Molecular orbitals for σ bonding in T_d complexes

- The set of *n* A–B σ bonds in AB_n (T_d *n* = 4) molecules are often thought of as independent entities.
- The concept of MO's allows us to begin with a very general and nonrestrictive framework that is in accord with all symmetry requirements allowing us to visualize (through computational methods) the physical geometry of the wave functions for different MO's in a molecule.
- First the symmetries of the MO's are determined followed by the identification of the AO's on A and B in AB_n
- The atomic orbitals on the central metal A, together with the corresponding *symmetry adapted linear combinations of ligand atomic orbitals* (SALCs) on the B atoms (or molecules if appropriate), that can be used to form MO's will have to form a basis for the representations that contribute to the reducible representation.
- Thus we begin by applying all of the symmetry operations in the molecular point group to the set of σ orbitals.

Point group

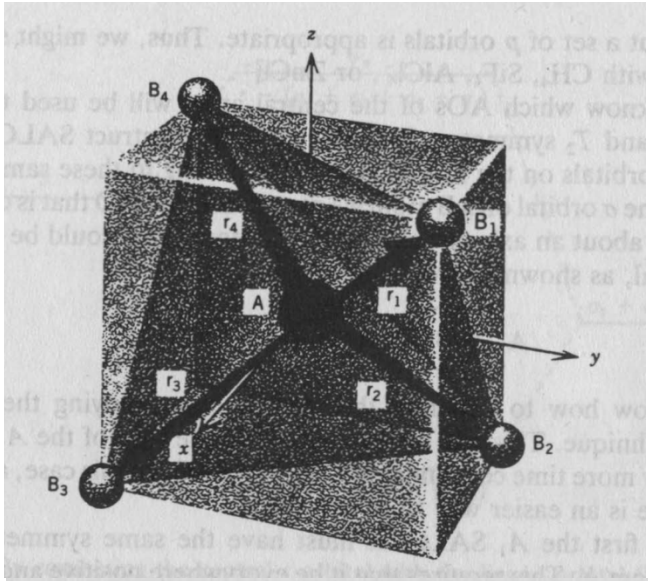
Symmetry operations of point group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

- For this purpose we may represent each σ orbital by a vector pointing from A to a B atom, and number these vectors r_1, r_2, r_3, r_4.
- Applying the identity operation we obtain:

$$
\begin{aligned}
r_1 &\rightarrow r_1 + 0r_2 + 0r_3 + 0r_4 \\
r_2 &\rightarrow 0r_1 + r_2 + 0r_3 + 0r_4 \\
r_3 &\rightarrow 0r_1 + 0r_2 + r_3 + 0r_4 \\
r_4 &\rightarrow 0r_1 + 0r_2 + 0r_3 + r_4
\end{aligned}
$$

which is a unit matrix with character χ (E) = 4 (all 4 vectors map onto themselves).



	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{tetra}	4	1	0	0	2

- If we rotate the set of vectors by $2\pi/3$ about the C_3 axis which is coincident with r_1 we get $\chi(C_3) = 1$ (only r_1 maps onto itself):

$$
\begin{aligned}
r_1 &\rightarrow r_1 + 0r_2 + 0r_3 + 0r_4 \\
r_2 &\rightarrow 0r_1 + 0r_2 + r_3 + 0r_4 \\
r_3 &\rightarrow 0r_1 + 0r_2 + 0r_3 + r_4 \\
r_4 &\rightarrow 0r_1 + r_2 + 0r_3 + 0r_4
\end{aligned}
$$

- The character of the matrix of the coefficients here $\chi(C_3) = 1$
- Proceeding in the same way for C_2, S_4 and σ_d we obtain the ligand AO representation Γ_{tetra} .

- Reference to the T_d character table shows that the Γ_{tetra} representation can be *reduced to*

$$\Gamma_{tetra} = A_1 + T_2$$ (….irreducible representations)

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{tetra}	4	1	0	0	2

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

- This means that the four σ MO's must be chosen so as to include an orbital of A_1 symmetry and a set of three orbitals belonging to the T_2 representation.
- The character table also tells us that AO's of the central metal atom falling into these categories are

A_1 orbitals	T_2 orbitals
$s\ (x^2 + y^2 + z^2)$	p_x, p_y, p_z dxy, dxz, dyz

- We therefore see that to form a complete set of tetrahedrally directed σ bonds, the central metal atom will have to provide an s orbital, as well as a set of p or d orbitals, or both.

