Lesson Overview
Advanced Bonding Theories

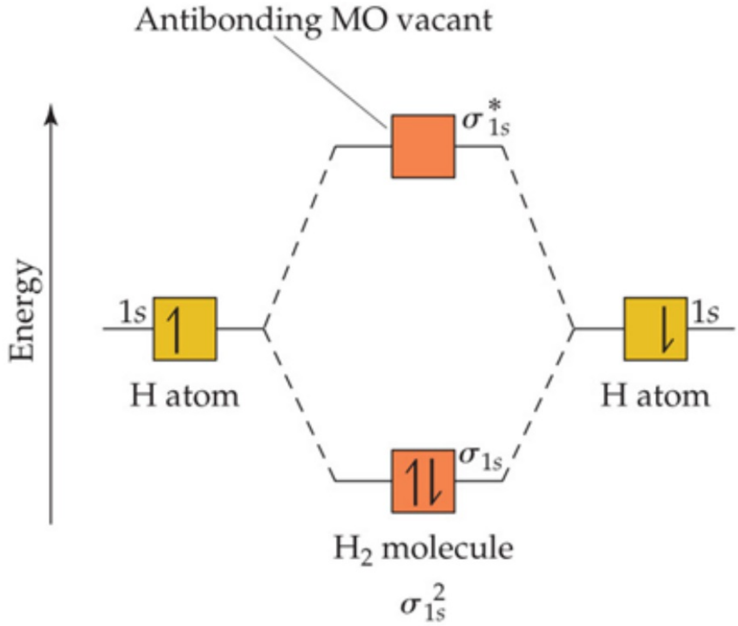
Objective: The student will be able to demonstrate how Molecular Orbital (MO) and Crystal Field (CF) Theories adjust for the failings of Valence-Bond (VB) and Valence-Shell Electron-Pair Repulsion (VSEPR) Theories.

Molecular Orbital Theory

What question does MO theory seek to answer?

