Lecture 9; CH 101: Inorganic Chemistry

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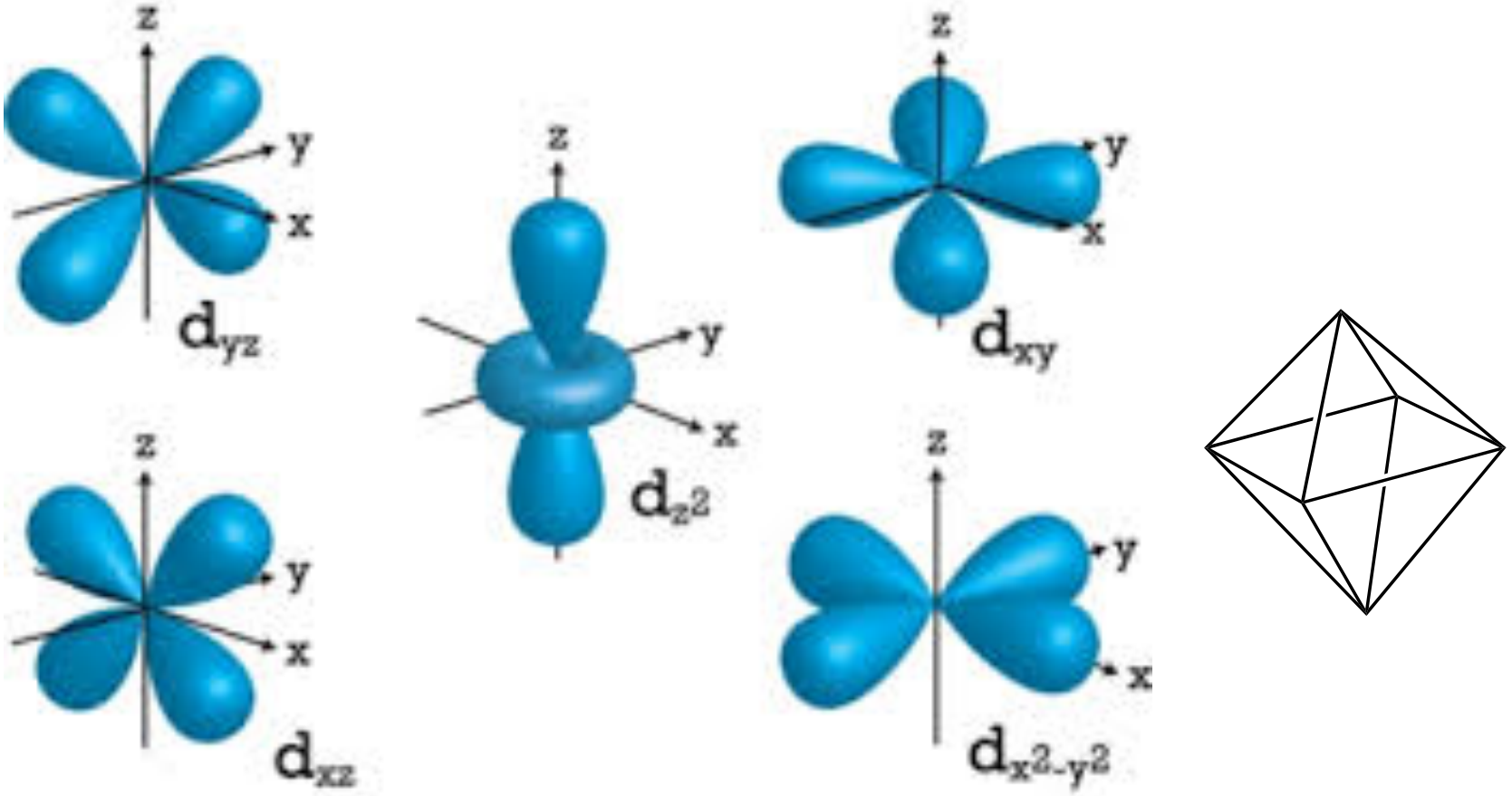
In neutral free atom, all d-orbitals have same energy (degenerate)



