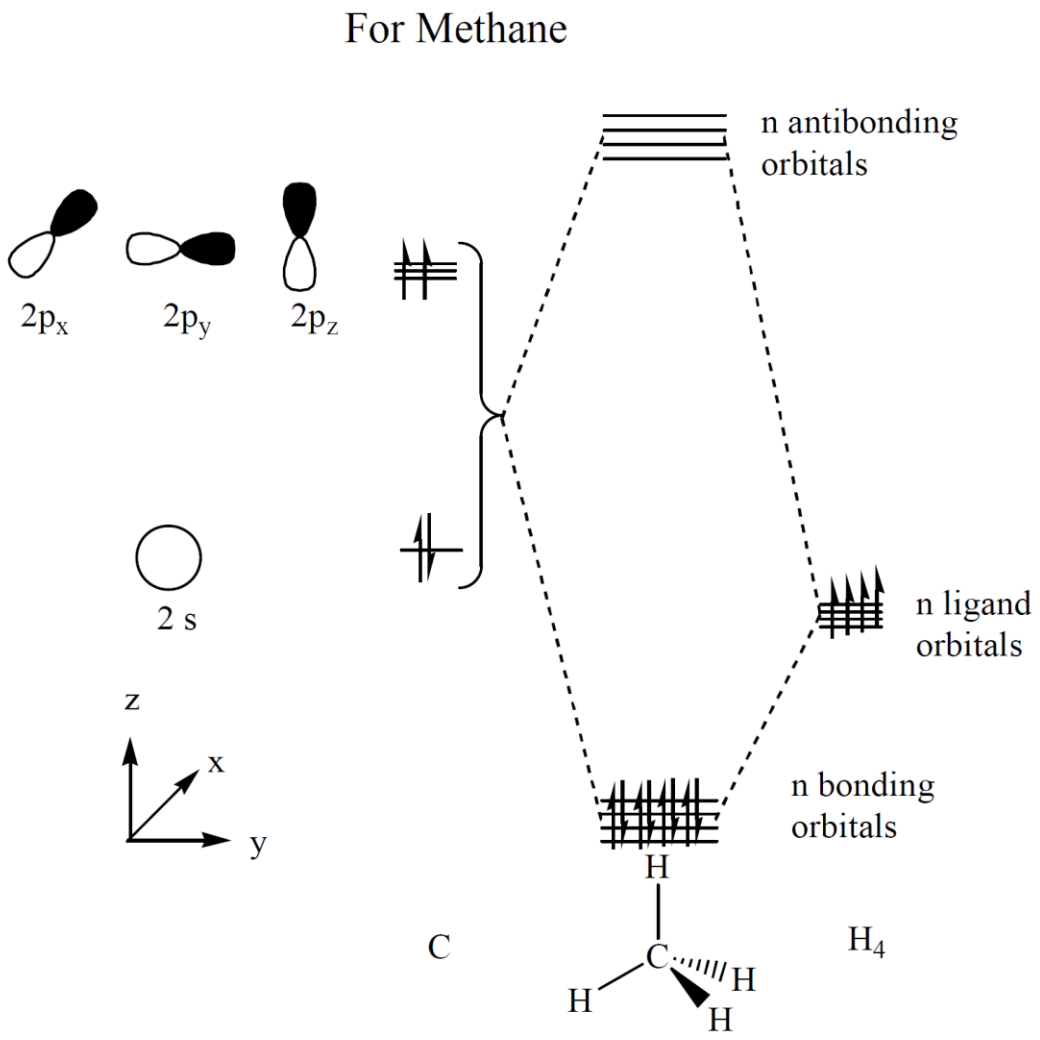
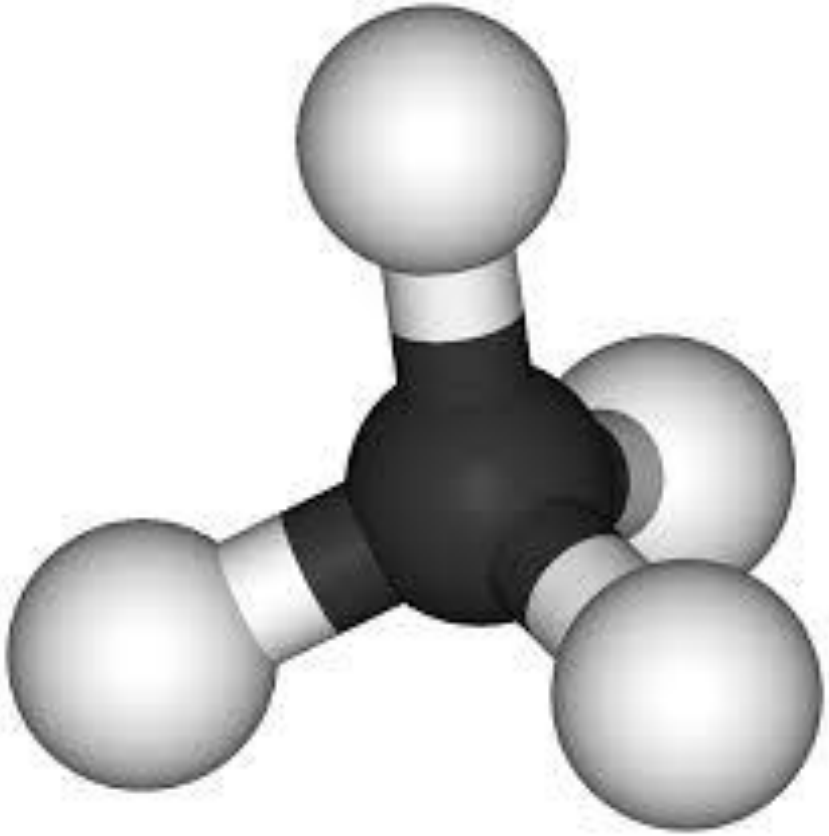
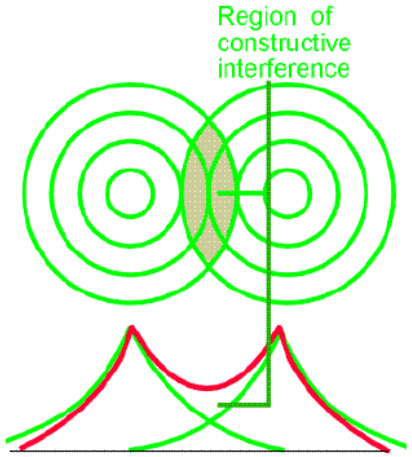
The Chemical Bond in Metal Complexes

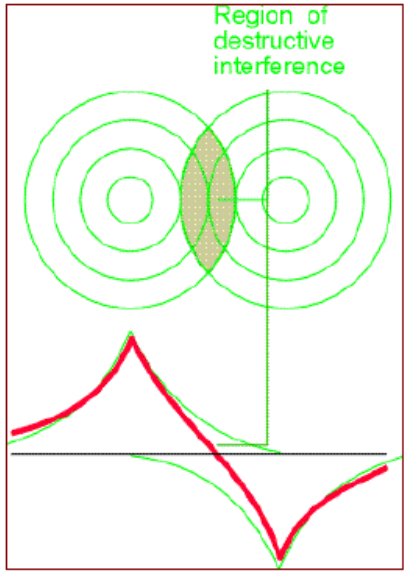
Covalent Bonds (organic molecules)

