Lecture 6

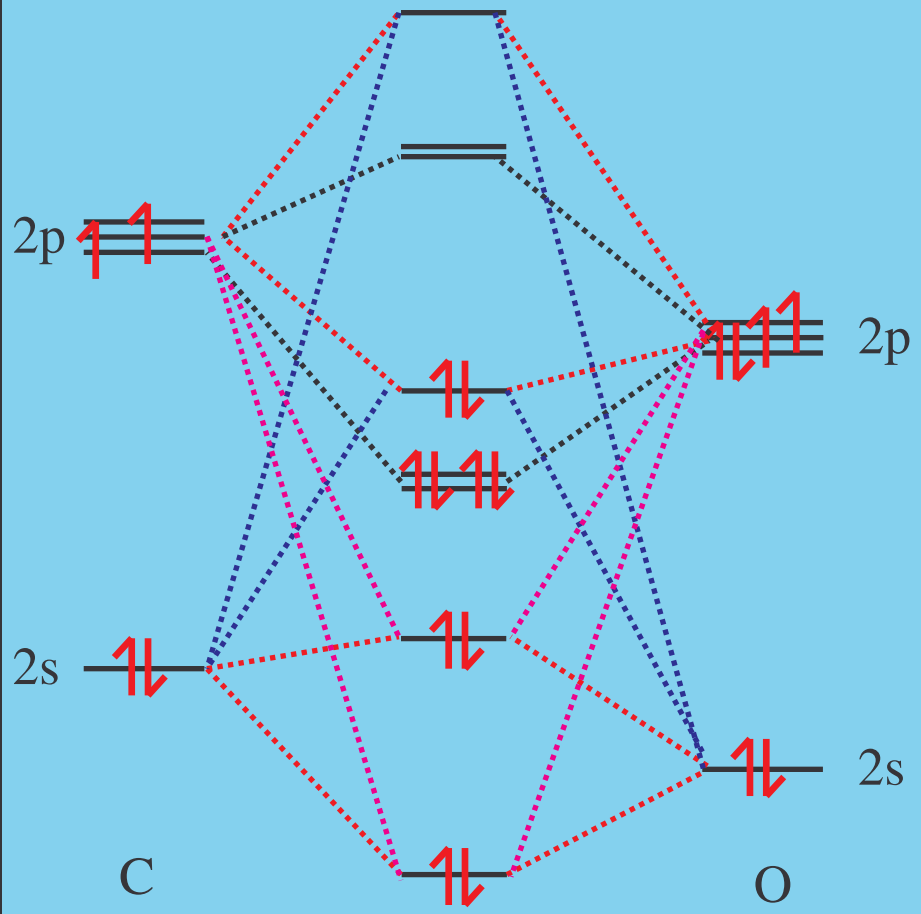
- How Molecular Oribital Theory enhances our understanding of the chemistry of transition metal complexes

- It can take into account:
- - covalent interactions
- - delocalisation
- - π-interactions

- Crystal Field Theory was a first approximation only

MO diagram for CO

- Same orbitals as homonuclear diatomics
  - different energies give rise to significant *2s* - *2p* mixing
  - confusing set of orbitals



4σ C-O anti-bonding (more C)

2π* π* (uneven – more carbon)

3σ Primarily carbon (p_z)

1π π bond (uneven – more oxygen)

2σ Primarily oxygen (p_z)

1σ C-O bonding interaction (more O)

The HOMO and LUMO of CO

- For chemical reactions the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital) are the most important.

