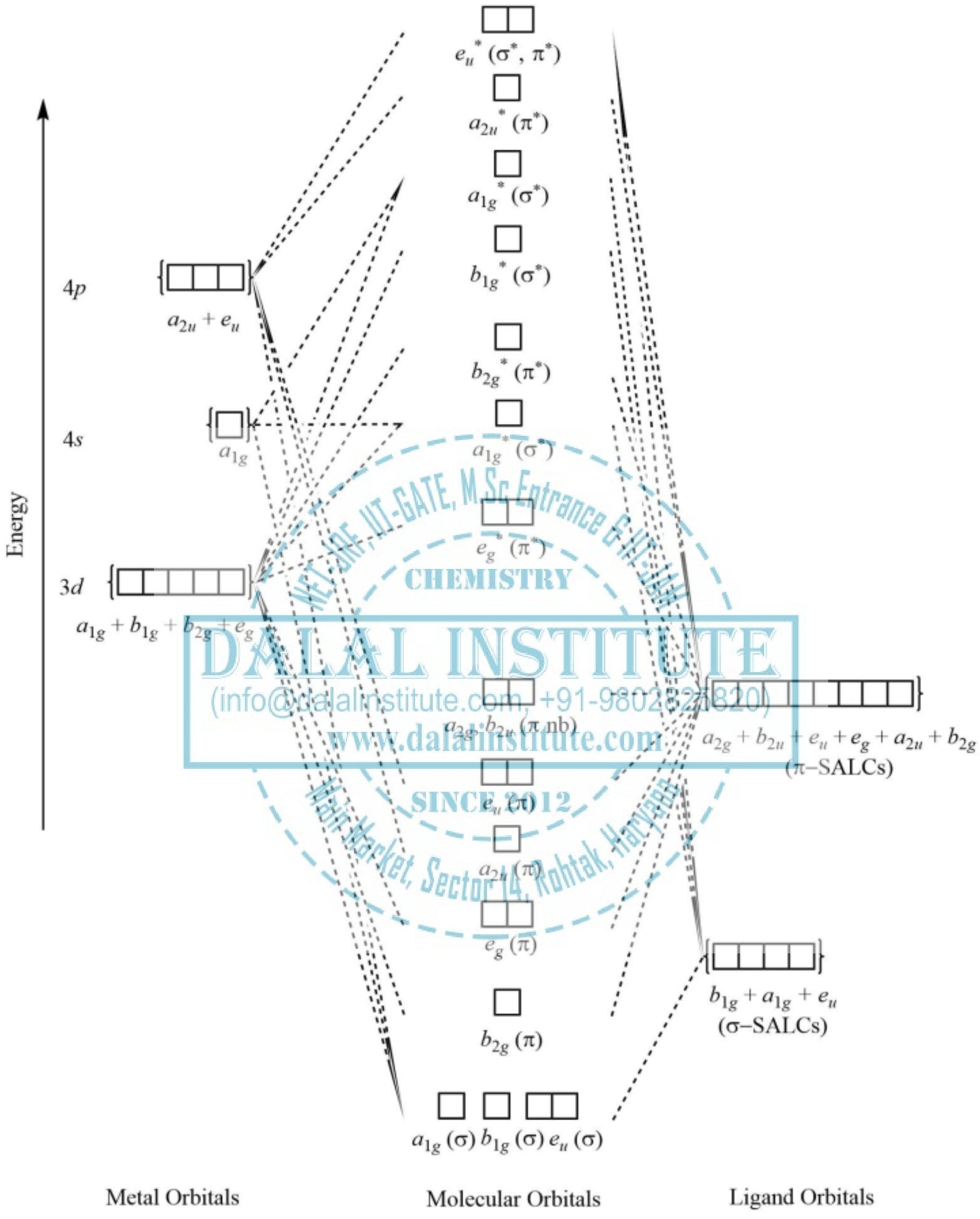
Energy
4p
$a_{2u} + e_u$
4s
a_{1g}
3d
$a_{1g} + b_{1g} + b_{2g} + e_g$
e_u^* (σ^*, π^*)
a_{2u}^* (π^*)
a_{1g}^* (σ^*)
b_{1g}^* (σ^*)
b_{2g}^* (π^*)
a_{1g}^* (σ^*)
e_g^* (π^*)
a_{2g}, b_{2u} (π nb)
e_u (π)
a_{2u} (π)
e_g (π)
b_{2g} (π)
a_{1g} (σ) b_{1g} (σ) e_u (σ)
$a_{2g} + b_{2u} + e_u + e_g + a_{2u} + b_{2g}$
(π–SALCs)
$b_{1g} + a_{1g} + e_u$
(σ–SALCs)
Metal Orbitals
Molecular Orbitals
Ligand Orbitals

Figure 25. The generation of π and σ-molecular orbitals in square-planar complexes.

