

# Lecture 4; CH 101: Inorganic Chemistry

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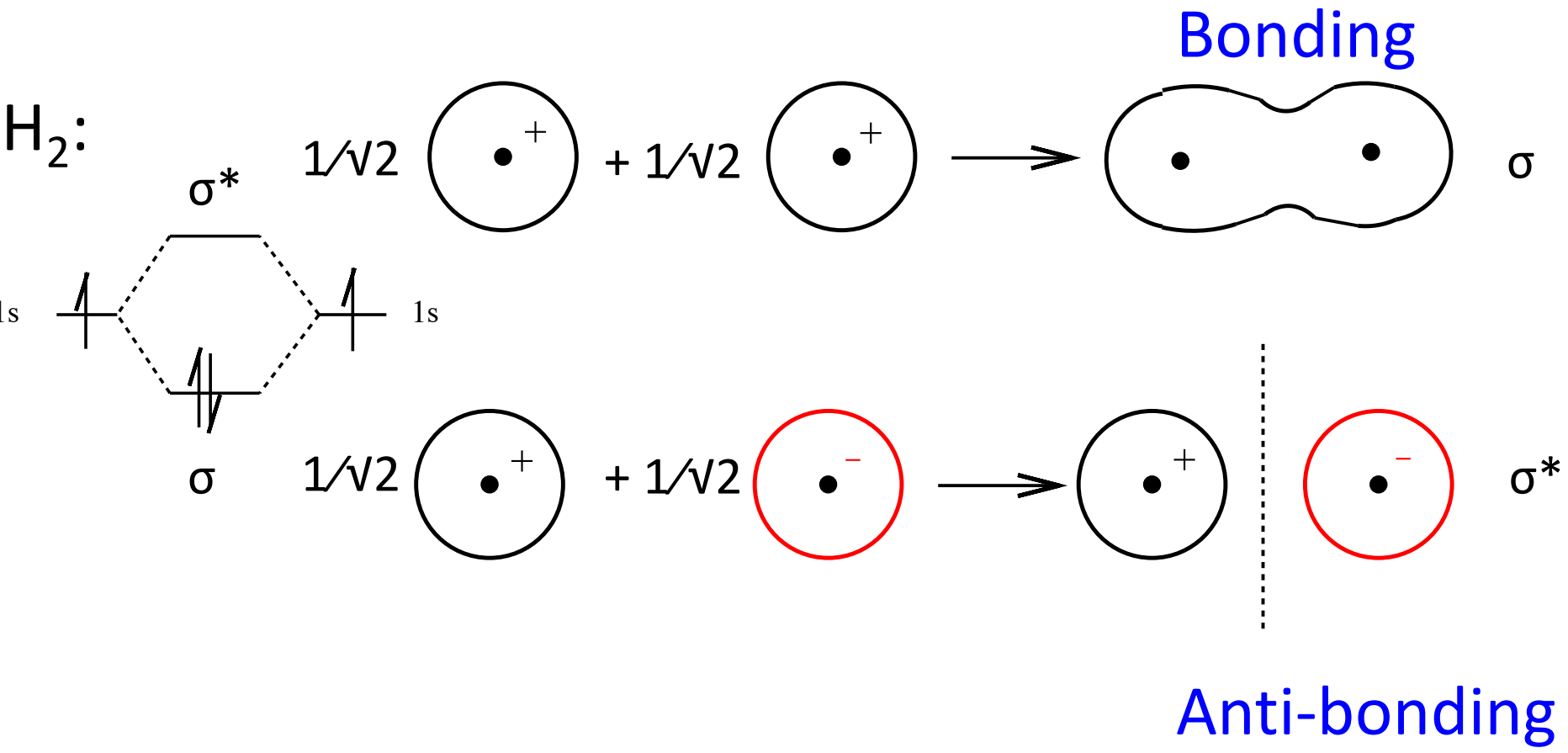
# Crystal Field Theory –

