# MOLECULAR ORBITAL THEORY

We shall now consider the qualitative aspects of the application of molecular orbital theory to complexes. The discussion will really include also the ligand field theory since this is perhaps best pictured as a theory, or even a series of theories, which combines the convenience and basic simplicity of CFT with the rigorousness and generality of MOT in whatever relative amounts seem to be necessary for the particular complex molecule or problem at hand. What is sometimes referred to as LFT is a modification of the CFT that allows certain parameters to be empirically altered to take account of covalence effects without explicitly introducing orbital overlap. This approach has been aptly termed *adjusted crystal field theory*, ACFT, by Cotton and Wilkinson[10] and we shall examine it briefly later.

As we have seen in Chapter 5, the molecular orbital theory can accommodate at one extreme the completely electrostatic situation which involves no orbital overlap to the maximum overlap at the other extreme, as well as all intermediate degrees of overlap. Of all the theoretical approaches to bonding this, then, is the most sophisticated and general and correspondingly the most difficult. Many approximations must be made in its quantitative application to the many-atom multielectron complex ion systems. Its usefulness in this area is very recent and is certain to increase in the future as better wave functions and computational methods become available.

The molecular orbital method employs the same central atom orbitals as does the VBT, but additionally it considers the available orbitals of the coordinated ligand atoms. Thus, excluding initially the π-bonding ligand

orbitals, for the case of six ligands around a central transition metal atom there will be a total of fifteen orbitals available for molecular orbital construction. These arise from nine orbitals on the metal atom and six orbitals from the ligands. For a particular complex, it is first necessary to establish which orbital overlaps are possible. Simply because of the inherent symmetry properties of the orbitals in the problem at hand some cannot overlap. It is only meaningful and proper to mathematically combine, for example by the LCAO method, orbitals that possess the same symmetries. In Table 10-10, we have listed according to symmetry class the metal atom orbitals for a $3d$ transition metal atom and the composite "symmetry" orbitals of the ligands for the regular octahedral case. The individual ligand orbitals are identified by the appropriate cartesian coordinate subscript designation from the following figure:
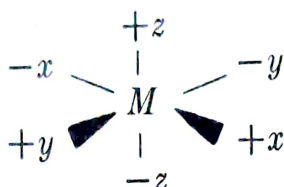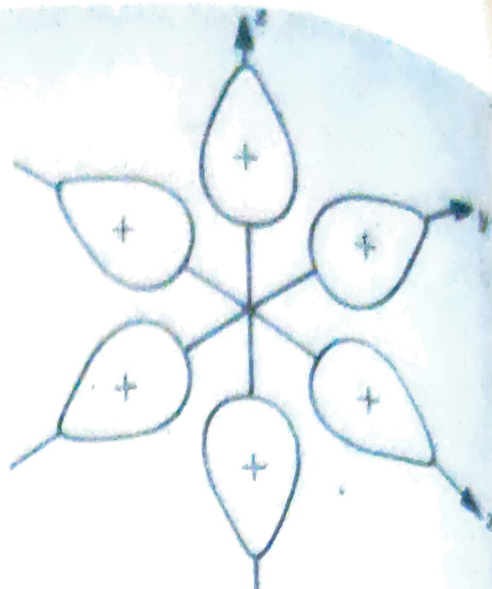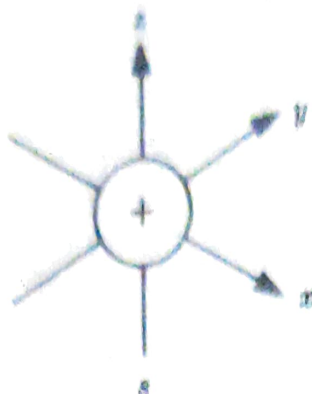