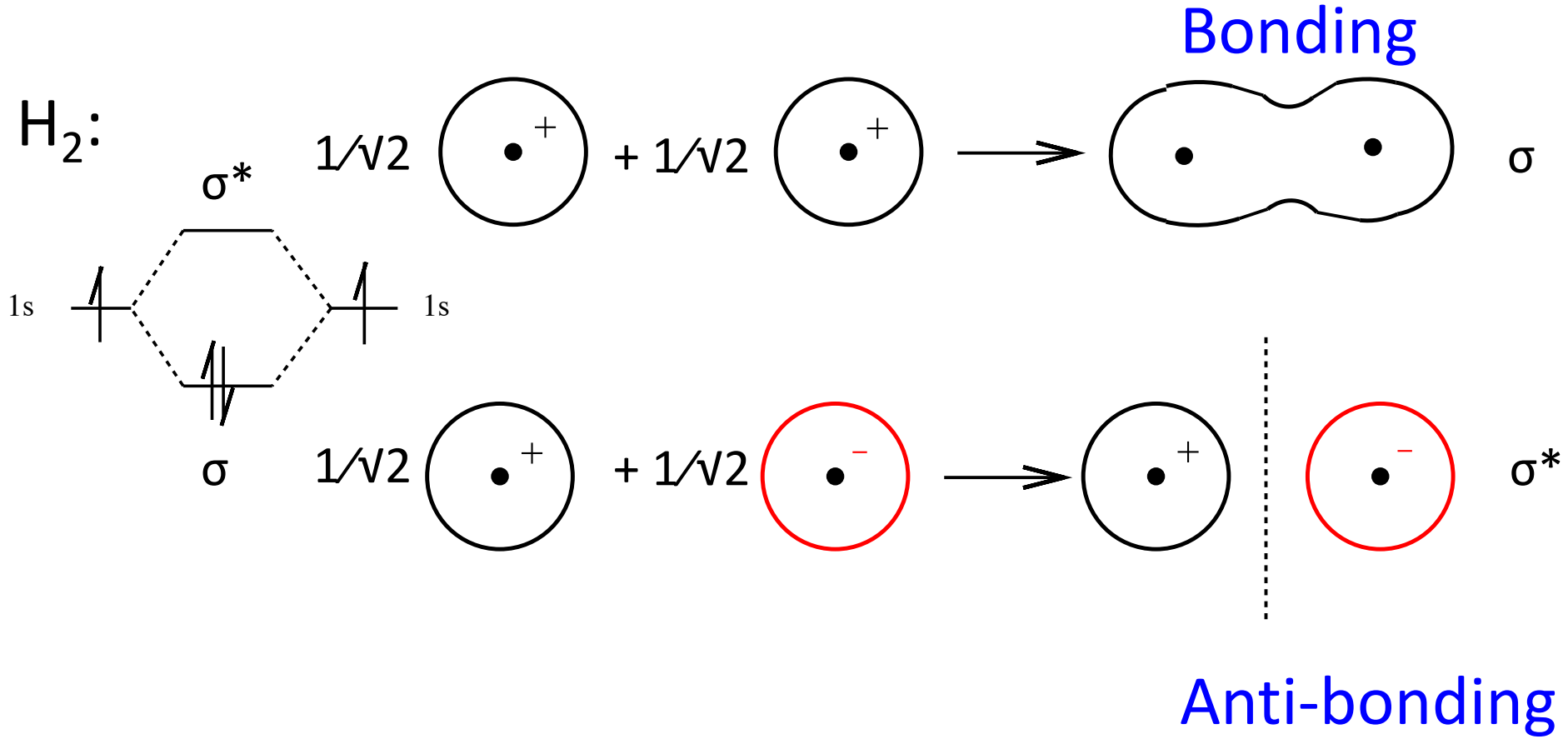
Crystal Field Theory –

- ✧ Gross over simplification and qualitative
- ✧ $d^{4,5,6,7}$ can be either high or low spin
- ✧ *High-field* ligands gives *low-spin* complexes
- ✧ Does not explain why certain ligands have a strong/weak ligand field
- ✧ Splitting of *d*-orbitals is considered as a “fact”

- ✧ Why is $W(NH_3)_6$ is not a stable compound?
- ✧ Why is $W(CO)_6$ is very air stable and unreactive?
- ✧ Why is $W(PMe_3)_6$ is very air-sensitive and reactive?
- ✧ Why d^0 systems such as Ti4+ cannot for stable carbonyl complexes?
- ✧ Is there a model that gives accurate electronic structure calculations?