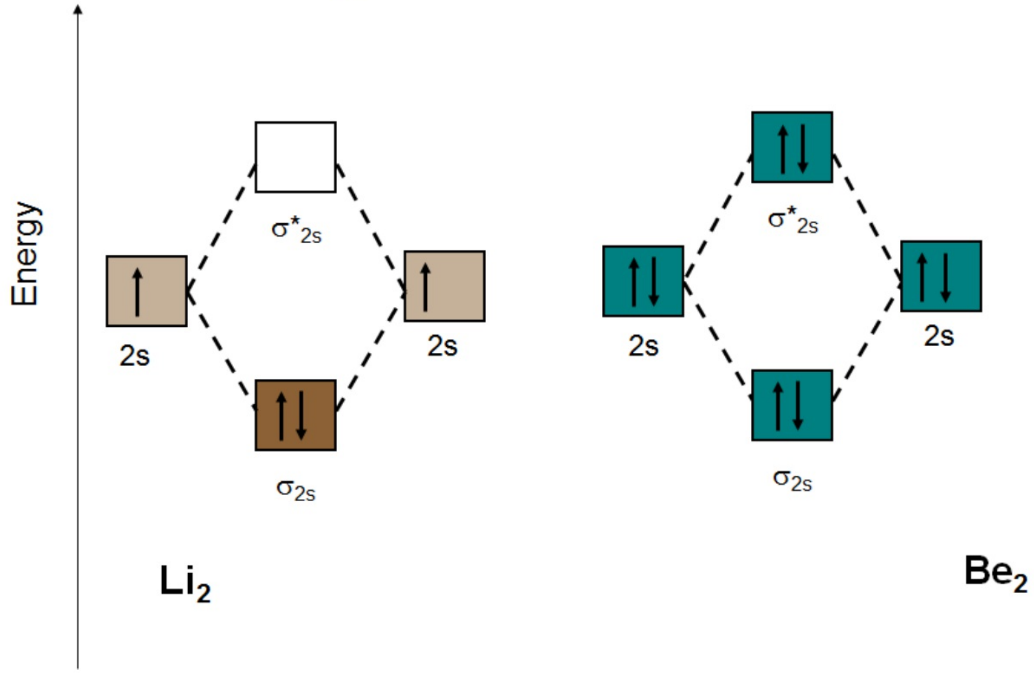
VB: bond order, resonance

VSEPR: shape of molecule



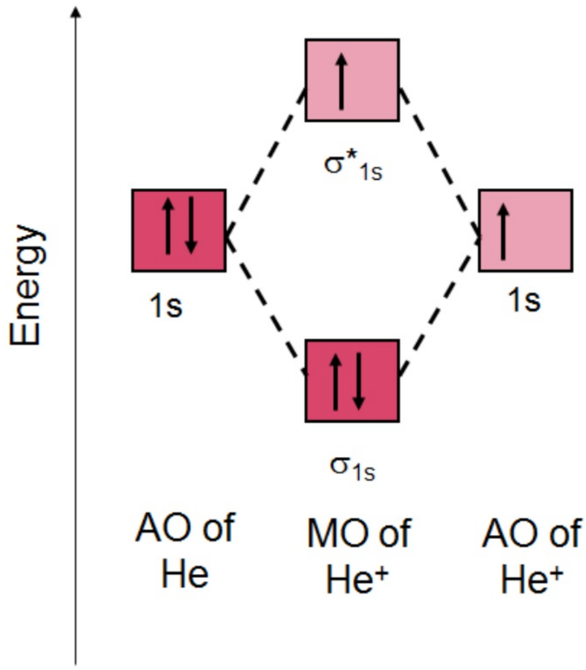
Molecular Orbital Theory Applications

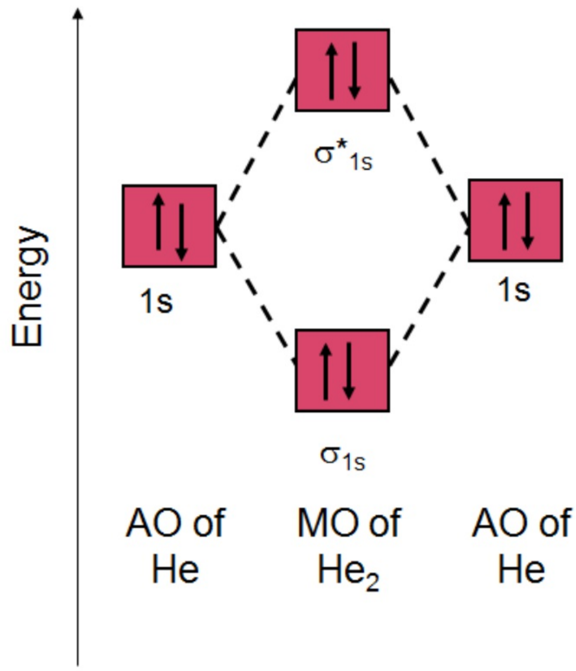
Use to predict the existence and/or stability of a substance through a bond order calculation.



