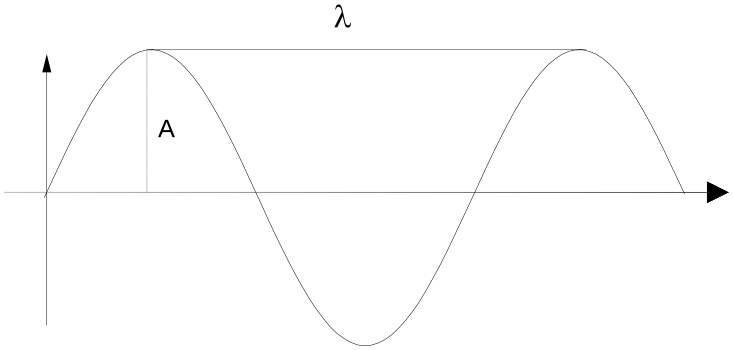
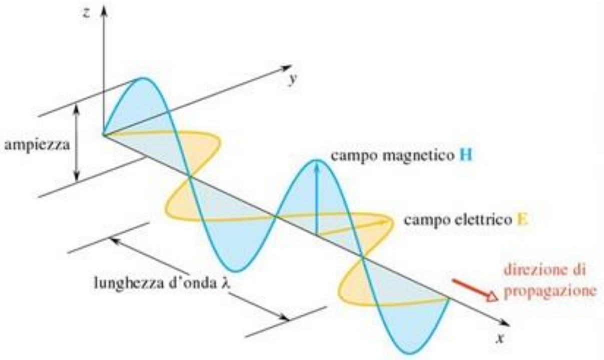
Onda



Lunghezza d'onda e Ampiezza

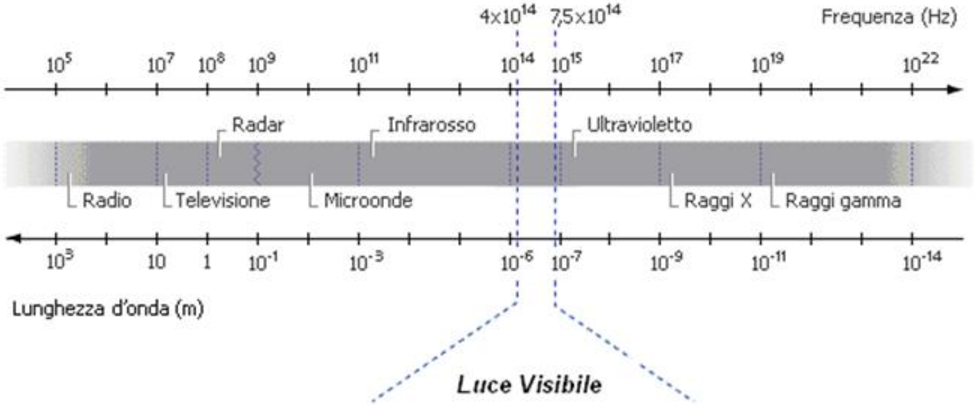
- λ = lunghezza d’onda → distanza tra due max o min successivi
- A = ampiezza
- ν = frequenza → numero di oscillazioni in 1 sec.

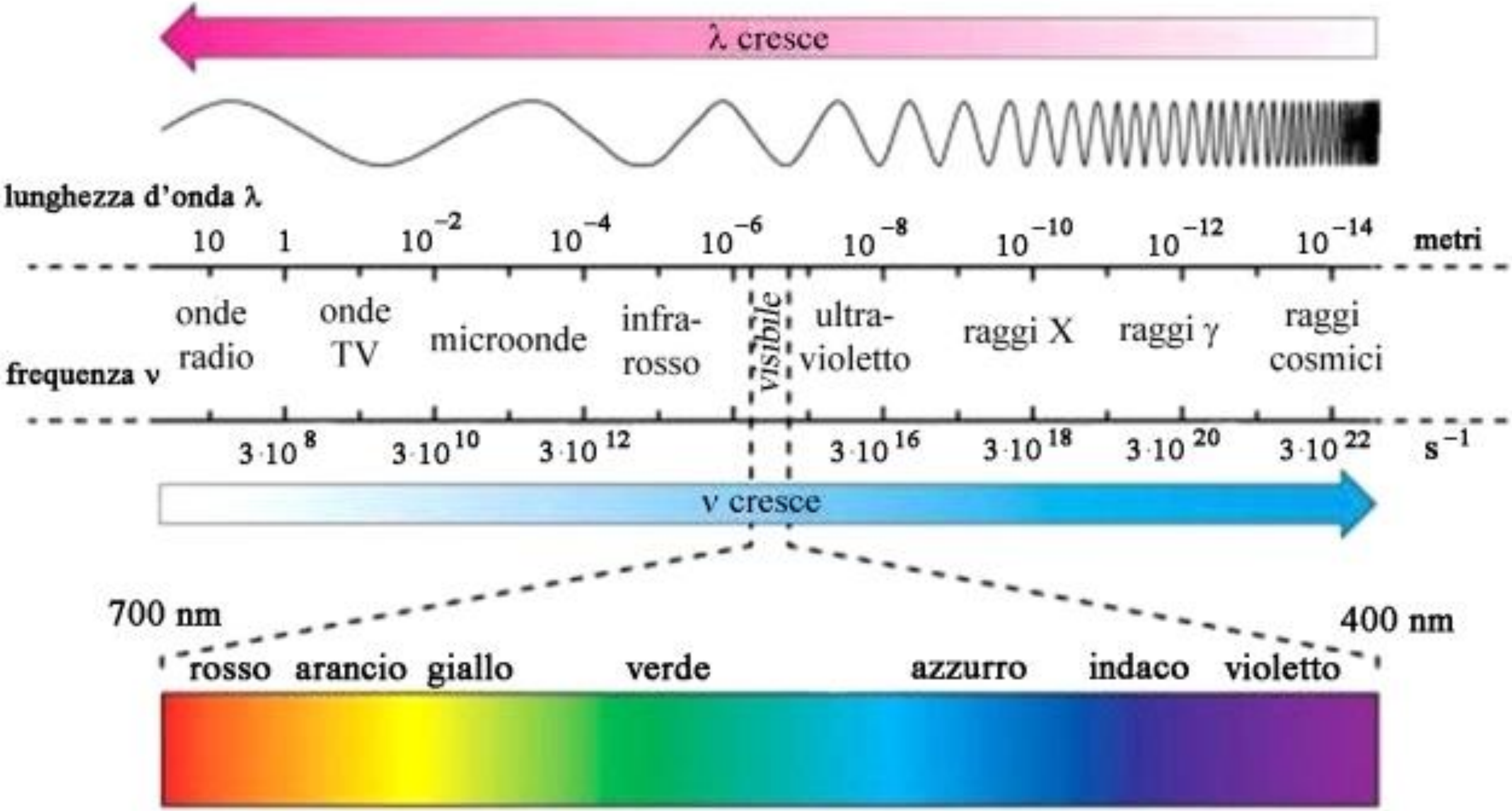
- c = velocità di propagazione della luce nel vuoto (3 x 10^5 km/s)