$\Gamma_{tetra} = A_1 + T_2$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

Construction of SALCs for σ bonding in T_d complexes

- Consider first the A_1 SALC. It must have the same symmetry of the s orbital on the central metal atom. This requires that it be everywhere positive and unchanged by all symmetry operations

$$A_1\,(s) = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$$

- The T_2 SALC's must match the symmetries of the p orbitals, i.e. must have positive amplitude where the p orbital is positive and negative amplitude where the p orbitals are negative

$$T_2 \begin{cases} (p_z) = \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4 \\ (p_x) = \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 \\ (p_y) = \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 \end{cases}$$

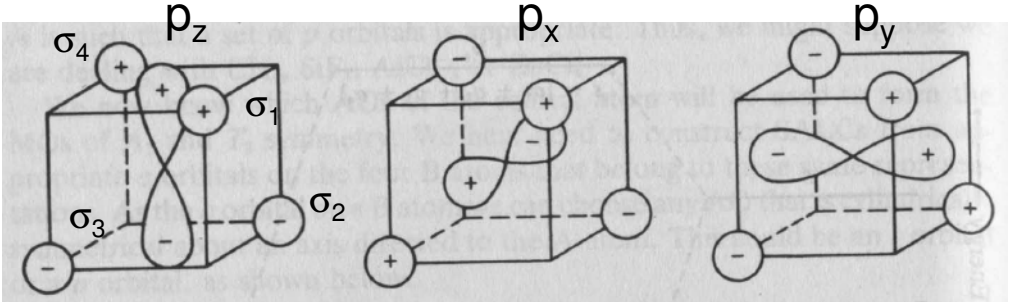


Figure 8.5 Qualitative representations of the three T_2 type σ MOs for an AB_4 molecule.

- Note: A_1 has zero nodes whereas T_2 has one node.

- We are now in a position to form the MO's by allowing overlap of the AO's on A with the SALCs of corresponding symmetry on the four B atoms.
- In each case we may bring the central orbital and the SALC together to give positive and negative overlap thus forming bonding and anti-bonding MO's respectively.