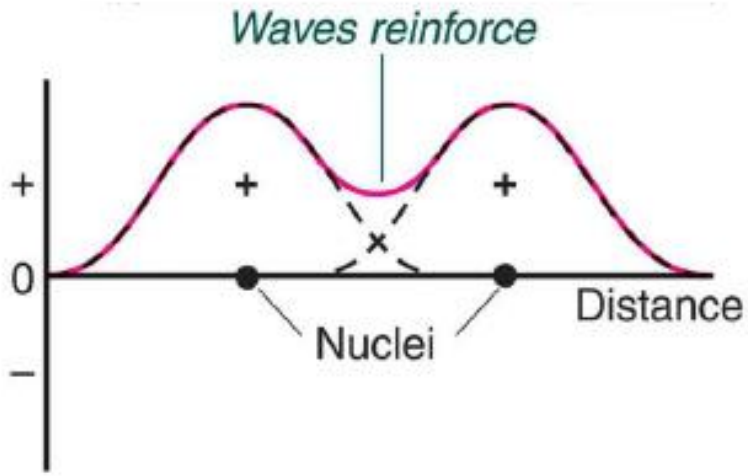


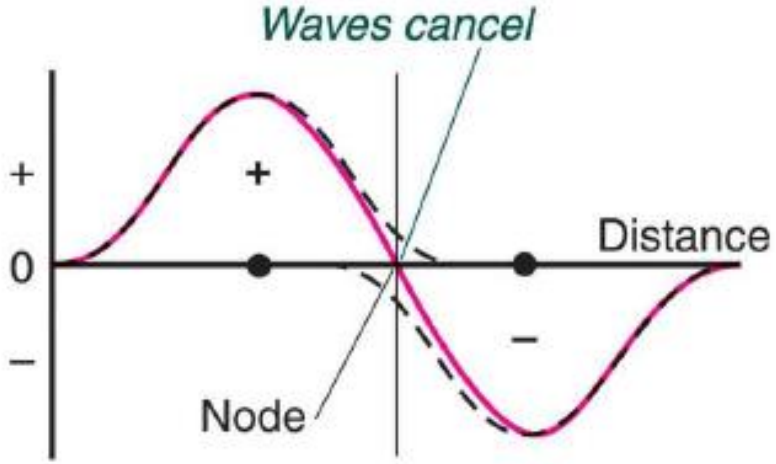


Molecular Orbitals (MO) combination of atomic wavefunctions

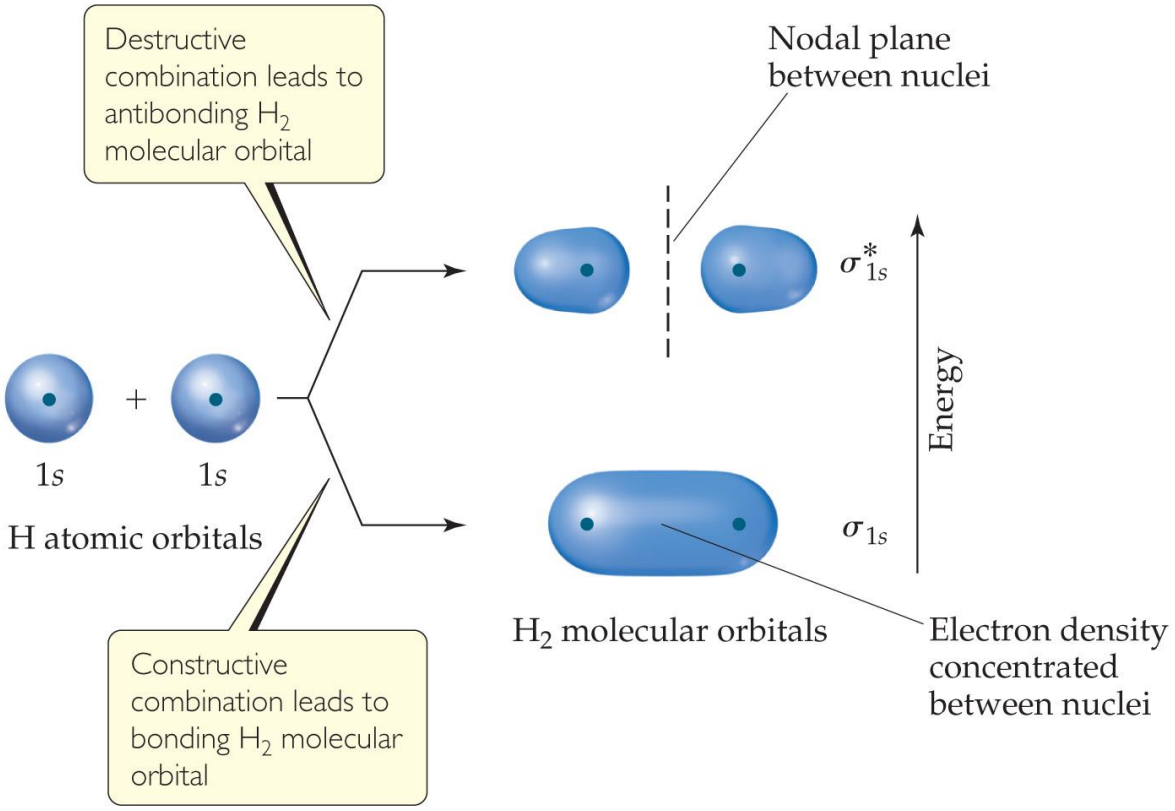


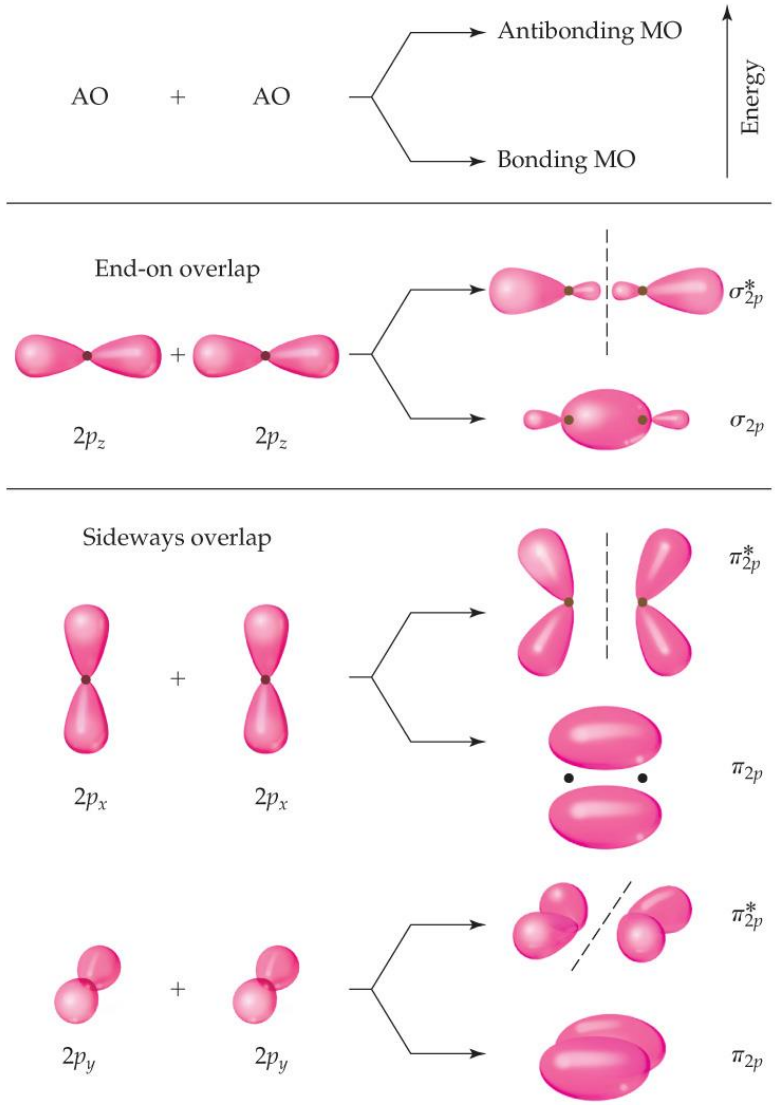




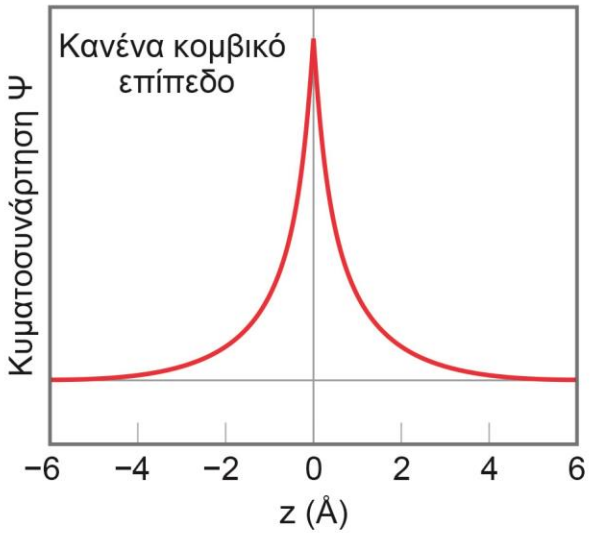


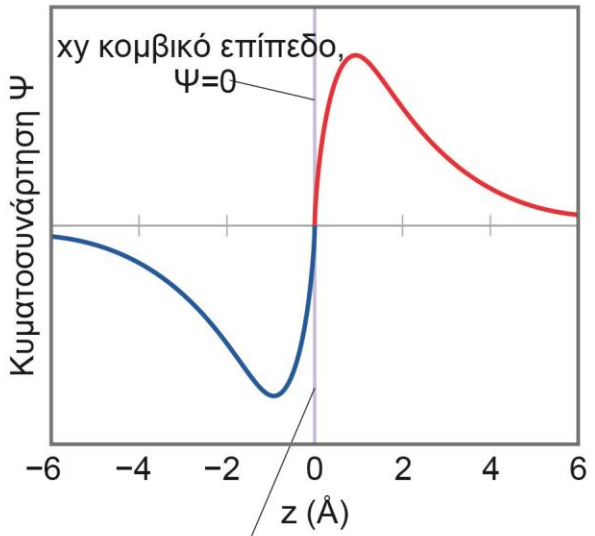
Molecular Orbitals (MO) combination of atomic wavefunctions

