Unit 3 – Deck 6

Inorganic

Orbitals interactions in metals: MO Theory of Bonding

Last Time

- Valence Bond Theory (atomic orbital hybridization schemes)
- Crystal Field Theory
- High-Spin States & Low-Spin
- Octahedral Field Splitting
- Crystal Field Stabilization Energy

Lecture Topics

- Ligand Field Theory
- Dative interactions between transition metals and π-donating ligands
- Dative interactions between transition metals and π-accepting ligands (metal $\mathrm{d}\pi$-backbonding)
- Ligand Field Stabilization Energies (LFSE)
- Demystifying the spectrochemical series

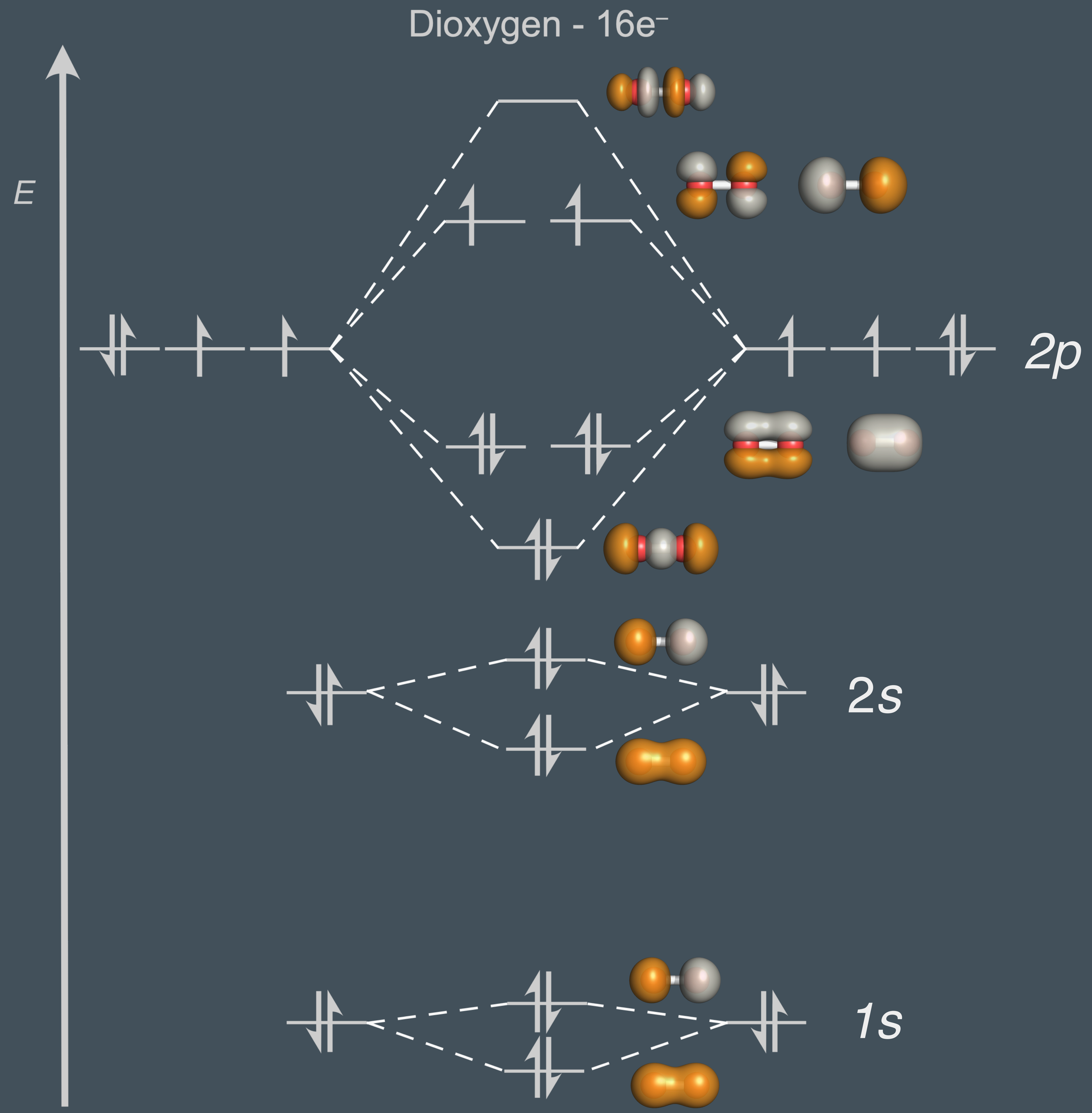
Molecular Orbital Theory

Molecular Orbital Theory is a quantum mechanical model or a molecule where the wavefunction of an electron in a molecule is calculated accounting for the 3D positions of all atoms in the compound.