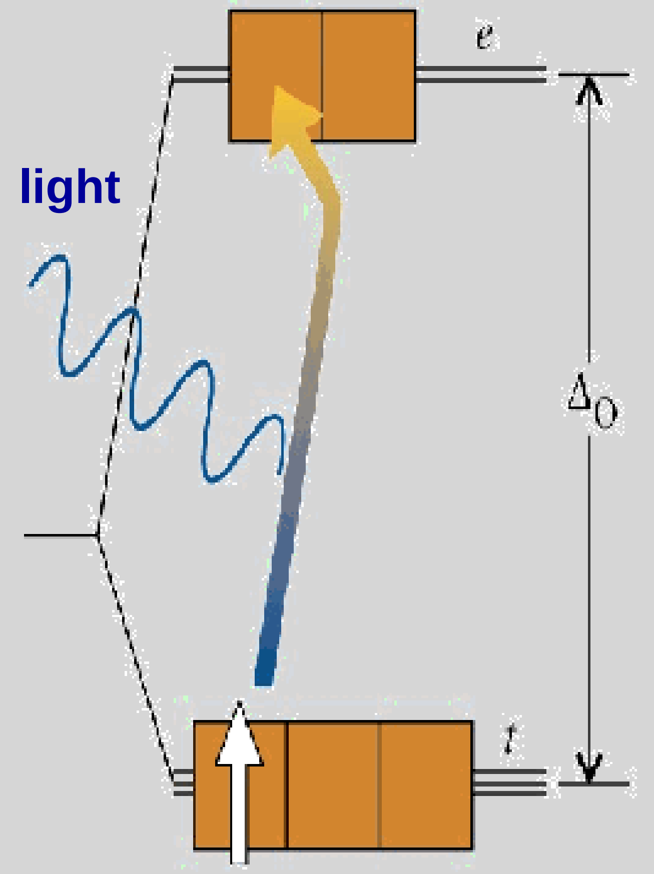
$$\lambda = \frac{c}{\nu} \qquad E = h\nu$$

Radiazione Elettromagnetica




λ cresce
lunghezza d'onda λ
10
1
10^−2
10^−4
10^−6
10^−8
10^−10
10^−12
10^−14
metri
onde radio
onde TV
microonde
infra-rosso
visibile
ultra-violetto
raggi X
raggi γ
raggi cosmici
frequenza ν
3·10^8
3·10^10
3·10^12
3·10^16
3·10^18
3·10^20
3·10^22
s^−1
ν cresce
700 nm
400 nm
rosso
arancio
giallo
verde
azzurro
indaco
violetto

The Effects of Ligands on Color

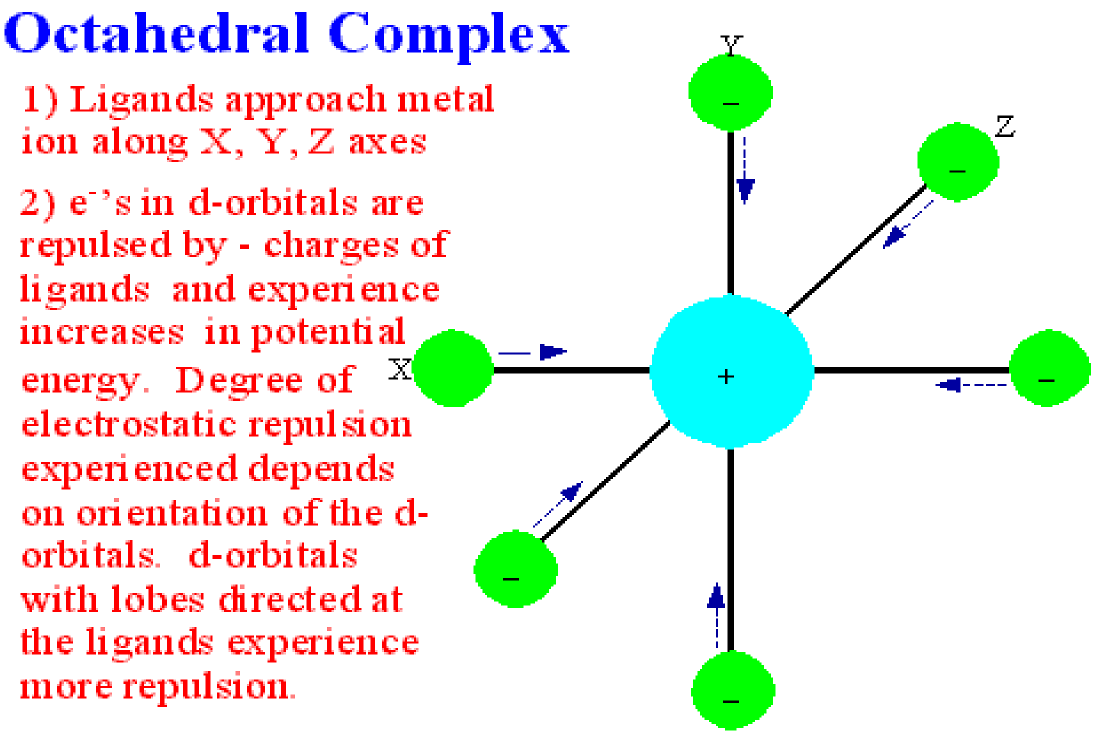


- The t-electron of the octahedral $[Ti(H_2O)_6]^{3+}$ complex can be excited into one of the e-orbitals if it absorbs a photon of energy equal to Δ_O.
- The wavelength of radiation absorbed can therefore tell the ligand field splitting energy.
- The wavelength of the photon is typically in the visible range.
- Therefore, the complex shows a color.

Aqueous Solutions of Cobalt(III) Complexes with Different Ligands

- Weak-field ligands (left) absorb low-energy red wavelengths and thus appear green.
- Strong-field ligands (right) absorb high-energy violet light and thus have colors near orange and yellow.

Cosa succede agli orbitali d del metalli in seguito alla coordinazione?
Teoria del campo cristallino



Octahedral Complex

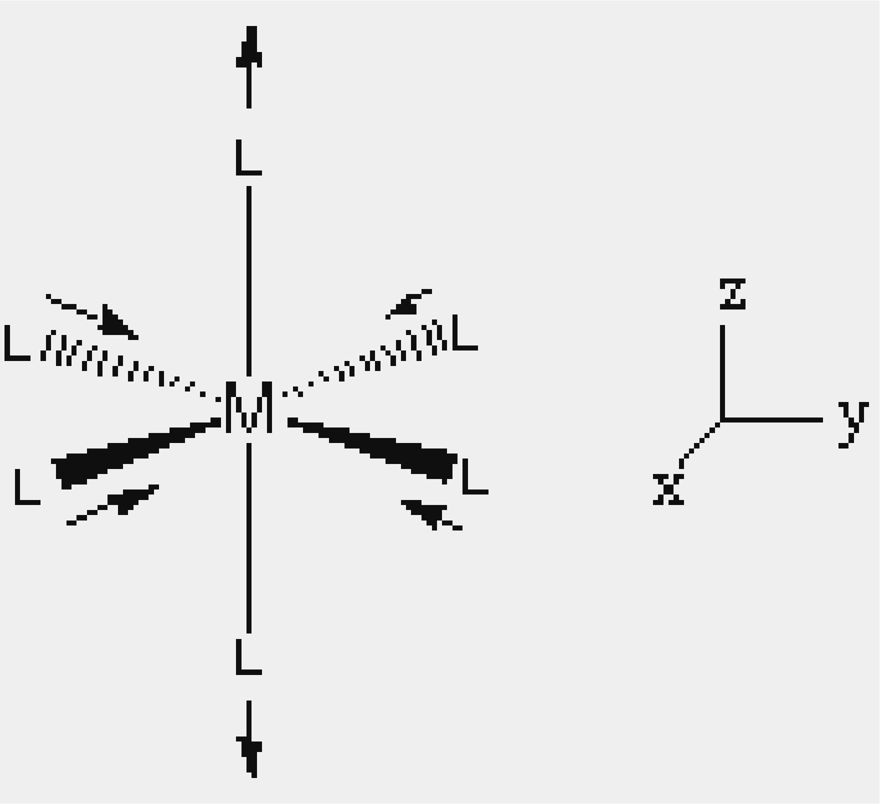
1) Ligands approach metal ion along X, Y, Z axes

2) e^-'s in d-orbitals are repulsed by - charges of ligands and experience increases in potential energy. Degree of electrostatic repulsion experienced depends on orientation of the d-orbitals. d-orbitals with lobes directed at the ligands experience more repulsion.