Thus, the nine significant metal atomic orbitals are designated as $\Phi_{3d_{xy}}$, $\Phi_{3d_{xz}}$, ... Φ_{4s}, ... Φ_{4p_z}. These nine orbitals fall into one of four symmetry classes, labeled according to their group theoretical origin: nondegenerate totally symmetric A_{1g}, a single orbital having the full symmetry of the molecule; doubly degenerate E_g, two orbitals equivalent except for spatial orientation; triply degenerate T_{1u}, three orbitals equivalent except for spatial orientation; and triply degenerate T_{2g}, three orbitals equivalent except for spatial orientation. The three T_{2g} orbitals are spatially oriented so as to be suitable only for π bonding in the octahedral system, that is, there are no ligand σ orbitals formed from orbitals having the T_{2g} symmetry, but the remaining six metal atom orbitals are all suitable for σ-bonding purposes. The subscripts g (from the German *gerade* meaning *even*) and u (from the German *ungerade* meaning *uneven*) are used to indicate whether the orbital is centrosymmetric or noncentrosymmetric, respectively.
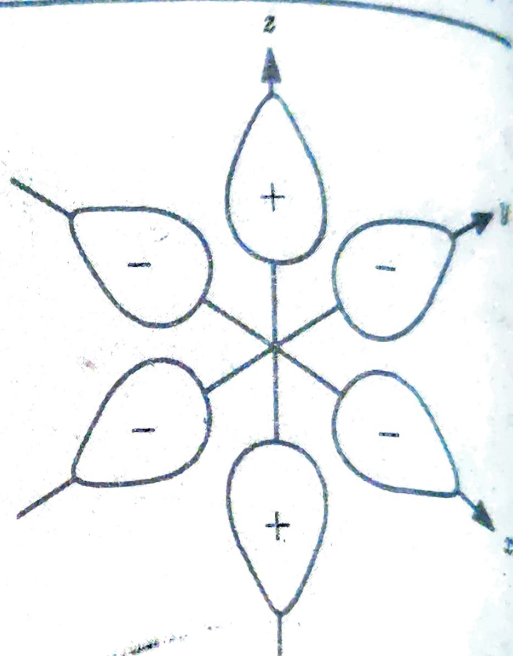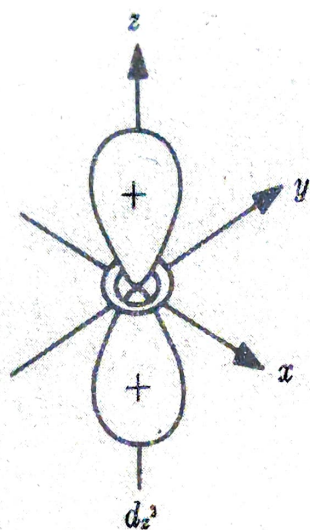
The six ligand σ orbitals must first be combined so as to form a set of six composite "symmetry" orbitals, each constructed to effectively overlap with a particular one of the six σ-bonding metal atom orbitals. These are sometimes designated as *ligand group orbitals*, *LGO's*, and methods for obtaining them may be found in two recent articles by Kettle.[36] The ligand composite σ orbitals are designated Σ_a, Σ_{z_1}...Σ_z, and these fall into the symmetry classes A_{1g}, E_g, and T_{1u}. (See Figure 10-14.) Then each metal atom orbital is combined with its matching symmetry ligand orbital by the LCAO method to yield a bonding and an antibonding MO pair of orbitals. (See Table 10-11 and Figure 10-15.) It is seen that the T_{2g} central atom orbitals remain nonbonding since they are not matched in symmetry by any composite ligand σ orbitals. However, we shall see shortly that it is just

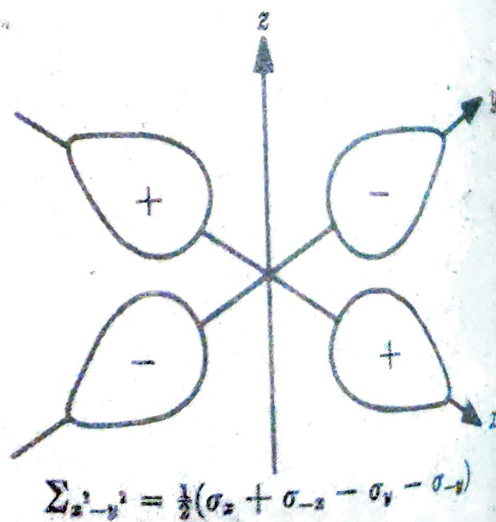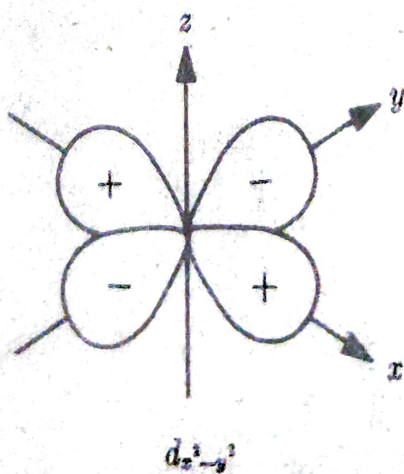**TABLE 10–10.** Symmetry Classification of Orbitals for Regular Octahedral Complexes.

