Molecular Orbital Theory

- Explain how atomic orbitals combine to form molecular orbitals.
- Distinguish between bonding, antibonding, and nonbonding orbitals based on constructive and destructive interference.
- Interpret simple MO diagrams (H_2, HeH^+, O_2) and relate orbital overlap to bond order and stability.
- Describe how orbital energy differences influence covalent, polar covalent, and ionic bonding character.
- Understand σ vs. π interactions and how orbital symmetry governs overlap strength.
- Recognize s–p mixing and its effect on molecular orbital energy ordering.
- Apply the concept of symmetry-adapted linear combinations (SALCs) to polyatomic molecules (e.g., BeH_2, CH_4).
- Define HOMO and LUMO and explain their importance in determining chemical reactivity.
- Identify how conjugated π systems (e.g., benzene) generate delocalized bonding and characteristic energy levels.

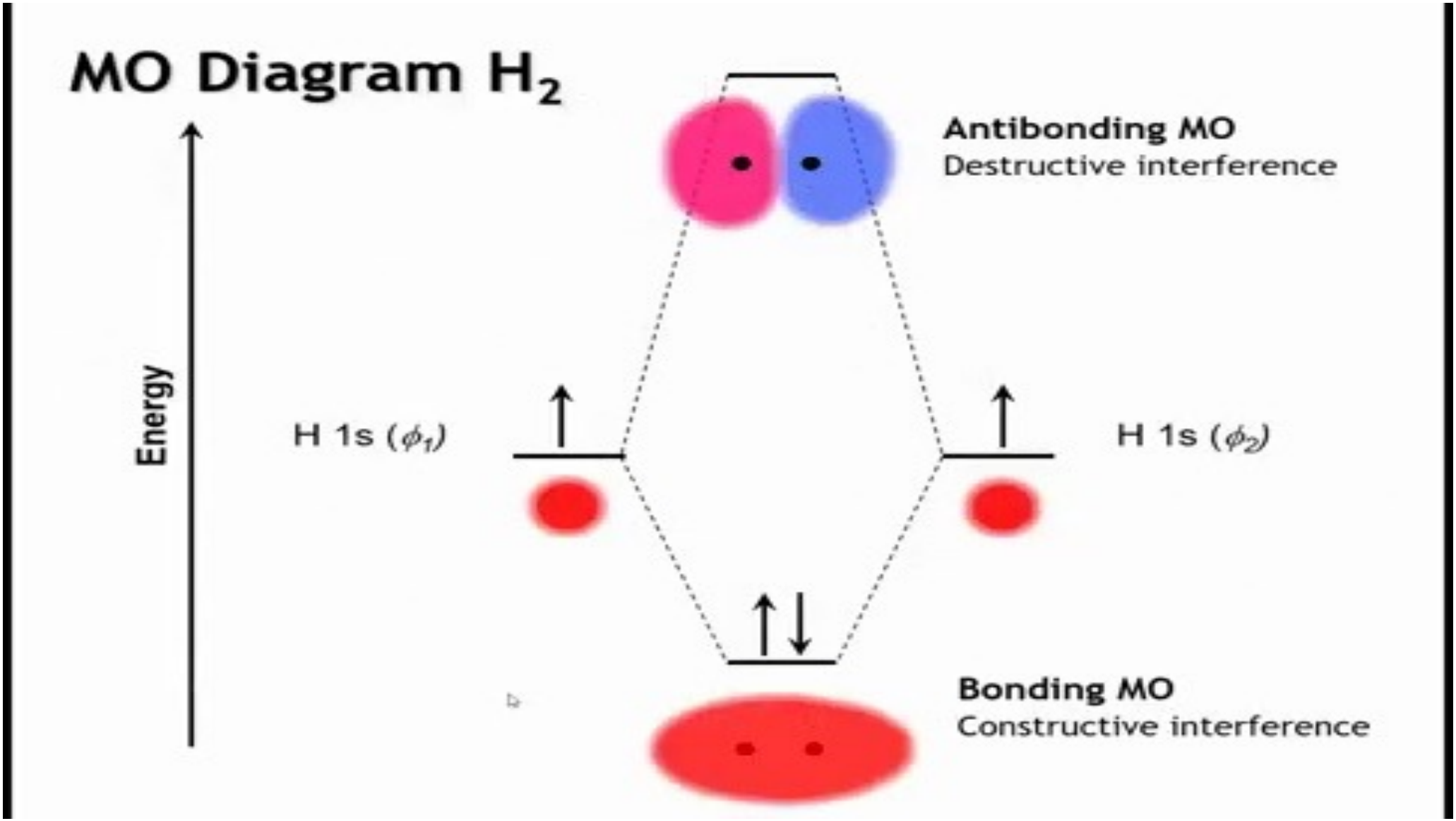
Molecular Orbitals

The electrons in an atom reside in atomic orbitals, each of which has a characteristic wavefunction.

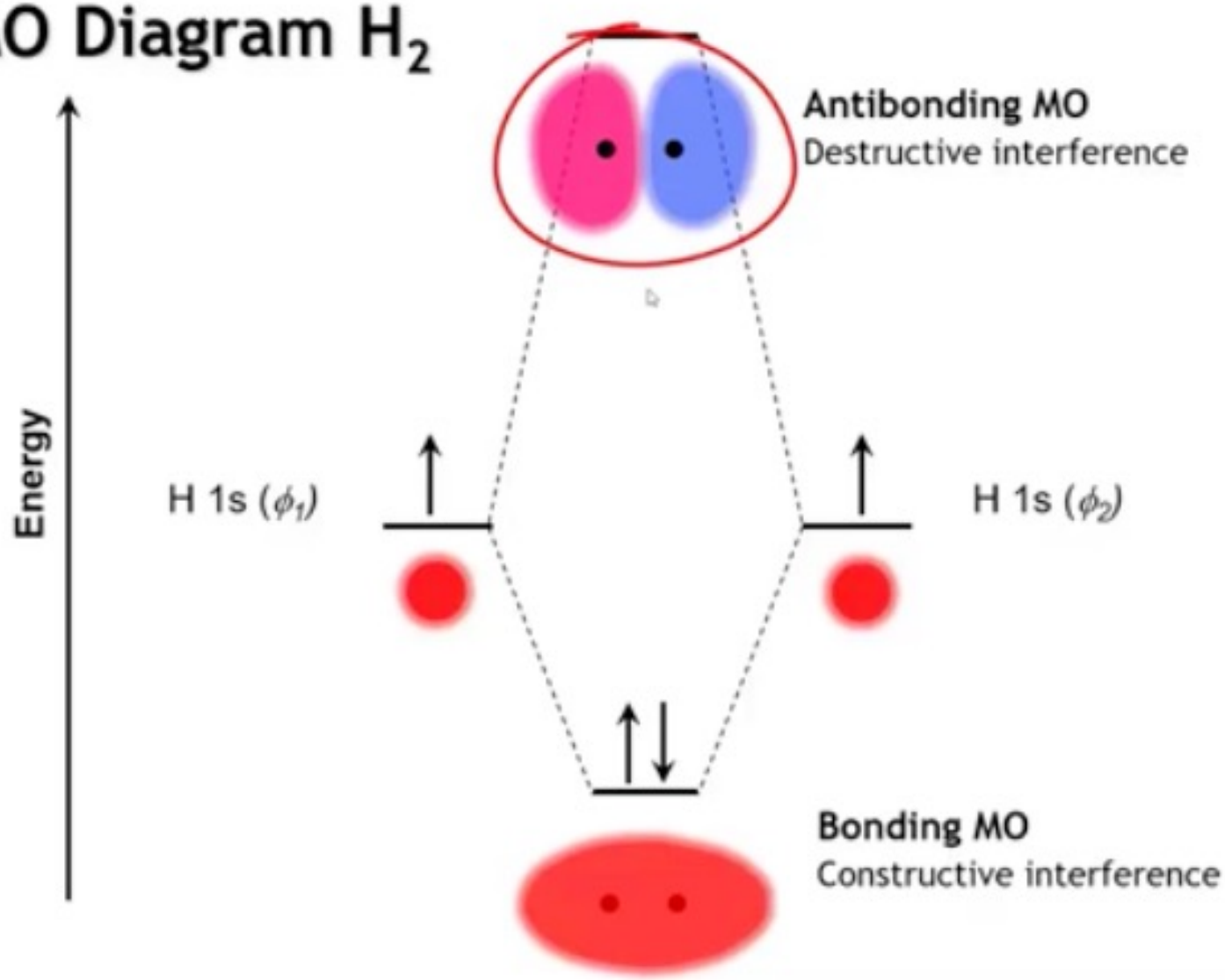
When atoms combine to form molecules we need new orbitals, **molecular orbitals**, that have their own wavefunctions.