Square Planar Coordination

Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane.

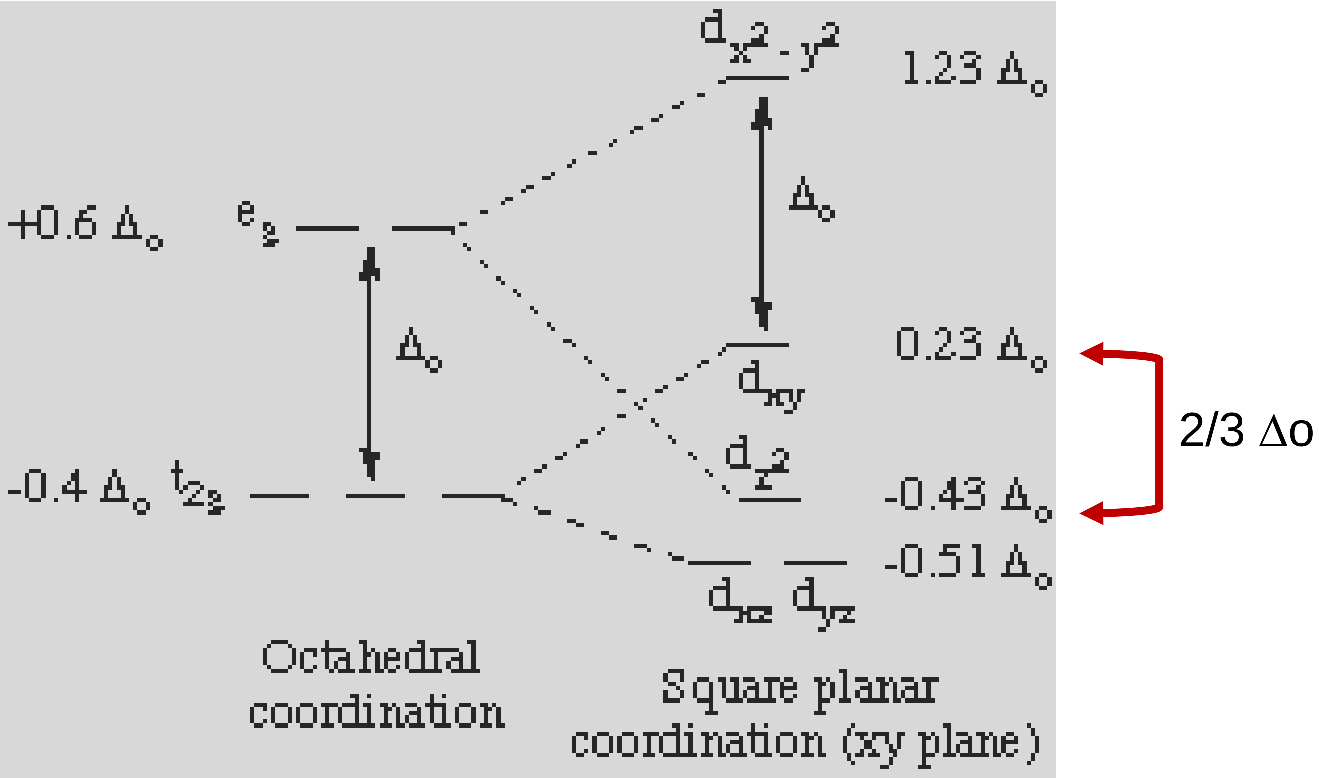
As the z-ligands move away, the ligands in the square plane move a little closer to the metal.



Orbital splitting

The orbital splitting diagram for square planar coordination can thus be derived from the octahedral diagram.

As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy. The dz^2 orbital falls the most, as its electrons are concentrated in lobes along the z-axis. The d_{xz} and d_{yz} orbitals also drop in energy, but not as much. Conversely, the dx^2-y^2 and the d_{xy} orbitals increase in energy.

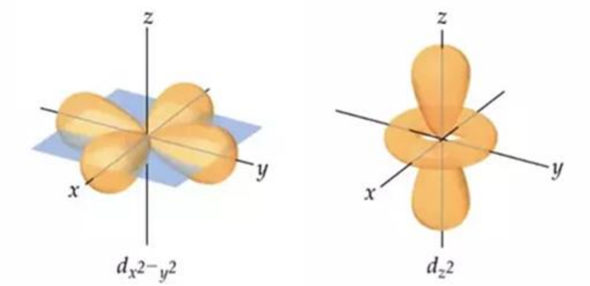


Square planar coordination is rare except for d8 metal ions.

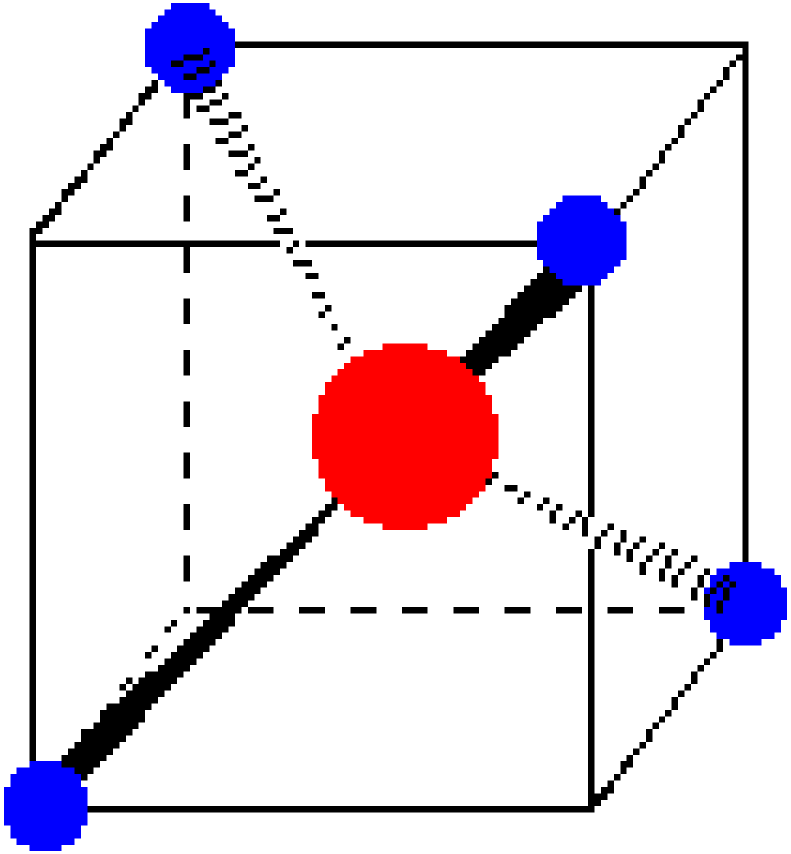
Among the d8 metal ions exhibiting square planar coordination are nickel(II), palladium(II), platinum(II), rhodium(I), iridium(I), copper(III), silver(III), and gold(III).