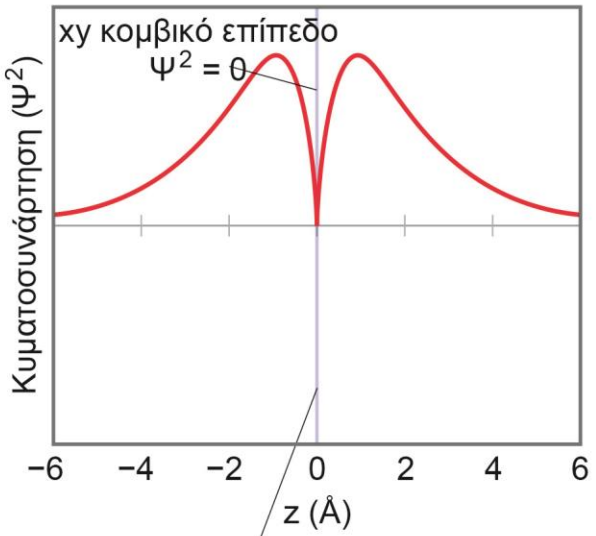


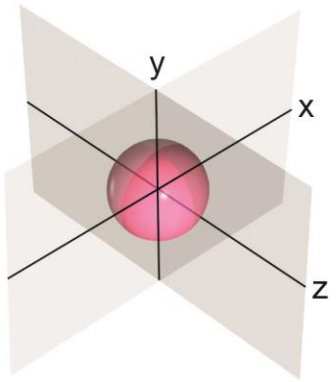


Molecular Orbitals (MO) combination of atomic wavefunctions

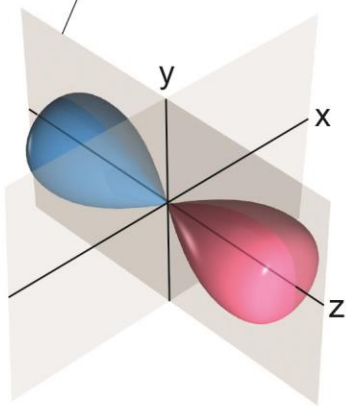




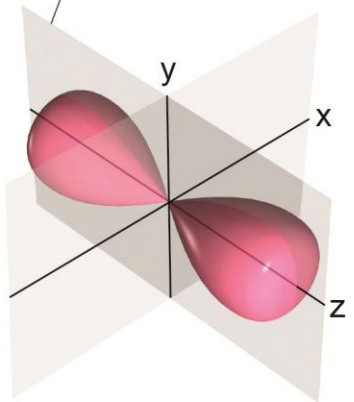




Τροχιακό 1s

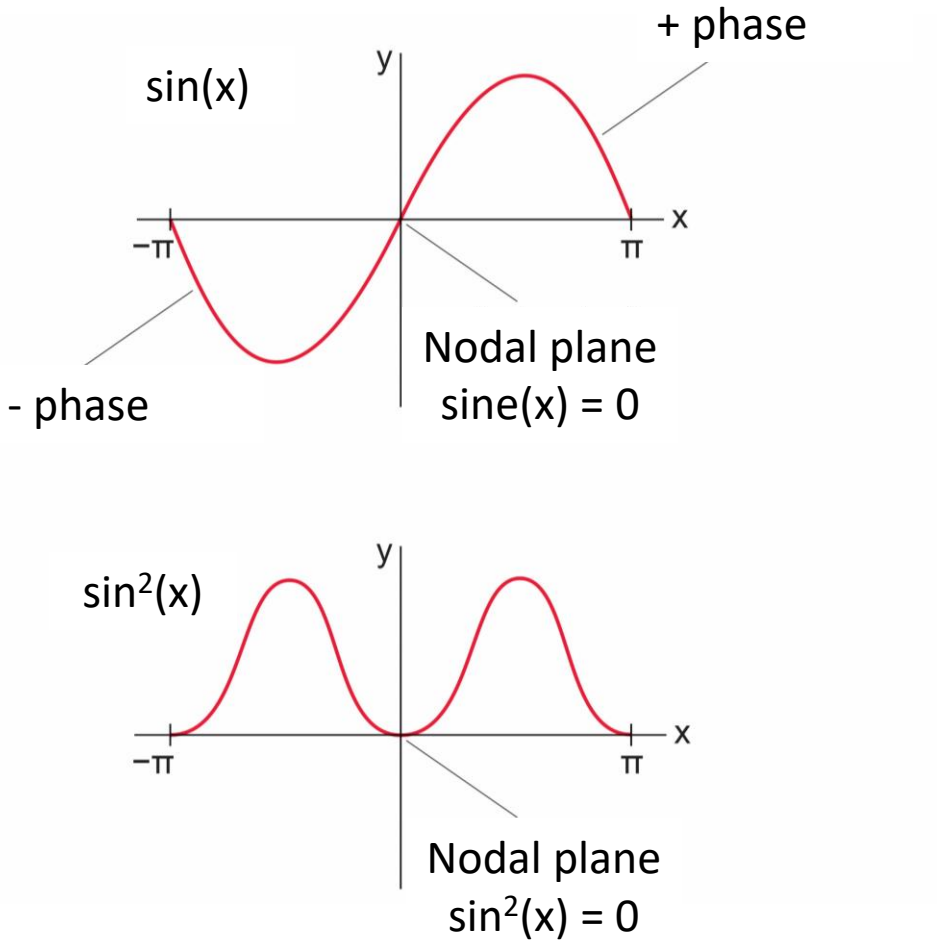


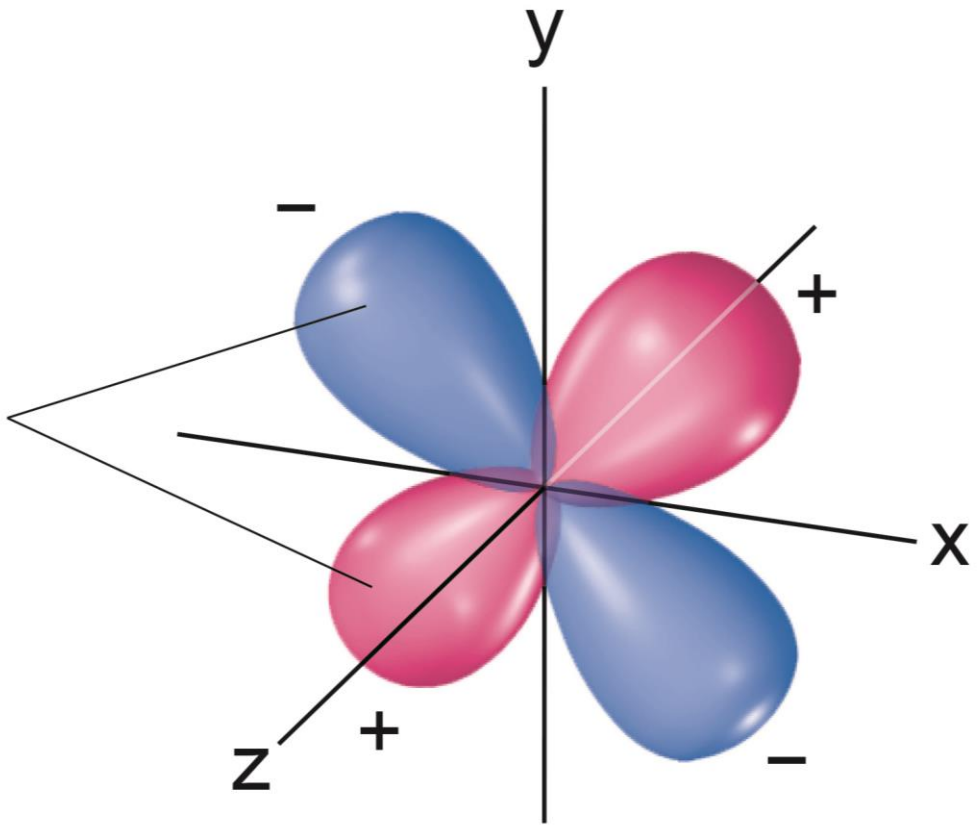
Τροχιακό $2p_z$



Τροχιακό $(2p_z)^2$