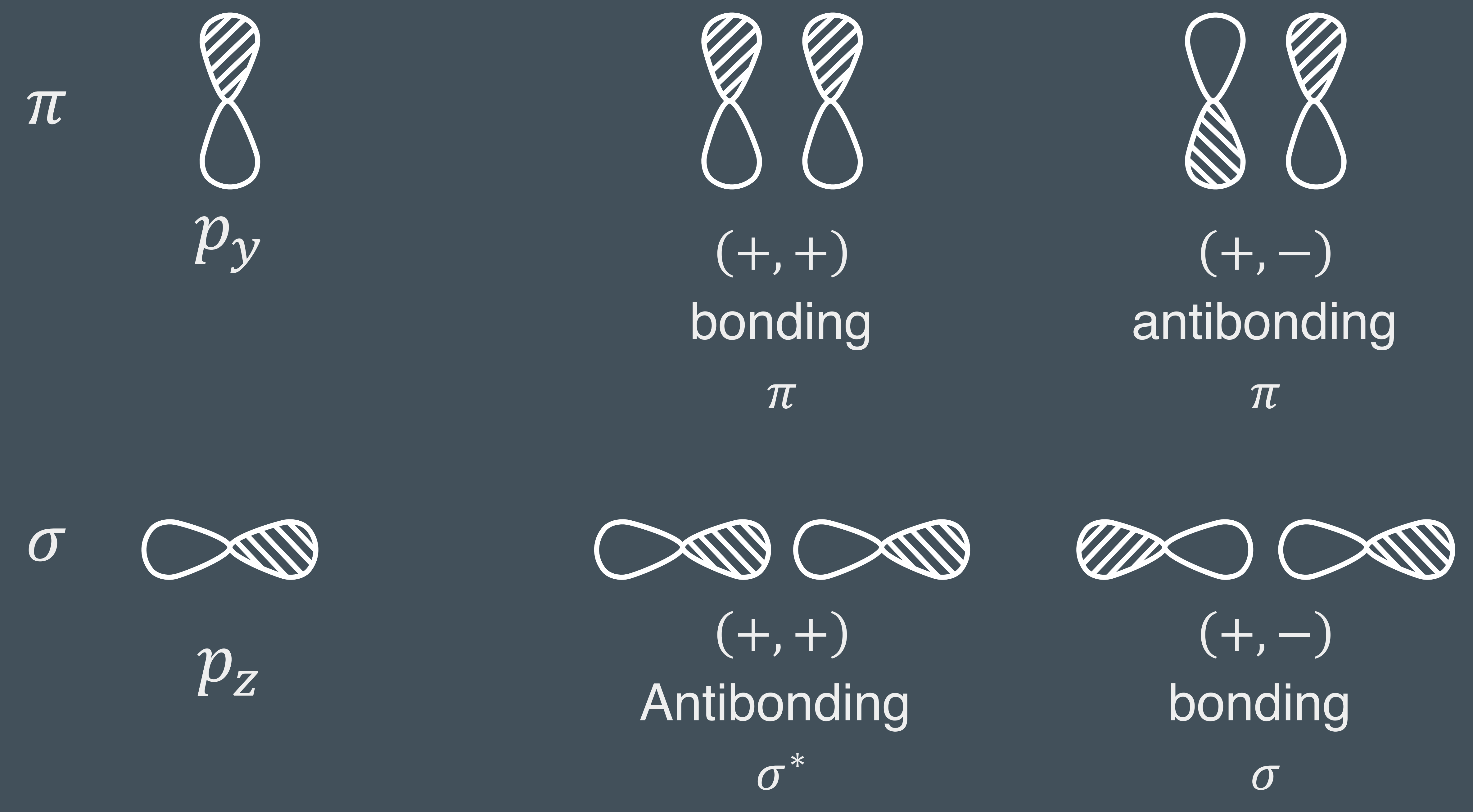
If the interactions of interest are metal–ligand bonds, MO Theory is also called Ligand Field Theory.

Crystal field theory explains the d-orbital splitting for σ-bonded metal complexes. Apart from its considerations of crystal field symmetry, it is largely empirical.