We will choose to describe molecular orbital wavefunctions as linear combination of atomic orbital wavefunctions (LCAO):

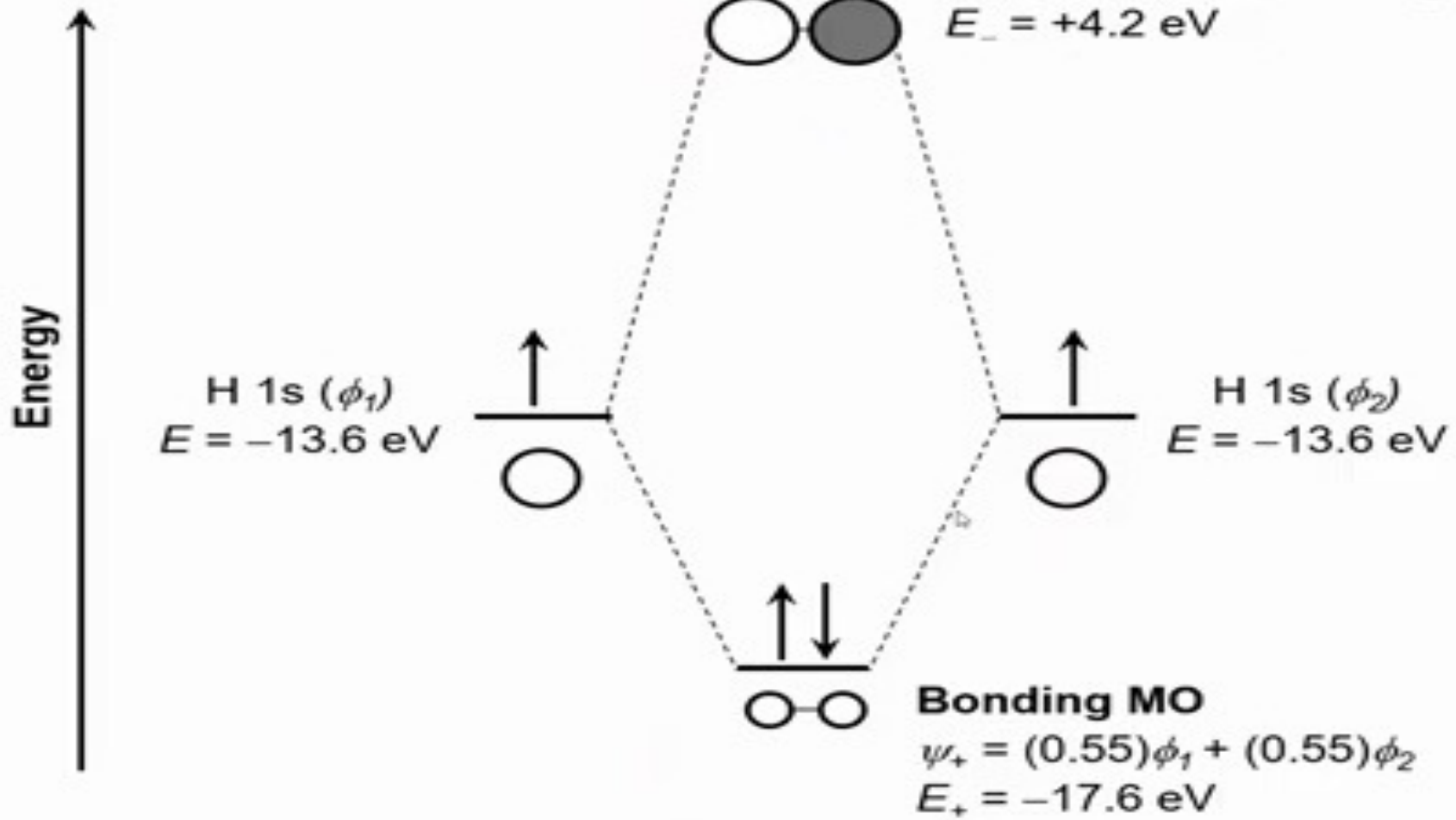
$$\psi_{MO} = \sum c_1\psi_{AO(1)} + c_2\psi_{AO(2)} + \ \ldots c_i\psi_{AO(i)}$$


MO Diagram H_2
Energy
H 1s (ϕ_1)
H 1s (ϕ_2)
Antibonding MO
Destructive interference
Bonding MO
Constructive interference