Copper(II) and silver(II), both d9 ions, are occasionally found in square planar coordination

Tetrahedral Coordination



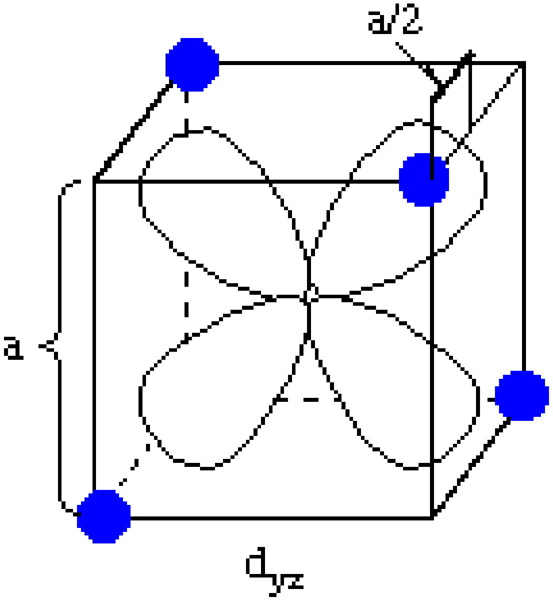
Imagine the metal atom inside a cube with its dz^2 and dx^2-y^2 orbitals pointing at the center of the cube faces.

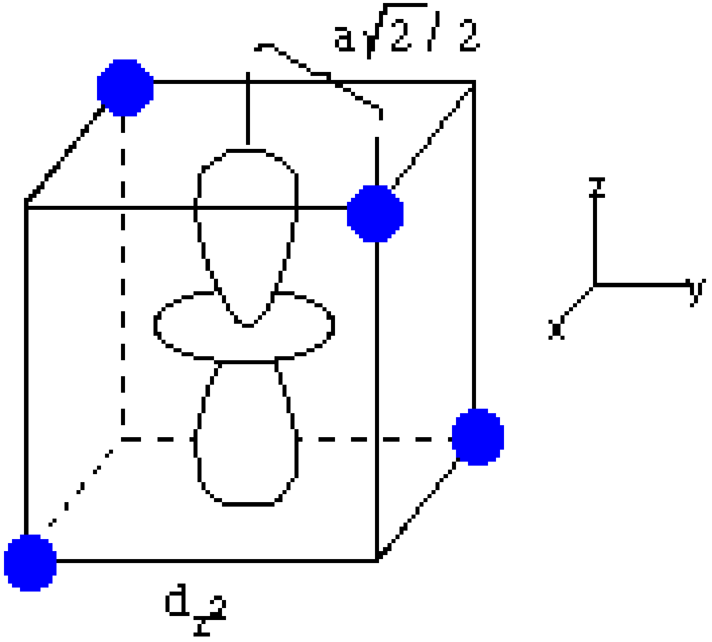


In a tetrahedral arrangement, the point charges approach via the four opposite corners of the cube.

The orbitals d_{xy}, d_{xz}, and d_{yz} are pointing towards the center of the cube edges (these are closer to the corner).

Different effect of the ligands



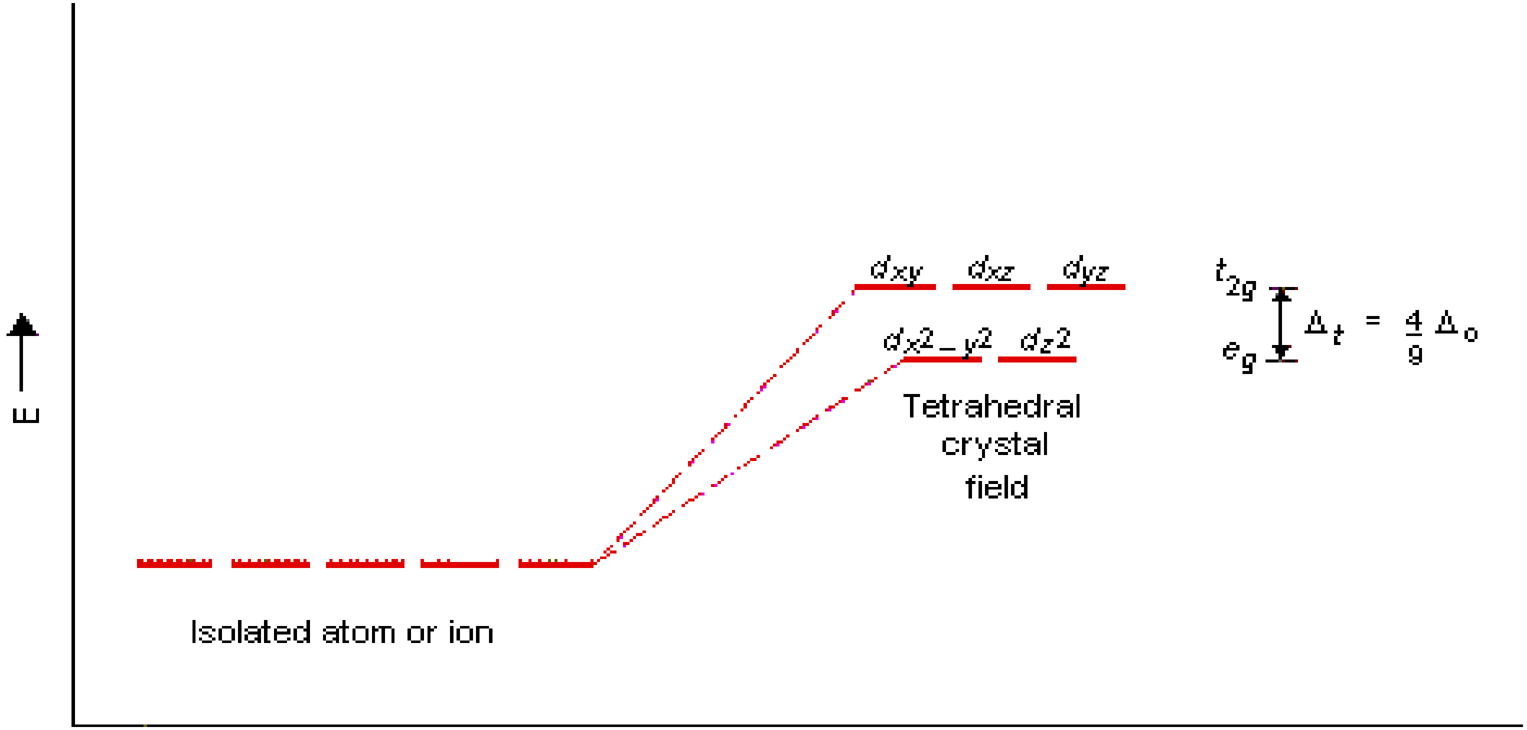


The d_{yz} orbital in tetrahedral coordination. Electrons in this orbital can approach within a distance of a/2 to ligand electrons.	The d_{z2} orbital in tetrahedral coordination: electrons in d_{z2} are further from the ligands than electrons in d_{yz}.

The d_{xz} and d_{xy} orbitals behave the same way as d_{yz}, whereas dx^2-y^2 behaves the same way as dz^2.