Symmetry Class	Metal Atomic Orbitals	Composite of Ligand σ Orbitals	Composite of Ligand π Orbitals
A_{1g}	Φ_{4s}	$\Sigma_a = \dfrac{1}{\sqrt{6}}(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$	—
E_g	$\Phi_{3d_{z^2}}$	$\Sigma_{z^2} = \dfrac{1}{2\sqrt{3}}(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$	—
	$\Phi_{3d_{x^2-y^2}}$	$\Sigma_{x^2-y^2} = \dfrac{1}{\sqrt{2}}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$	—
T_{1u}	Φ_{4p_x}	$\Sigma_x = \dfrac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$	$\pi_x = \dfrac{1}{\sqrt{2}}(\pi_{x,y} + \pi_{x,-y} + \pi_{x,z} + \pi_{x,-z})$
	Φ_{4p_y}	$\Sigma_y = \dfrac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$	$\pi_y = \dfrac{1}{\sqrt{2}}(\pi_{y,z} + \pi_{y,-z} + \pi_{y,x} + \pi_{y,-x})$
	Φ_{4p_z}	$\Sigma_z = \dfrac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$	$\pi_z = \dfrac{1}{\sqrt{2}}(\pi_{z,x} + \pi_{z,-x} + \pi_{z,y} + \pi_{z,-y})$
T_{2g}	$\Phi_{3d_{xy}}$	—	$\pi_{xy} = \dfrac{1}{\sqrt{2}}(\pi_{y,x} - \pi_{y,-x} + \pi_{x,y} - \pi_{x,-y})$
	$\Phi_{3d_{xz}}$	—	$\pi_{xz} = \dfrac{1}{\sqrt{2}}(\pi_{x,z} - \pi_{x,-z} + \pi_{z,x} - \pi_{z,-x})$
	$\Phi_{3d_{yz}}$	—	$\pi_{yz} = \dfrac{1}{\sqrt{2}}(\pi_{z,y} - \pi_{z,-y} + \pi_{y,z} - \pi_{y,-z})$

A_{1g}

$$\Sigma_s = \frac{1}{\sqrt{6}}(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$$

E_g

d_{z^2}

$$\Sigma_z = \frac{1}{2\sqrt{3}}(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$$
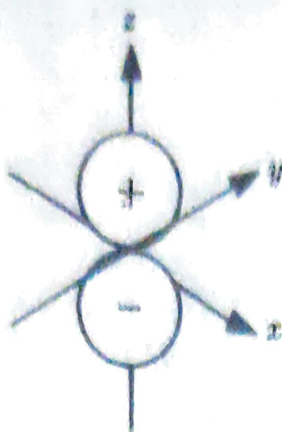
$d_{x^2-y^2}$

$$\Sigma_{x^2-y^2} = \tfrac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$
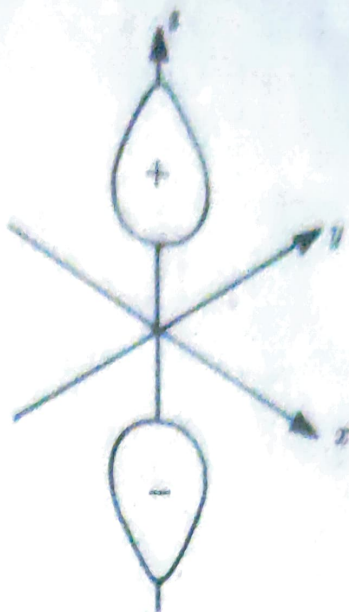
FIGURE 10-14