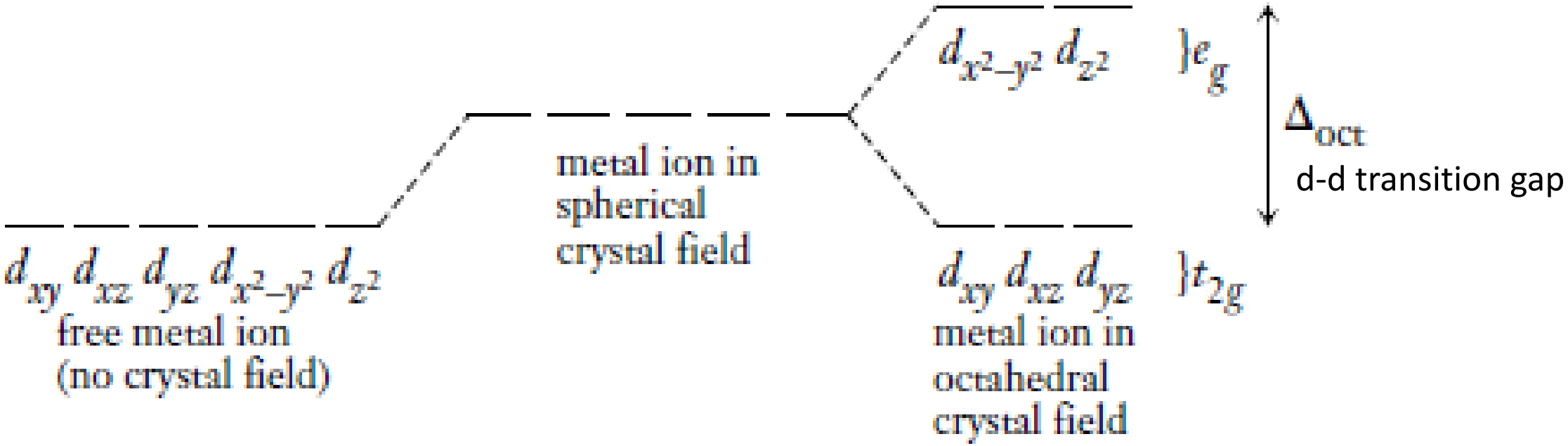
Molecular Orbitals (MO) combination of atomic wavefunctions



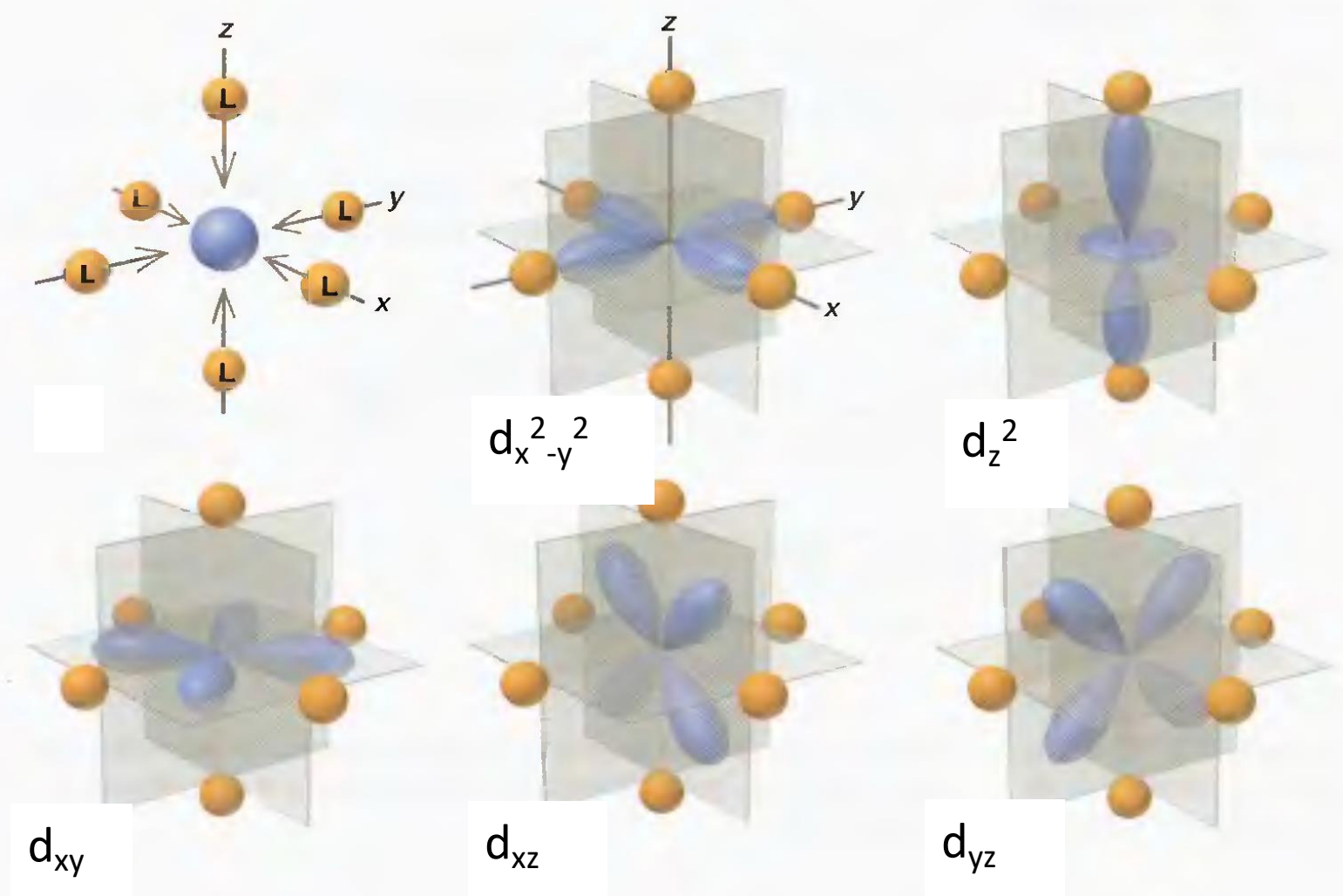


d_{xy} orbital

Crystal-field Splitting in octahedral field



Interaction of the t_{2g} and e_g orbitals in an octahedral crystal field



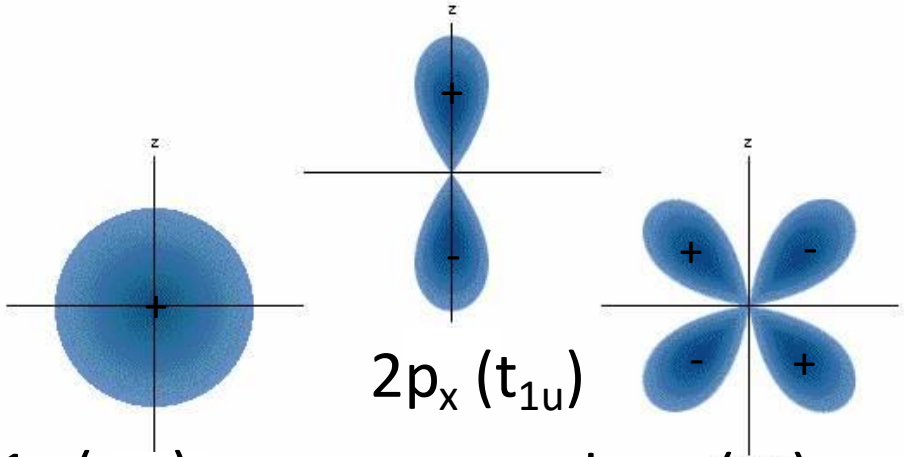
e_g symmetry

t_{2g} symmetry

Symbols of wavefunctions(orbitals)