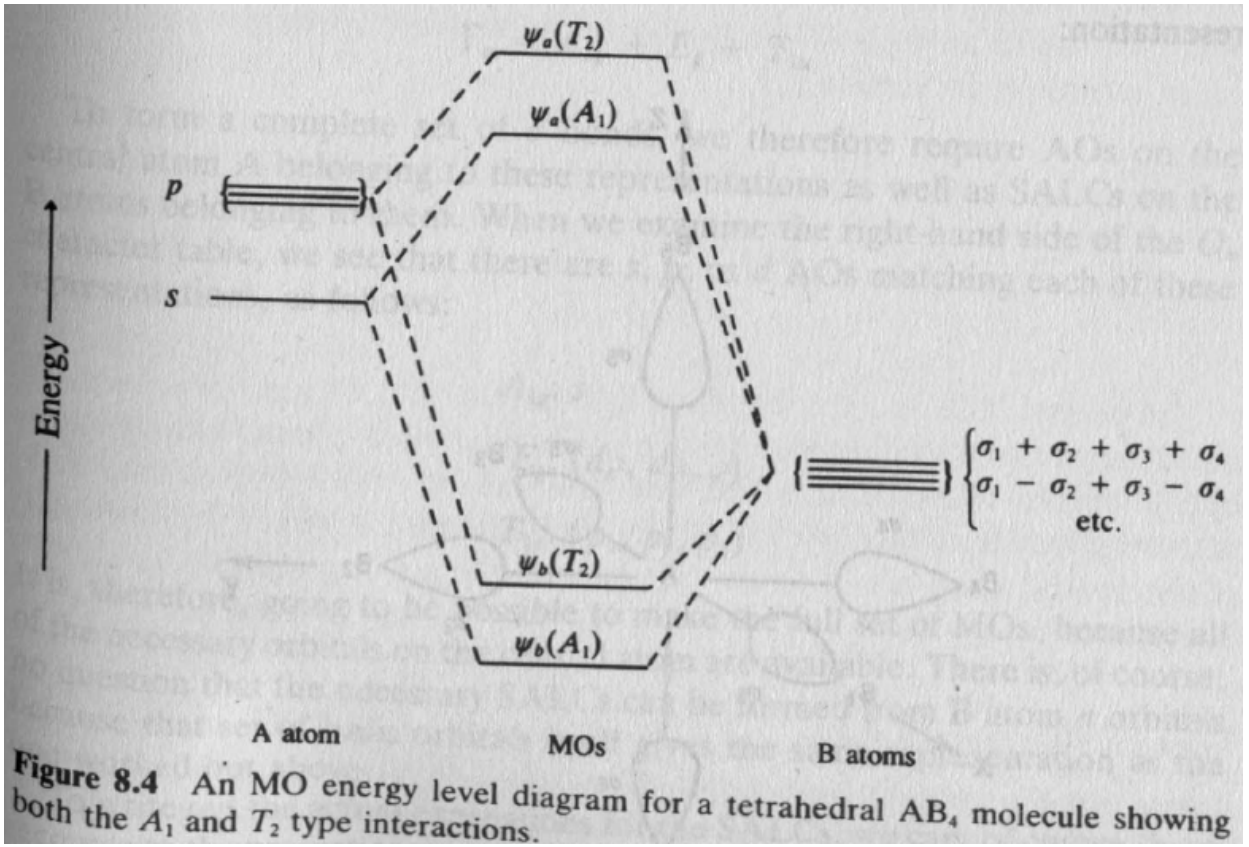


Figure 8.4 An MO energy level diagram for a tetrahedral AB_4 molecule showing both the A_1 and T_2 type interactions.

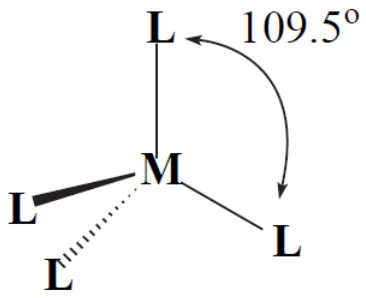
Steps for construction of MO correlation diagram for transition metal complexes

1. Firstly determine metal oxidation state and calculate metal and ligand electron counts.
2. Draw the metal valence atomic orbitals, e.g. 3d, 4s and 4p orbitals (coordinates may be chosen arbitrarily but must be kept consistent throughout).
   - Assign Mulliken symbols from point group character table.
   - Check for proper assignments by degeneracy requirements.
3. Draw ligand SALC's
   - Assign Mulliken symbols from irreducible representations.
   - Check for proper assignments by degeneracy requirements.
4. Match ligand irreducible representations with metal atomic orbitals for σ and π bonding interactions.
5. Check for non-bonding metal/ligand orbitals.
6. Construct MO correlation diagram
7. Fill electrons and check with original metal/ligand electron count in step 1.