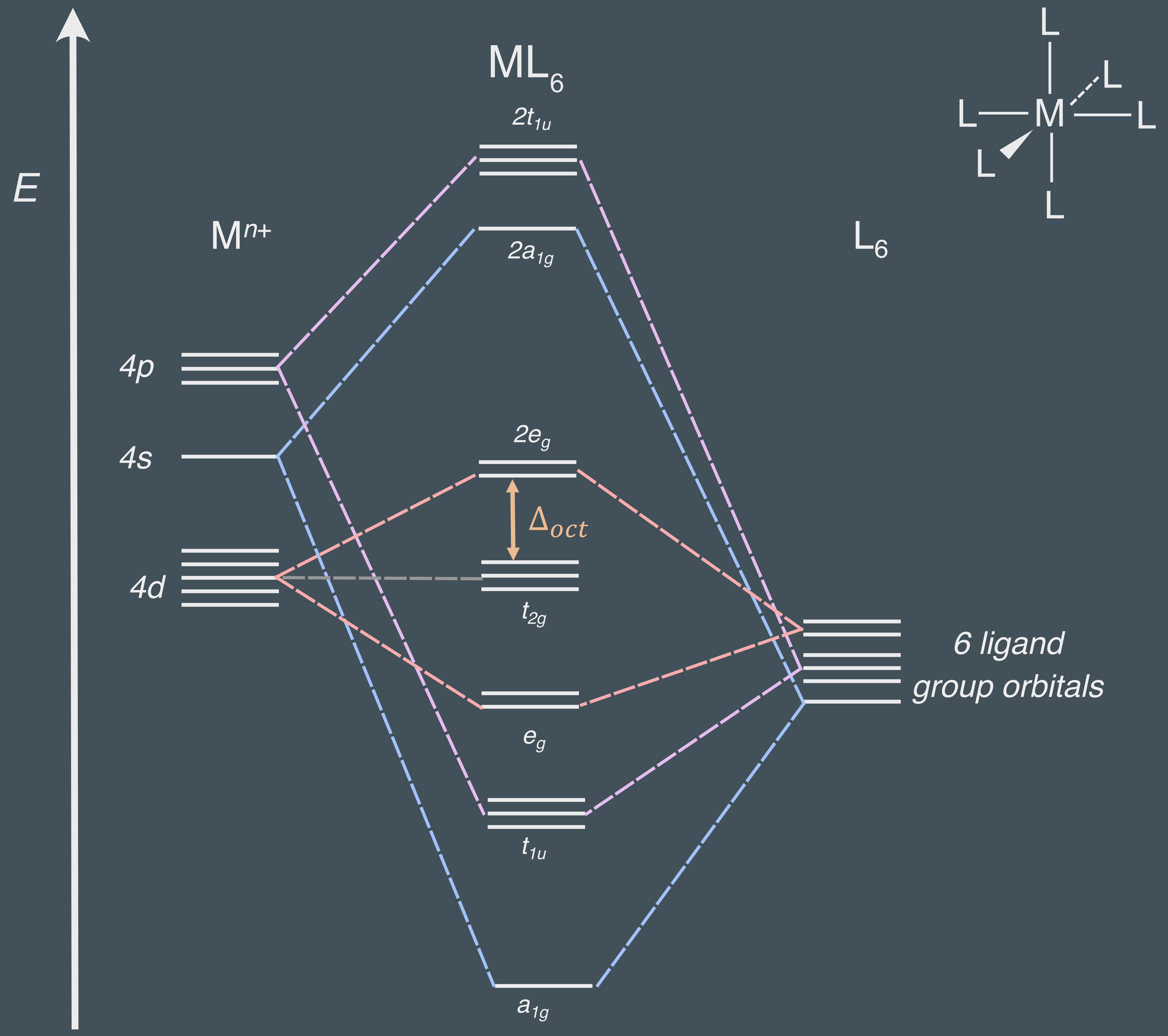
Molecular Orbital Theory



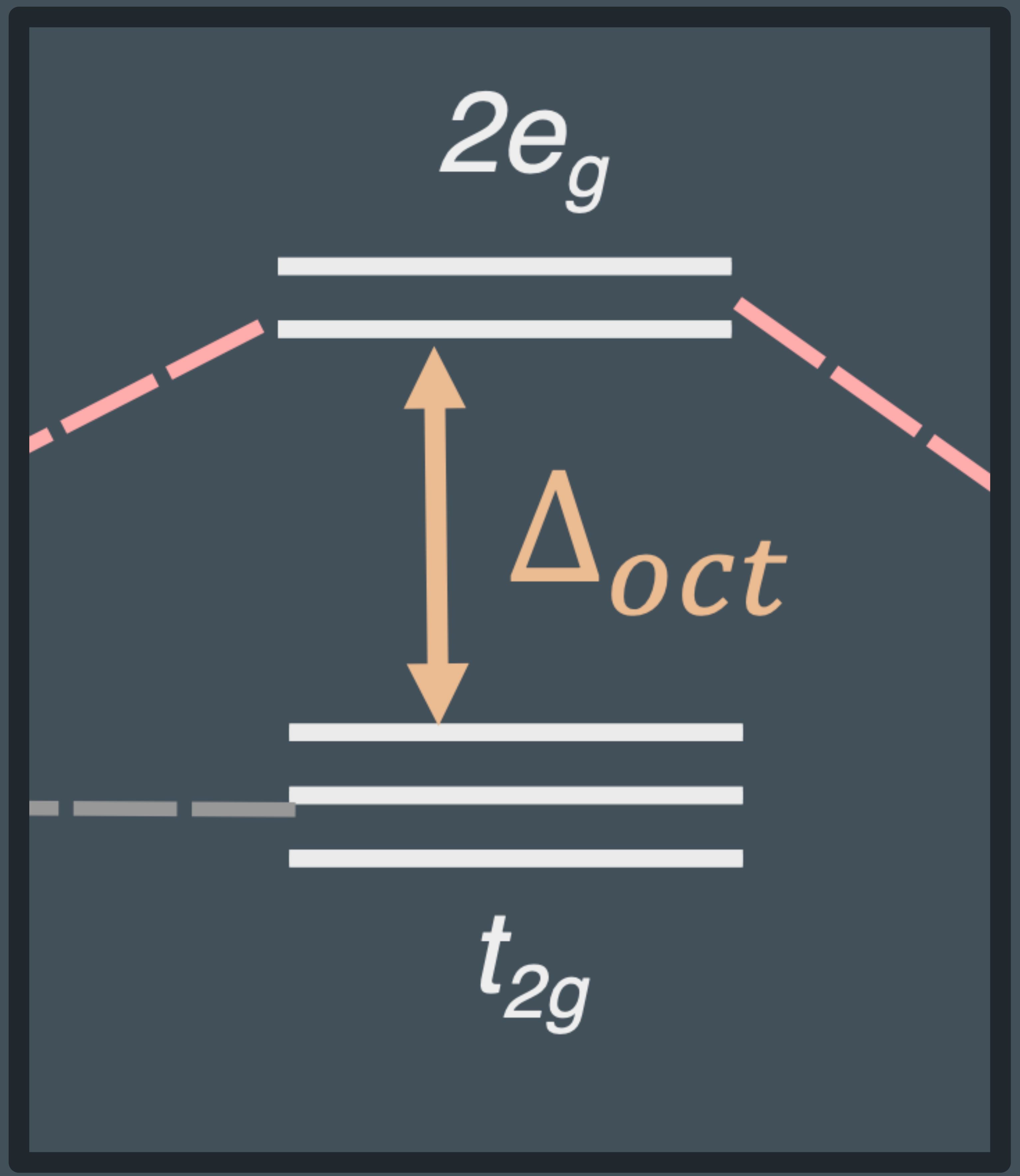
1. When 2 atoms interact the electron wavefunctions for each atom combine to form 2 new molecular orbitals.
2. One of the new orbitals forms with the two orbitals having the *same parity* (+, +) while the other new molecular orbital has *opposite parity* (+, –)



MO for O_h Ligand field



Octahedral σ–bonded complexes



MO for O_h Complexes

Trends for **octahedral σ–bonded complexes**:

1. Low spin complexes occupy the a_{1_g}, t_{1_u}, e_g and t_{2_g} and e_g^* MO's following the Aufbau principle and Hund's rule without need to consider electron pairing energy.
2. High spin complexes occupy the a_{1_g}, t_{1_u}, e_g, t_{2_g}, and e_g^* MO's. Add electrons following the Aufbau principle and Hund's rule. For filling t_{2_g}, and e_g^* maximize spin across both t_{2_g}, and e_g^* then continue to follow Aufbau and Hund.
3. The 12 ligand electrons occupy the a_{1_g}, t_{1_u}, and e_g MO's.
4. Occupancy of the t_{2_g}, and e_g^* MOs corresponds to the number of valence electrons on the metal ion.

