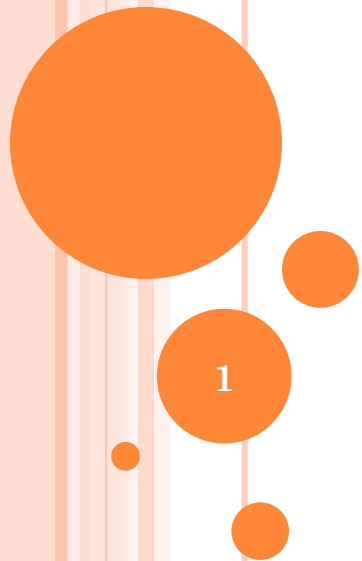


MO diagram using Group Theory



1

Contribution to character per unshifted atom in Γ_{3N}

Symmetry Operation R	$\chi(R)$
E	3
i	-3
σ	1
C_n	$1 + 2 \cos (360/n)^\circ$
S_n	$-1 + 2 \cos (360/n)^\circ$

Γ_p is exactly like x, y, z as seen in the derivation of Γ_{3N}



Molecular Orbital Approach –Group Theory :

Single central atom, A or M ----- AB_n or MX_n

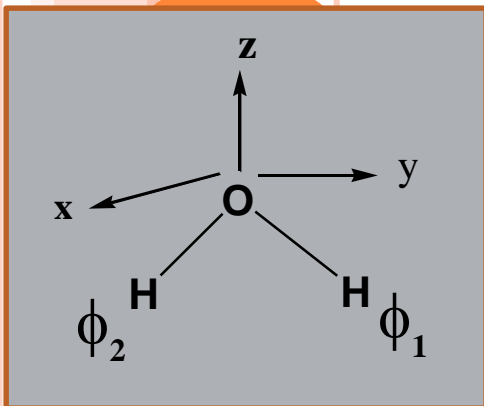
Pendant atoms B or X

σ – bonding in AB_2 / MX_2 or AB_6 / MX_6

IRs to which the atomic orbitals of the central atom give rise are listed in the character table for the relevant point group.

When there is a match in symmetry between the central atom AO and a possible linear combination of ligand orbitals, interaction occurs leading to bonding and anti-bonding orbitals. When there is no match, orbitals remain non-bonding.

AX_2 , eg. H_2O , Bent molecule-----point group C_{2v} ie. Oxygen has s- and p-orbitals only.



From Character table for Water, AOs of Oxygen : $2s$ and $2p_z$ are Bases for A_1 IR $2p_x$ is for B_1 $2p_y$ is for B_2

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Lower case Mulliken symbols used for all orbitals by convention

$2s, 2p_z$ ----- a_1

$2p_x$ ----- b_1

$2p_y$ ----- b_2

H has 1s atomic orbital

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_2	1	-1	-1	1	y, R_x	yz
Γ_σ	2	0	0	2		

$$\Gamma_\sigma = a_1 + b_2$$

$$\Psi_{a1} = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2)$$

$$\Psi_{b2} = \frac{1}{\sqrt{2}} (\phi_1 - \phi_2)$$

Take ϕ_1 as basis set and using projection operator we get two SALCs :

An approximation : Oxygen 2s and 2p orbitals are independent, and the 2s orbitals are too tightly bound (low in energy to take part in MO formation)

Therefore, Ψ_{a1} and $2p_z$ form bonding and anti-bonding Mos
 Ψ_{b2} and $2p_y$ form bonding and anti-bonding Mos
 $2p_x$ forms non-bonding MOs