Character table for the T_d point group

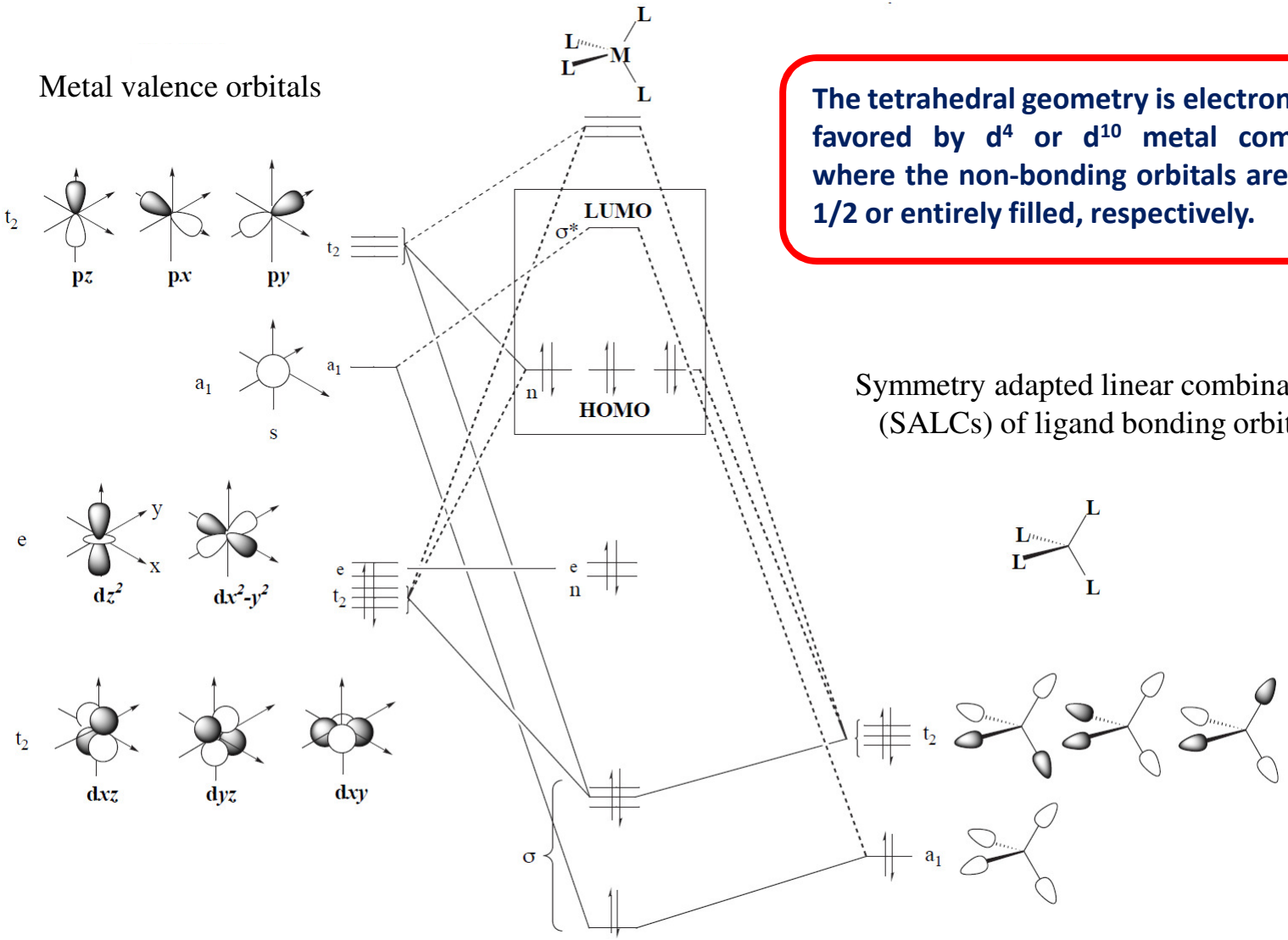
TABLE 10-10
Representations of Tetrahedral Orbitals

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1			$x^2 + y^2 + z^2$
A_2	1	−1	1	−1			
E	2	−1	2	0			$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1		(R_x, R_y, R_z)	
T_2	3	0	−1	−1		(x, y, z)	(xy, yz, xz)
Γ_σ	4	1	0	0		$A_1 + T_2$	
Γ_π	8	−1	0	0		$E + T_1 + T_2$	



tetrahedral

MO description of σ only bonding in a T_d transition metal complex



The tetrahedral geometry is electronically favored by d^4 or d^{10} metal complexes where the non-bonding orbitals are either 1/2 or entirely filled, respectively.