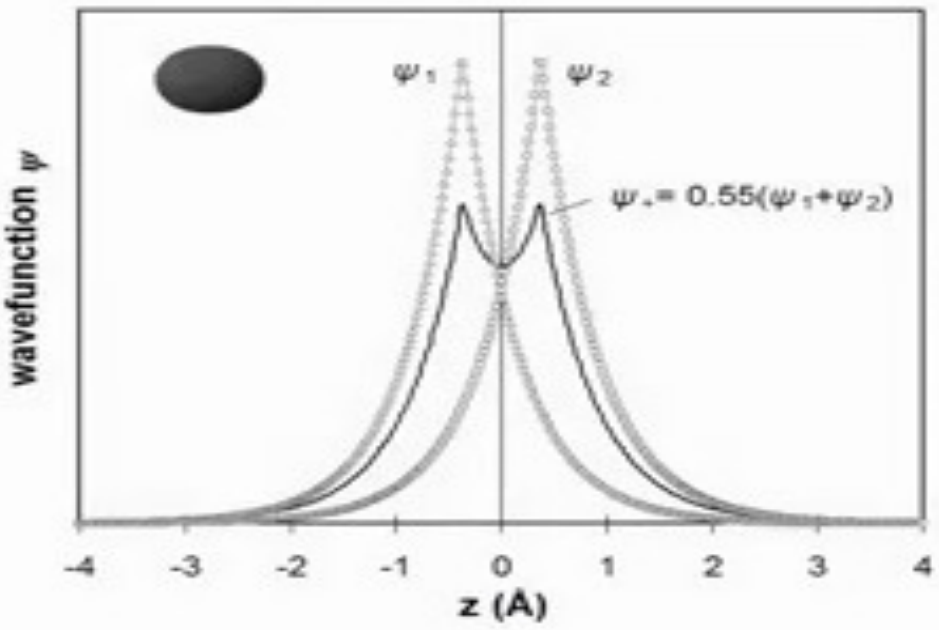
MO Diagram H_2



MO Diagram H_2

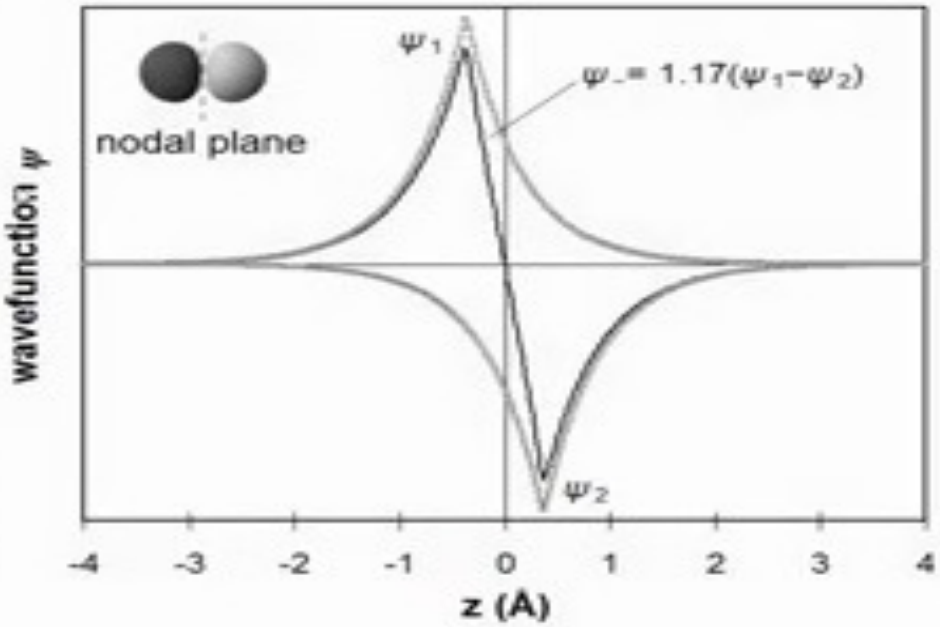


Molecular Orbital Wavefunctions



Bonding MO

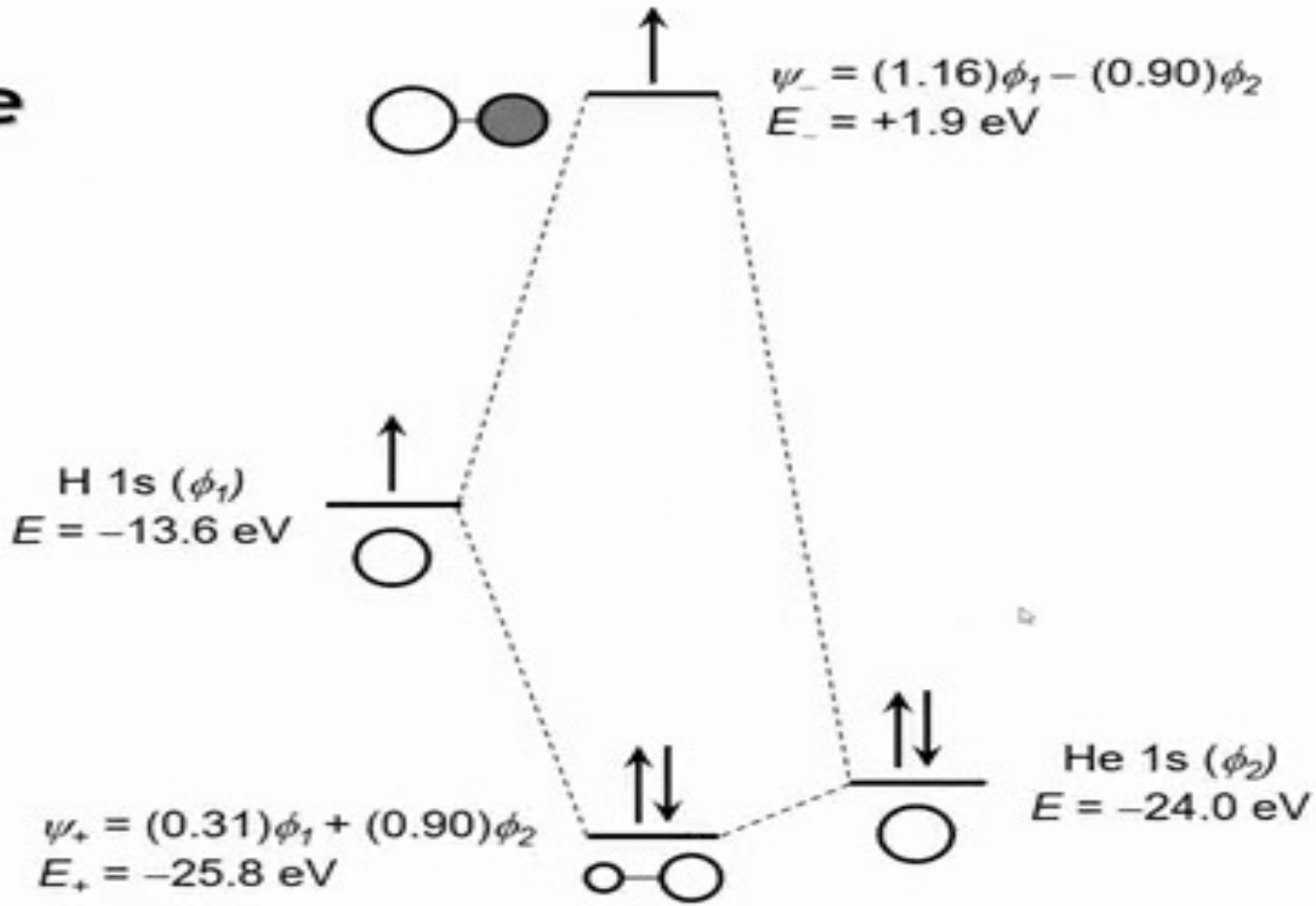
- Constructive interference
- Increases e^- between nuclei
- Lower energy



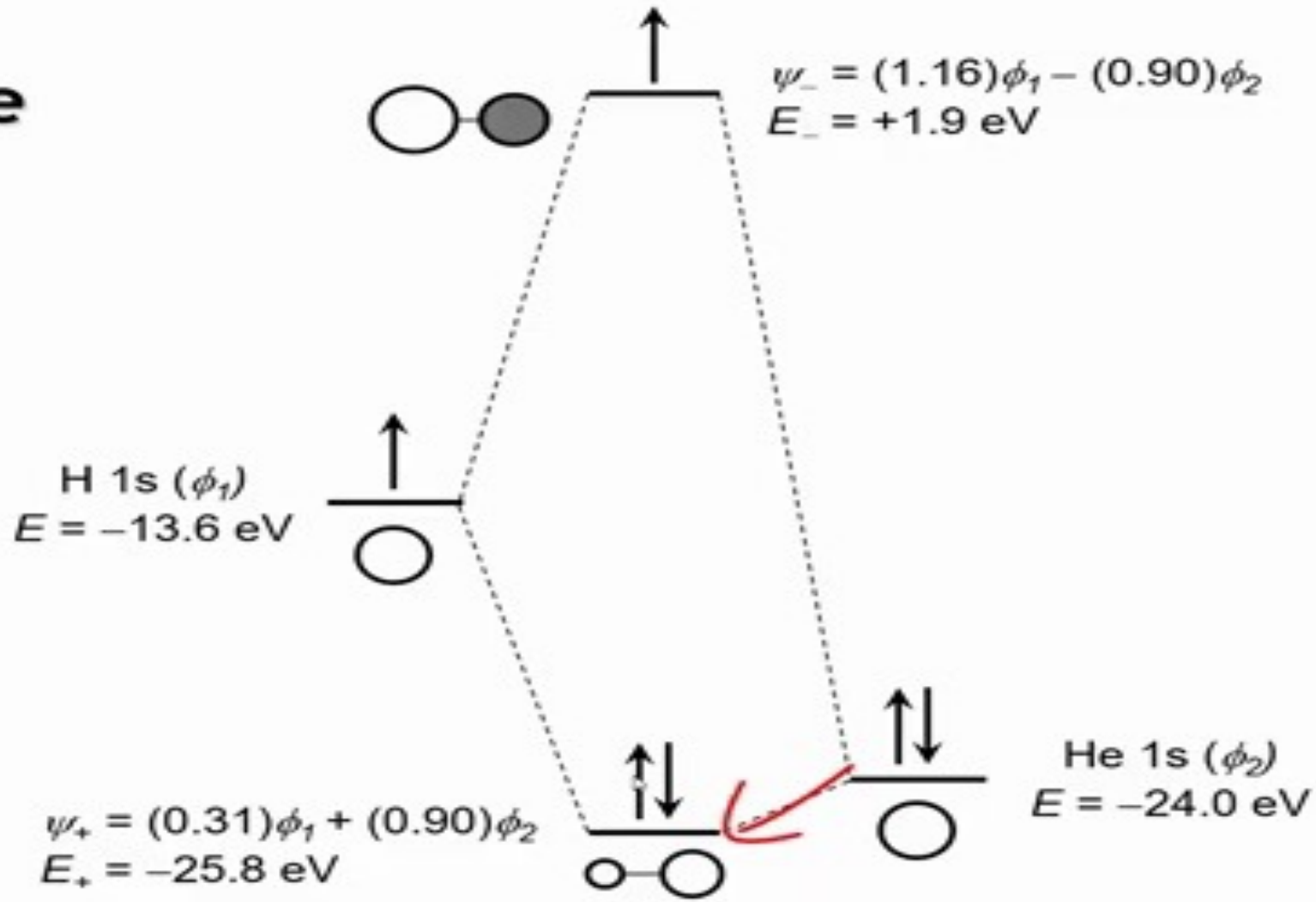
Antibonding MO

- Destructive interference
- Nodal plane between nuclei
- Higher energy

HHe


$\psi_- = (1.16)\phi_1 - (0.90)\phi_2$
$E_- = +1.9$ eV
H 1s (ϕ_1)
$E = -13.6$ eV
$\psi_+ = (0.31)\phi_1 + (0.90)\phi_2$
$E_+ = -25.8$ eV
He 1s (ϕ_2)
$E = -24.0$ eV