Ligand Field

✧ Conventional Molecular Orbital (MO) Theory

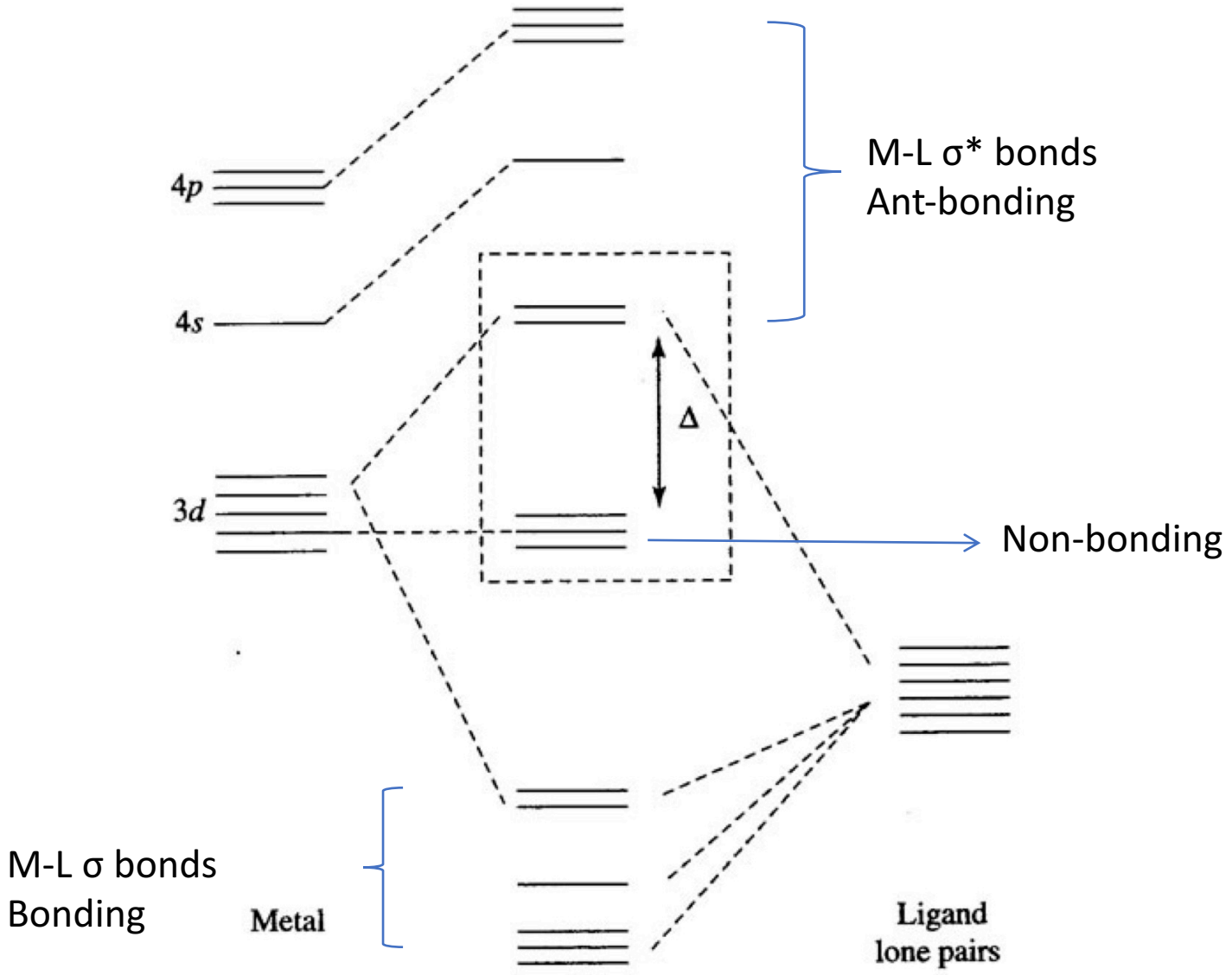


Ligand Field

- ✧ One *s*, three *p* and five *d*-orbitals of the isolated ion is taken into consideration

- ✧ 6 pure σ-donor ligands(NH_3) – 6 lone pair orbitals (6 ligand group atomic orbitals - LGAO)

- ✧ Octahedral case;
  One *s*, three *p* and two d_σ (dsp_σ) have right symmetry to interact with 6 LGAO's


4p
4s
3d
Δ
M-L σ* bonds
Ant-bonding
Non-bonding
M-L σ bonds
Bonding
Metal
Ligand
lone pairs