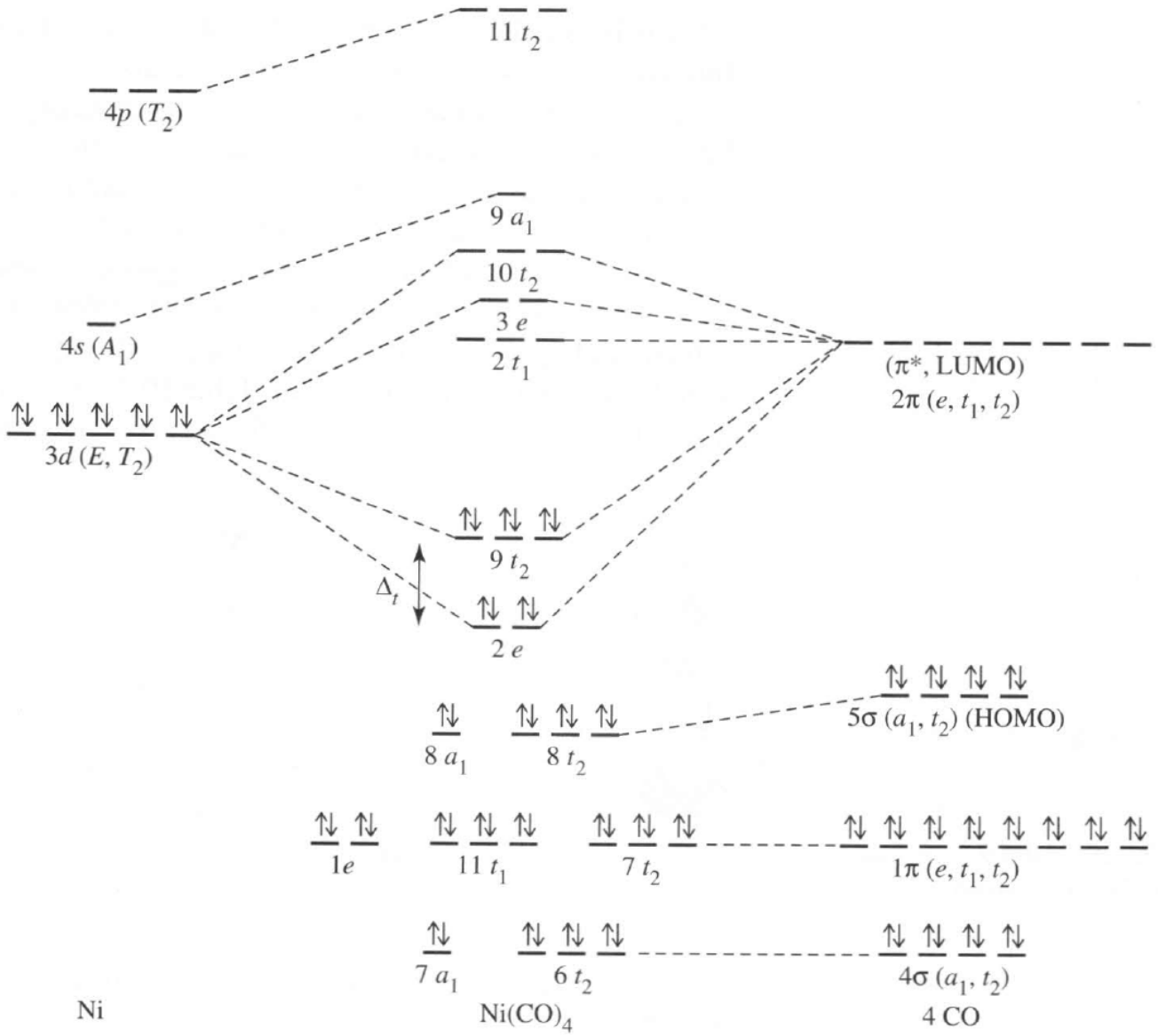
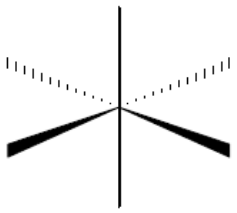


FIGURE 10-18 Molecular Orbitals for Tetrahedral $Ni(CO)_4$. C. W. Bauschlicher, Jr., and P. S. Bagus, *J. Chem. Phys.*, **1984**, *81*, 5889, argue that there is almost no σ bonding from the 4*s* and 4*p* orbitals of Ni, and that the d^{10} configuration is the best starting place for the calculations, as shown here. G. Cooper, K. H. Sze, and C. E. Brion, *J. Am. Chem. Soc.*, **1989**, *111*, 5051, include the metal 4*s* as a significant part of σ bonding, but with essentially the same net result in molecular orbitals.