HHe


$\psi_- = (1.16)\phi_1 - (0.90)\phi_2$
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H 1s (ϕ_1)
$E = -13.6$ eV
He 1s (ϕ_2)
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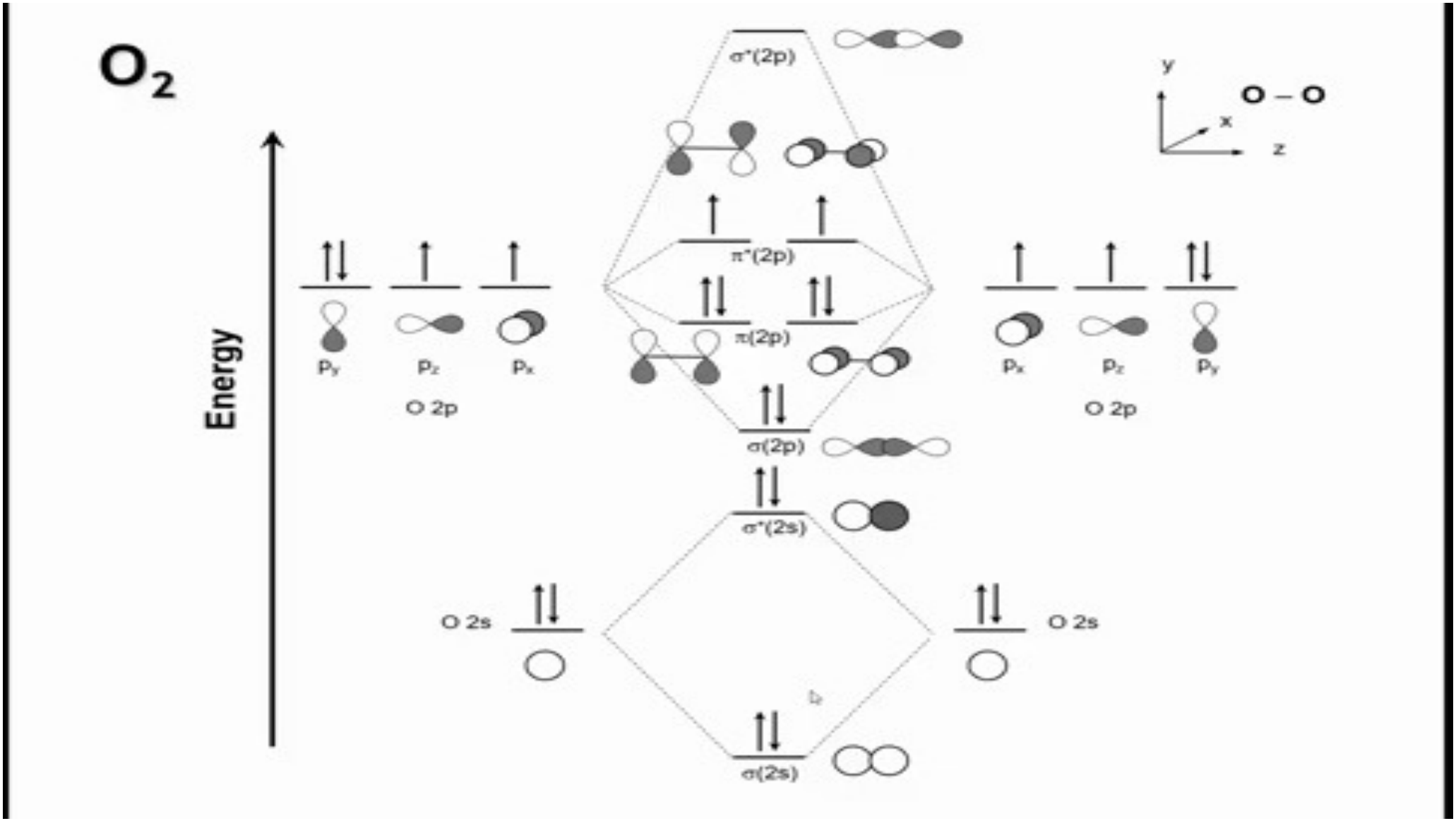

O2
Energy
σ*(2p)
π*(2p)
π(2p)
σ(2p)
σ*(2s)
σ(2s)
O 2s
O 2s
O 2p
O 2p
py
pz
px
px
pz
py
y
x
z
O – O

s-p Mixing of the σ/σ* orbitals

σ* *s–p* mixing

more antibonding
σ* (2*p*) destabilized, *E* ↑

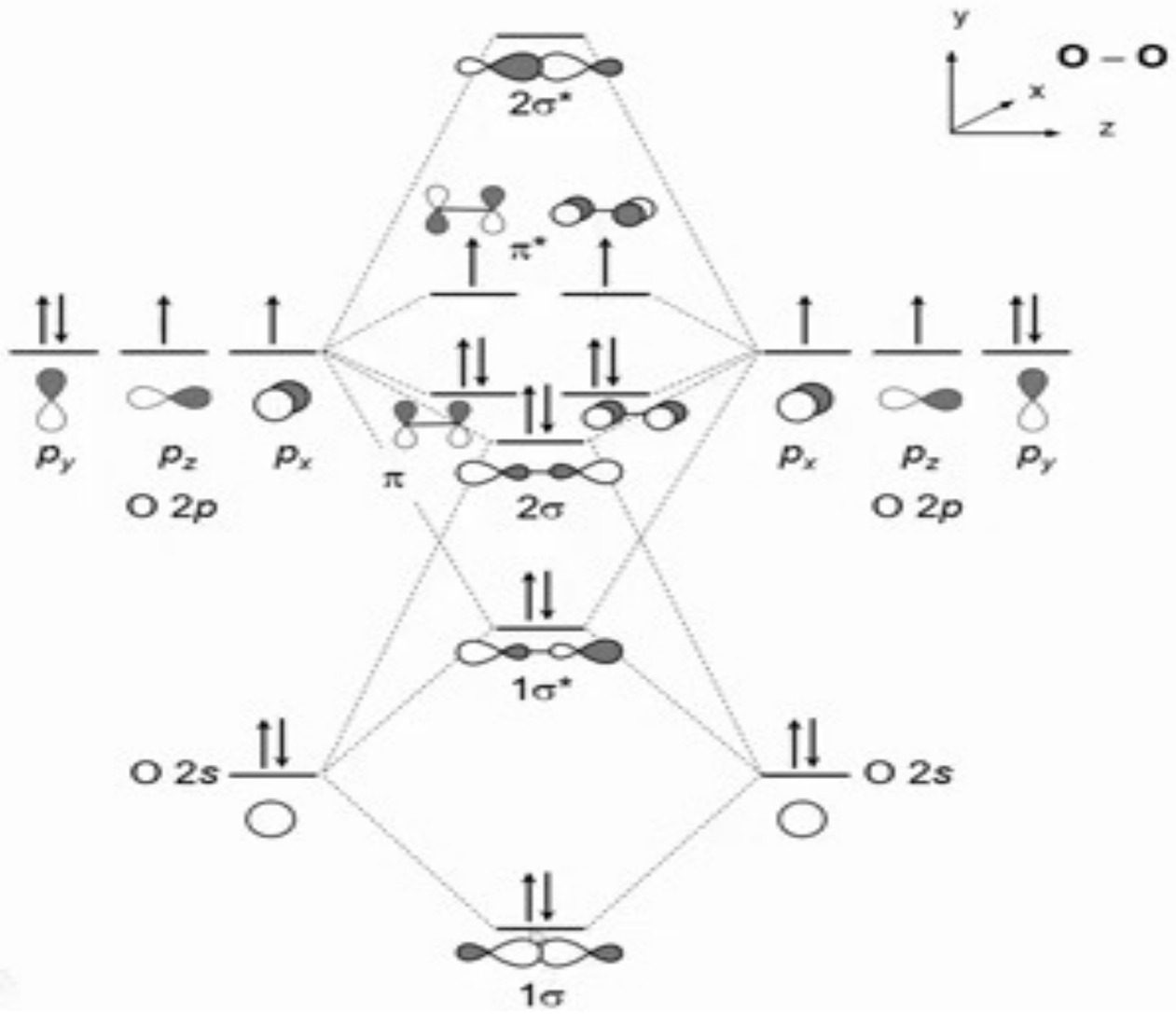
less antibonding
σ* (2*s*) stabilized, *E* ↓