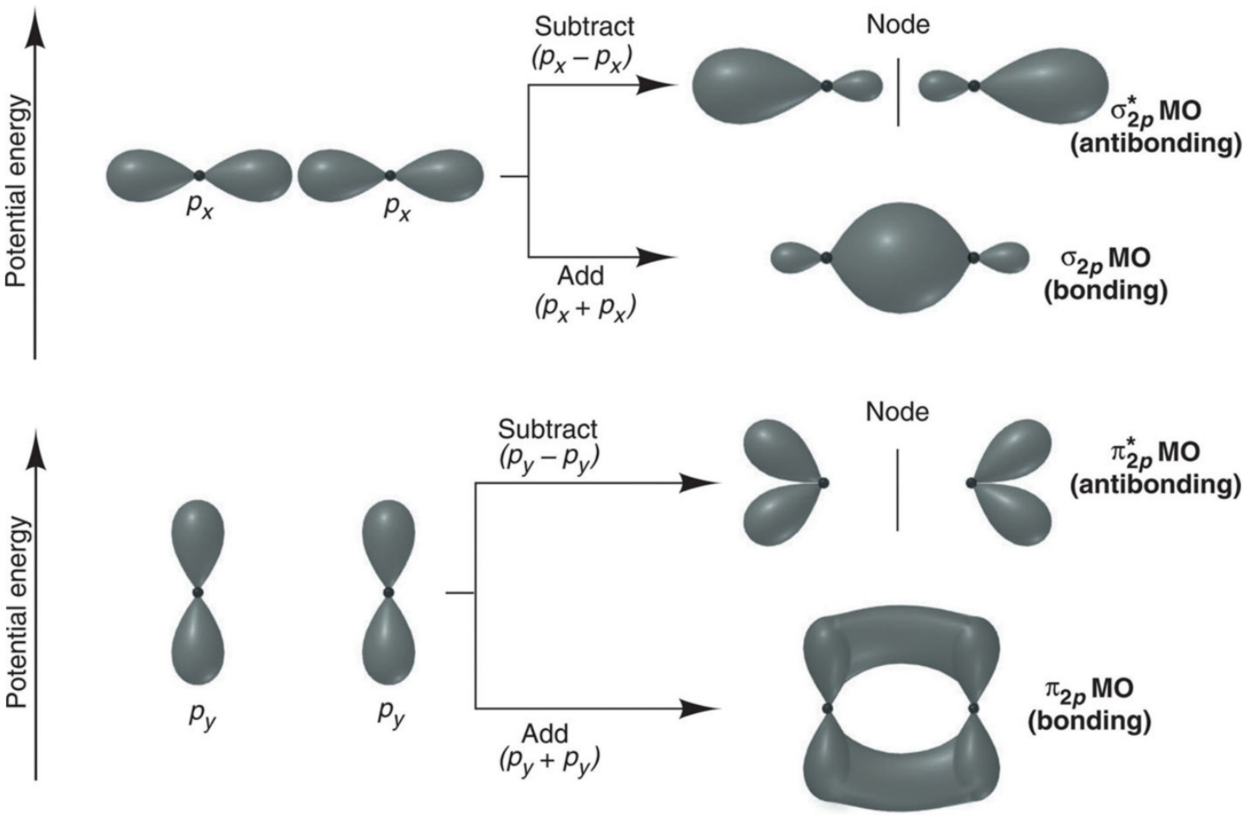
Molecular Orbital Examples

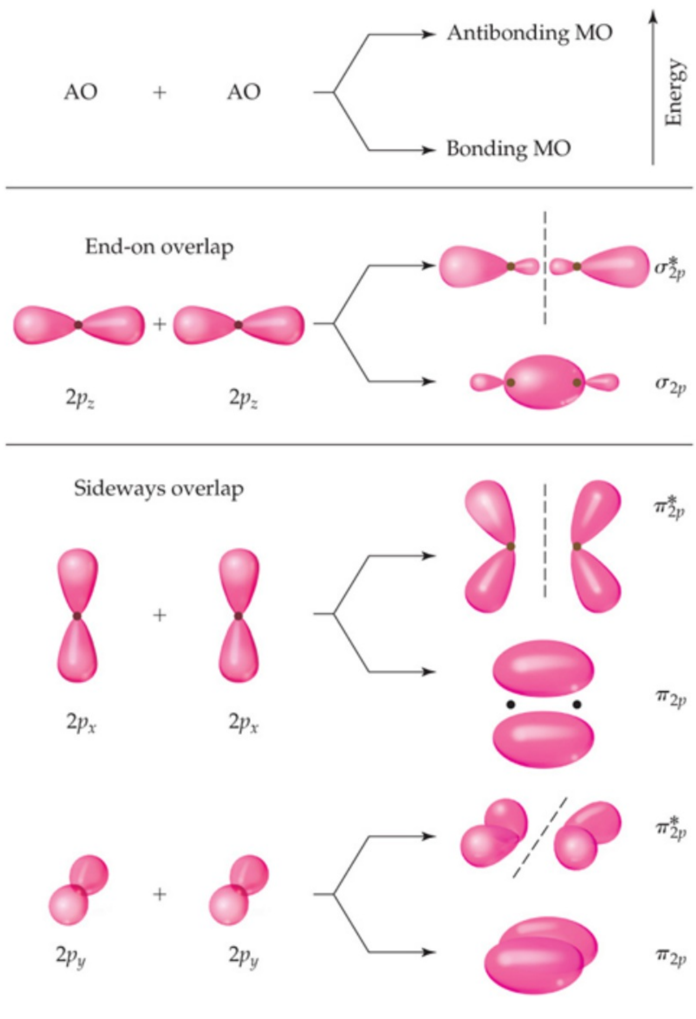
Determine whether these two molecules exist based on a BO calculation:



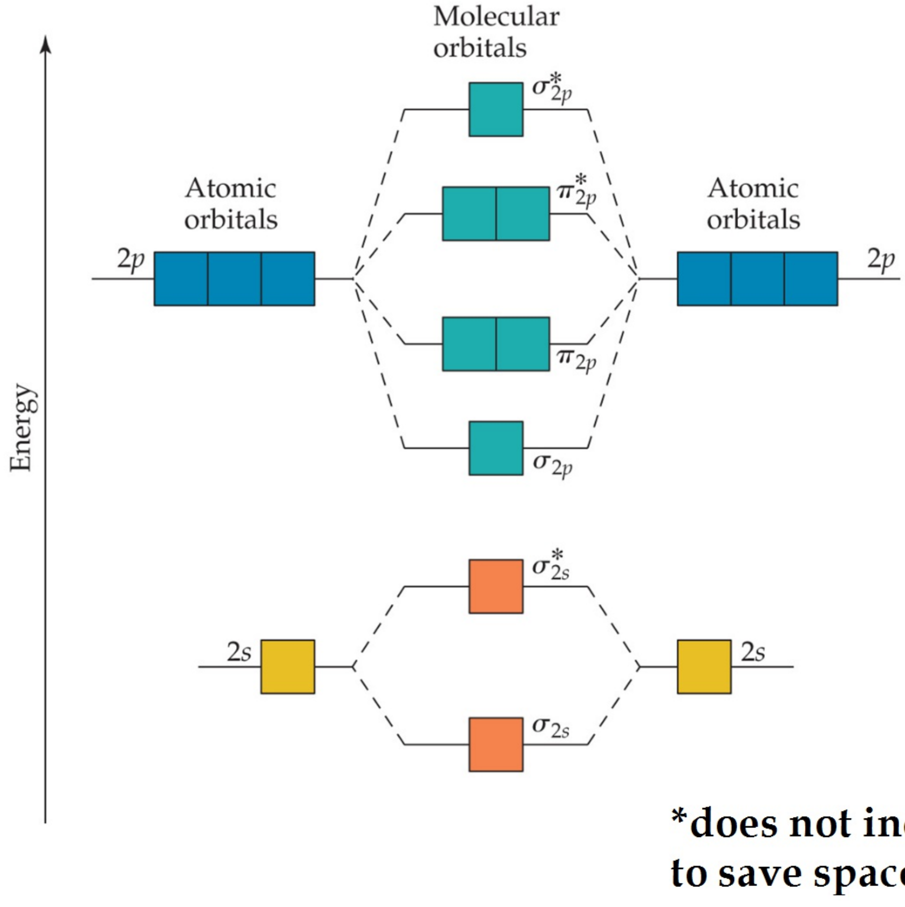


Bonding and Anti-bonding



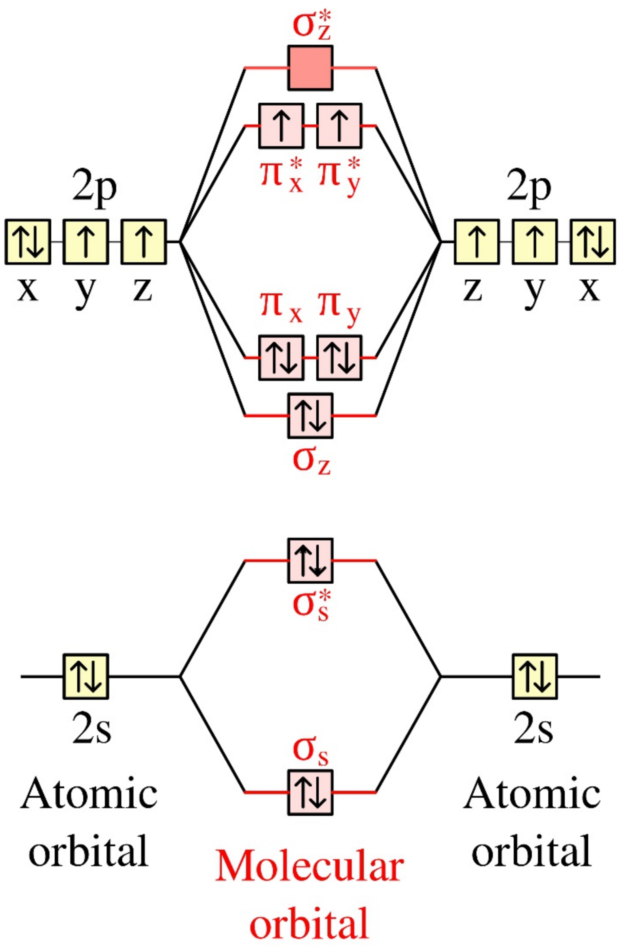

AO
+
AO
Antibonding MO
Bonding MO
Energy
End-on overlap
$2p_z$
$2p_z$
σ^*_{2p}
σ_{2p}
Sideways overlap
$2p_x$
$2p_x$
π^*_{2p}
π_{2p}
$2p_y$
$2p_y$
π^*_{2p}
π_{2p}