Character table for the O_h point group

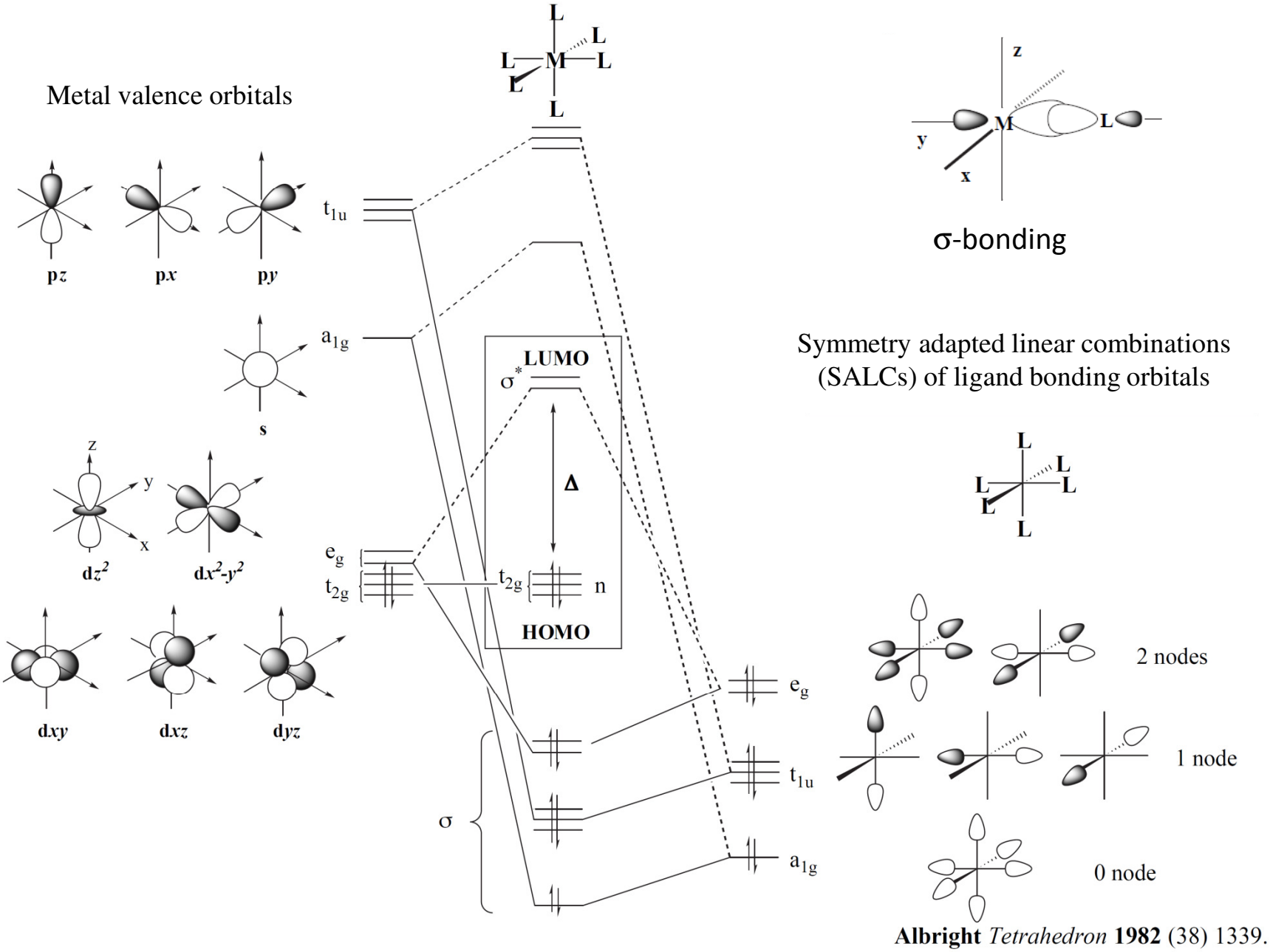
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$X^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1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