The Six Metal Atom σ Orbitals, on the Left in Each Case, and Their Matching Ligand Composite Symmetry Orbitals, on the Right in Each Case.
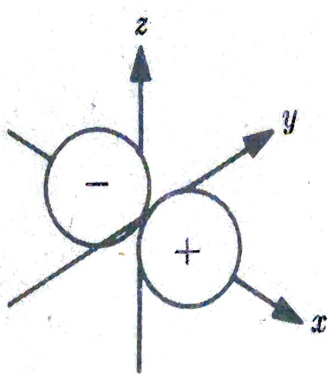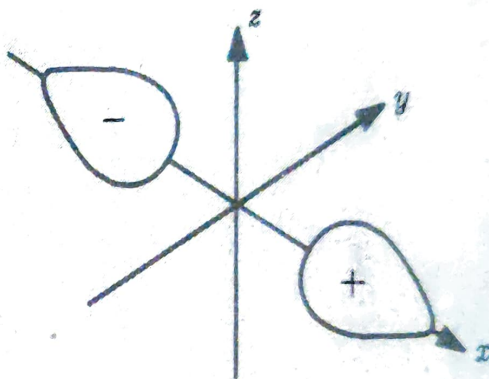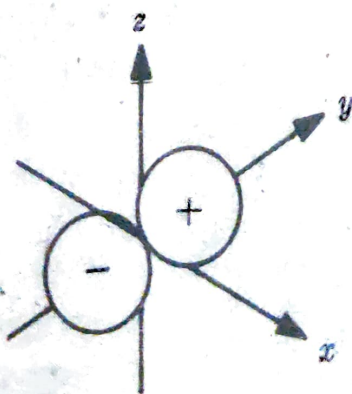
p_z

$\Sigma_z = \dfrac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$
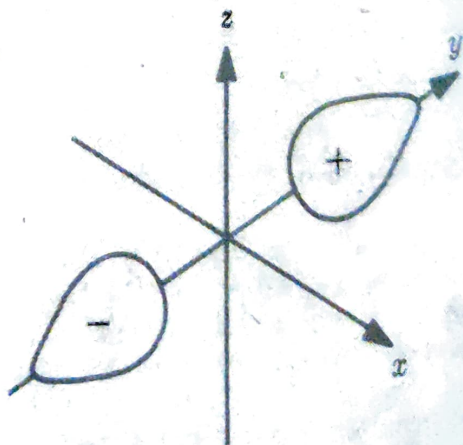
T_{1u}

p_x

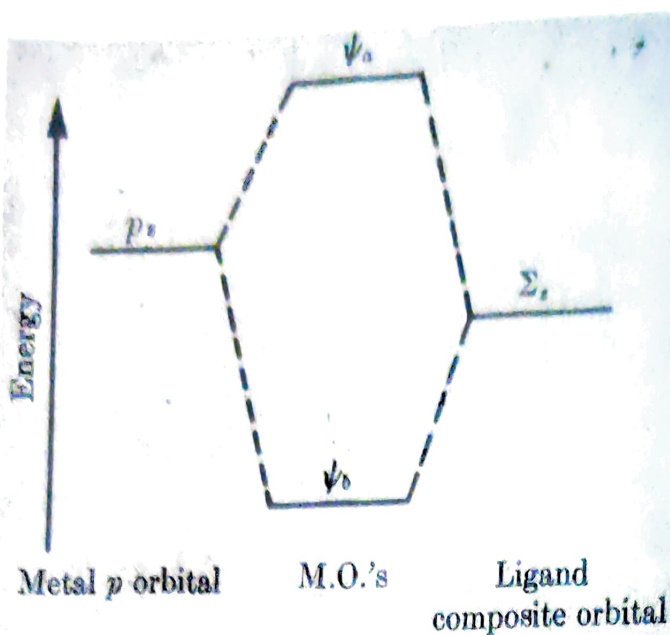$\Sigma_x = \dfrac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$