- ✧ 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  $Ti^{4+}$  cannot form 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  $\sigma$ -donor ligands( $\text{NH}_3$ ) – 6 lone pair orbitals (6 ligand group atomic orbitals - LGAO)
- ✧ Octahedral case;  
One  $s$ , three  $p$  and two  $d_\sigma$  ( $dsp_\sigma$ ) have right symmetry to interact with 6 LGAO's

# MO Diagram: $O_h$

## $O_h$ with $\sigma$ -donor Ligands

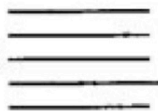
4p



4s



3d



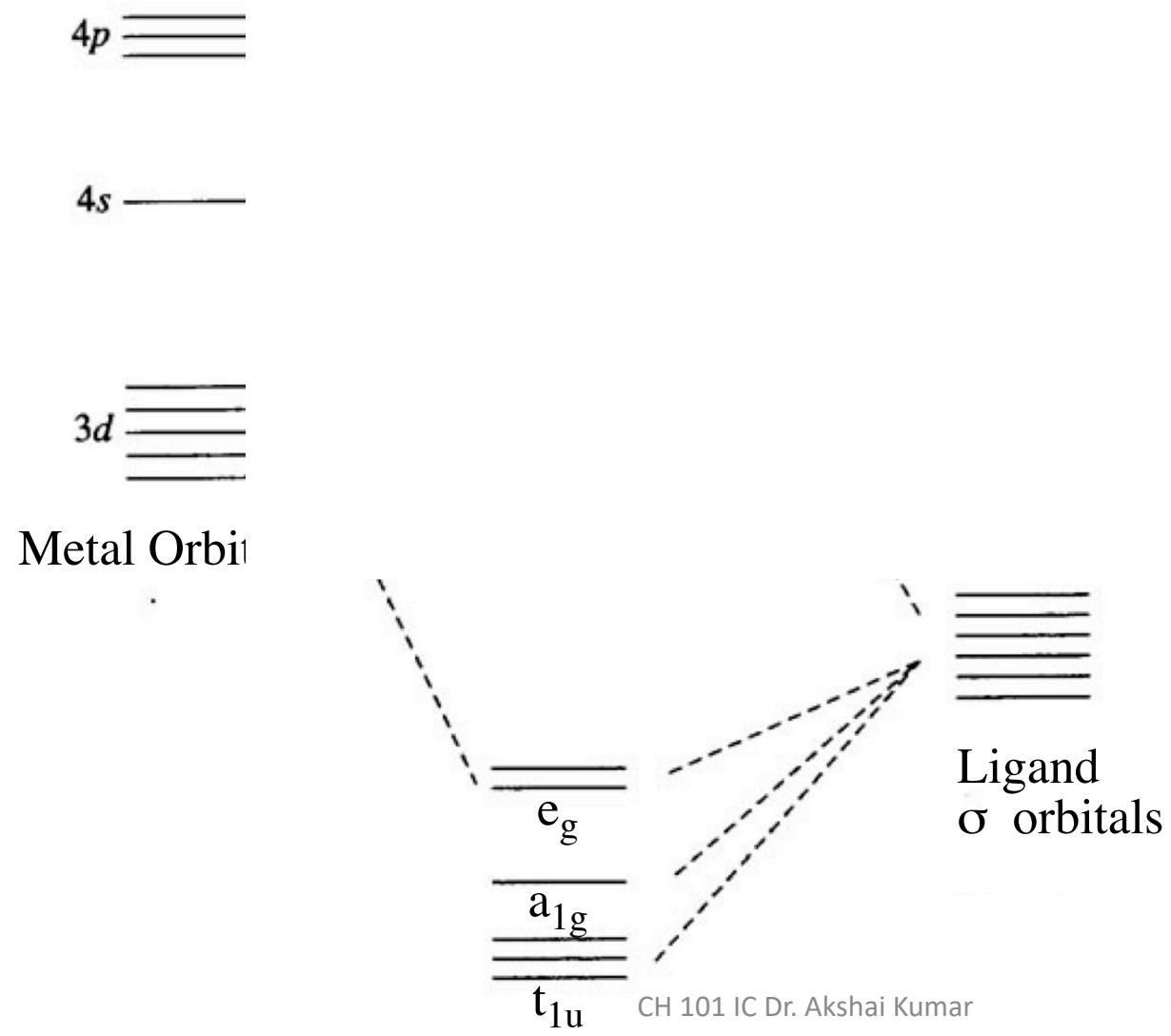