HOMO – 3σ

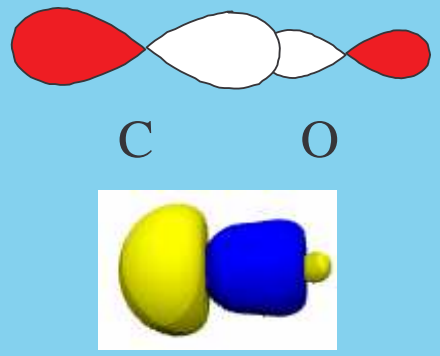
low energy Oxygen orbitals

makes 2σ → mainly O p_z

→ in 3σ mainly C p_z

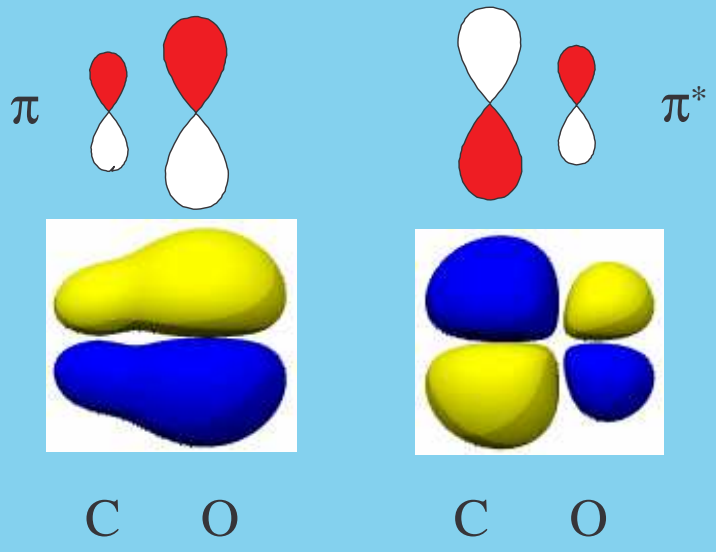
Some anti-bonding mixes in due to *sp* mixing

3σ



LUMO – 2π*

Comes from standard π interaction however lower oxygen orbital means π has has more oxygen and π* more carbon



Interaction of the CO 3σ with *d* orbitals

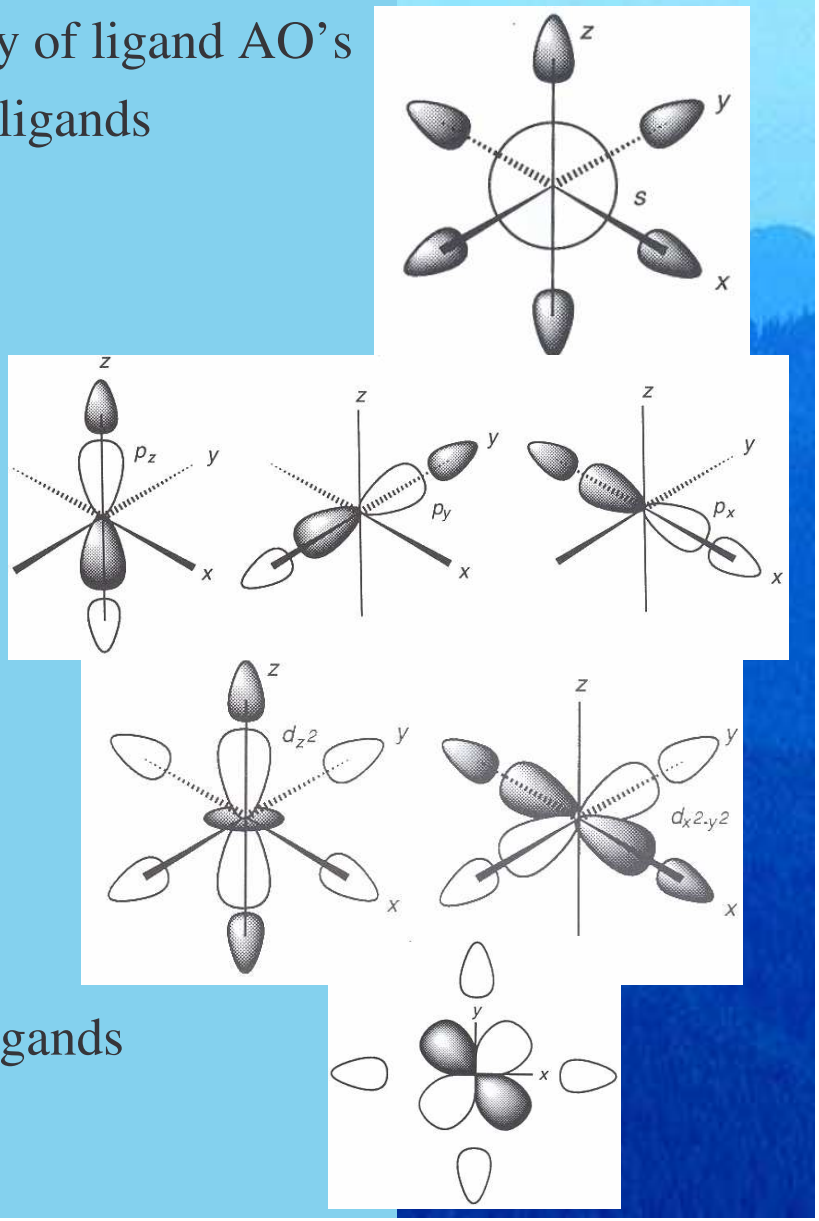
- Three sets of interaction based on symmetry of ligand AO's
  - Generally applicable to σ bonding TM ligands