5. What is stabilized by forming of the metal complex the metal ion or the ligands?

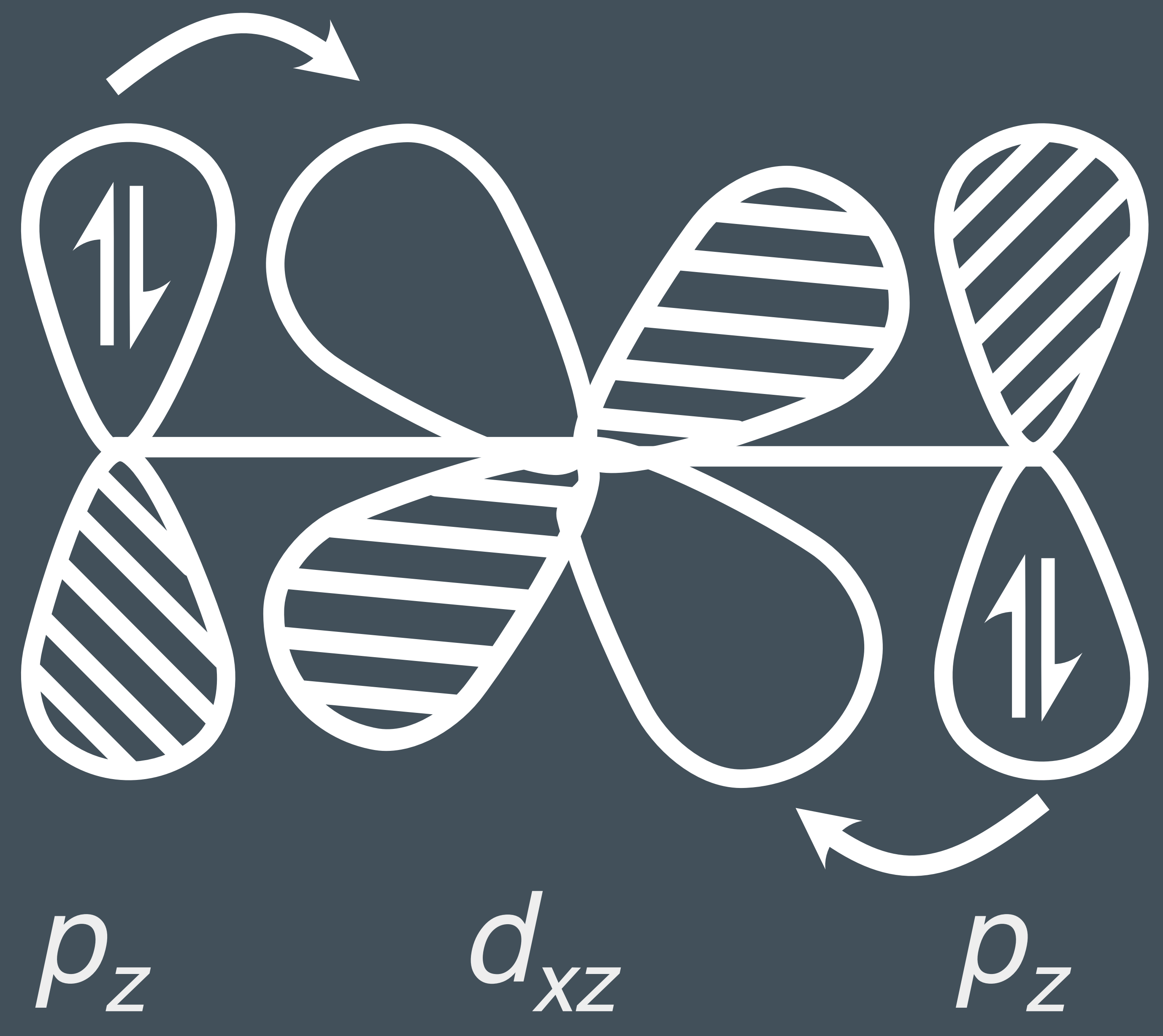
π bonding in O_h Complexes

Octahedral complexes with π–bonding

In some octahedral complexes, the d_{xy}, d_{yz}, and d_{xz} (t_{2g}) orbitals on the metal overlap with ligand *p* orbitals to exhibit π–bonding.

Two Types of π-Bonding

A **π–donor ligand** donates electrons to the metal center in an interaction that involves a filled ligand orbital and an empty metal orbital.