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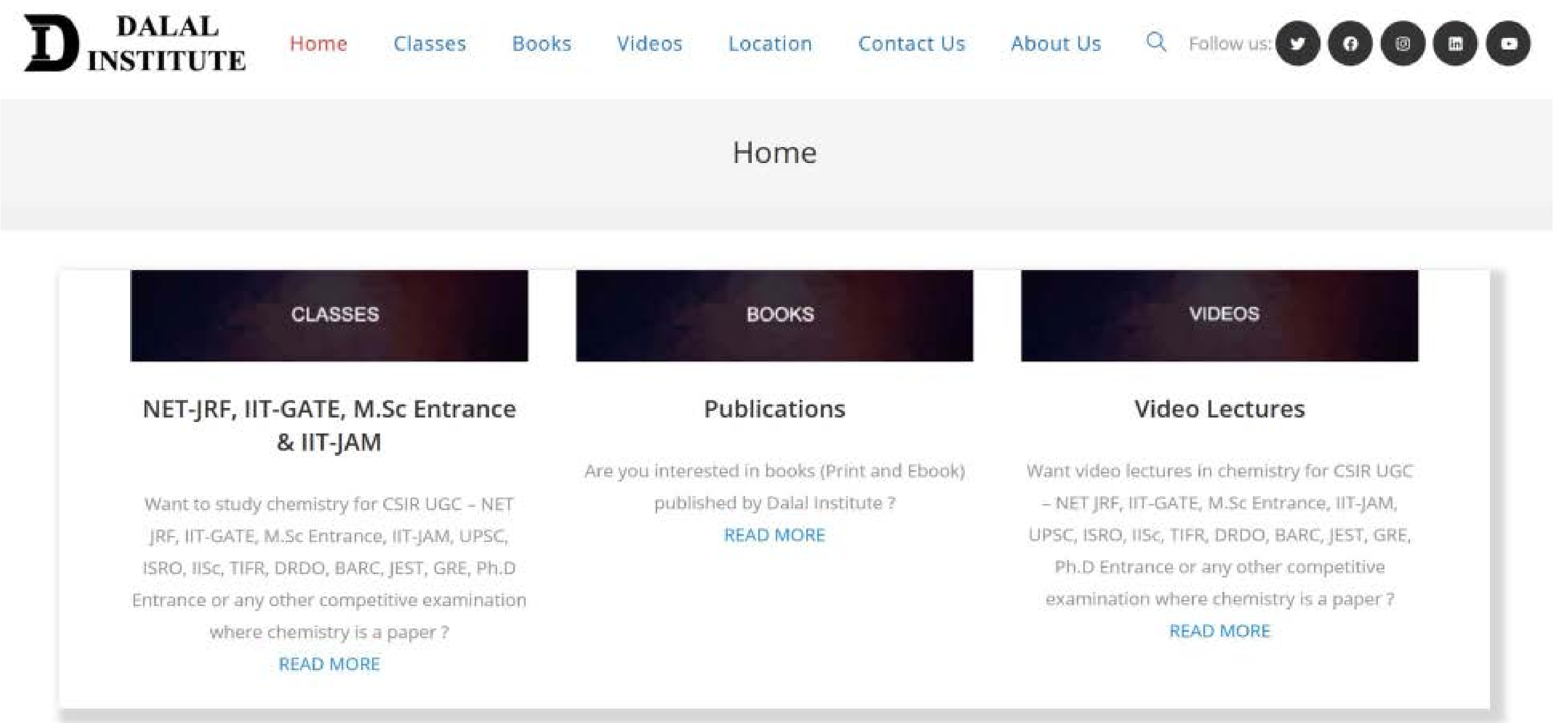

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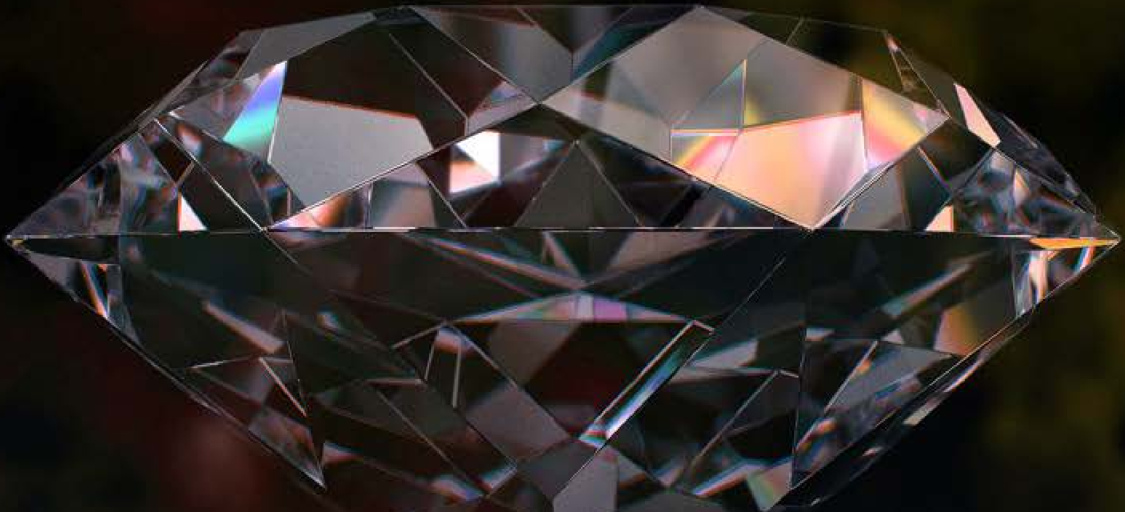

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