MO diagrams* introducing *p* orbitals



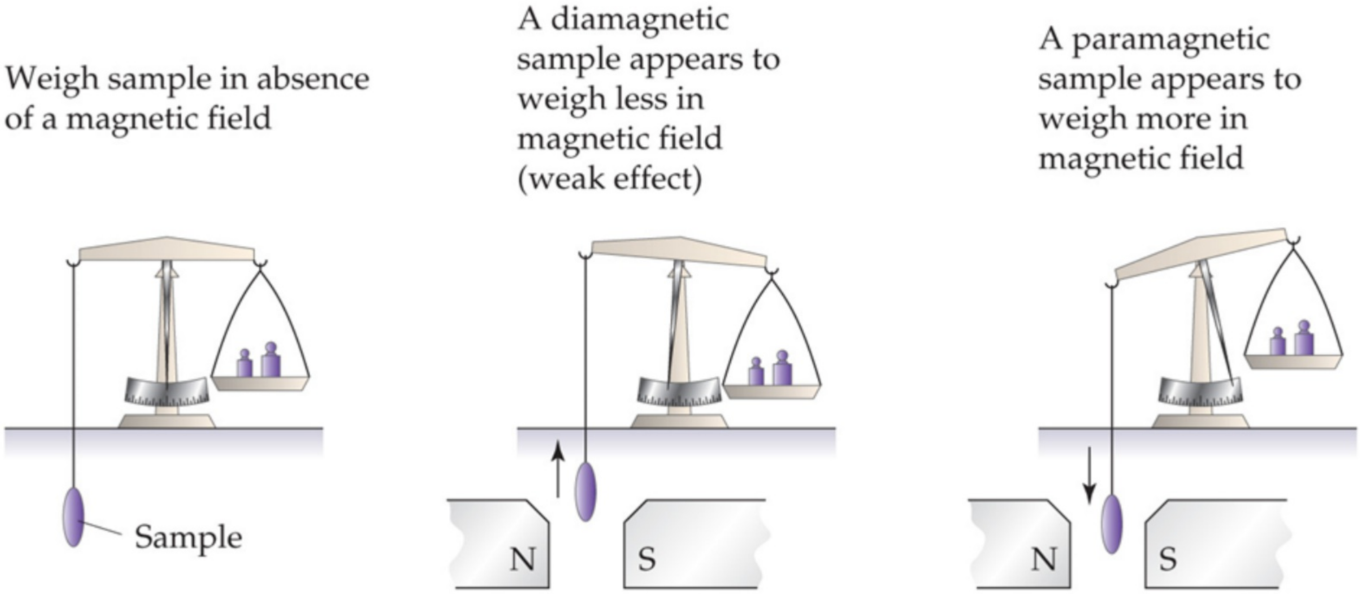
***does not include 1*s* orbital to save space**