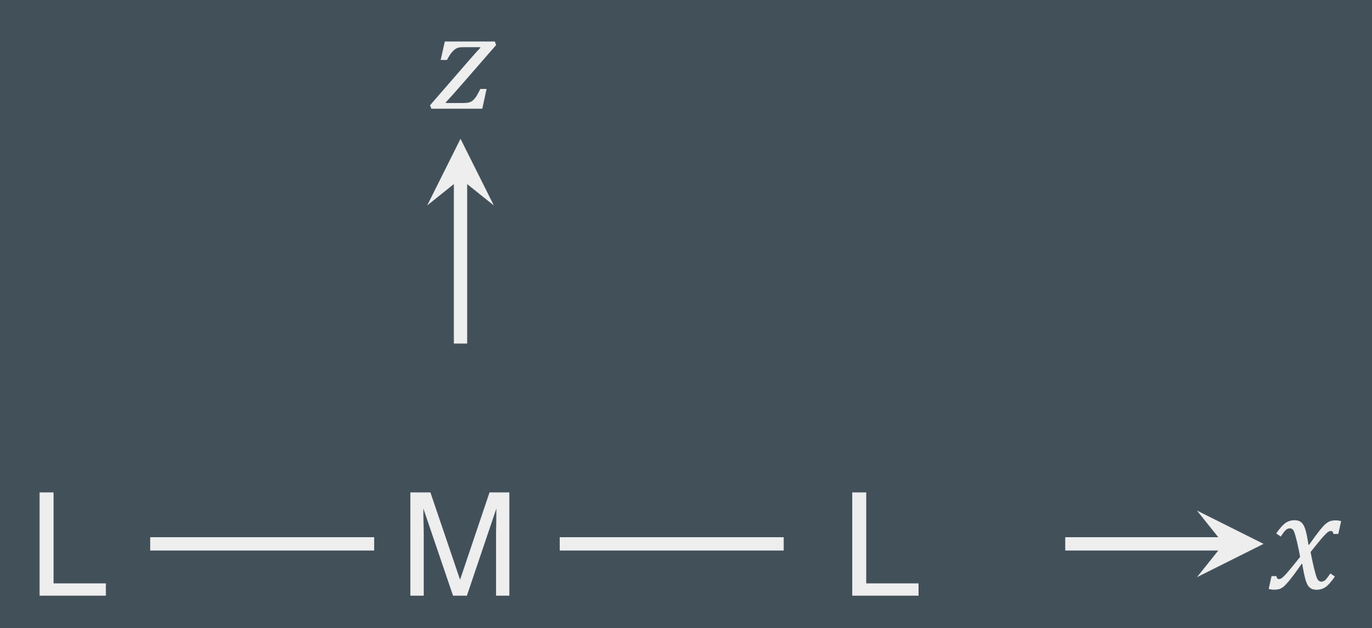


Filled ligand donor orbitals are stabilized by donation into empty/partially filled d-π orbitals

Two Types of Ligands

Octahedral complexes
with π–bonding

A **π–acceptor ligand** accepts electrons from the metal center in an interaction that involves a filled metal orbital and an empty ligand orbital.