For pure σ-donating ligands d_π of CFT is non-bonding in MO

Similarly, d_σ of CFT is M-L σ anti-bonding in MO

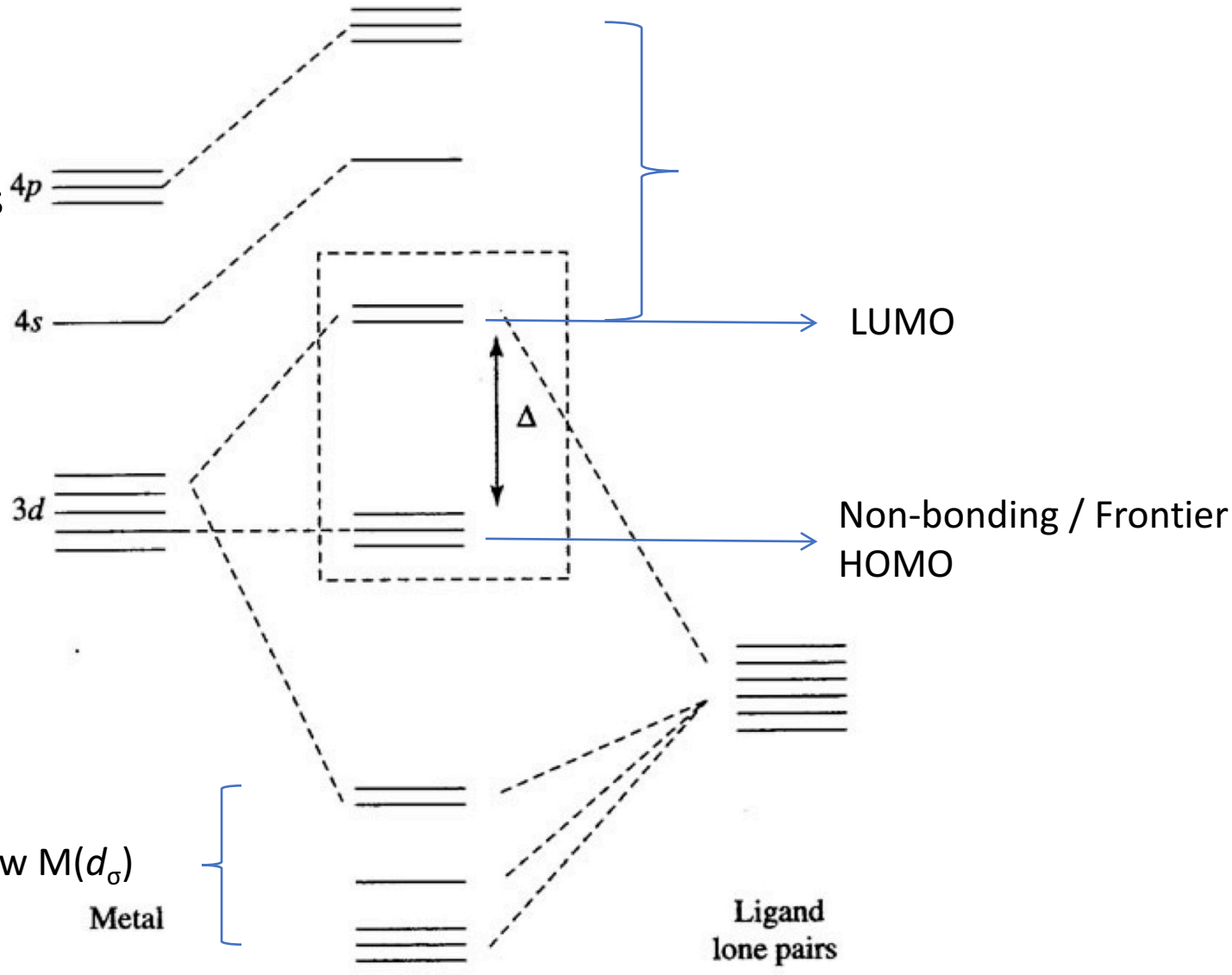
d^6 complex; 6e from metal, 12 e from ligand

18 e occupy the levels up to d_π

Splitting increases with increase in strength of M-L σ-bond

High-field σ-donating ligands form strong σ-bonds

As most bonding (and therefore "chemistry") occurs in the valence (or "frontier") orbitals of a compound, most reactions of metal complexes occur at the metal centre.



L(σ) always lies below M(d_σ)

More L character

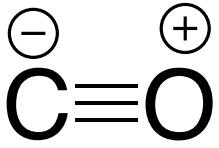
$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PPh_3 < CO, H < SnCl_3^-$$

← low Δ high Δ →

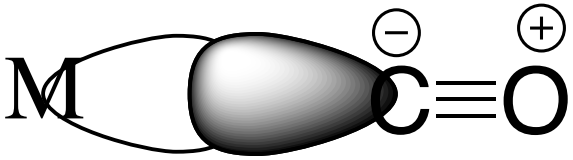
← π donor π acceptor/strong σ donor →

How about ligands that also have π-acceptors? CO?

Bonding in Metal Carbonyls

Valence bond structure of CO; 

(formally, a carbanion)



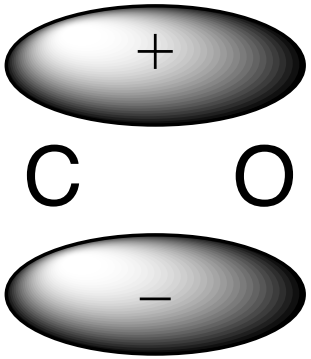
Vague explanation of M-CO bonding. Does not describe why transition metals form much stronger bonds with CO than main group metals

$H_3B \leftarrow : C \equiv O$ 23 kcal/mol

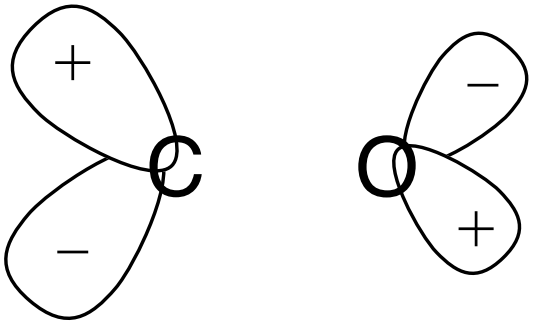
$(CO)_5W \leftarrow : C \equiv O$ 42.5 kcal/mol