MO Diagram for Water-----next page



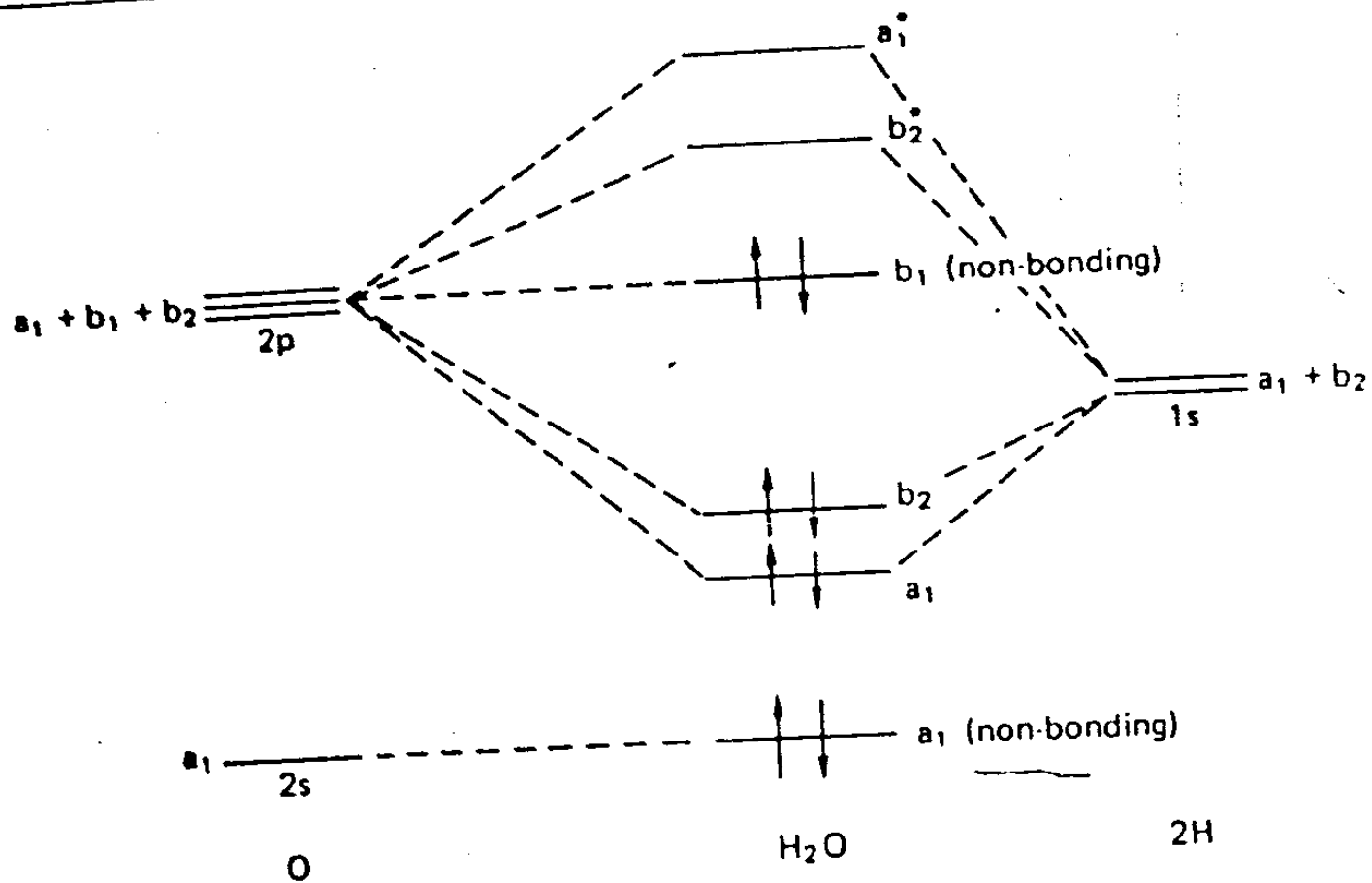