Metal Orbitals



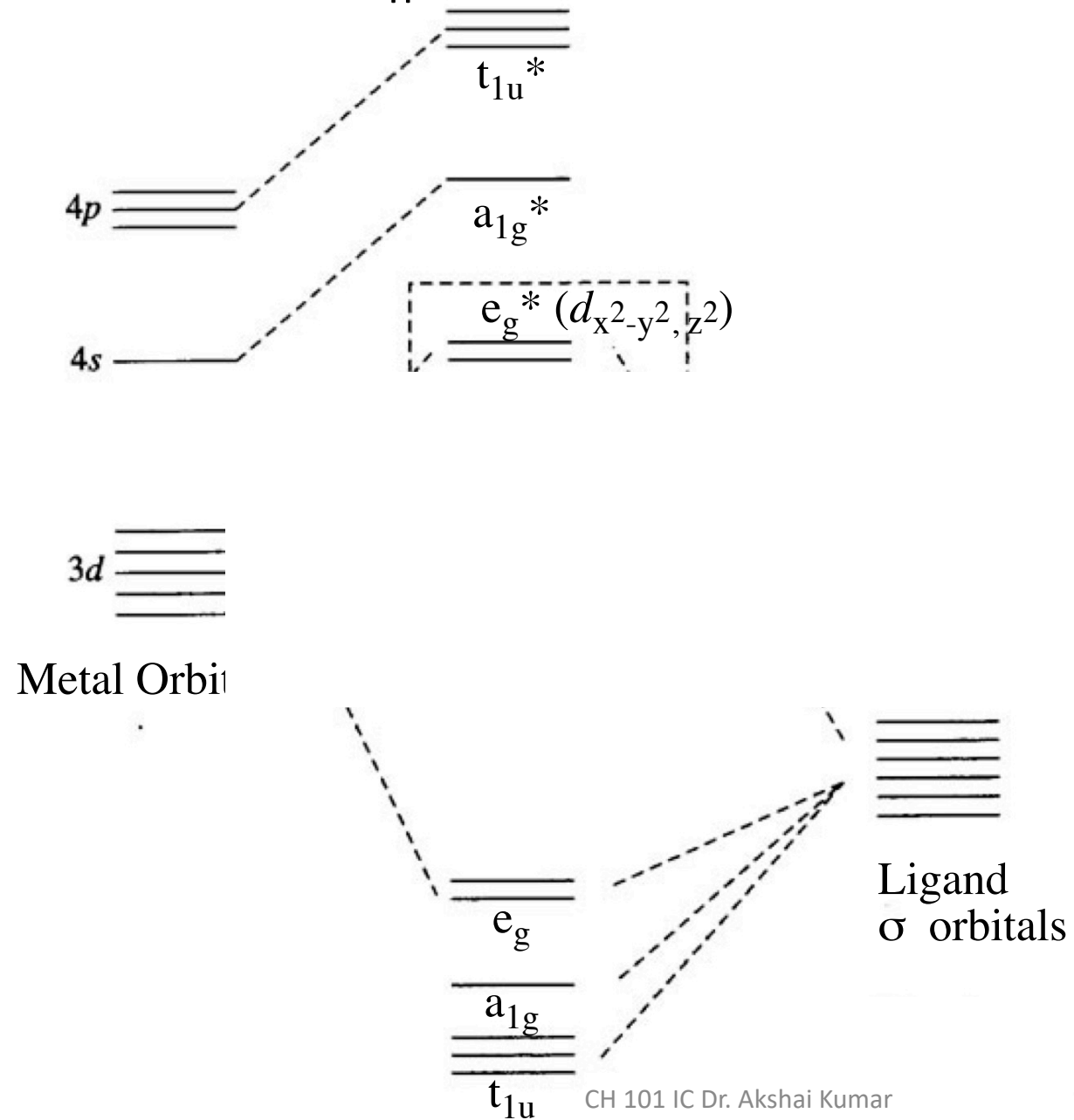
Ligand  
 $\sigma$  orbitals

MO Diagram:  $O_h$

$O_h$  with  $\sigma$ -donor Ligands



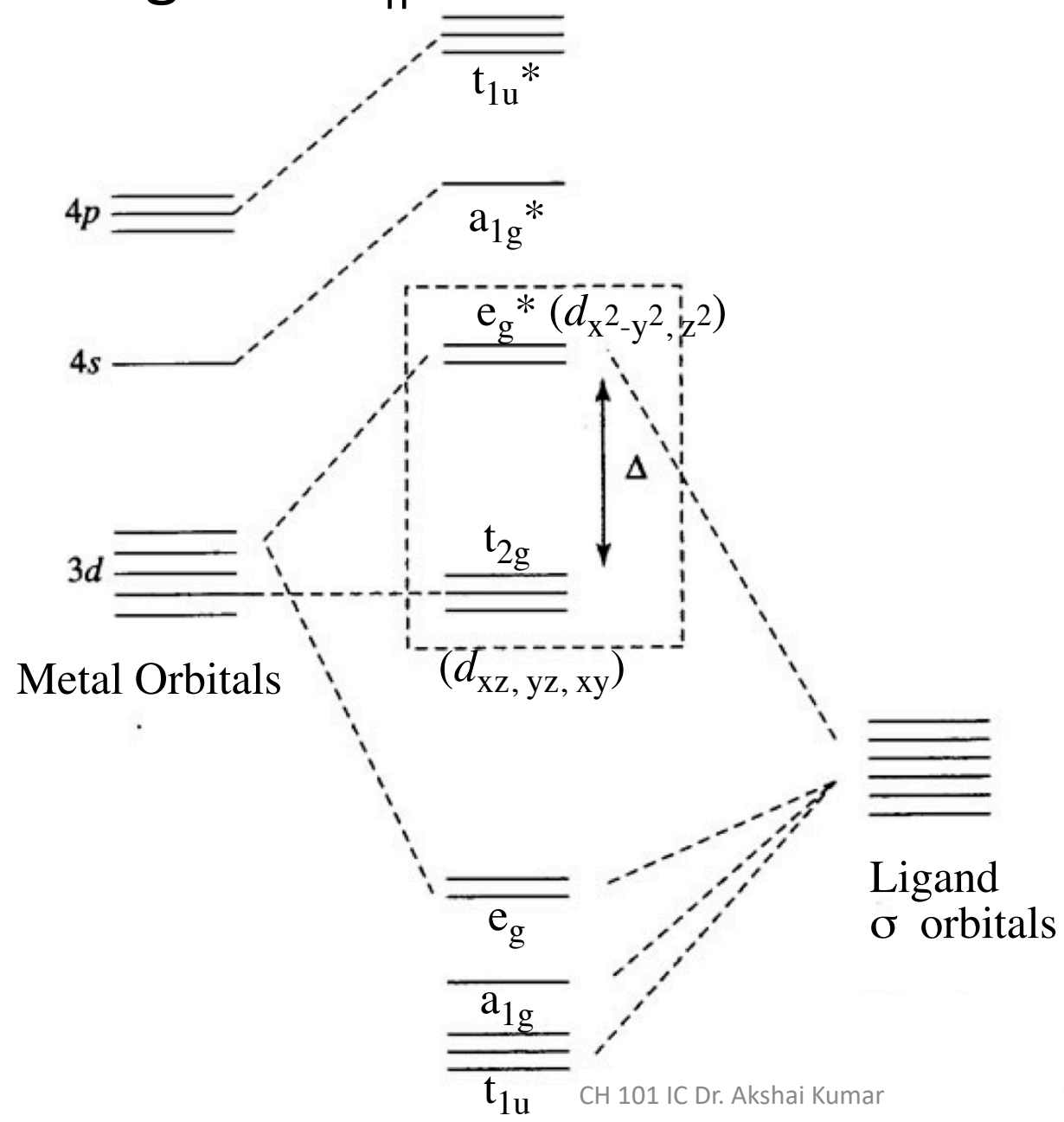
# MO Diagram: $O_h$ $O_h$ with $\sigma$ -donor Ligands