O_2: Valence Bond Diagram



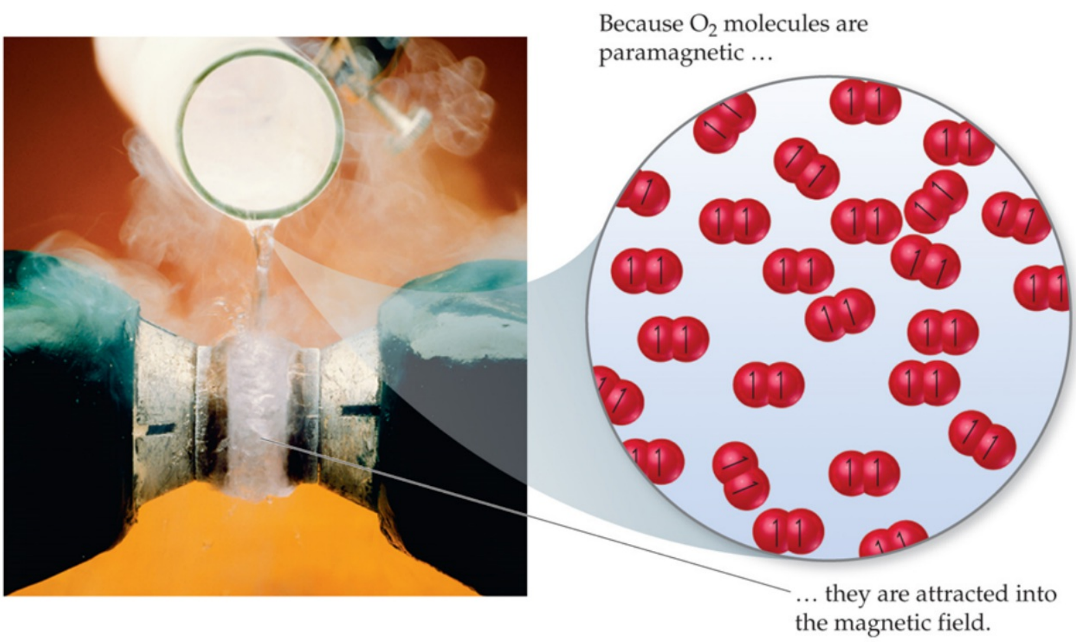
para & diamagnetism

Paramagnetism vs. Diamagnetism

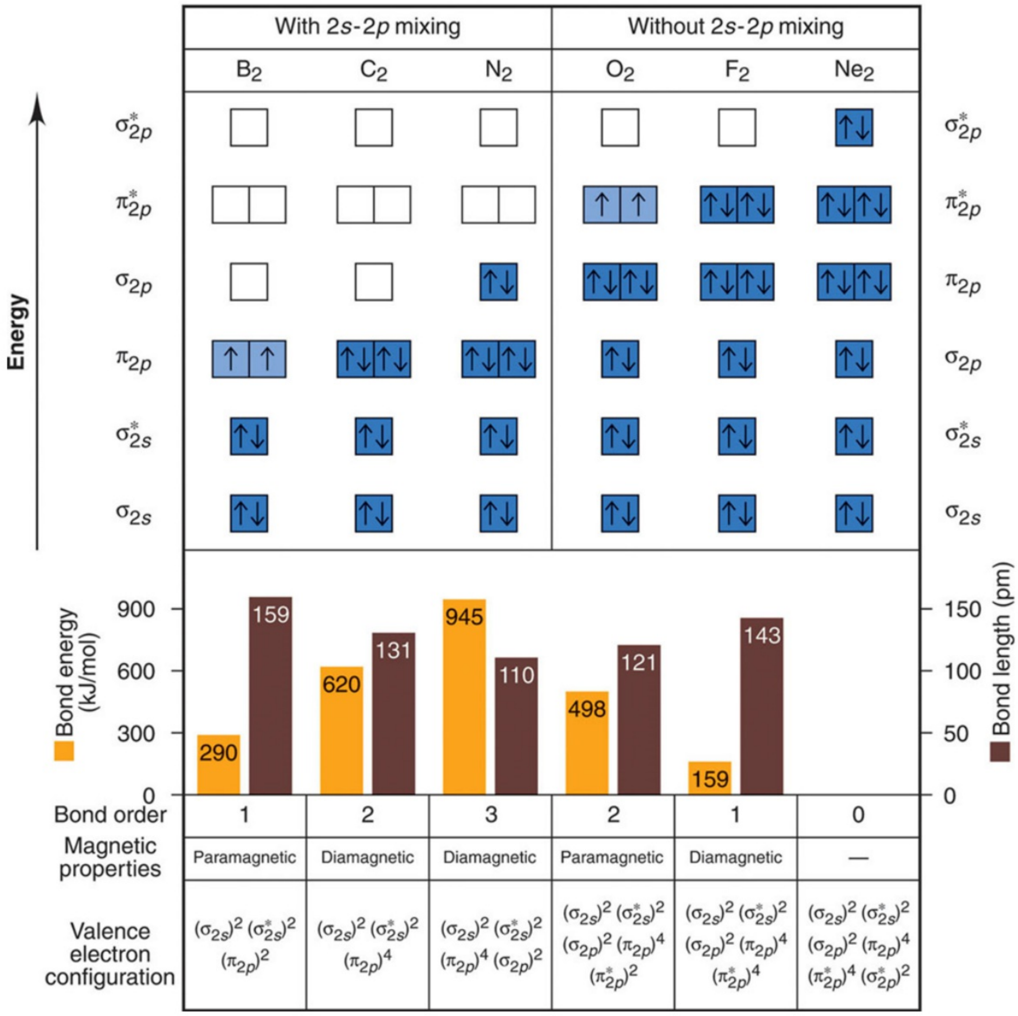


Due to the attraction or repulsion of the magnetic field

The paramagnetic nature of O_2



Comment: VB theory vs. MO theory.



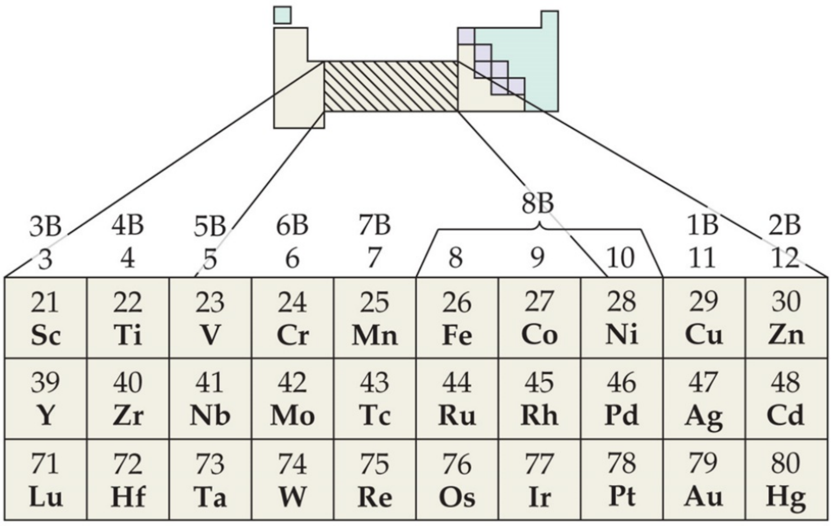
With 2s-2p mixing
Without 2s-2p mixing
B2
C2
N2
O2
F2
Ne2
Energy
σ*2p
π*2p
σ2p
π2p
σ*2s
σ2s
Bond energy (kJ/mol)
Bond length (pm)
900
600
300
0
150
100
50
290
159
620
131
945
110
498
121
159
143
Bond order
1
2
3
2
1
0
Magnetic properties
Paramagnetic
Diamagnetic
Diamagnetic
Paramagnetic
Diamagnetic
—
Valence electron configuration
(σ2s)2 (σ*2s)2 (π2p)2
(σ2s)2 (σ*2s)2 (π2p)4
(σ2s)2 (σ*2s)2 (π2p)4 (σ2p)2
(σ2s)2 (σ*2s)2 (σ2p)2 (π2p)4 (π*2p)2
(σ2s)2 (σ*2s)2 (σ2p)2 (π2p)4 (π*2p)4
(σ2s)2 (σ*2s)2 (σ2p)2 (π2p)4 (π*2p)4 (σ*2p)2