$(PR_3)_2ClIr \leftarrow : C \equiv O$ > 70 kcal/mol

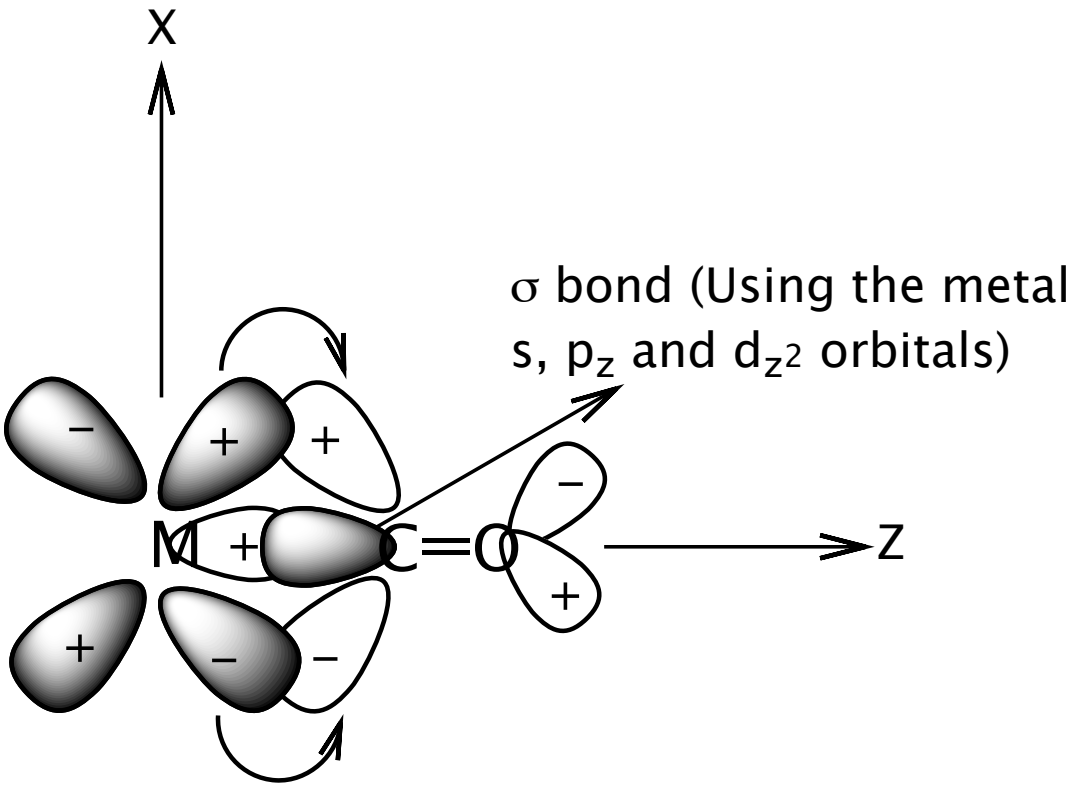
π



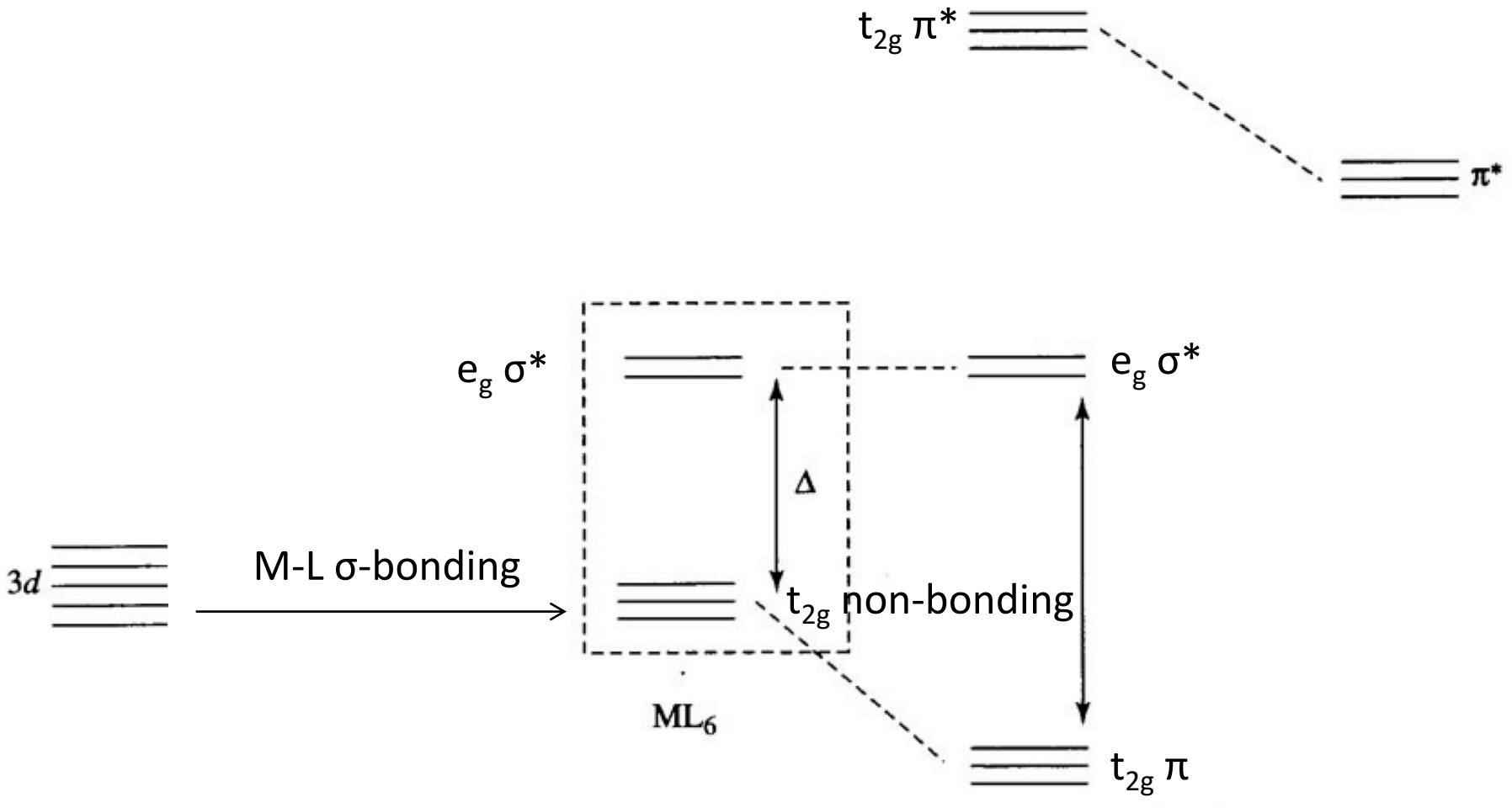
π*



Bonding in Metal Carbonyls



Metal-Ligand π-bonding