Orbital splitting

The resulting d-orbital splitting diagram for tetrahedral coordination is the inverse of the diagram for octahedral coordination



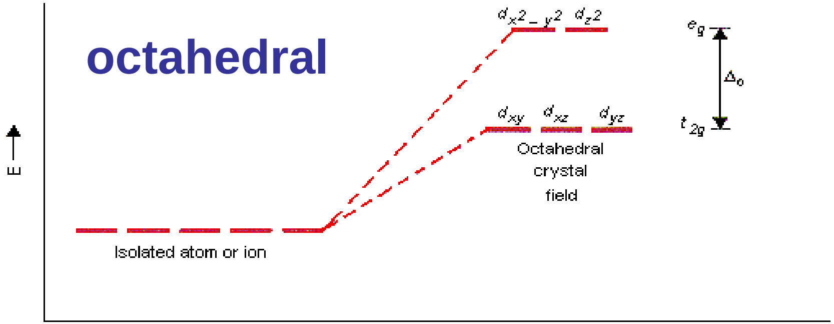
The splitting in a tetrahedral field is much smaller than the splitting in an octahedral case. Thus, tetrahedral complexes, if given an option, always assume a high spin configuration

Tetrahedral Complexes

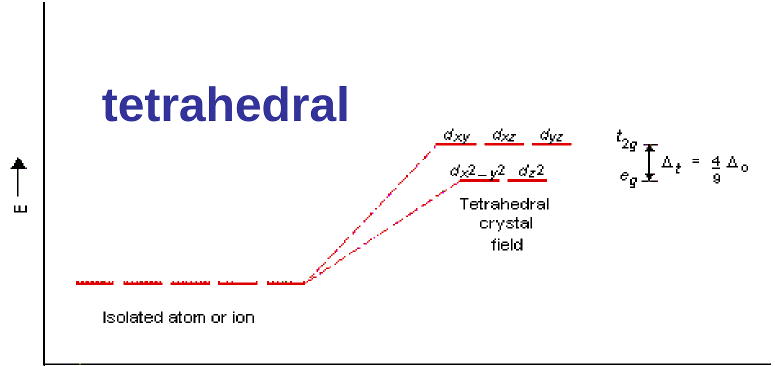
- Tetrahedral complexes are almost always high-spin.
- They do not have enough ligands to give a large ligand field splitting even if the ligands are classified as strong-field ligands.
- Δ_T is typically less than half as large as Δ_O because the *d*-orbitals do not point so directly at the ligands and also because there are fewer repelling ligands.

Summary

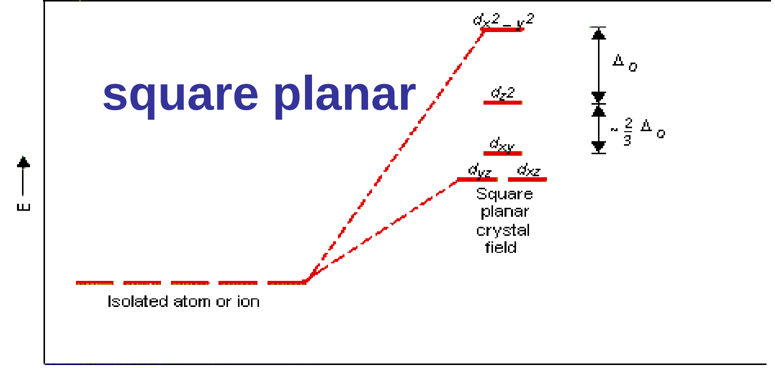
Electrostatic "field" of ligands increases energy of valence d-orbitals *via* electrostatic repulsion



-6 ligands approach along faces of cube (i.e., along x,y,z axes)
-e_g orbitals most repelled



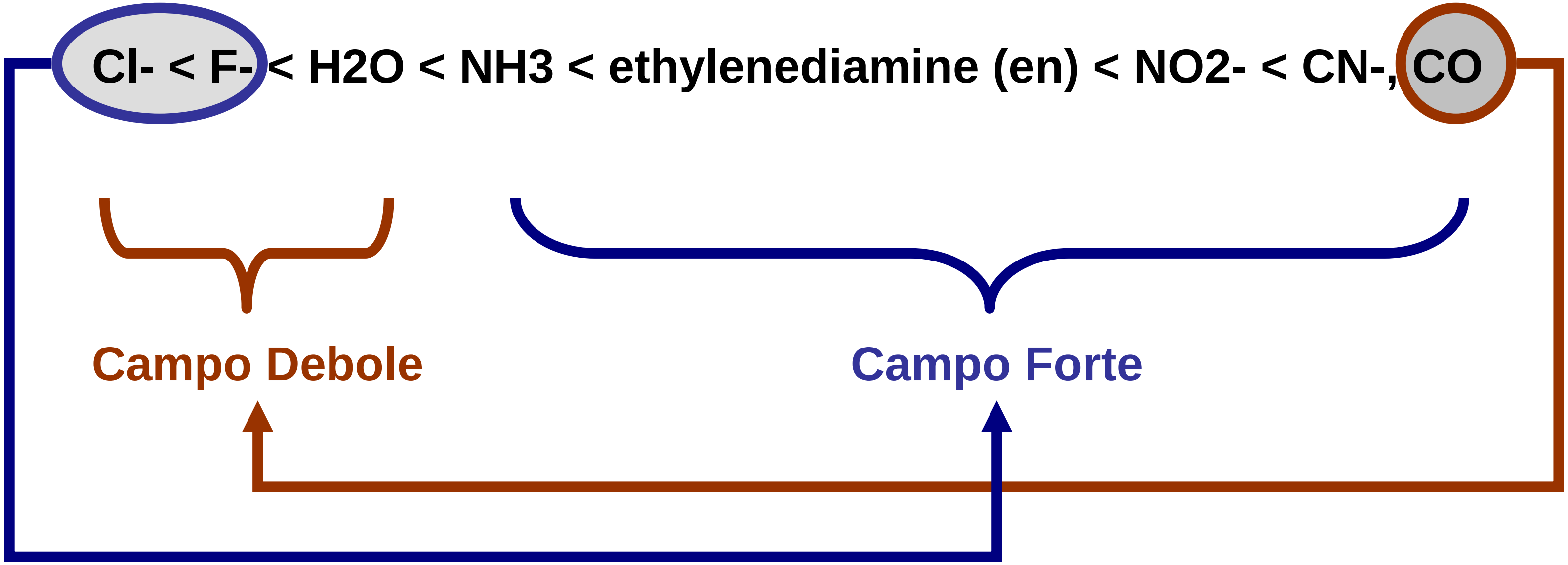
-4 ligands approach from opposing corners of cube
-t_{2g} orbitals raised in energy by electrostatic repulsion