p_y

$\Sigma_y = \dfrac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$

FIGURE 10-14 (Continued)
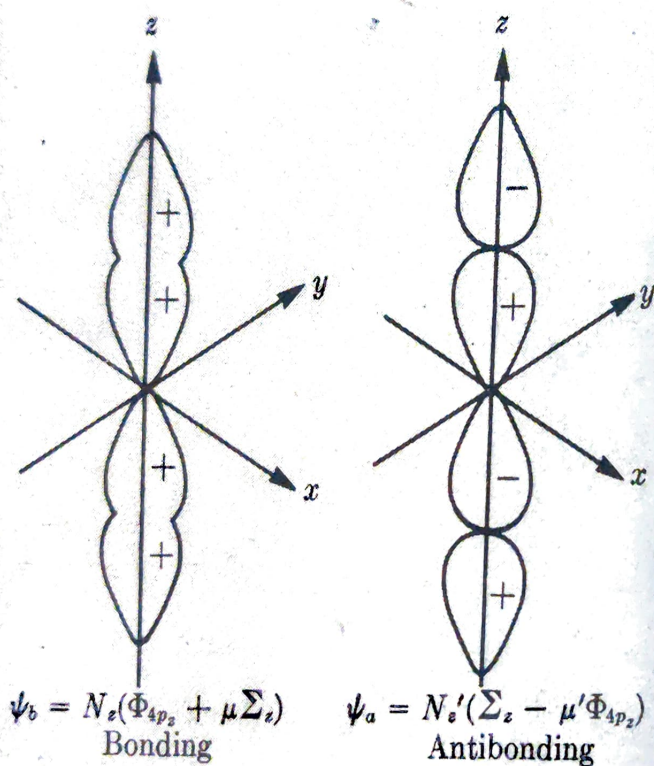
FIGURE 10-15

(a) Relative Energies of a Metal p Orbital, Its Matching Ligand Symmetry Orbital and the Resulting Bonding and Antibonding σ Molecular Orbitals. (b) Combinations of Appropriate Metal and Ligand T_{1u} Symmetry Orbitals to Form the Bonding (above) and Antibonding MO's.

these metal atom orbitals which can become π-bonding provided that the ligands possess matching symmetry π-bonding orbitals.

A molecular orbital (MO) energy level diagram, which results from a

TABLE 10-11. Molecular Orbitals for Regular Octahedral Complexes Neglecting π Bonding.

Symmetry Class	Bonding Orbitals	Nonbonding Orbitals	Antibonding Orbitals
A_{1g}	$N_o(\Phi_s + \lambda\Sigma_s)$	—	$N_o'(\Sigma_s - \lambda'\Phi_s)$
T_{1u}	$N_o(\Phi_{px} + \mu\Sigma_x)$ $N_o(\Phi_{py} + \mu\Sigma_y)$ $N_o(\Phi_{pz} + \mu\Sigma_z)$	— — —	$N_o'(\Sigma_x - \mu'\Phi_{px})$ $N_o'(\Sigma_y - \mu'\Phi_{py})$ $N_o'(\Sigma_z - \mu'\Phi_{pz})$
E_g	$N_{o+y^2}(\Phi_{3d_{x^2-y^2}} + \nu\Sigma_{x^2-y^2})$ $N_o(\Phi_{3d_{z^2}} + \nu\Sigma_{z^2})$	— —	$N'_{x^2-y^2}(\Sigma_{x^2-y^2} - \nu'\Phi_{3d})$ $N'_{z^2}(\Sigma_{z^2} - \nu'\Phi_{3d})$
T_{2g}	— — —	$\Phi_{3d_{xy}}$ $\Phi_{3d_{xz}}$ $\Phi_{3d_{yz}}$	— — —

mathematical treatment of the type outlined qualitatively above, for a hypothetical regular octahedral complex ignoring π bonding, is shown in Figure 10–16. The exact ordering of the strongest, that is, lowest energy, bonding levels is uncertain due to the uncertainties in obtaining the necessary exchange integrals. In general it may be assumed that, to a first approximation, the energies of the bonding and antibonding MO's lie equal energy distances below and above, respectively, the mean value of the energies of the combining orbitals. Furthermore, it may be assumed that if an MO is much nearer to one of the AO's or LGO's used in its construction than to the other one, it will have much more the character of the nearer one. Thus, the six σ-bonding MO's are considered to have more the character of ligand atom orbitals than metal atom orbitals, and we therefore consider electrons in these orbitals to be mainly "ligand electrons." Likewise, any electrons occupying any of the antibonding MO's are considered to be predominately "metal electrons," and any electrons in the non-σ-bonding T_{2g} orbitals will be purely metal electrons, providing, of course, that no ligand π orbitals exist to overlap these T_{2g} orbitals.

We see then from the MO diagram that the T_{2g} and E_g^* levels, both containing mainly metal atom orbitals, are split apart (qualitatively) in the same manner they were by the purely electrostatic arguments from the CFT. All that has changed in this limited portion of the energy diagram is that in the MOT the E_g^* orbitals are not *pure* metal atom d orbitals. Furthermore, in the CFT the splitting arises from only *electrostatic* and symmetry considerations whereas in the MOT the splitting arises from *covalent bonding* and symmetry considerations.