Figure 10.3 Qualitative molecular orbital energy level diagram for H₂O



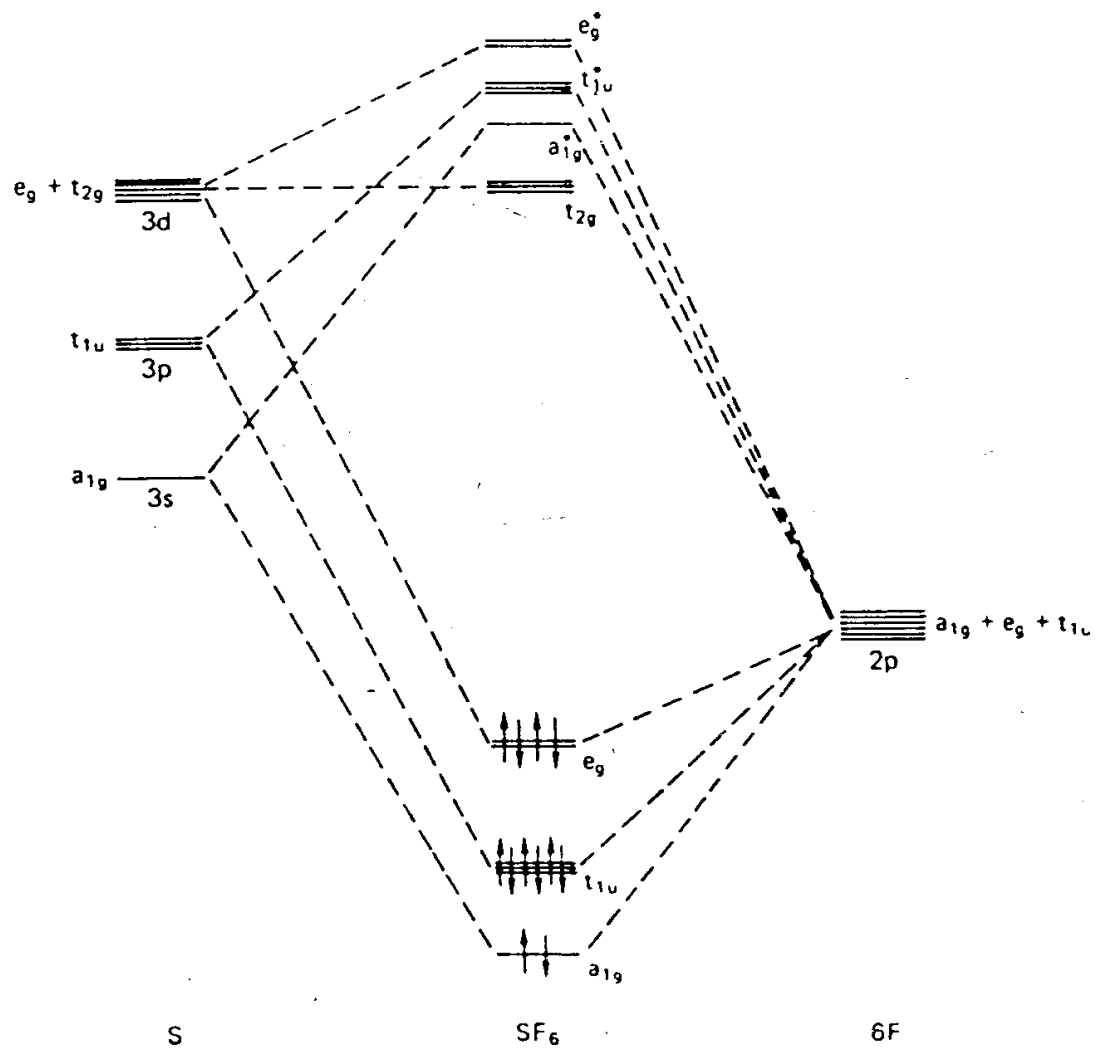
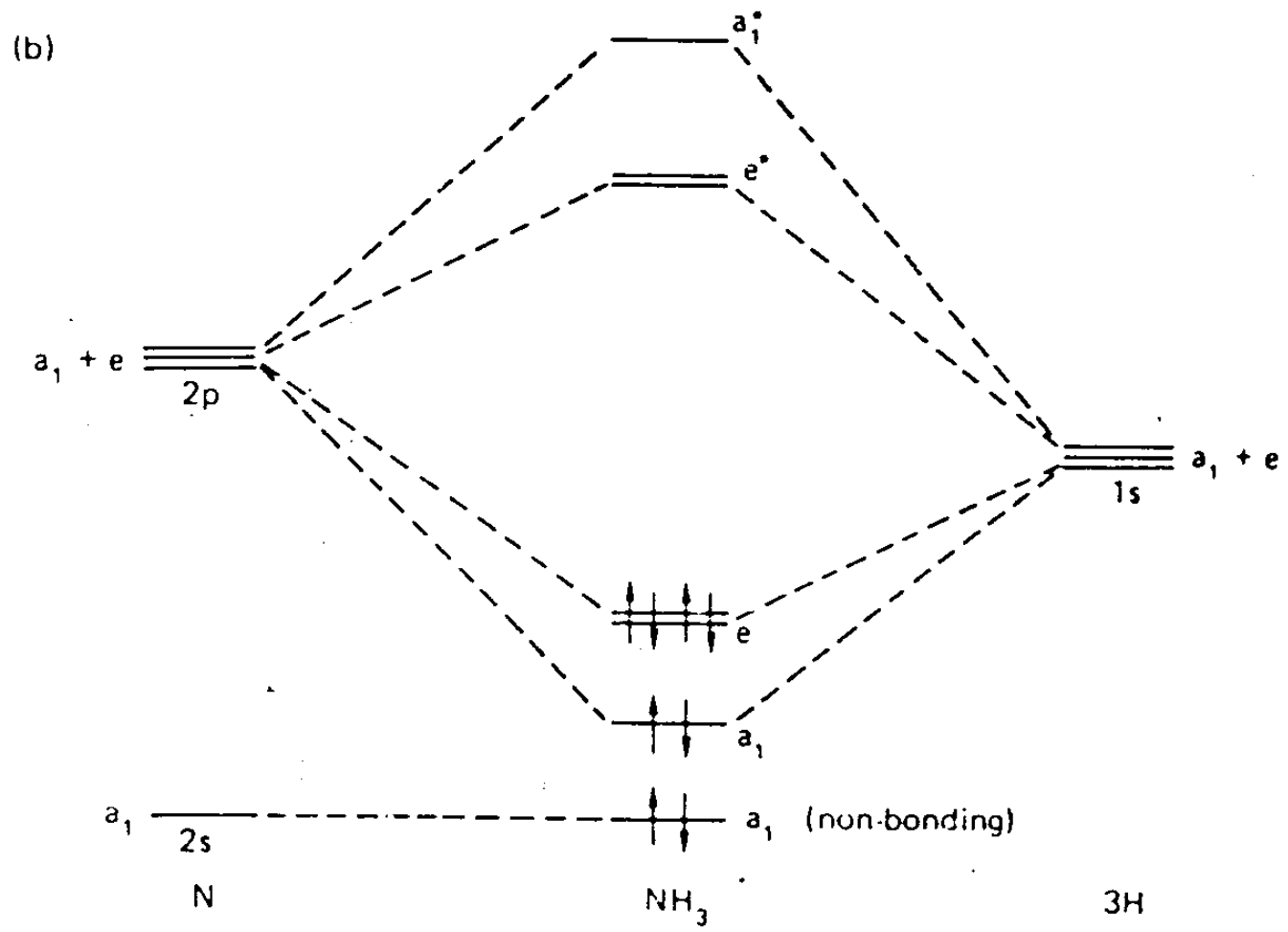