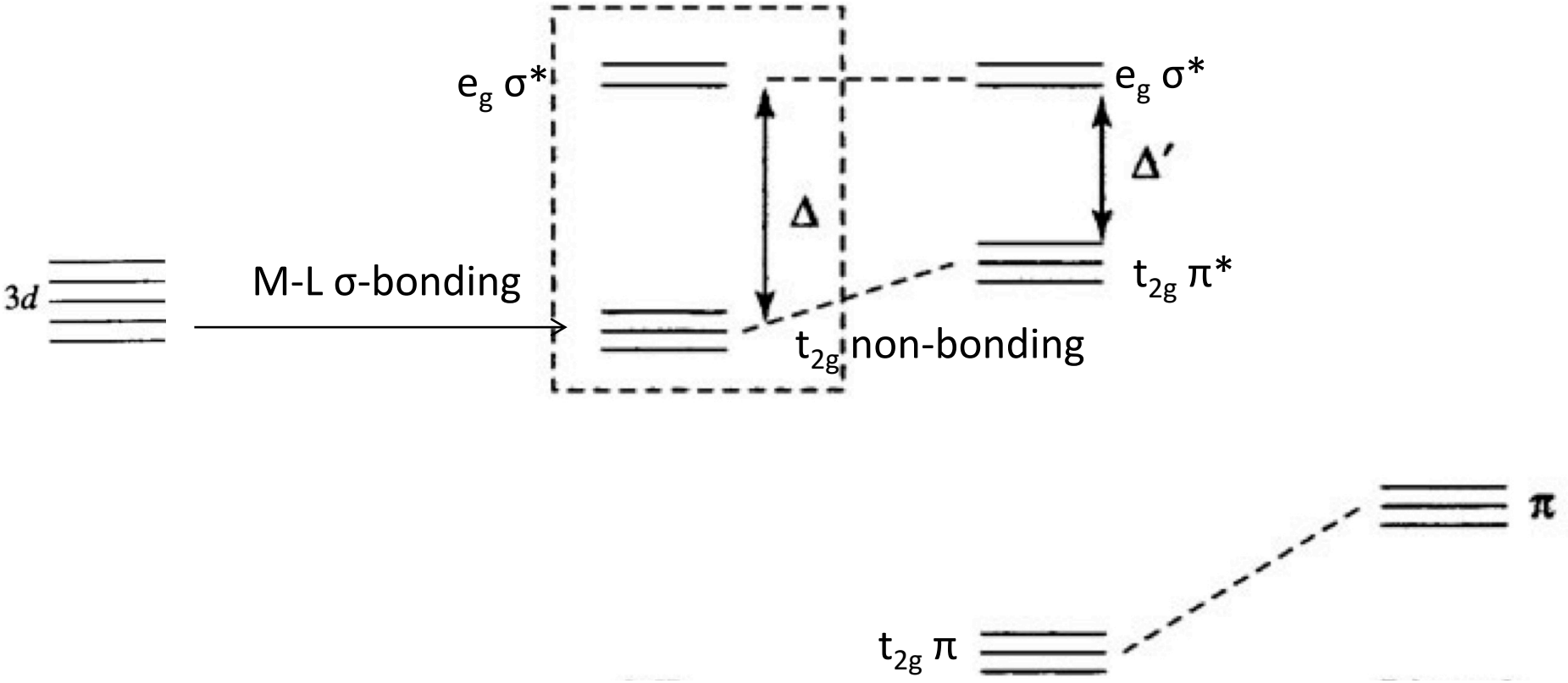
M **L**

Ligands that are π-donors are Low-Field
(OR^-, F^- and Cl^-)

d_π electrons are destabilized. Repulsion between two filled orbitals in case of d^6 