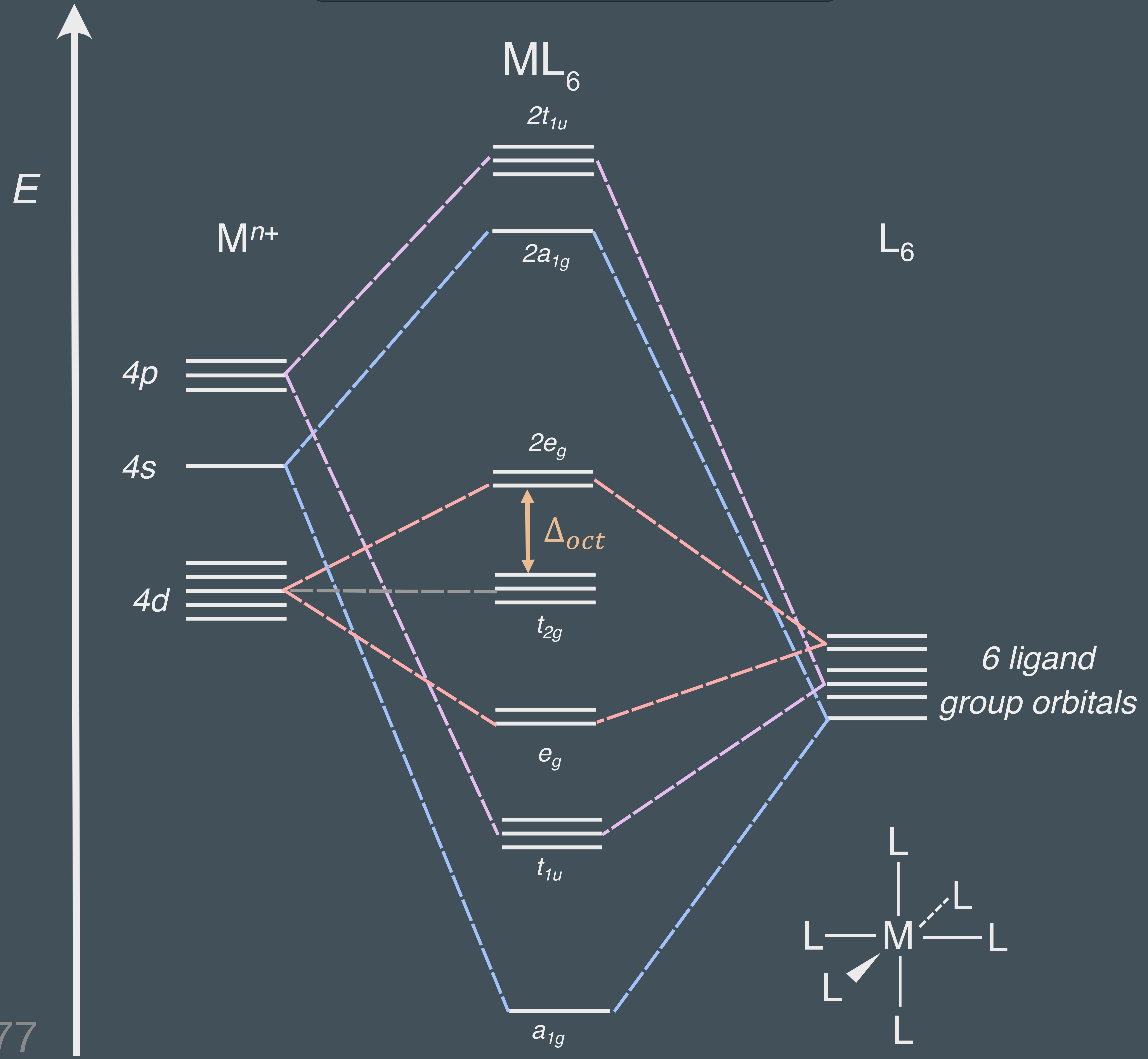
π–Donor Ligand Examples

Octahedral complexes with π–bonding

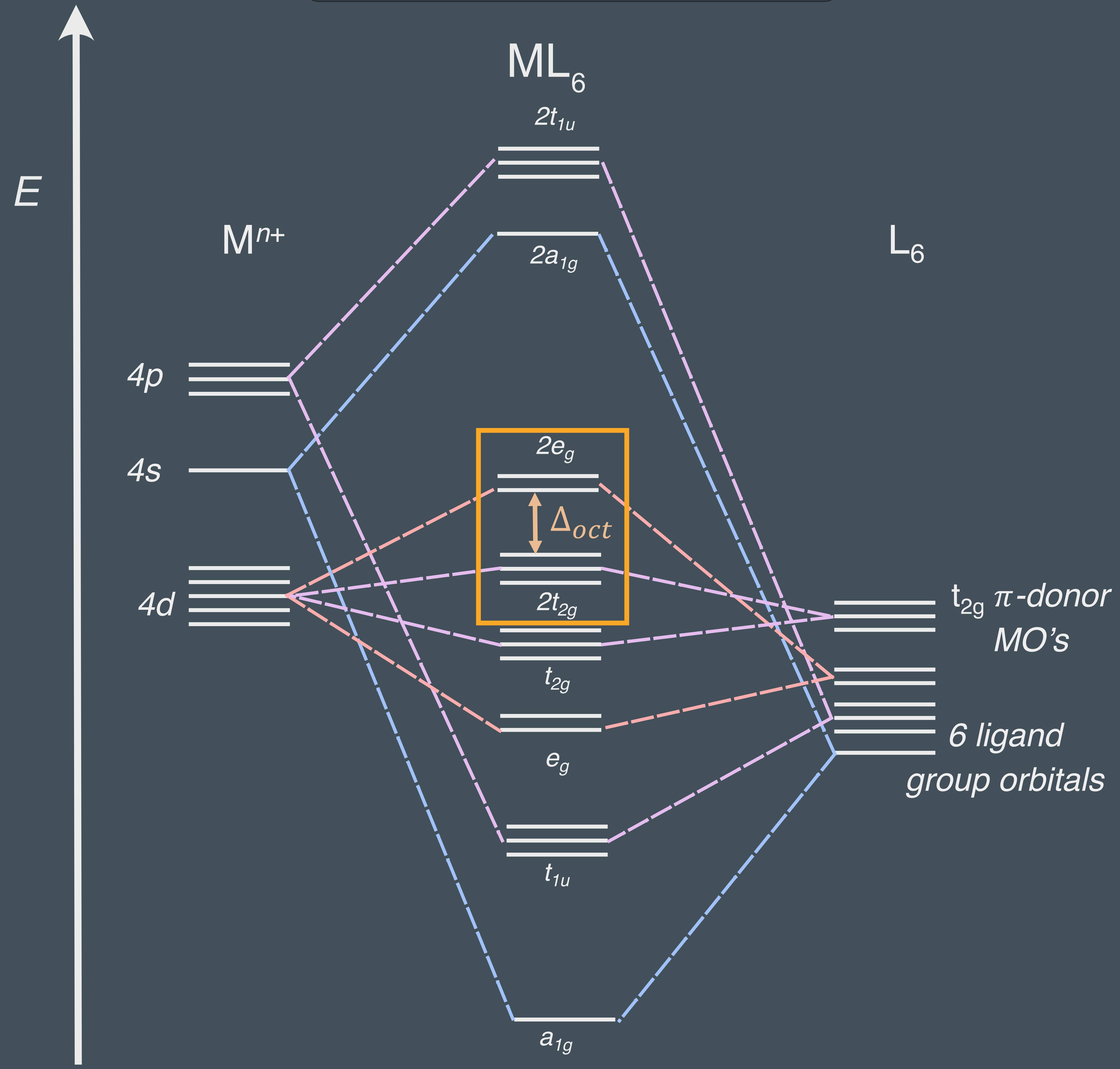
A **π–donor ligand** donates electrons to the metal center in an interaction that involves a filled ligand orbital and an empty metal orbital.