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

$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

MO description of σ only bonding in an O_h transition metal complex

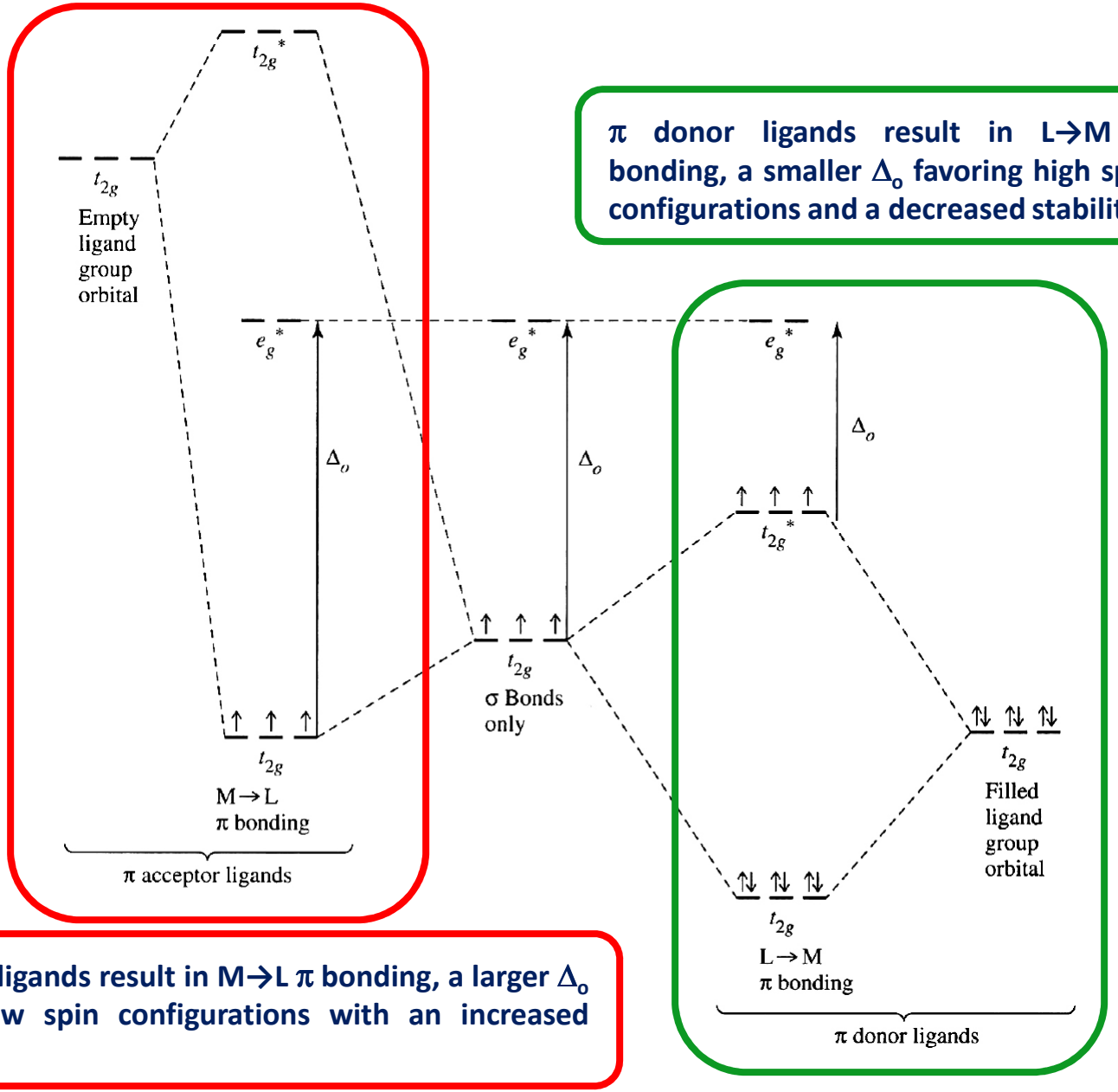


σ-bonding

Symmetry adapted linear combinations (SALCs) of ligand bonding orbitals

Albright *Tetrahedron* **1982** (38) 1339.

Summary of π-bonding in O_h complexes



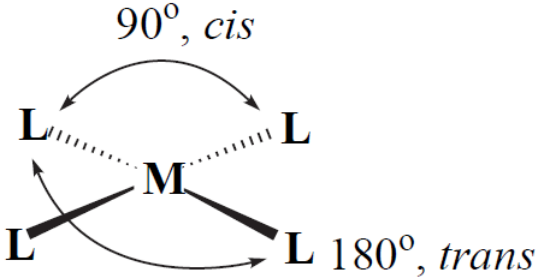
π donor ligands result in L→M π bonding, a smaller Δ_o favoring high spin configurations and a decreased stability.

π acceptor ligands result in M→L π bonding, a larger Δ_o favoring low spin configurations with an increased stability.

Character table for the D_{4h} point group

TABLE 10-9
Representations and Orbital Symmetry for Square-Planar Complexes

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	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	R_z	
B_{1g}	1	−1	1	1		1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1		1	−1	1	−1	1		xy
E_g	2	0	−2	0		2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1		−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1		−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1		−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1		−1	1	−1	1	−1		
E_u	2	0	−2	0		−2	0	2	0	0	(x, y)	