resulting in lowering of Δ and weaker M-L bonds
(compared to that in case of π-acceptors)

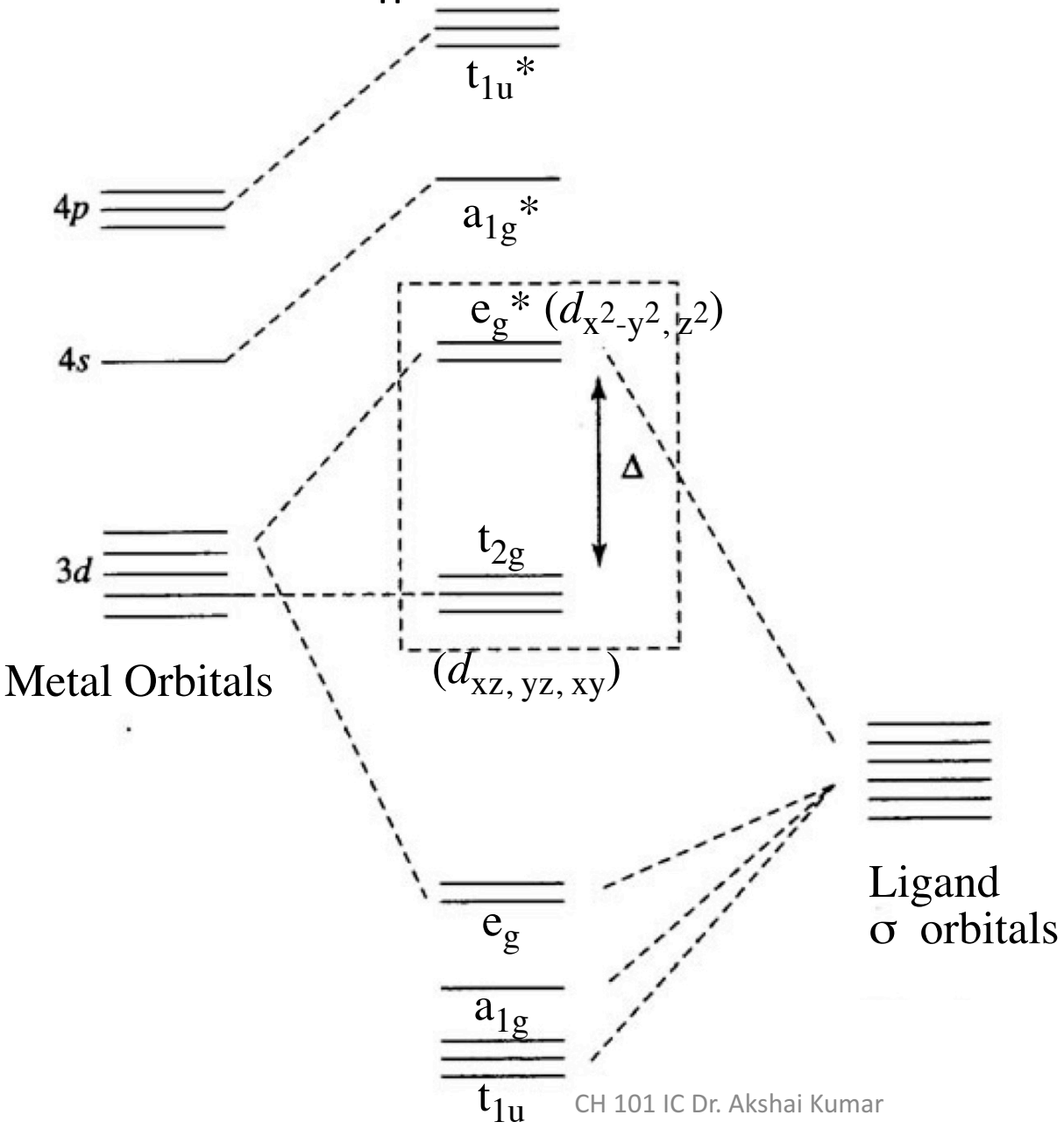
But stronger bonds in case of d^0 metals $[TiF_6]^{2-}$
$W(OMe)_6$