-4 ligands approach along faces of cube

-d(x^2-y^2) orbital most affected by electrostatic repulsion, followed by dz^2

Limiti della teoria del campo cristallino



Cl- < F- < H2O < NH3 < ethylenediamine (en) < NO2- < CN-, CO

Campo Debole

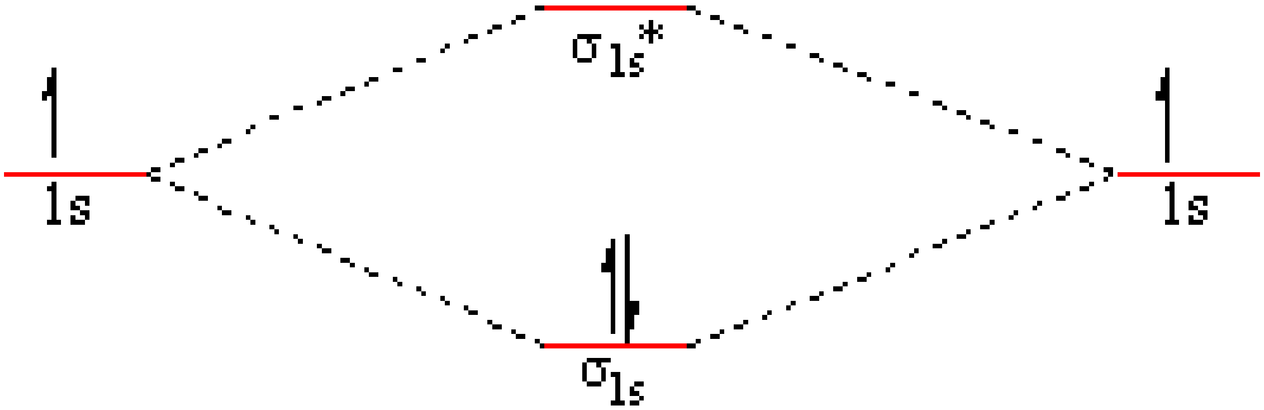
Campo Forte

Leganti carichi come fluoruri e cloruri dovrebbero generare un campo forte

Leganti come il CO dovrebbero generare un campo debole

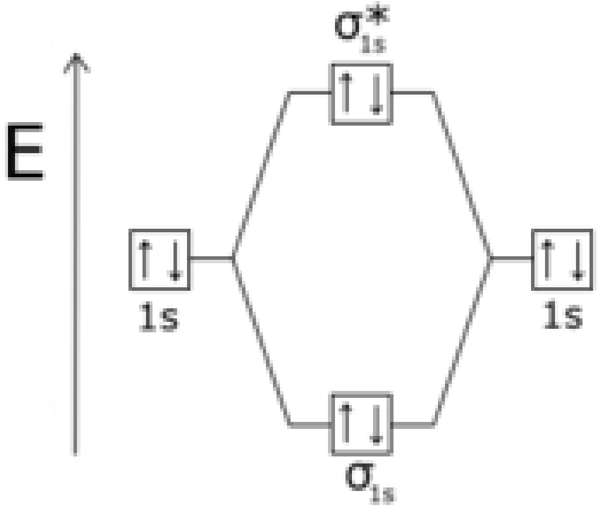
Teoria dell’orbitale molecolare

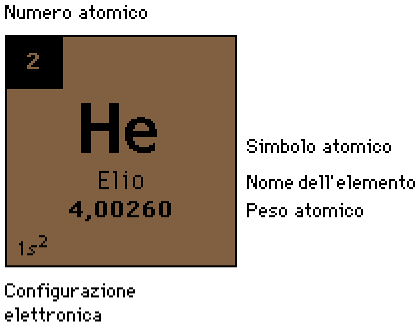
La molecola H_2

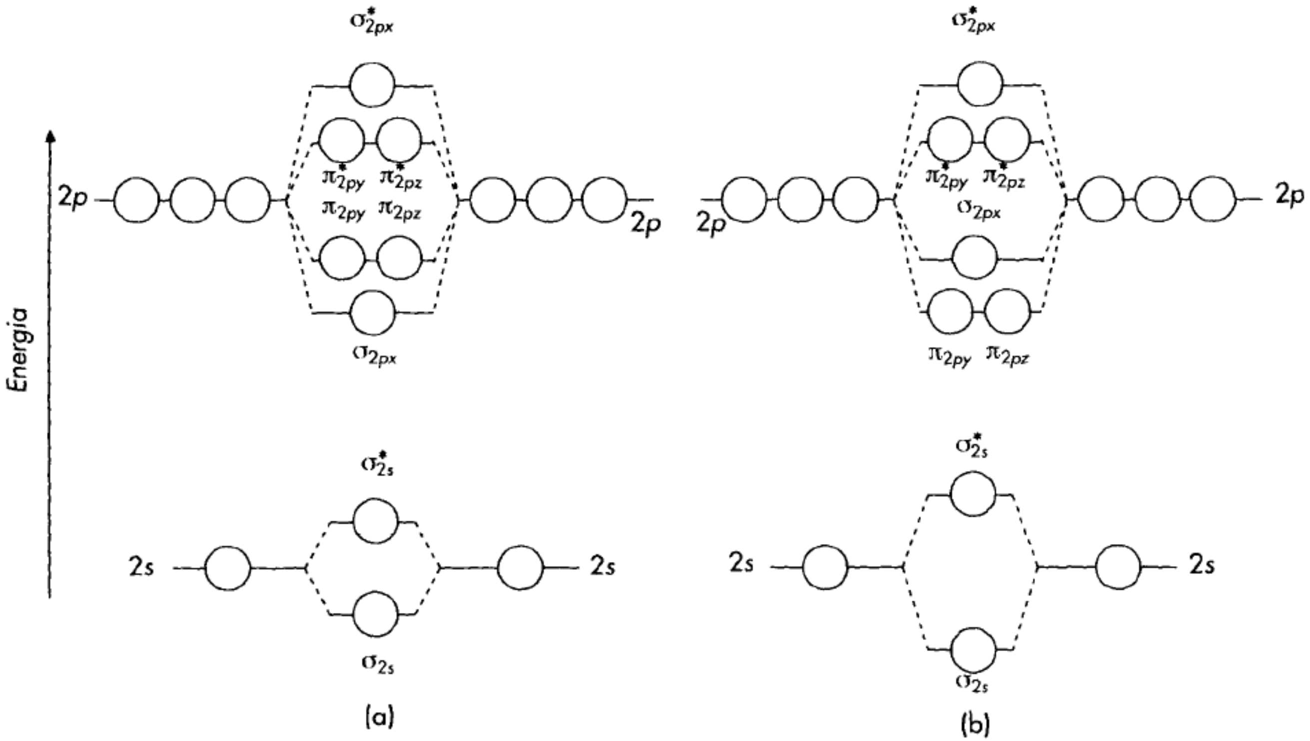


Orbitale molecolare di antilegame

Orbitale molecolare di legame







· a) Energie degli orbitali molecolari di O_2, F_2, Ne_2. b) Energie degli orbitali molecolari di Li_2, Be_2, B_2, C_2, N_2.