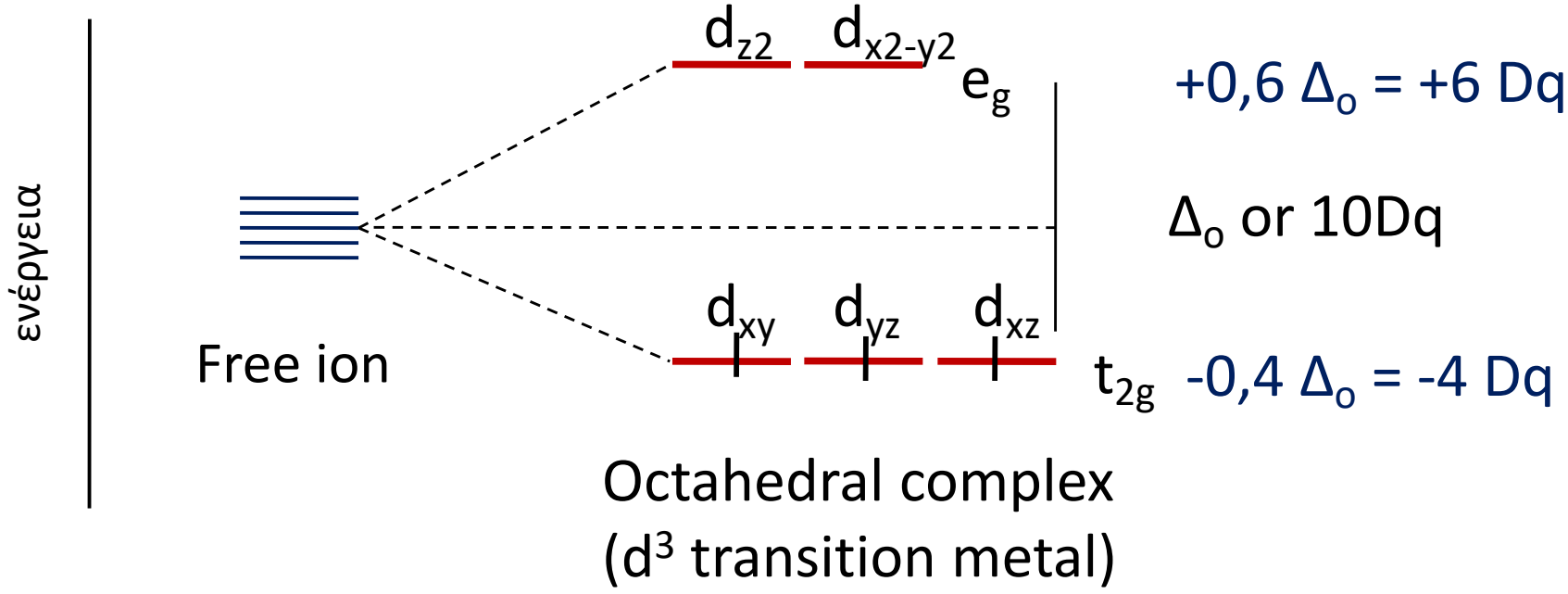
Symmetry descriptrors a, b, e, t, g relate to the symmetry of the orbitals

a = singly degenerate orbital, symmetrical to the main axis
b = singly degenerate orbital, anti-symmetrical to the main axis
e = doubly degenerate orbital
t = triply degenerate orbital
g = symmetrical with respect to the inversion center
u = anti-symmetrical with respect to the inversion center



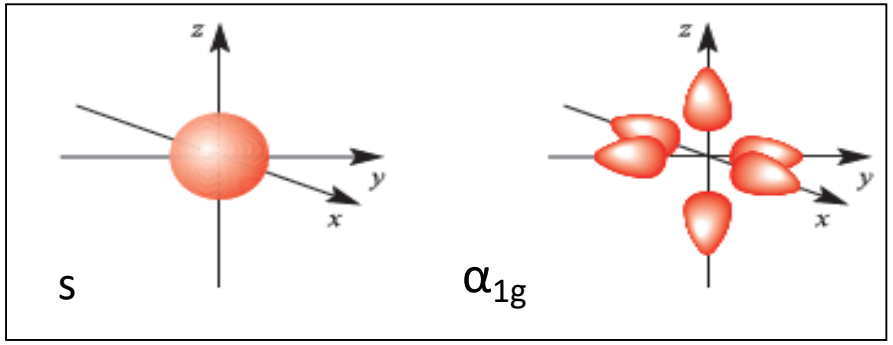
1s (a_{1g}) $2p_x$ (t_{1u}) d_{x2-y2} (e_g)

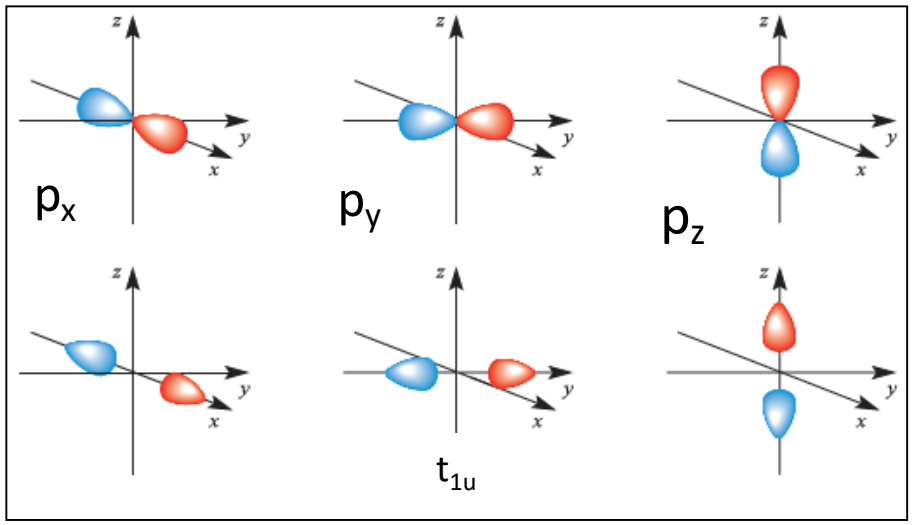
Octahedral crystal field

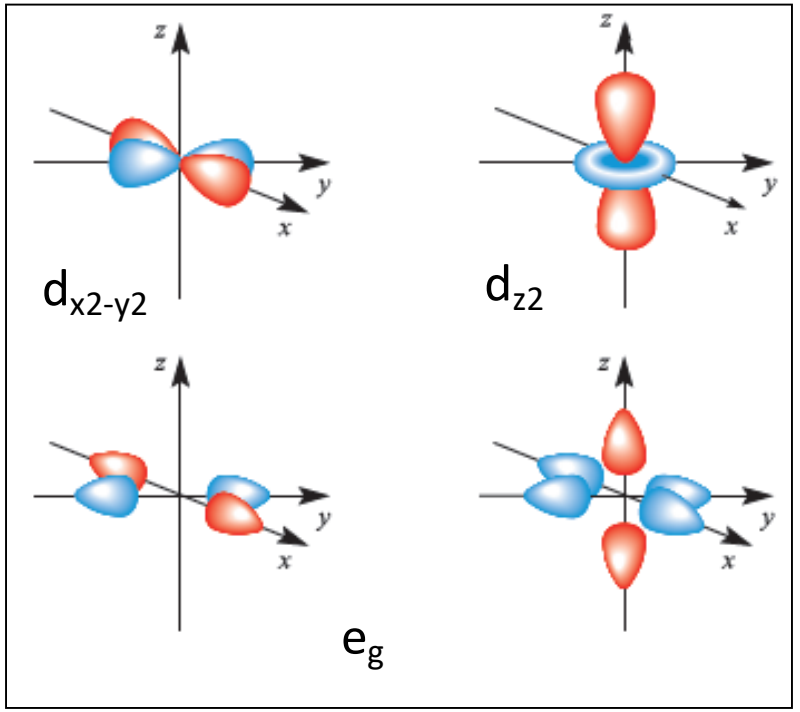


Symmetry of atomic orbitals (metal vs ligands)