Ligands that are π-donors are Low-Field (OR^-, F^- and Cl^-)

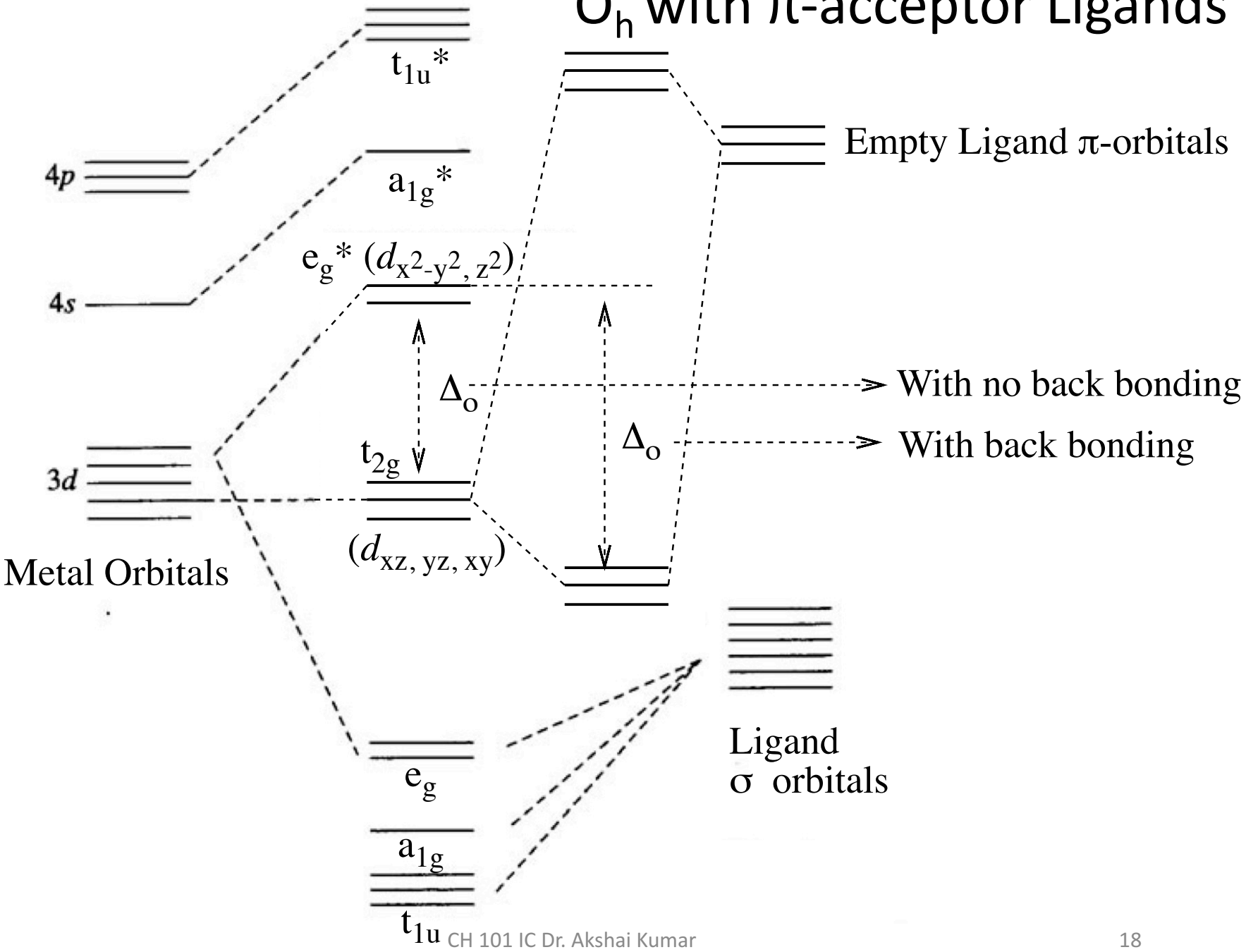


MO Diagram: O_h

O_h with σ -donor Ligands



O_h with π-acceptor Ligands



O_h with π-donor Ligands