MO Diagram:  $O_h$

$O_h$  with  $\sigma$ -donor Ligands



For pure  $\sigma$ -donating ligands  $d_\pi$  of CFT is non-bonding in MO

Similarly,  $d_\sigma$  of CFT is M-L  $\sigma$  anti-bonding in MO

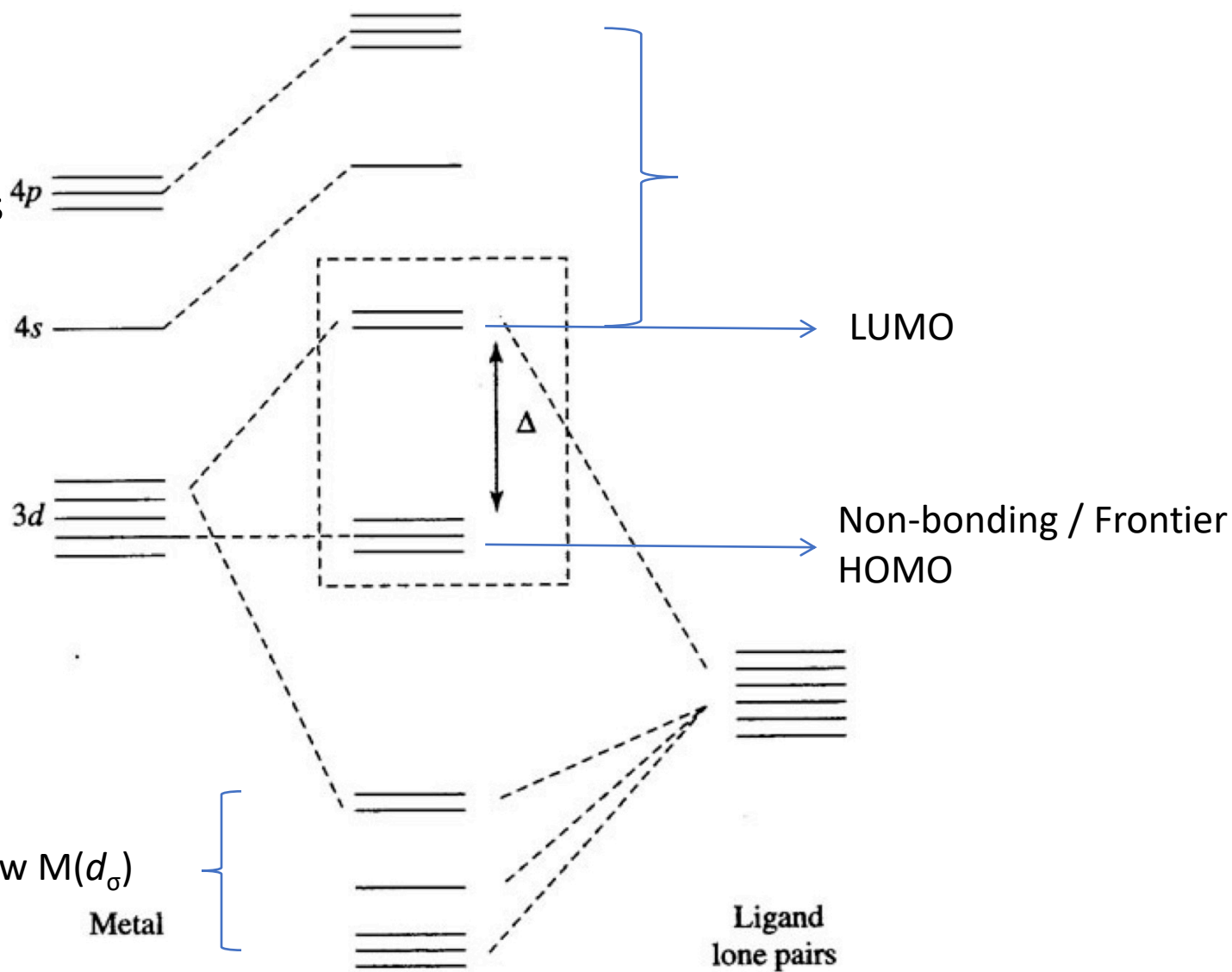
$d^6$  complex; 6e from metal, 12 e from ligand