Large 2s–2p interaction				Small 2s–2p interaction			
	B_2	C_2	N_2		O_2	F_2	Ne_2
σ^*_{2p}				σ^*_{2p}			↑↓
π^*_{2p}				π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}			↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓

	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

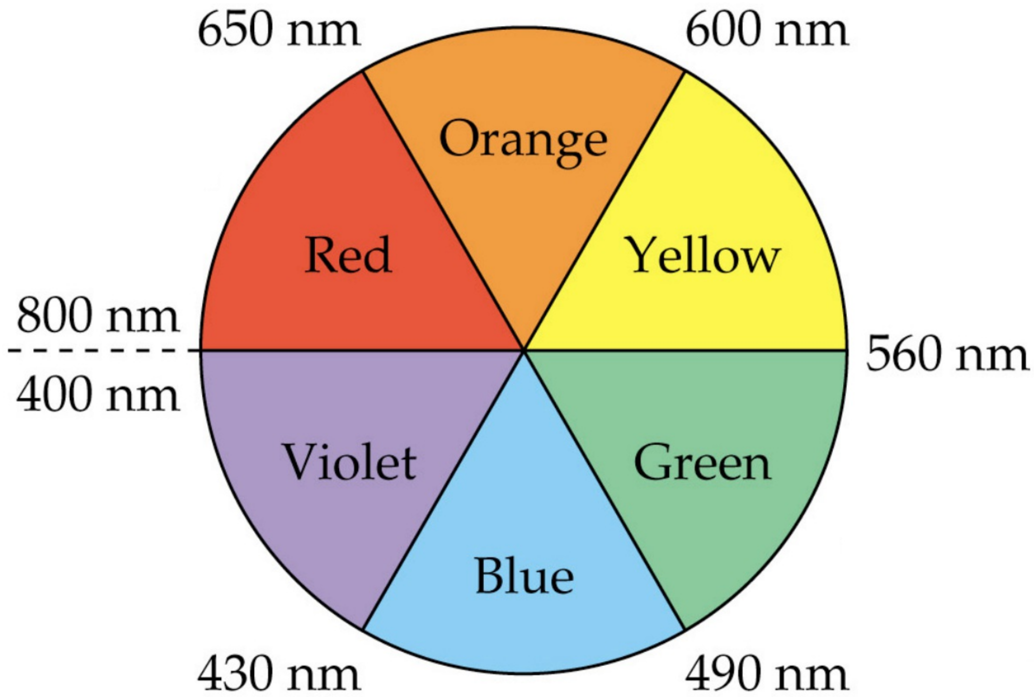
Crystal Field Theory

A model for bonding in transition-metal complexes which accounts for their magnetic properties and colors.



VB & MO Theory fall short in their explanations

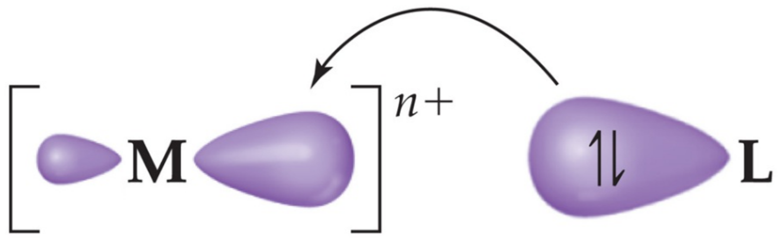
The Color Wheel & Color Theory (it's not just for art class)



An object will have a particular color because (1) it reflects light of that color, or (2) it absorbs light of the complementary color.

Metal-Ligand Interactions

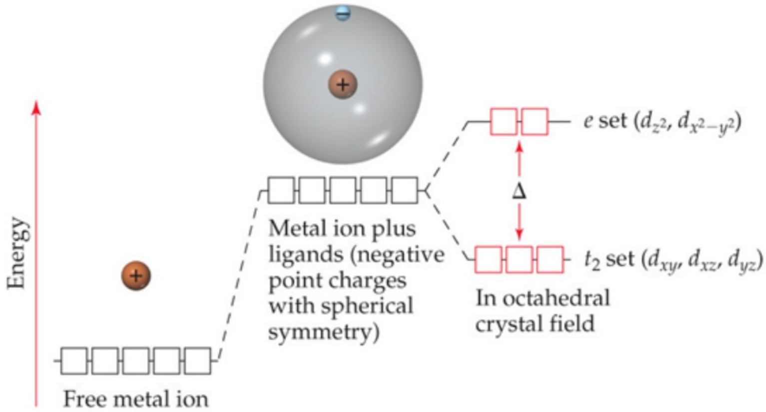
Complexes are a product of Lewis acid-base interactions. The metal ion attracts ligands, which donate electrons to an empty orbital.

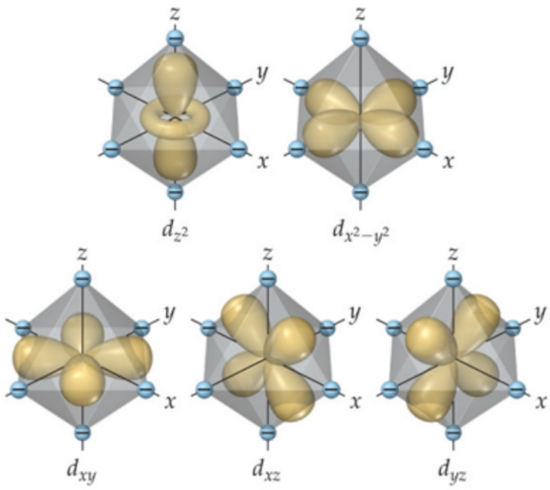


The interactions can be metal - ionic ligand or a metal - neutral ligand, meaning the IMFs change depending on the ligand.