MO's for O_h Ligand Field | π-Donors

σ only ligands



π–donor ligands

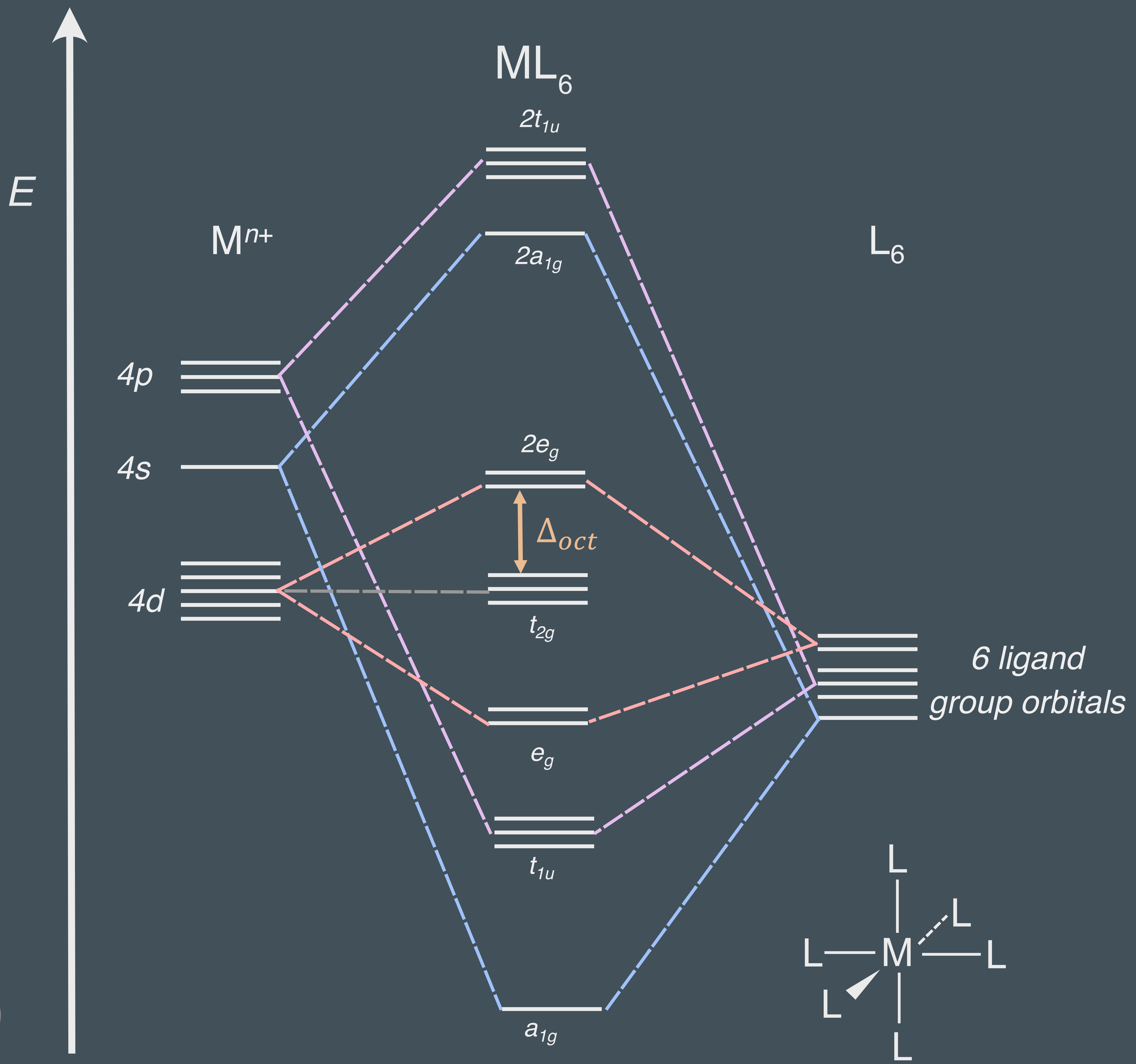


π–Acceptor Ligand Examples

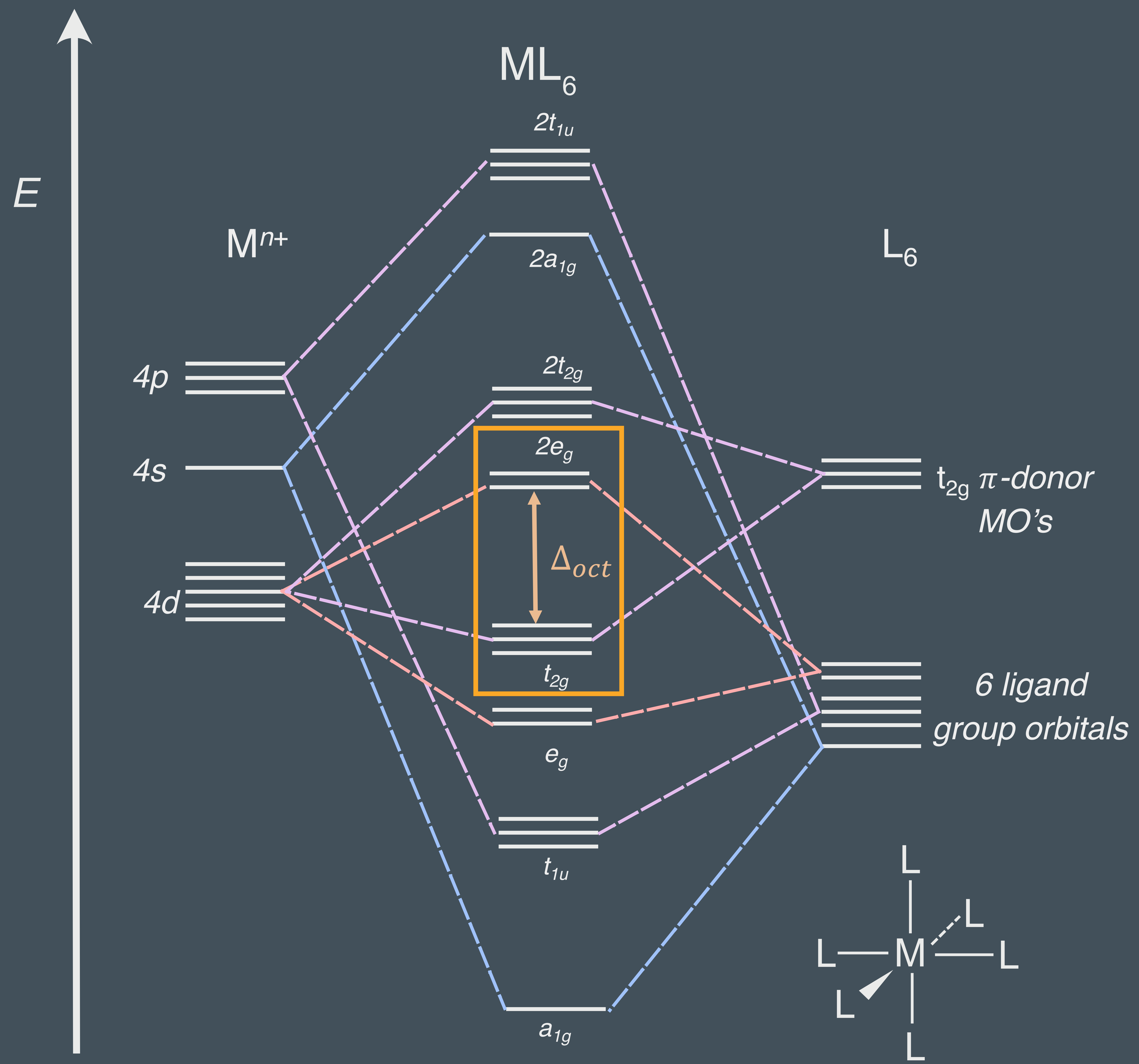
A **π–acceptor ligand** accepts electrons from the metal center in an interaction that involves a filled metal orbital and an empty ligand orbital.

MO's for O_h Ligand Field | π-Acceptors

σ only ligands



π–acceptor ligands



π–Bonding Summary

Metal–ligand π–bonds arise from two possible scenarios:

1. *back-donation* (aka *backbonding*)of electrons from a filled metal *d*-orbital to vacant antibonding π^* orbitals on the ligand.

2. A filled ligand π orbital donating to an empty metal *d*-orbital (usually a weaker interaction)

Which type of bonding can stabilize electron rich metal complexes?