σ *s–p* mixing

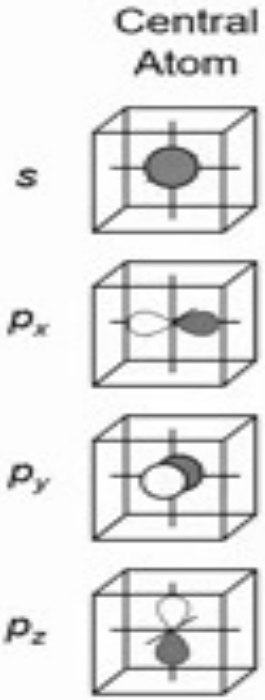
less bonding
σ (2*p*) destabilized, *E* ↑

more bonding
σ (2*s*) stabilized, *E* ↓

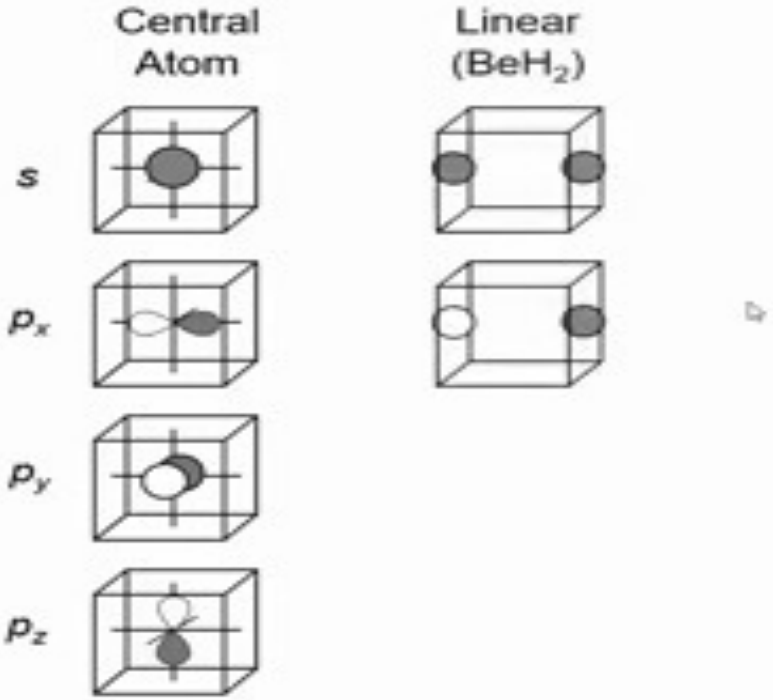
O_2



Beyond diatomics

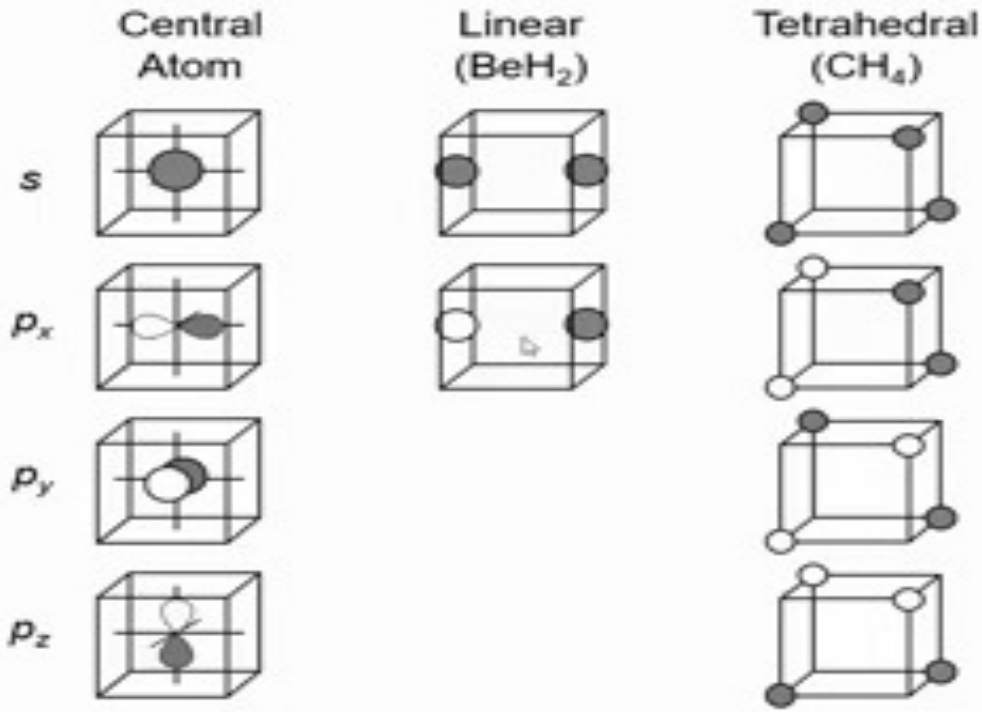


Beyond diatomics



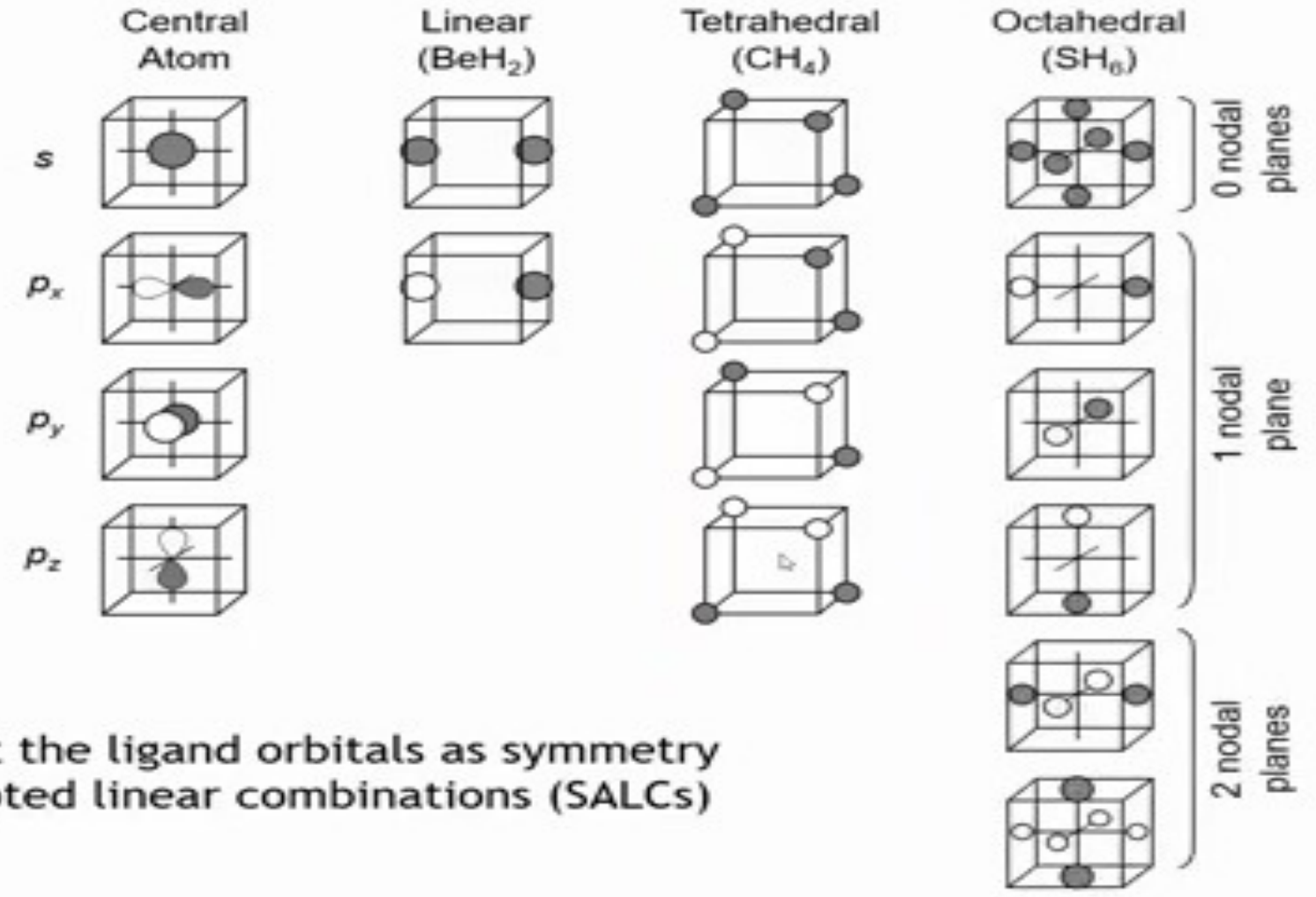
Treat the ligand orbitals as symmetry adapted linear combinations (SALCs)