Metal atom orbitals   Molecular orbitals   Composite ligand orbitals
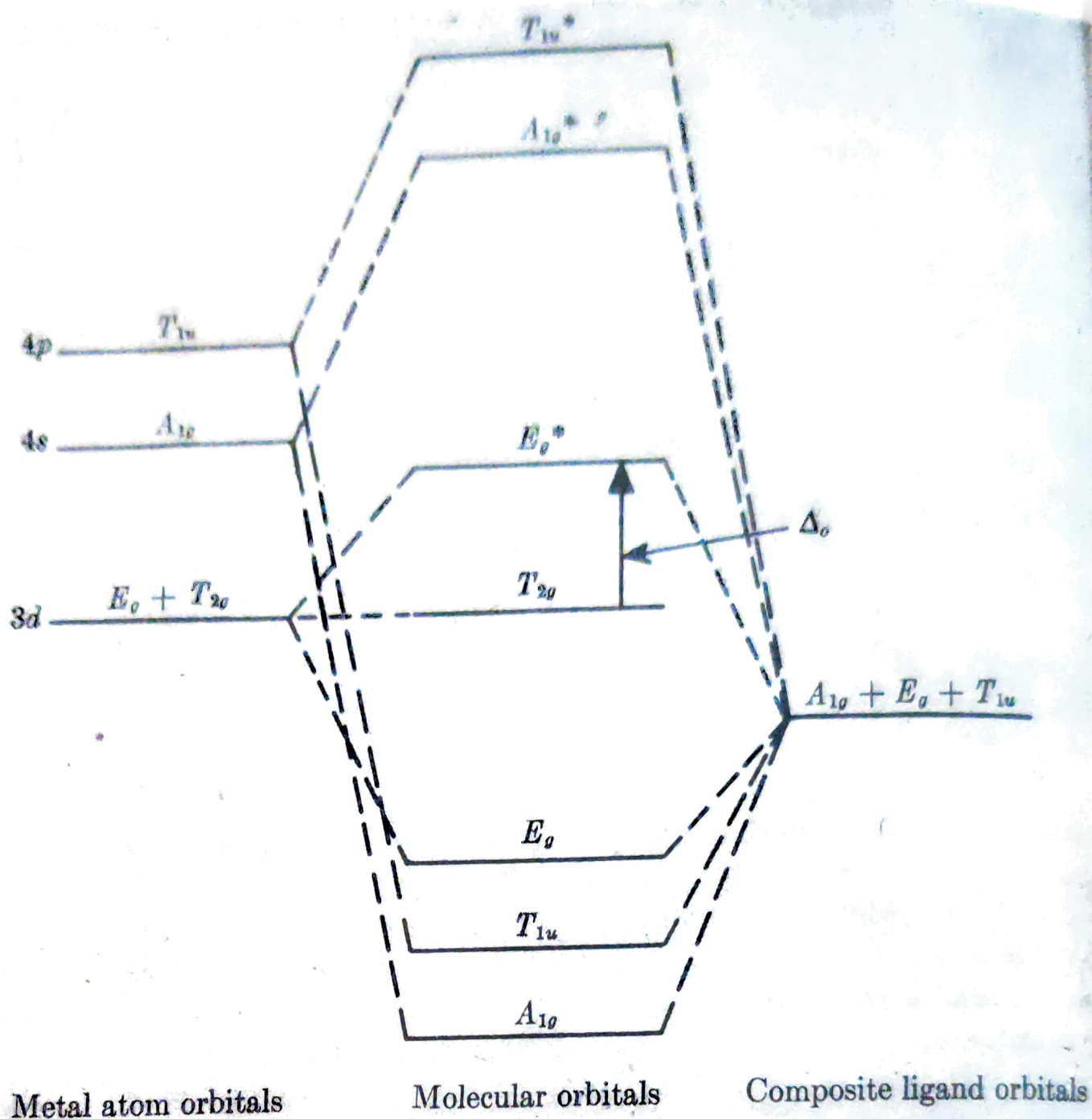
FIGURE 10-16

Energy Level Diagram for a Hypothetical Regular Octahedral Complex Formed between a $3d$ Metal Atom and Six Identical Ligands Which Do Not Possess π Orbitals.

What is more important, however, is that the MOT energy level diagram contains much more information than the CFT one. For example, the antibonding levels above the E_g^* set also represent terminal levels for electronic transitions originating in T_{2g} (or below), and electrons in the bonding levels may be excited into higher levels yielding so-called *charge-transfer* bands. Neither of these phenomena can be dealt with by the CFT. And of course, the CFT also cannot consider π bonding and all of its consequences.