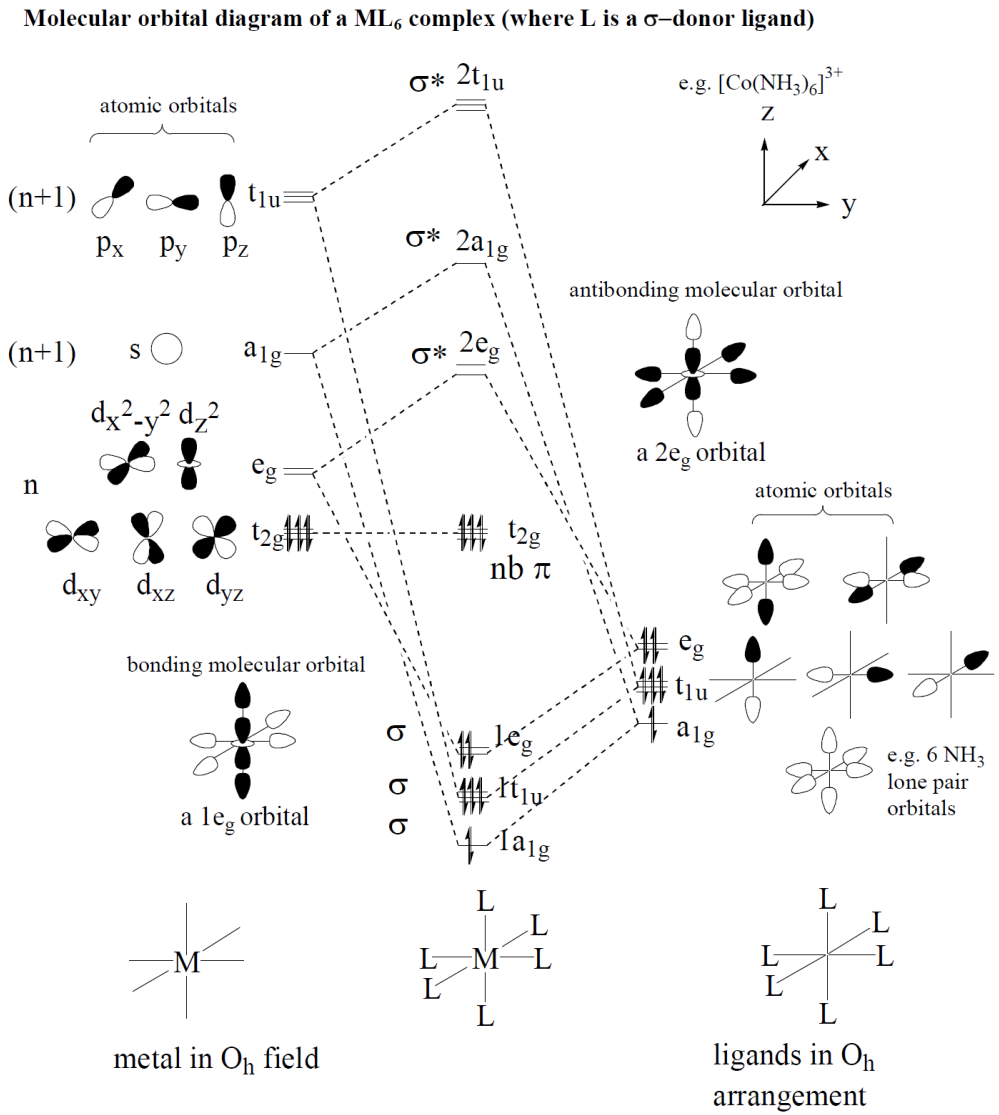
Only orbitals with the exact same symmetry combine

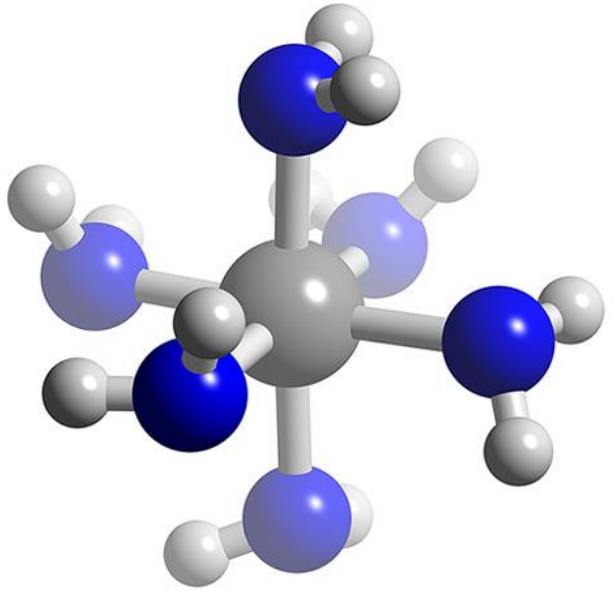


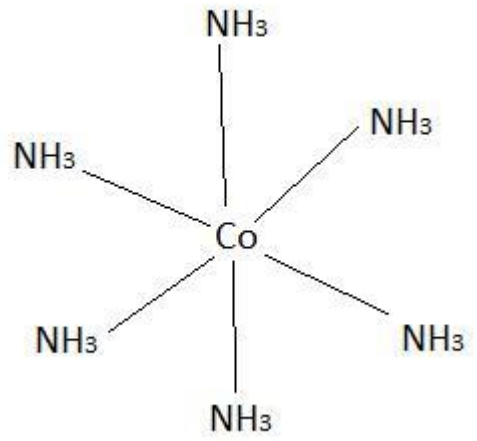




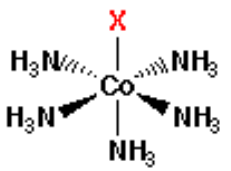
Dative Bonds (coordination chemistry)







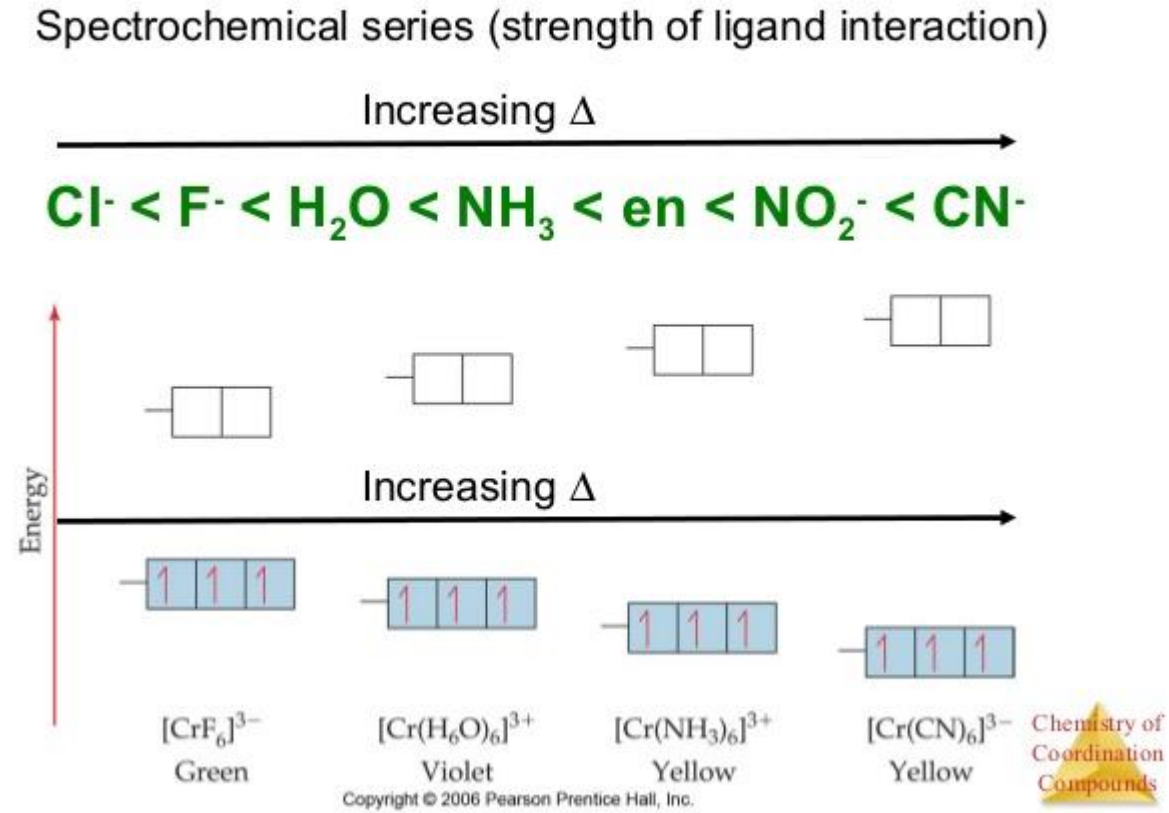
Spectrochemical Series



$CO > CN^- > NO_2^- >$ phen, biby $>$ en $> NH_3$,
py $>$ NCS $> H_2O > C_2O_4^{2-} > OH^- >$ urea $>$
F^- , $N_3^- > NO_3^- > Cl^- > SCN^- > Br^- > I^-$