Beyond diatomics



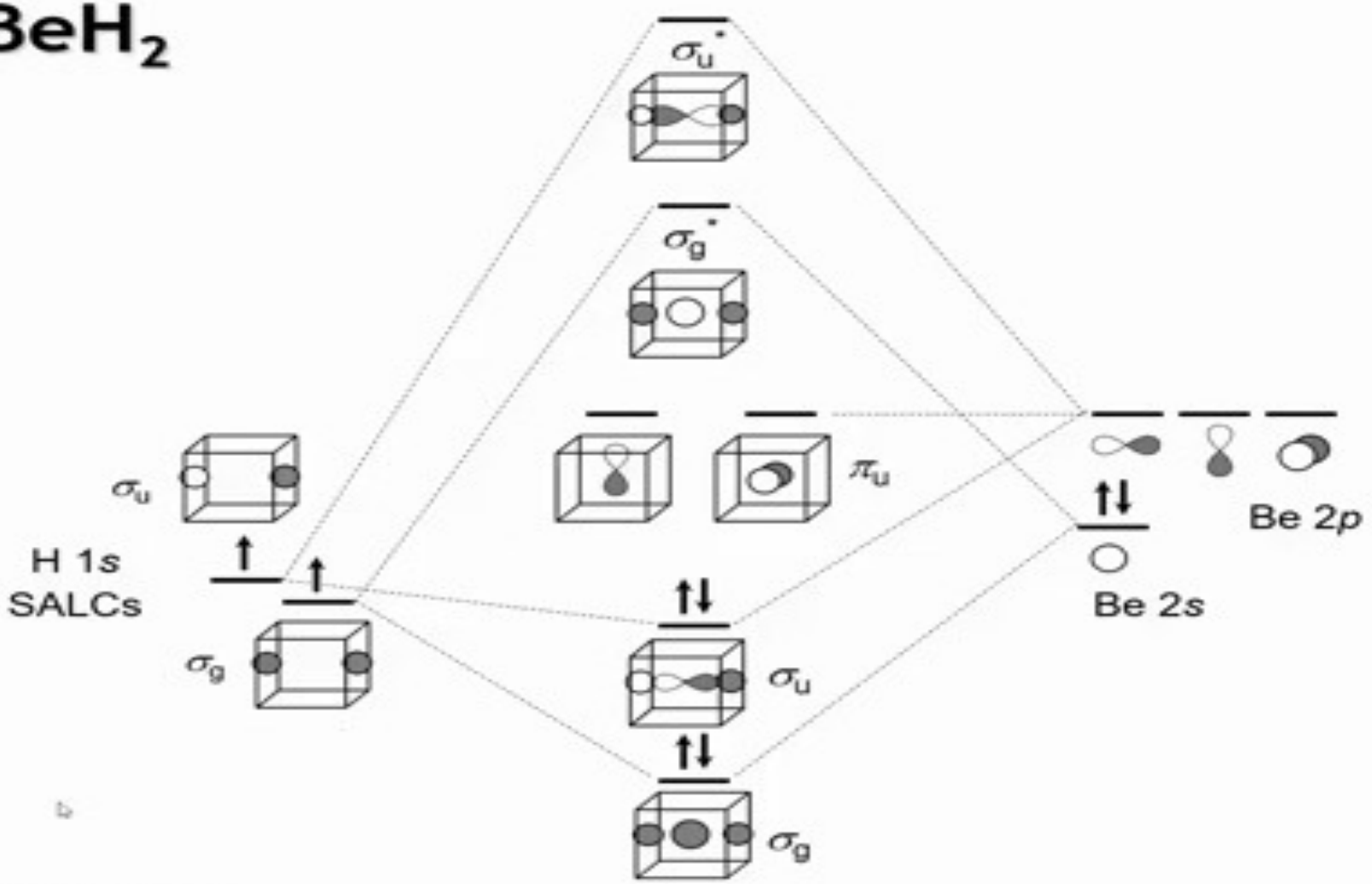
Treat the ligand orbitals as symmetry adapted linear combinations (SALCs)

Beyond diatomics

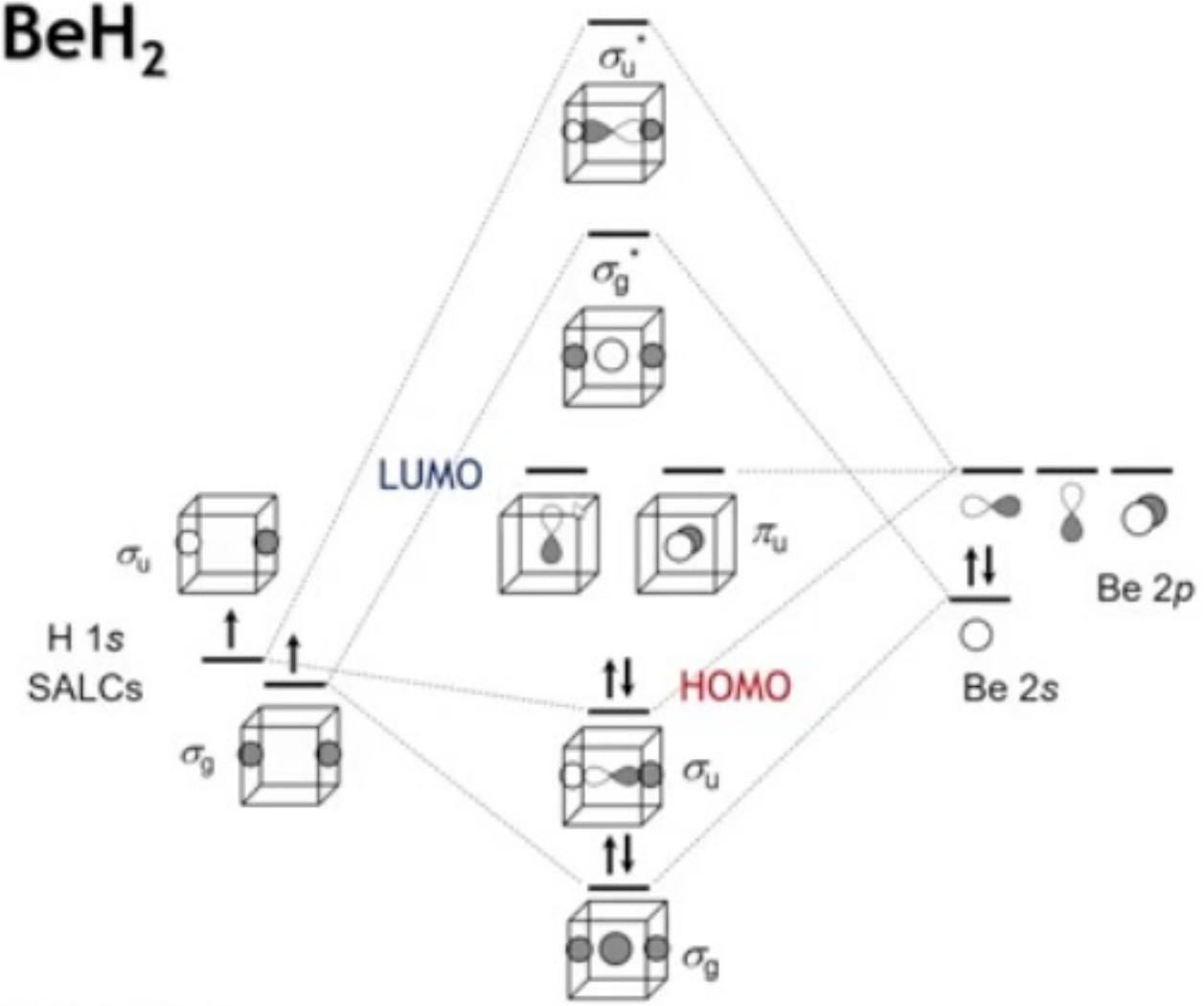


Treat the ligand orbitals as symmetry adapted linear combinations (SALCs)