- a_{1g} all ligand AO's in phase
  - Interaction with s orbital → 1

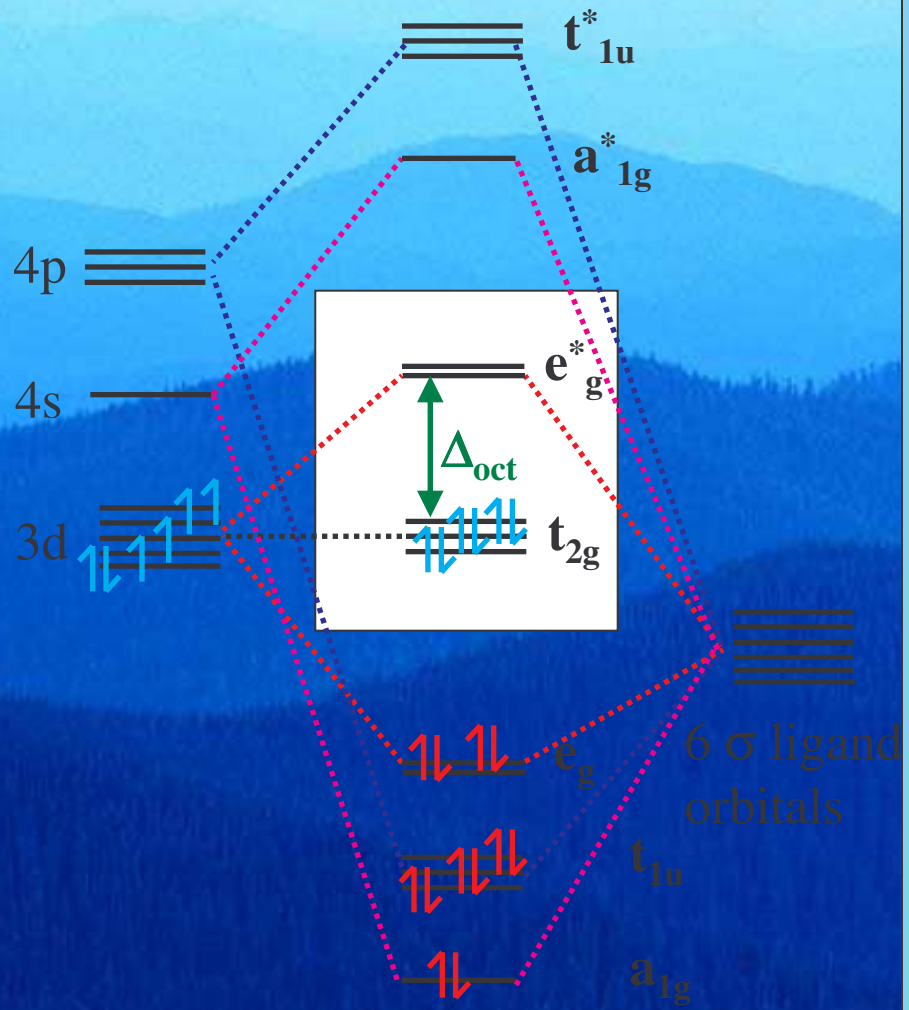
- t_{1u} ligands in one axis contribute
  - With opposite phase – one nodal plane
  - Interaction with *p* orbitals → 3

- e_g ligand phases have two nodal planes
  - Interact with d_{z^2} $d_{x^2-y^2}$ → 2