Figure 10.14 Qualitative molecular orbital energy level diagram for SF₆

Diagram for p-block elements

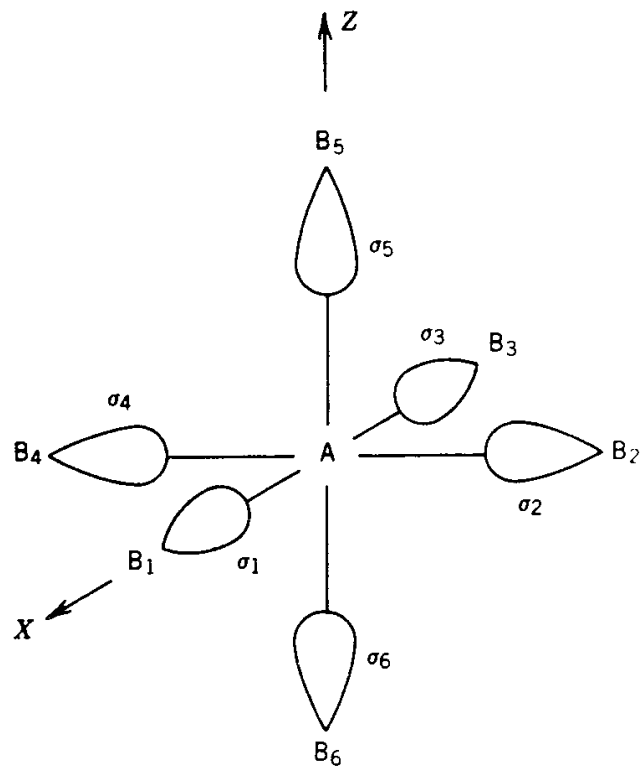




C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$



AB₆, Octahedral Molecule



$$\Gamma_{\sigma} = A_{1g} + E_g + T_{1u}$$

$$A_{1g}: s$$

$$E_g: (d_{z^2}, d_{x^2-y^2})$$

$$T_{1u}: (p_x, p_y, p_z)$$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
Γ_{σ}	6	0	0	2	2	0	0	0	4	2

Octahedral Molecule : O_h point group : ML_6

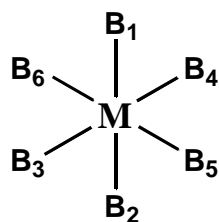
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

From Character table : $4s - a_{1g}$

$3d_{x^2-y^2}, 3d_{z^2} - e_g$

$3d_{xy}, 3d_{yz}, 3d_{zx} - t_{2g}$

$4p_x, 4p_y, 4p_z - t_{1u}$



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
Γ_{SALC}	6	0	2	2	0	0	0	0	4	2		

$$\Gamma_{SALC} = A_{1g} + E_g + T_{1u}$$

So total 6 SALCs for Octahedral molecule

4s, 4p and $(3d_{x^2-y^2}, 3d_{z^2})$ AOs of metal form bonding
And anti-bonding MOs