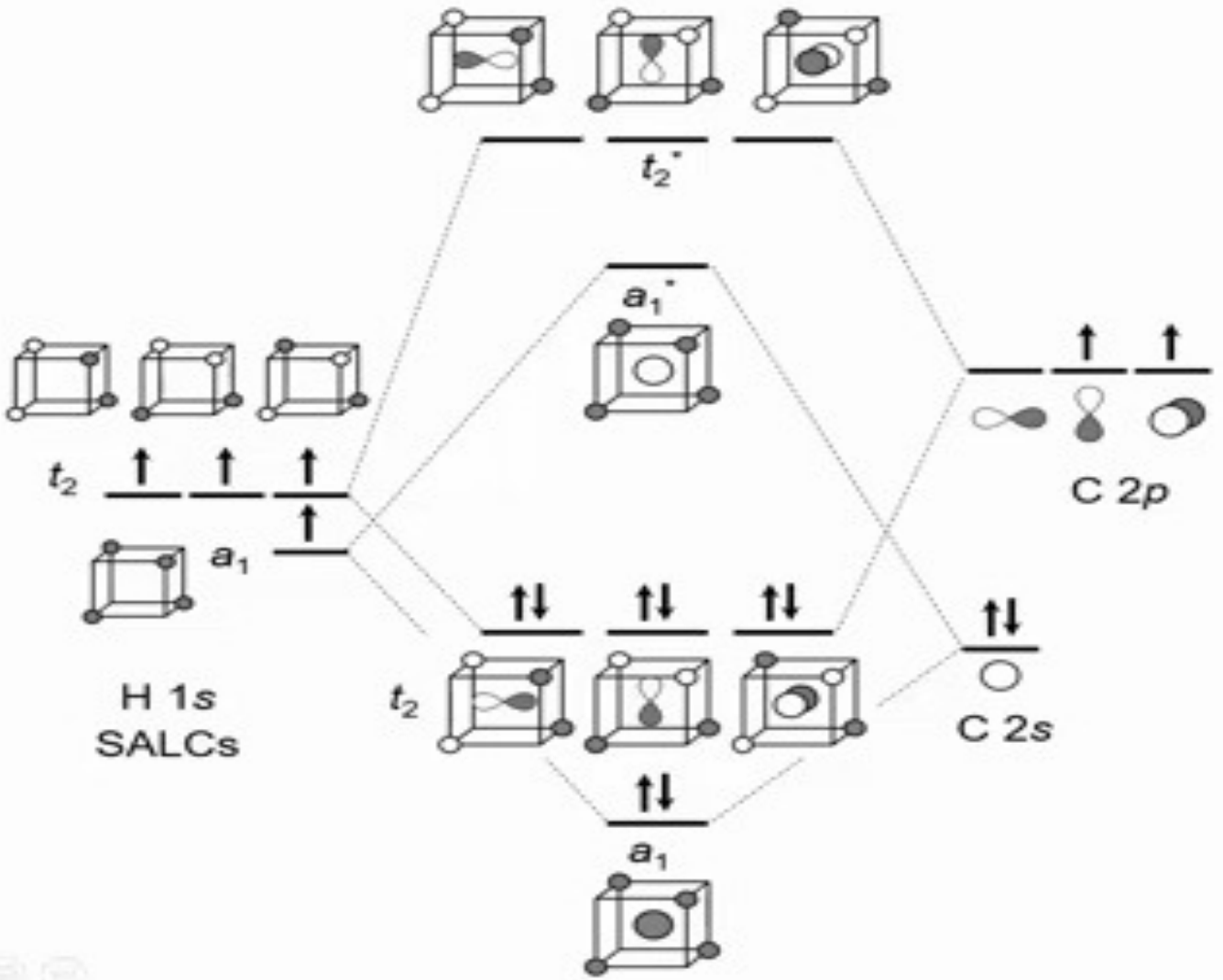
BeH_2



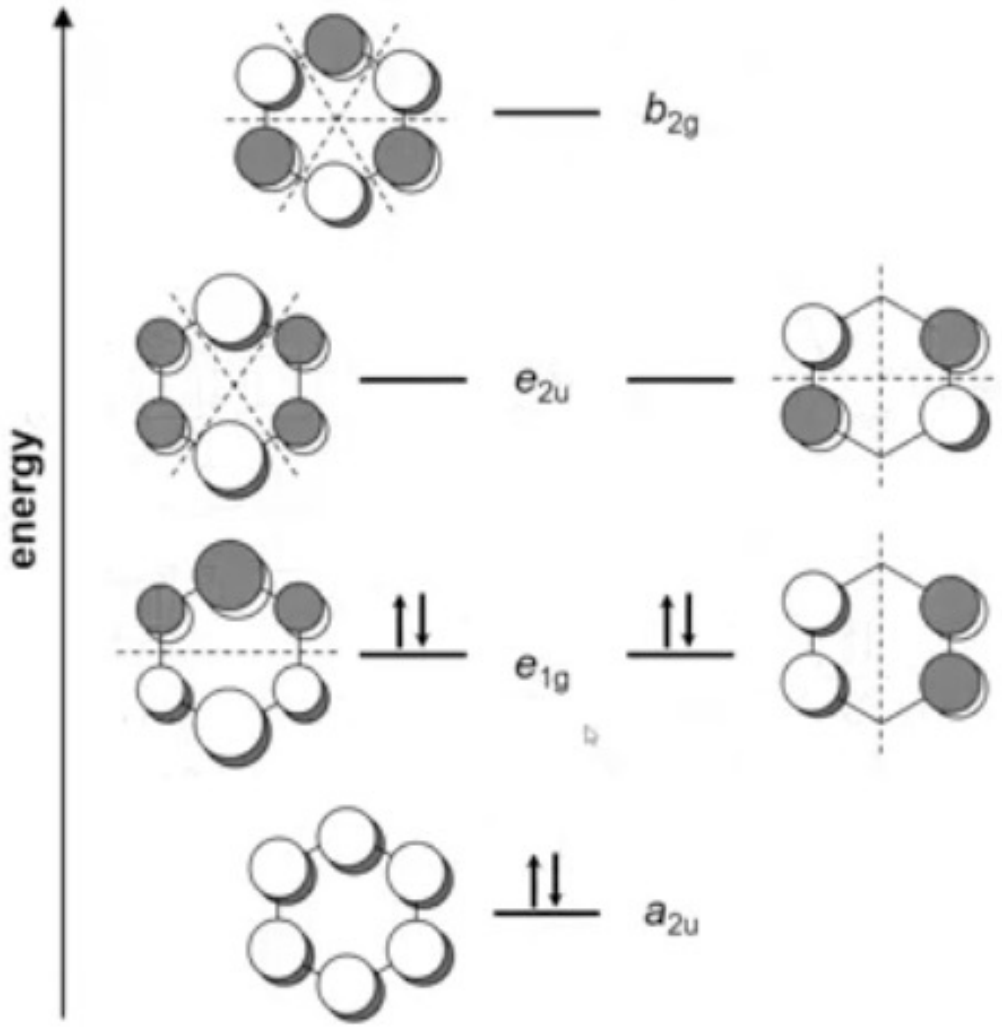
BeH_2


σ_u^*
σ_g^*
LUMO
π_u
σ_u
H 1s
SALCs
HOMO
σ_u
σ_g
σ_g
Be 2p
Be 2s

CH_4



Delocalized pi-bonding in benzene



Summary — Molecular Orbital Theory

- Molecular orbitals (MOs) form from **linear combinations of atomic orbitals (LCAO)**; electrons are described by delocalized wave functions over the entire molecule.
- **Bonding MOs** arise from constructive interference (increased electron density between nuclei → stabilization).
- **Antibonding MOs** arise from destructive interference (nodal plane between nuclei → destabilization).
- Energy splitting between bonding and antibonding orbitals increases with **orbital overlap** and decreases with **energy mismatch**.
- **Polarity** arises when orbitals of unequal energy mix, giving partial ionic character.
- **σ and π bonds** differ by overlap geometry: σ bonds form along the internuclear axis, π bonds form side-on.
- **s–p mixing** alters MO energy ordering, notably in lighter diatomics (C_2, N_2).
- For polyatomic molecules, **ligand orbitals combine into SALCs** that mix with central-atom orbitals of matching symmetry.
- **HOMO and LUMO** define the frontier orbitals controlling reactivity and optical transitions.
- In **conjugated π systems**, delocalization spreads bonding over many atoms, producing evenly spaced energy levels (e.g., benzene).