The Fajans Tsuchida Spectrochemical Series (variation of Δ_o with X)

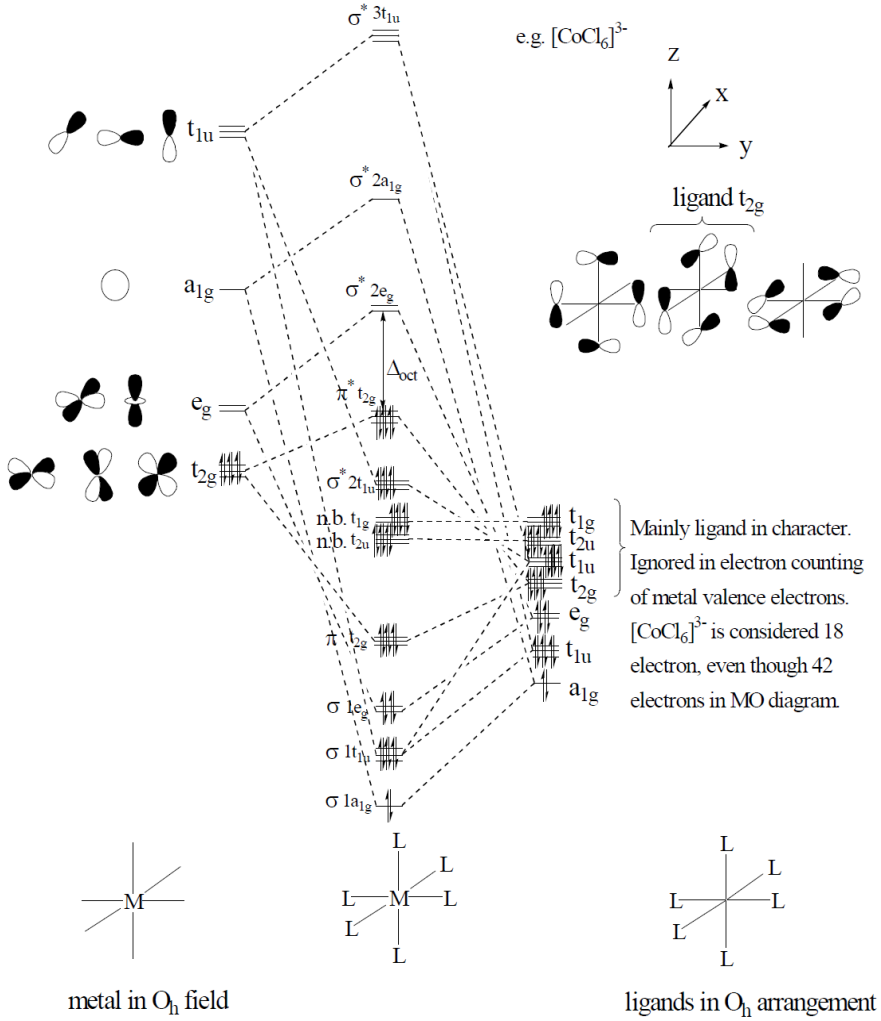
R. Tsuchida, Bull. Chem. Soc. Jpn. **1938** 13, 388 - 400 ; 434 - 450 and 471 - 480



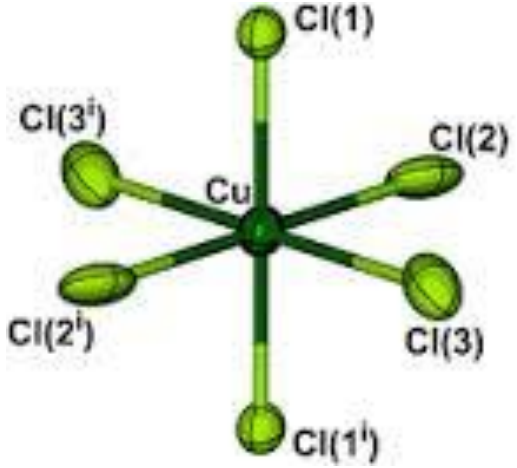
Dative Bonds (coordination chemistry)

What effect do π-acceptors and π-donors have on the chemistry of metal complexes?

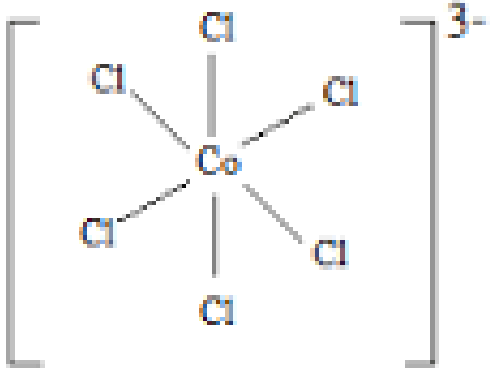
MO diagram of O_h complex with π-donor ligands



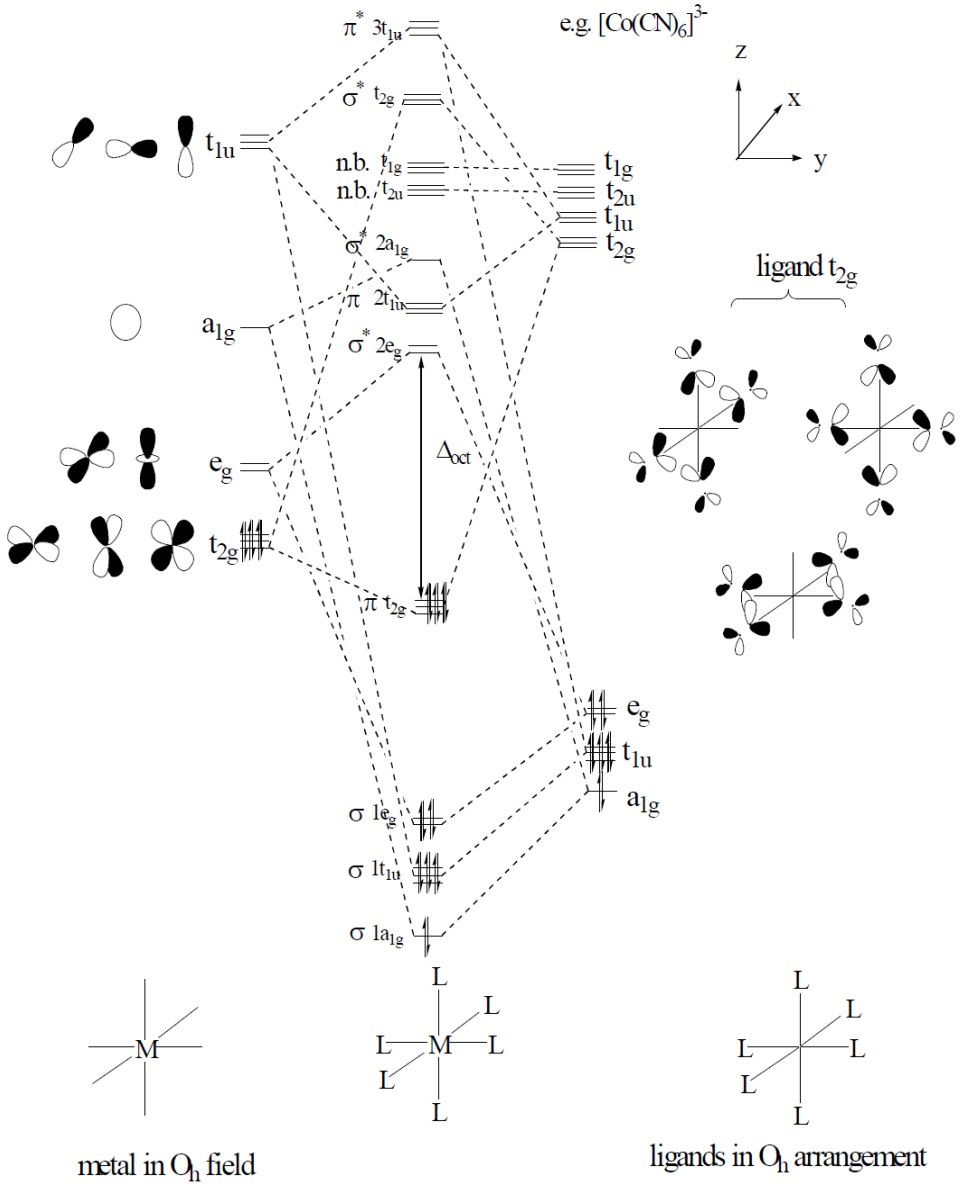
Note the effect on the t_{2g} d-orbitals in comparison to the σ-only case. These t_{2g} orbitals have risen in energy, closer to the e_g level, resulting in a reduction of Δ_{oct} (10 Dq).