Metal-Ligand Interactions

Although the metal ligand is attracted to the ligand's electrons, the metal ion's *d* electrons are repulsed by the ligands.

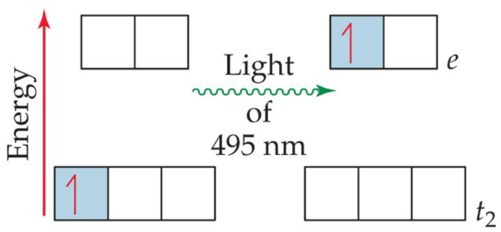


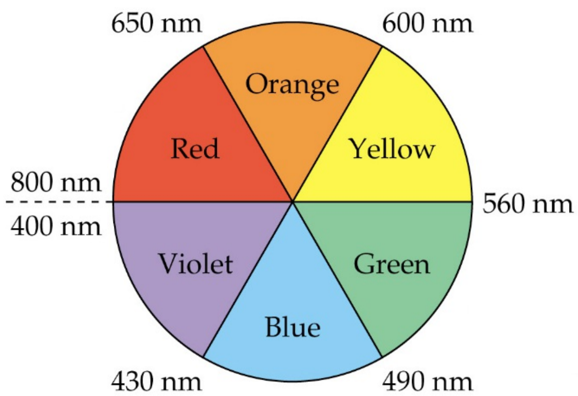


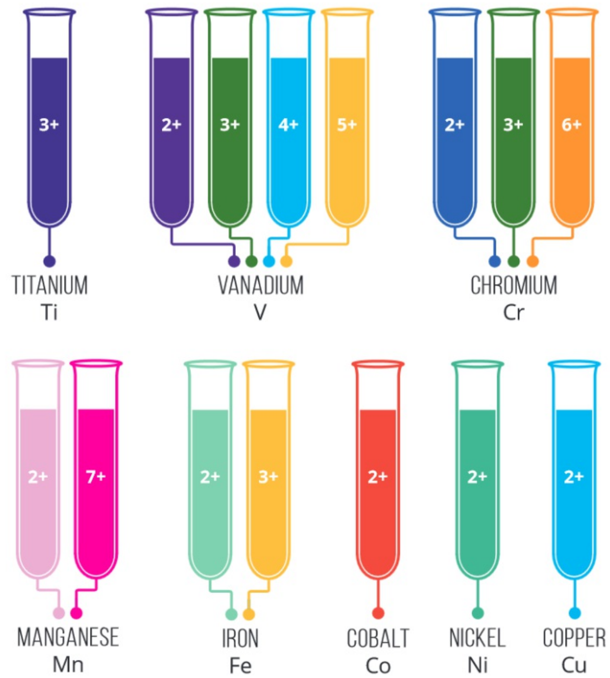
Octahedral complexes: The electron (ligand) group geometry is also an important factor.

CF Theory & Color

The energy gap (Δ) between e and t_2 orbital sets is the same order of magnitude as the energy of a photon of visible light.







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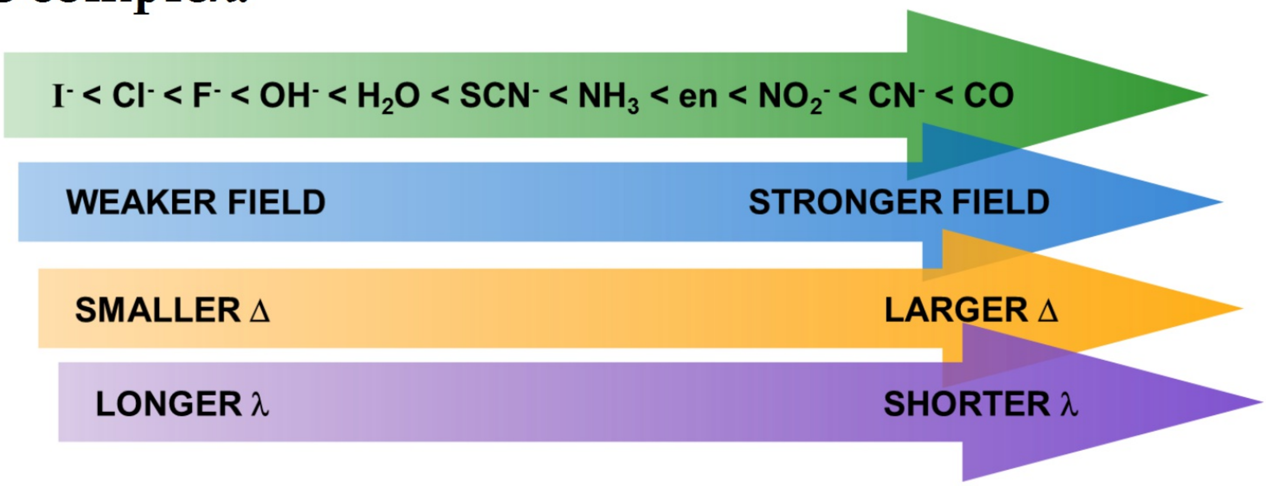
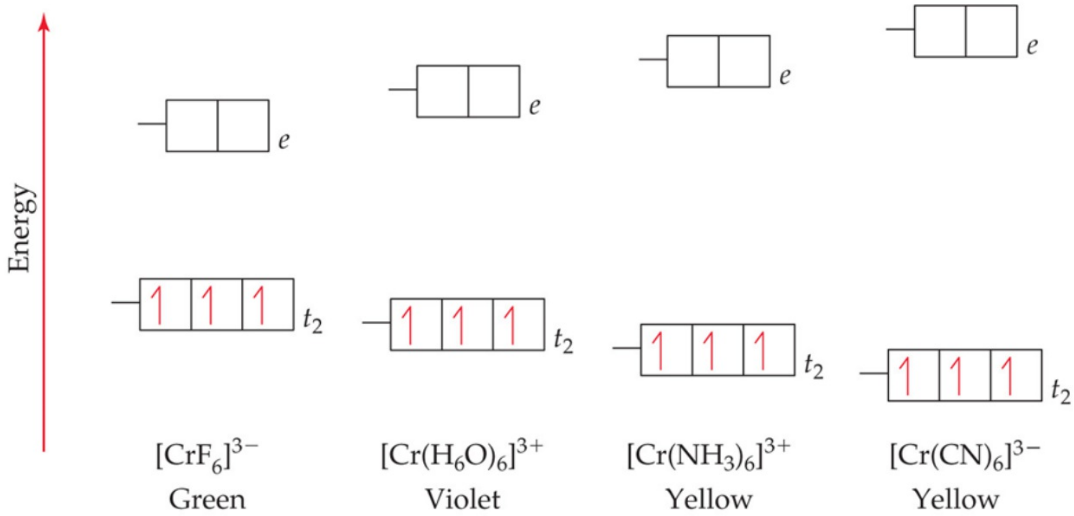
The Spectrochemical Series