- Three remaining *d* orbitals point between ligands
  - zero overlap



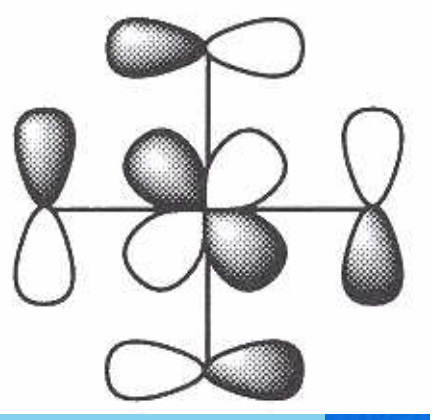
MO diagram for Tm $(\sigma\text{-L})_6$



- Electrons from filled σ orbitals on the ligands fill all the bonding orbitals
- d electrons fill t_{2g} (n.b.) and e^*_g
- Example is d^6 – e.g. Co^{3+}
- These are the orbitals considered in ligand field theory.
- Note the e^*_g is anti-bonding
- The size of Δ_{oct} is important
- We need to look at π interactions

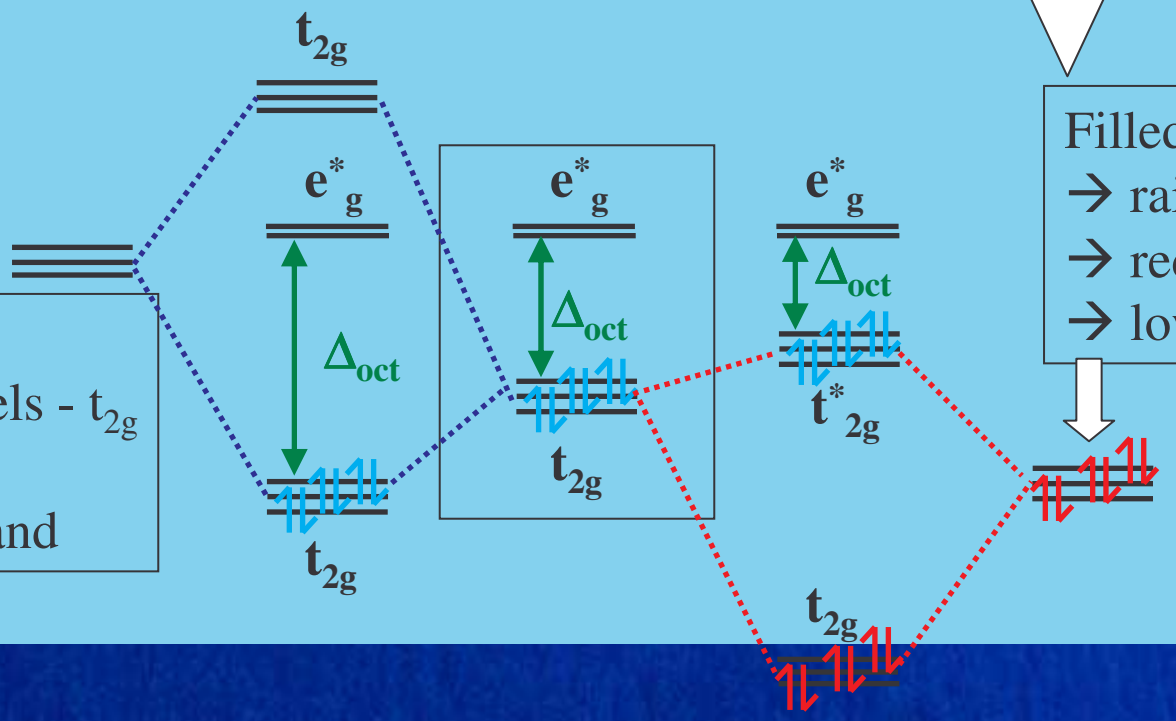
π interactions with TMs – High and Low Field Explained

- Orbitals with π character can interact with the t_{2g} *d* orbitals
  - Must be correct symmetry (t_{2g}) → 3 arrangements possible



- Two situations
  - Ligand orbitals are low energy and filled (e.g. F)
  - Ligand orbitals are high energy and empty (e.g. CO)

Empty p orbitals
→ Lowers d levels - t_{2g}
→ Large Δ_{oct}
→ high field ligand



Filled p orbitals
→ raises d levels -t^*_{2g}
→ reduces Δ_{oct}
→ low field ligand