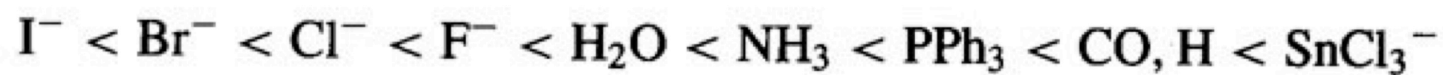
18 e occupy the levels up to  $d_\pi$

Splitting increases with increase in strength of M-L  $\sigma$ -bond

High-field  $\sigma$ -donating ligands form strong  $\sigma$ -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.





← low  $\Delta$

high  $\Delta$  →

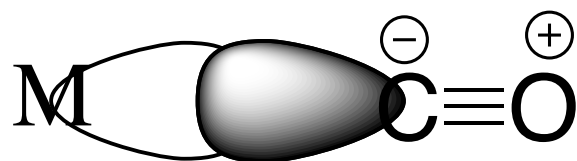
←  $\pi$  donor

$\pi$  acceptor/strong  $\sigma$  donor →

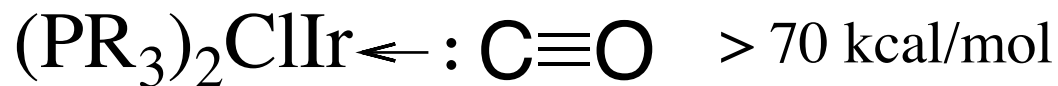
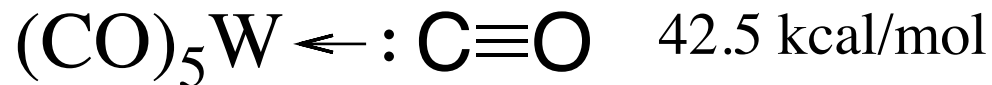
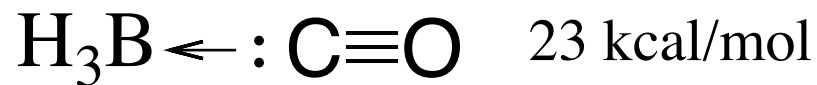
How about ligands that also have  $\pi$ -acceptors? CO?

## Bonding in Metal Carbonyls

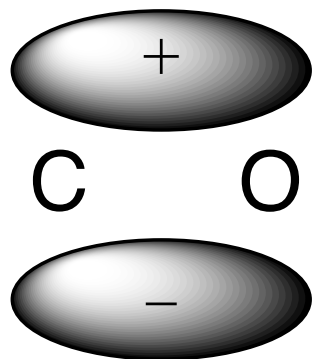
Valence bond structure of CO;  $\overset{\ominus}{\text{C}} \equiv \overset{\oplus}{\text{O}}$   
(formally, a carbanion)