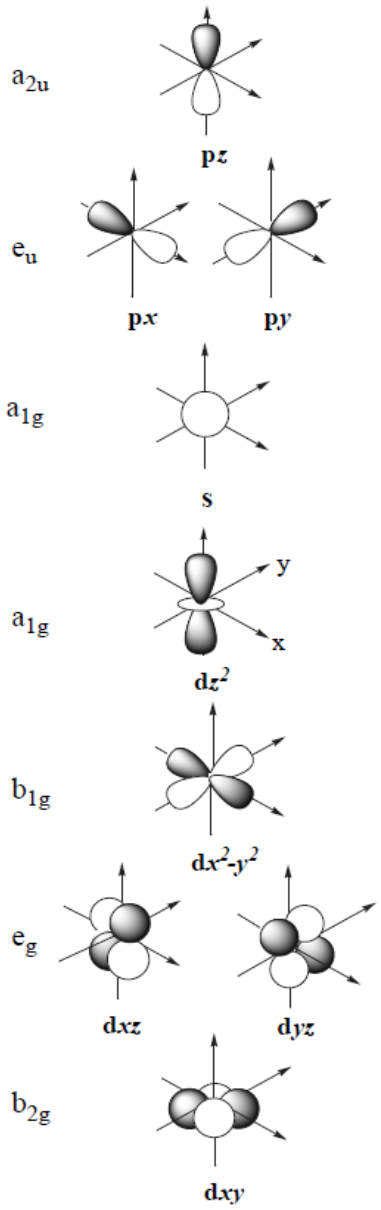


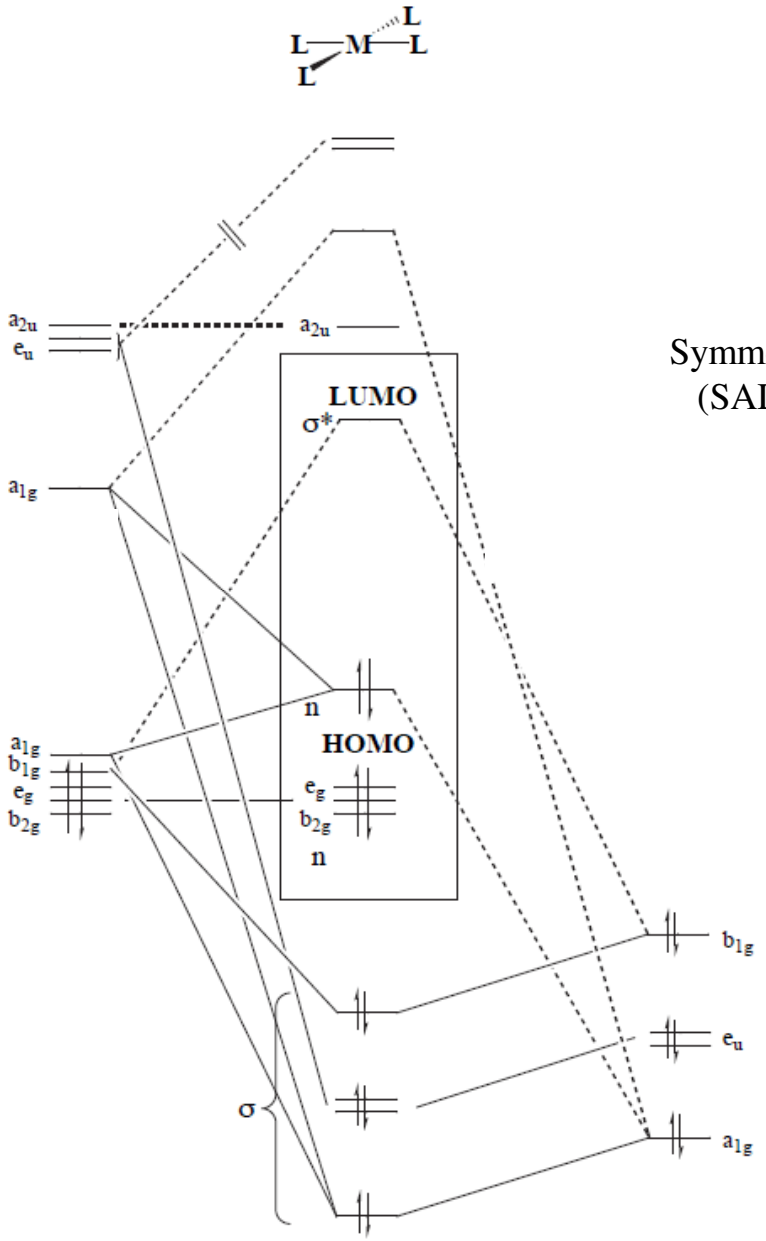
square planar

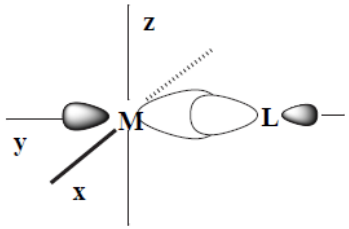
$$\Gamma_\sigma = A_{1g} + E_u + B_{1g}$$

MO description of σ only bonding in a square planar D_{4h} transition metal complex

Metal valence orbitals







σ-bonding

Symmetry adapted linear combinations (SALCs) of ligand bonding orbitals