Molecular orbitals of O_h Complexes

A few trends in π–bonded octahedral complexes:

1. Δ_{oct} decreases on going from pure σ–complex to one containing π–donor ligands

2. For a complex with π–donor ligands, increased π–donation stabilizes the lowest t_{2_g} level (*ligand based*) and destabilizes the higher energy $t^*_{2_g}$ level *(metal based).* This decreases Δ_{oct} .

3. For a complex with π–acceptor ligands, increased π–acceptance stabilizes the t_{2_g} level. This increases Δ_{oct} .

4. Δ_{oct} values are relatively large for complexes containing π–acceptor ligands. They are also likely to be low spin.

Crystal Field Limitations

So far we have assumed all ligands are identical (homoleptic), therefore our implementation of CFT only works for simple complexes.

CFT does not explain *how* or *why* particular ligands are placed where they are in the spectrochemical series.

Ligand Field Theory (LFT)

LFT is an extension of crystal field theory which is freely parameterized rather than taking a localized field arising from point charge ligands.

What does that mean?

1. Like CFT, LFT focuses on the *d*-orbitals only.

2. Like CFT, LFT uses Δ_{oct}.

3. Unlike CFT, LFT is 100% delocalized (MO theory in metal complexes).

The Spectrochemical Series - Ligands

Δ_{oct} increases along spectrochemical series:

$I^- < Br^- < [NC\mathbf{S}]^- < Cl^- < F^- < [OH]^- < [ox]^{2-} \approx H_2O < [\mathbf{N}CS]^- < NH_3 < en < bpy < phen < [CN]^- \approx CO$

Weak Field Ligands
(Smaller Δ_{oct})

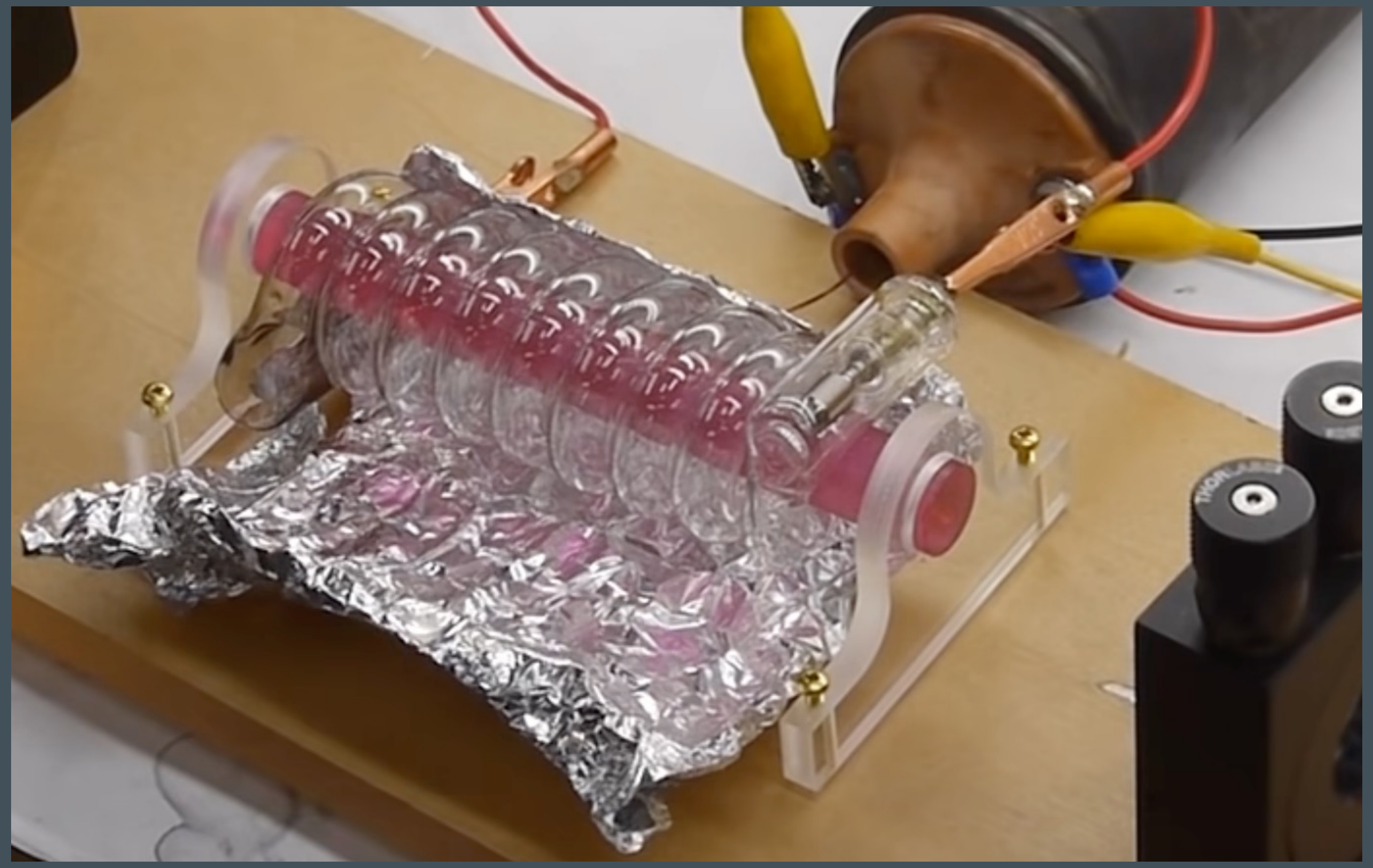
Strong Field Ligands
(Larger Δ_{oct})

Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)

The spectrochemical series is an empirical generalization that can also be applied to metal ions.

Electronic Spectra

To predict the electronic spectra of metal complexes we must account for both the ligand field splitting of the d-orbitals, their multielectron configuration, and other (usually higher energy) electronic transitions in the molecules



Applied Science
https://www.youtube.com/@AppliedScience