Teoria del campo dei leganti

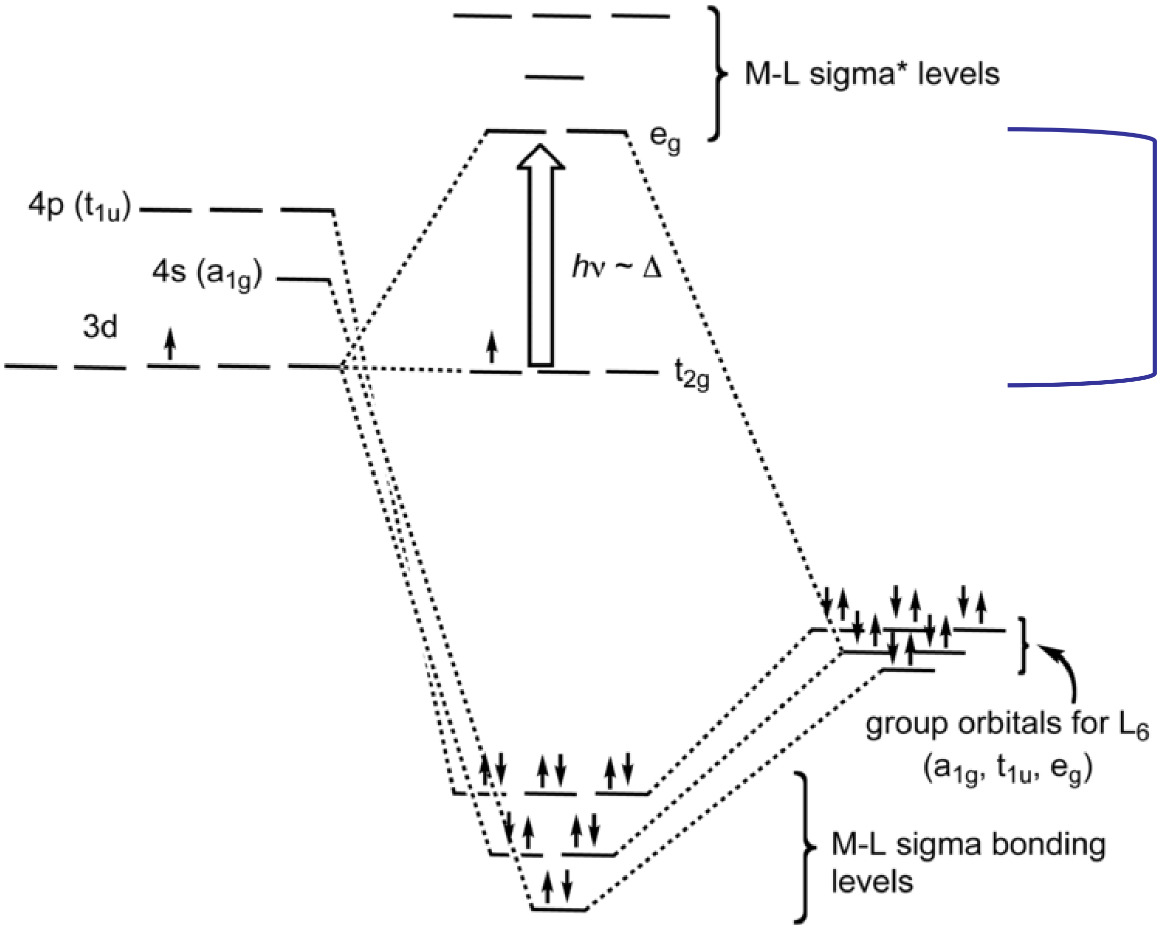
5d (n)
1s (n+1)
3p (n+1)

Orbitali del metallo	**MO**	**Orbitali dei leganti**
	N antileganti	
9 orbitali	**9-N non leganti**	**N orbitali**
	N leganti	

Nel caso di coordinazione 6 questo schema corrisponde a: **6 leganti, 3 non leganti** e **6 antileganti**

Orbitale	Simmetria
s	a_{1g}
p_x, p_y, p_z	t_{1u}
d_{xy}, d_{yz}, d_{zx}	t_{2g}
$d_{x^2-y^2}$, d_{z^2}	e_g

- a_{1g} (non degenere) $\Rightarrow \sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6$
- t_{1u} (triplamente degenere) $\Rightarrow \sigma_1-\sigma_3$, $\sigma_2-\sigma_4$, $\sigma_5-\sigma_6$
- e_g (doppiamente degenere)



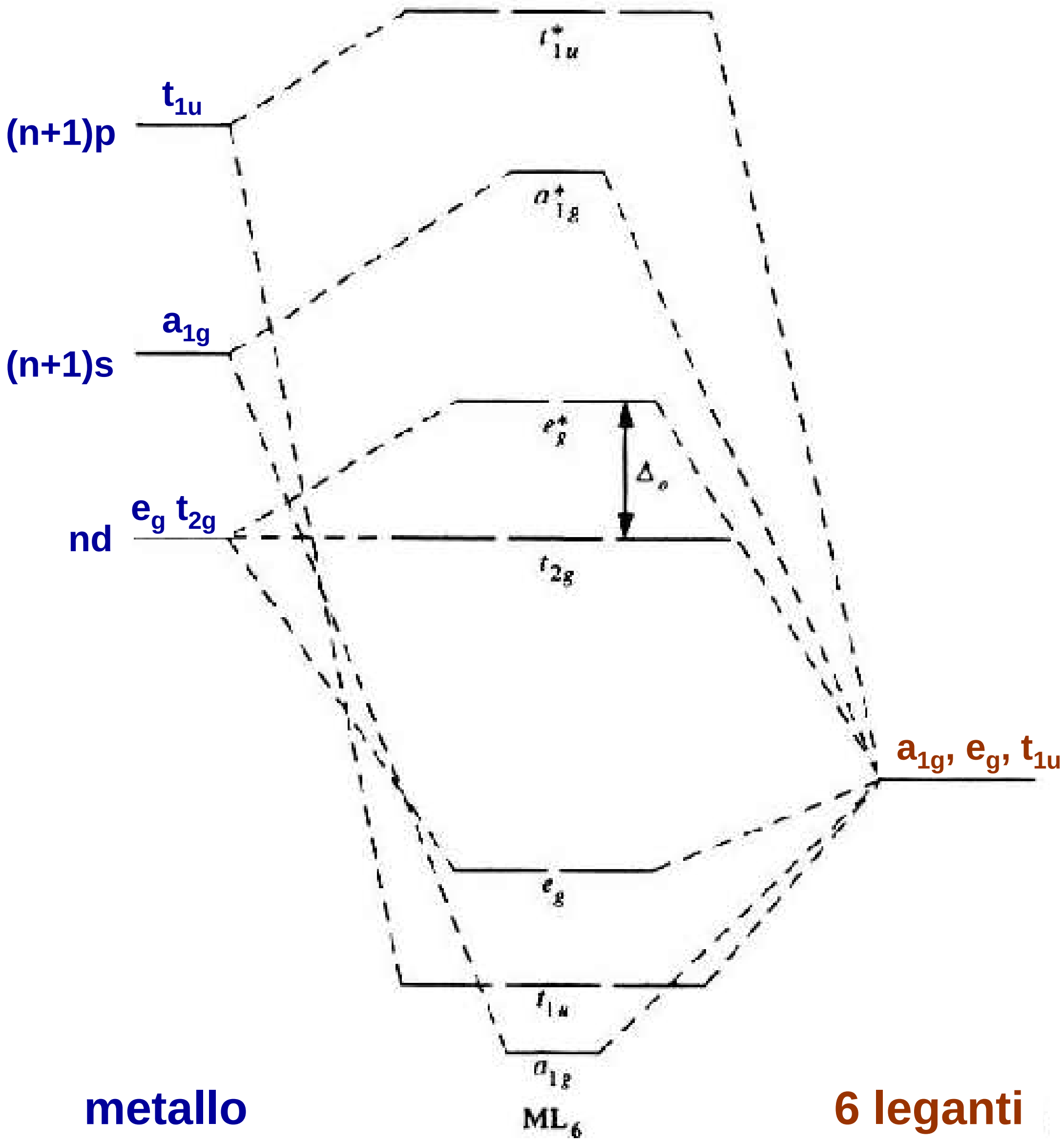
Δo = HOMO - LUMO

Regola dei 18 elettroni (ottetto + 5 orbitali d)