$(3d_{xy}, 3d_{yz}, 3d_{zx})$ form non-bonding MOs



For TM or heavier main
Group elements

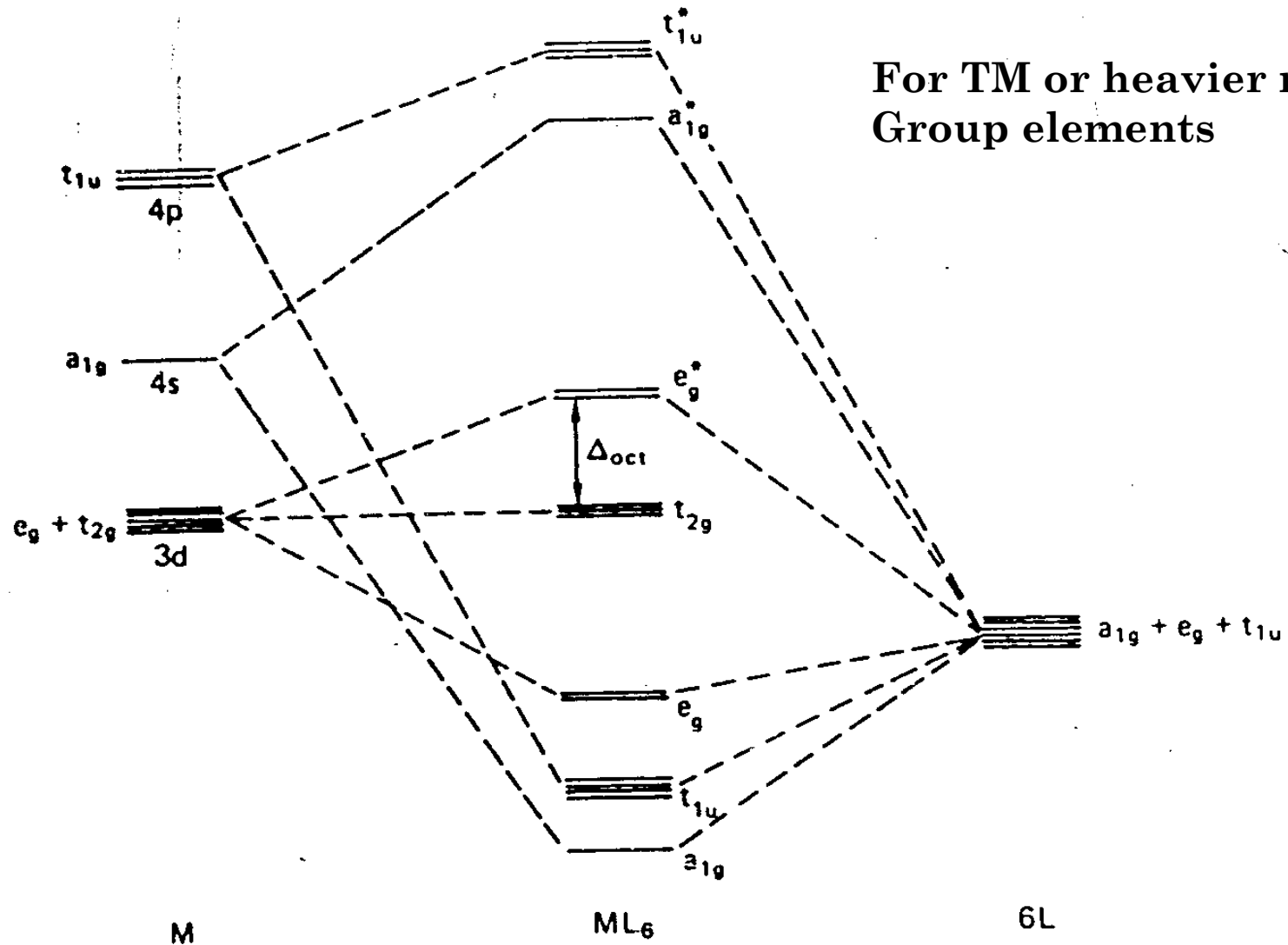


Figure 10.13 Qualitative molecular orbital energy level diagram (σ -bonding only) for an octahedral transition metal ML_6 complex



SOME POINTS :

- Relative energies of 3d, 4s and 4p orbitals is known
- Ligand orbitals are lower in energy than M-orbitals
- All bonding MOs are closer in energy to the ligand than to metal AOs so ligand Electrons go to these orbitals and metal electrons go to non-bonding and anti-Bonding orbitals
- Bonding MOs are less in energy than a.b. MOs
- n.b. MOs have energies between b and a.b. MOs
- The ones belonging to totally symmetric representation tend to lie lowest
- MOs tend to rise as the number of nodes increases. Mos with no nodes lie lowest And those with greatest nodes lie highest in energy
- Valence orbitals of an atom with more electronegativity are lower in energy Than one which has lesser EN. Also separation between 2s and 2p is greater Than in elements earlier in the period due to increased core charge as we Move across the row of the periodic table

π -interactions have less effective overlap than σ -interactions, π -bonding has Higher energy than σ -bonding MOs while π^* has lower energy than σ^* in case of Similar AOs