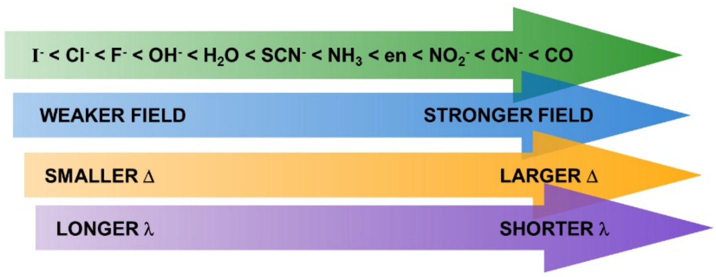
How are the exact colors determined?
Color depends on both the metal and ligand present in the complex.



The ligand will determine the energy gap (Δ).

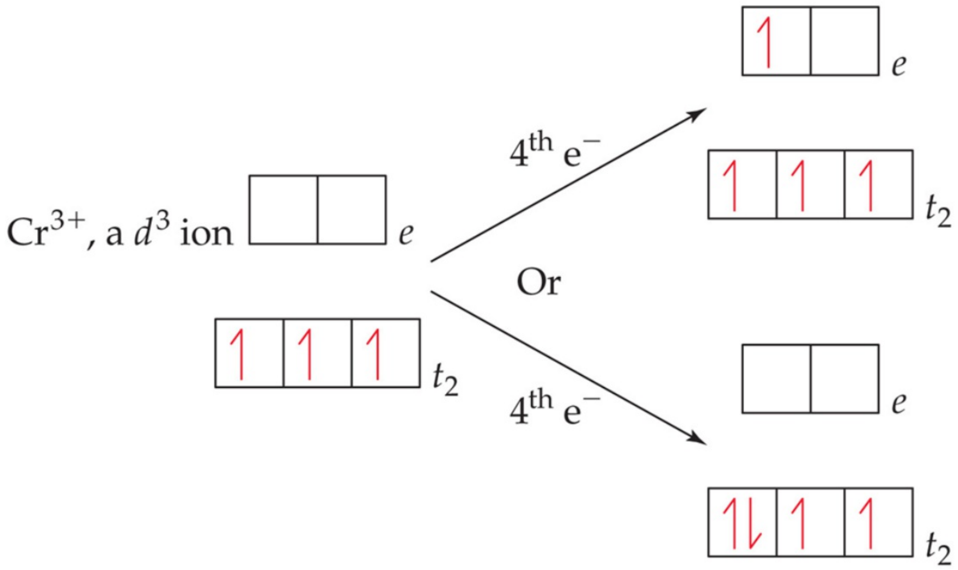
Example of Changing Color





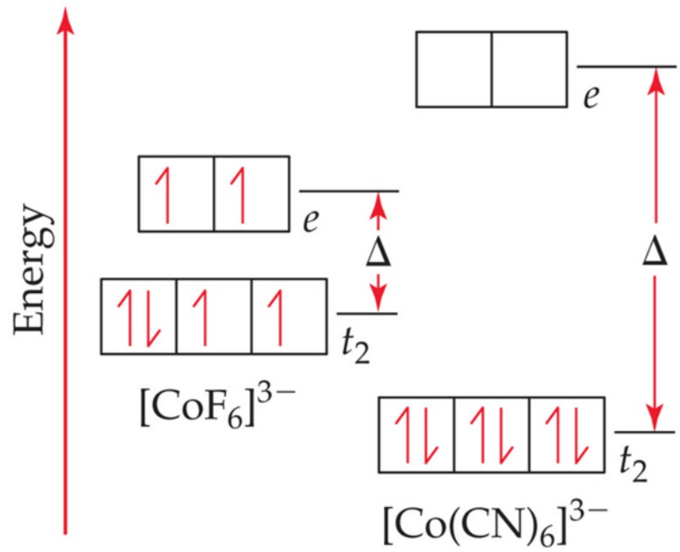
Electron Configurations in Octahedral Complexes

What happens if we add a fourth electron to the Cr system? (from previous slide)



The Spectrochemical Series

Weaker field ligands impart a smaller difference between the "e" and "t_2" orbital sets



Opposite is true for strong field ligands!

Tetrahedral and Square-Planar Complexes