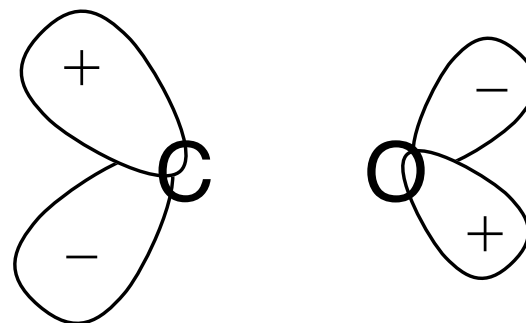
Vague explanation of M-CO bonding. Does not describe why transition metals form much stronger bonds with CO than main group metals



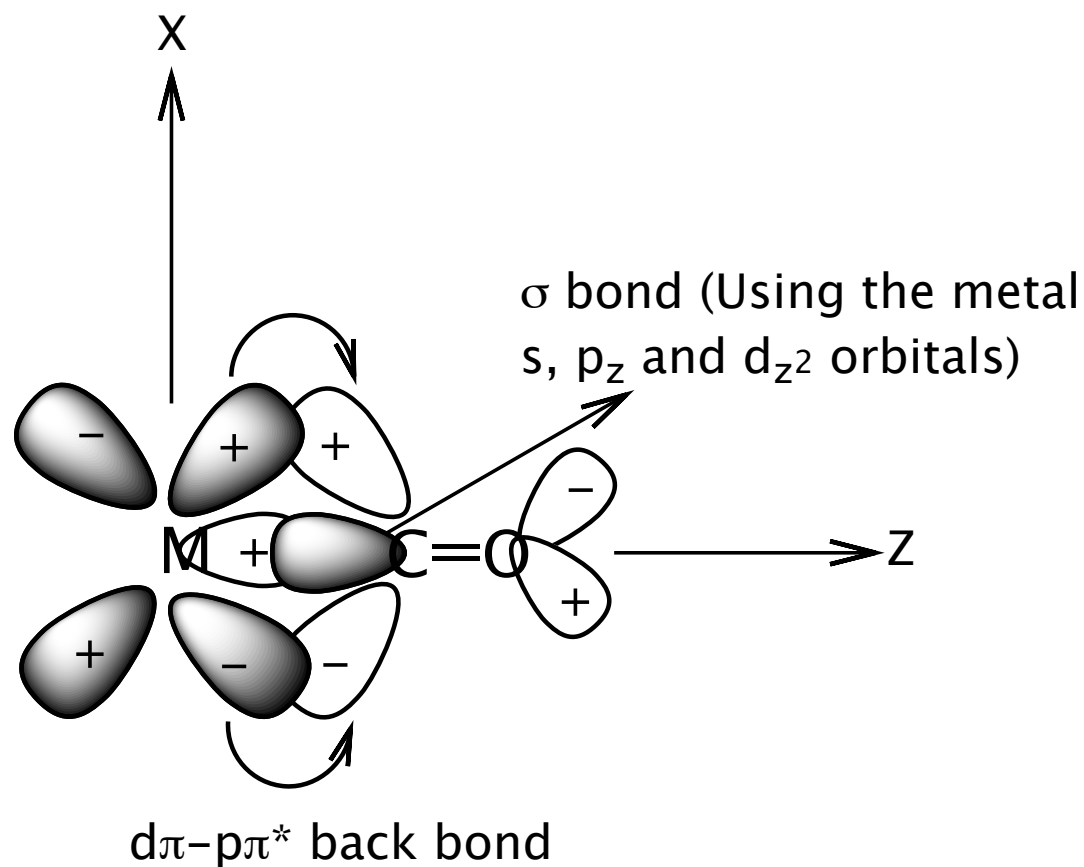