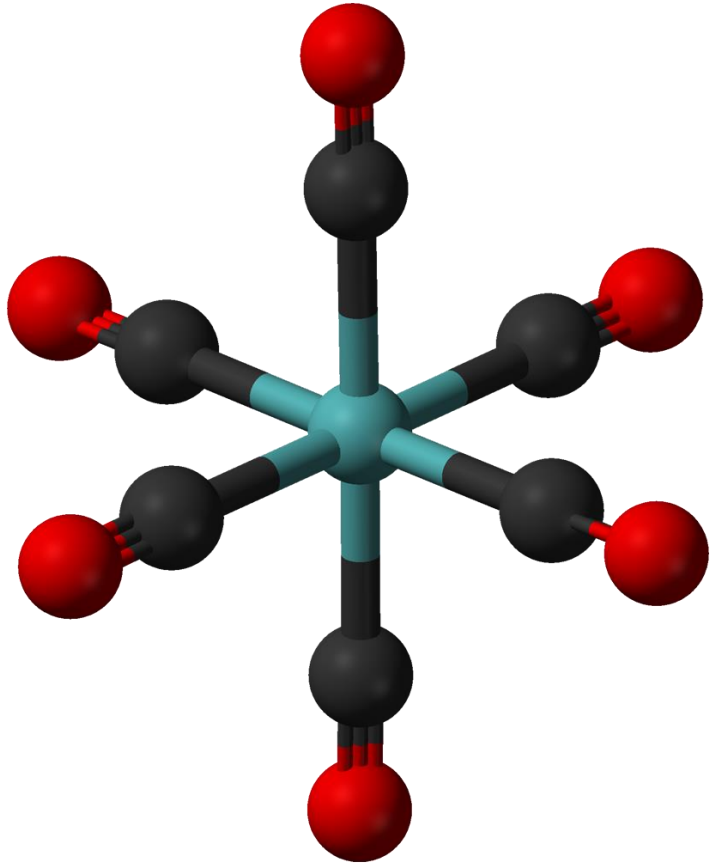


Cu–Cl(1) = 2.278(1)
Cu–Cl(2) = 2.603(1)
Cu–Cl(3) = 2.608(1)



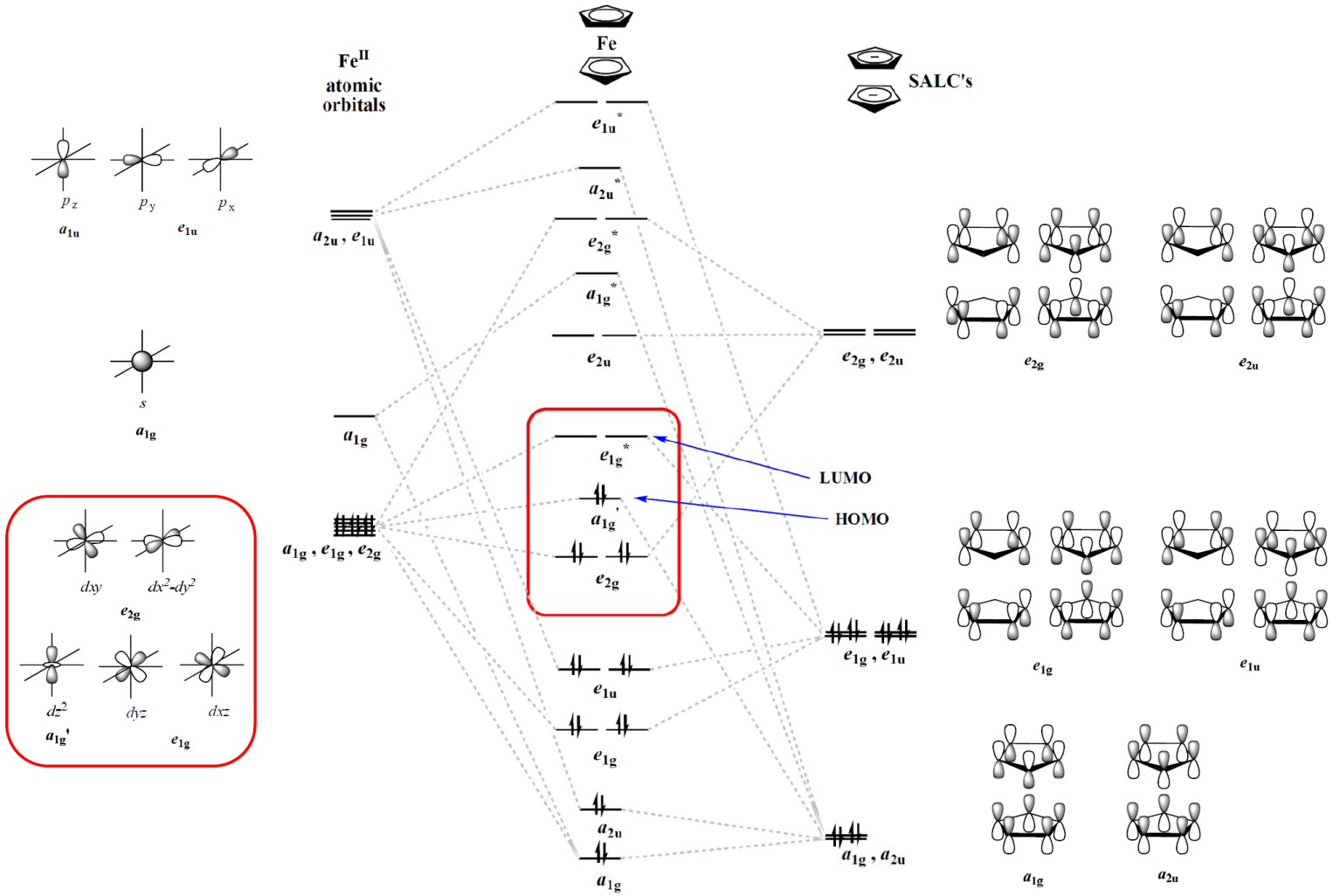
Dative Bonds (organometallic chemistry)

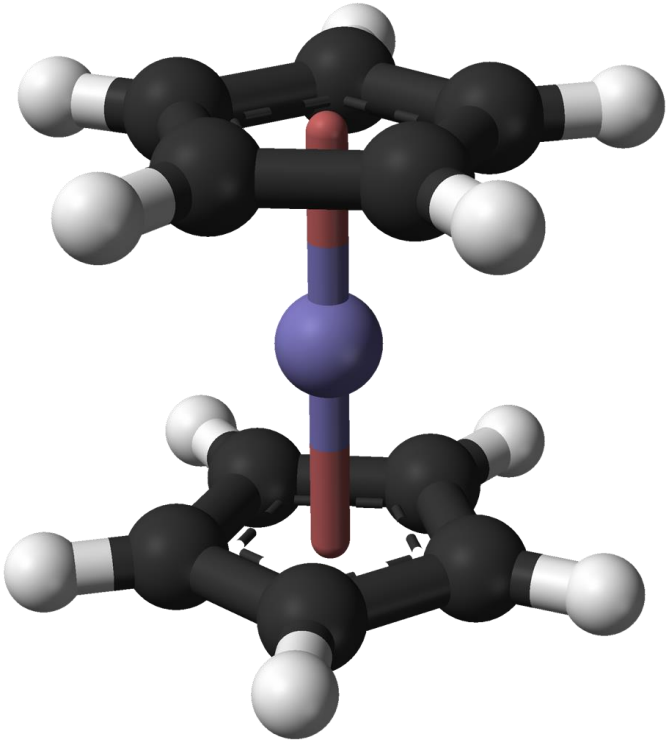




Dative Bonds (Metal-π electrons)

A qualitative molecular orbital diagram for ferrocene (D_{5d})





Metal-π electrons bond is still a σ-bond