Orbitali non leganti

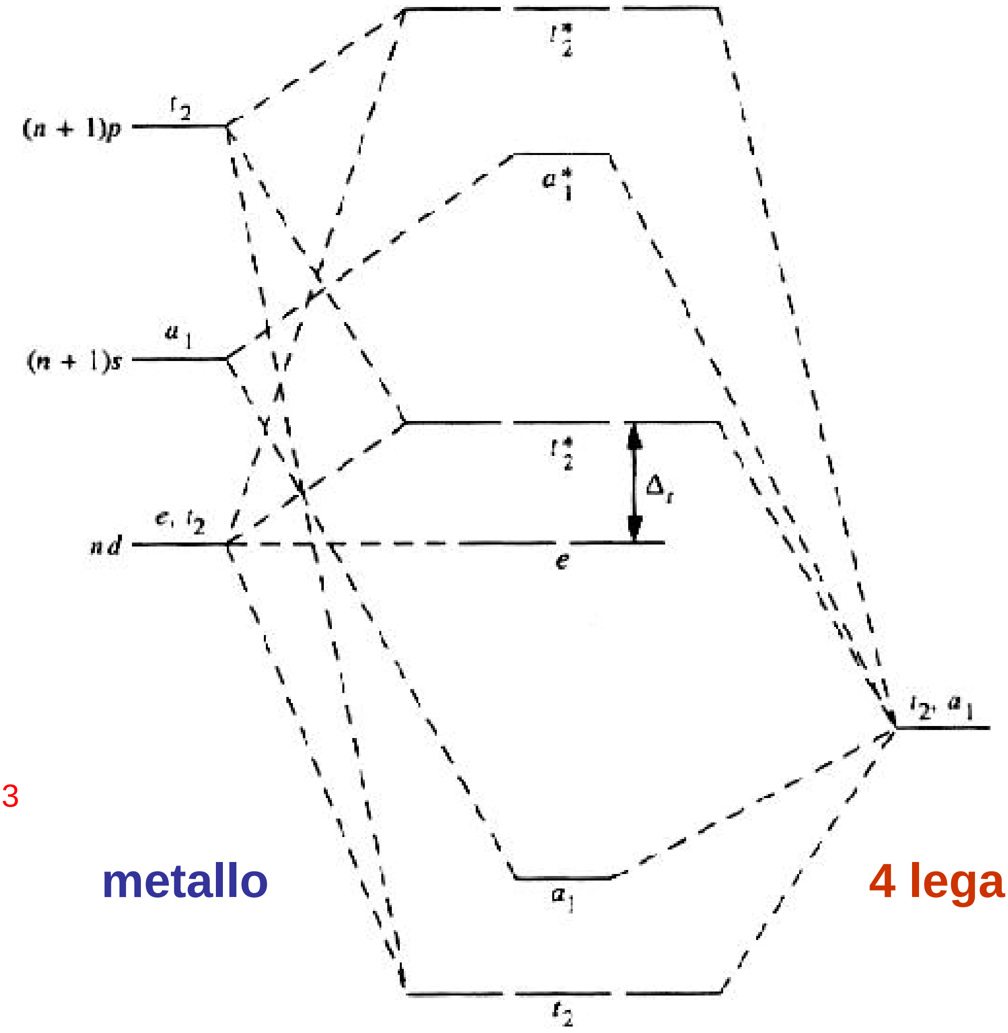
Orbitali molecolari in un complesso ottaedrico

Combinazioni di orbitali di adatta simmetria



N. Orbitali: 9+6 = 15

Orbitali molecolari in un complesso tetraedrico

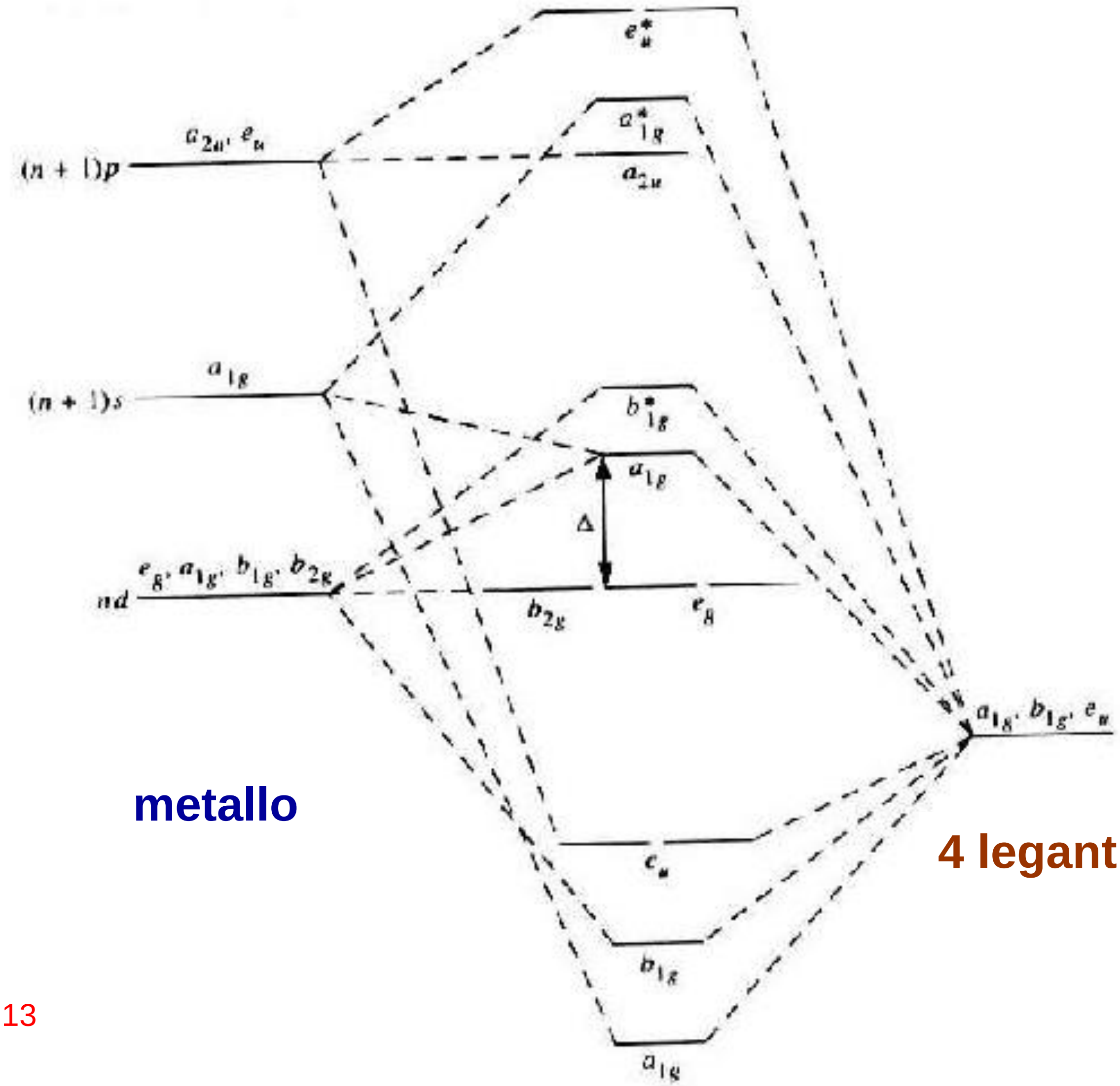


N. Orbitali: 9+4 = 13

metallo

4 leganti

Orbitali molecolari in un complesso planare quadrato



metallo

4 leganti

N. Orbitali: 9+4 = 13