$\pi$



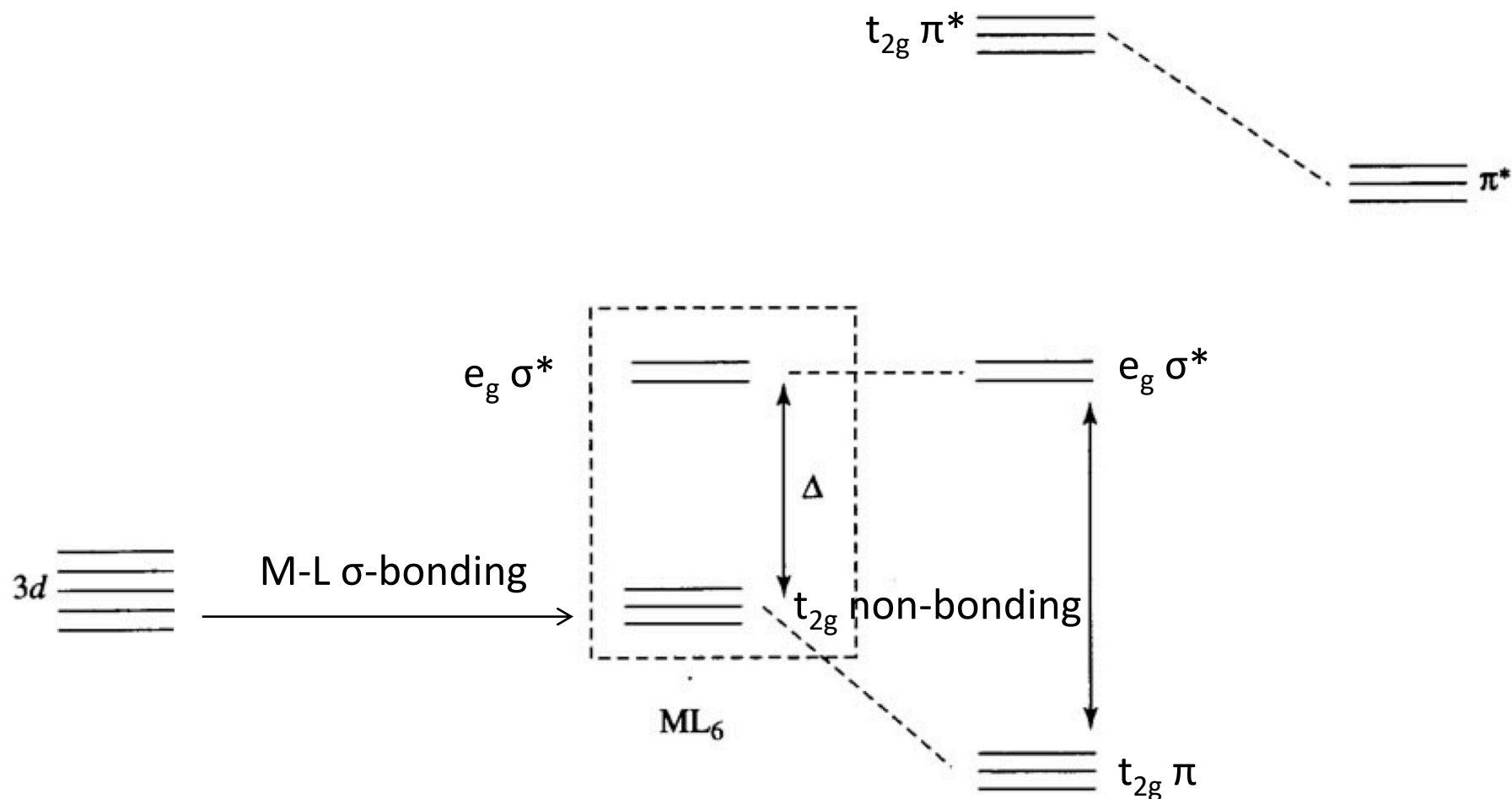
$\pi^*$



# Bonding in Metal Carbonyls



# Metal-Ligand $\pi$ -bonding



**M**

**L**



# $O_h$ with $\pi$ -acceptor Ligands