Homework: 5.7 – 5.13, 5.15

How does σ–π splitting differ for p orbitals in O_2, and what determines the energy separation between bonding and antibonding orbitals?

How does σ–π splitting differ for p orbitals in O_2, and what determines the energy separation between bonding and antibonding orbitals?

For O_2, p_z orbitals overlap head-on to form σ and σ* orbitals, while p_x and p_y overlap side-on to form π and π* orbitals. The σ orbitals experience greater overlap, producing a larger bonding–antibonding energy gap. The more spatial overlap between atomic orbitals, the greater the energy splitting between bonding and antibonding MOs. s–p mixing ($\sigma_2 s$–$\sigma_2 p$ interaction) further modifies these energy levels.

What is a symmetry-adapted linear combination (SALC), and how does it simplify the construction of molecular orbitals in polyatomic molecules?

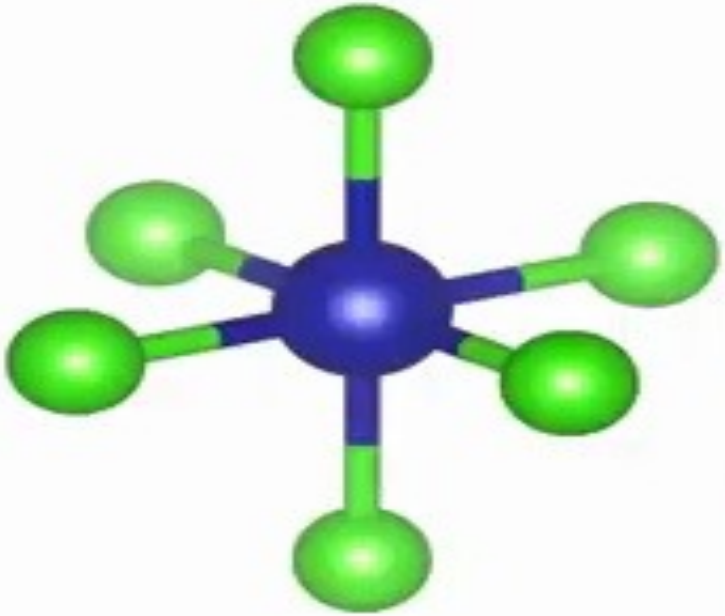
What is a symmetry-adapted linear combination (SALC), and how does it simplify the construction of molecular orbitals in polyatomic molecules?

A SALC is a combination of ligand orbitals grouped according to symmetry, allowing them to interact only with central atom orbitals of matching symmetry. For example, in BeH_2, one SALC interacts with the Be 2s orbital and another with the Be 2p_z orbital, forming bonding and antibonding pairs while other p orbitals remain nonbonding. This approach generalizes MO theory beyond diatomic molecules to complex geometries like tetrahedral (CH_4) and octahedral (SH_6) systems.

MO Theory Part II

- Understand how molecular orbital theory applies to transition metal complexes with **octahedral** and **tetrahedral** symmetry.
- Identify which **atomic orbitals** on the metal and ligands participate in bonding interactions.
- Construct **ligand group orbitals (SALCs)** for octahedral and tetrahedral complexes and determine which metal orbitals they can mix with.
- Explain the formation of **σ-bonding, π-bonding, and nonbonding** molecular orbitals in metal–ligand systems.
- Interpret how **energy matching** between metal and ligand orbitals governs bonding strength and orbital participation.
- Describe the **splitting pattern of d orbitals** (t_2g/e_g in octahedral, e/t_2 in tetrahedral) and relate it to bonding interactions.
- Compare the **magnitude and direction** of orbital splitting in octahedral vs. tetrahedral geometries.
- Connect molecular orbital diagrams to **crystal field theory** concepts and identify the **frontier orbitals** relevant to reactivity.

Octahedral complex, $CrCl_6^{3-}$



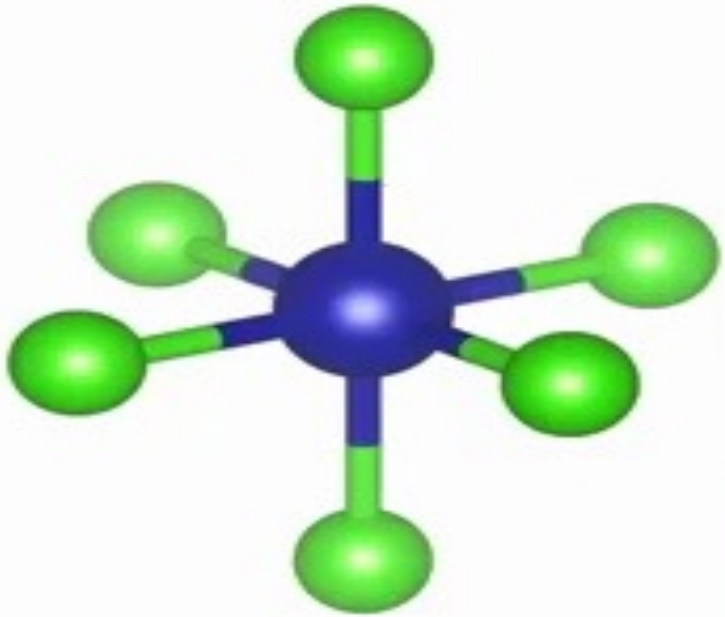
Cl
3s −29.1
3p −13.7
(in eV)

Ti
4s −6.0
4p ----
3d −10.7
(in eV)

• • •

Zn
4s −8.1
4p ----
3d −20.6
(in eV)

Octahedral complex, $CrCl_6^{3-}$



Cl
3s −29.1
3p −13.7
(in eV)

18 Cl 3p AOs

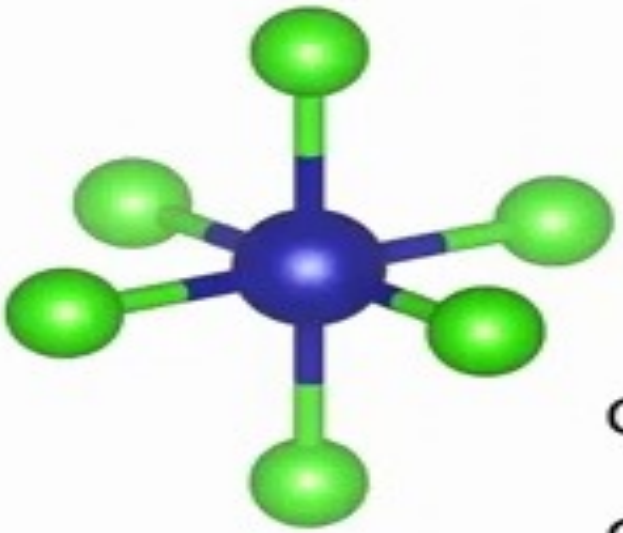
Ti
4s −6.0
4p ----
3d −10.7
(in eV)

• • •

Zn
4s −8.1
4p ----
3d −20.6
(in eV)

5 Cr 3d, **1** Cr 4s, **3** Cr 4p Aos

Electron counting $CrCl_6^{3-}$

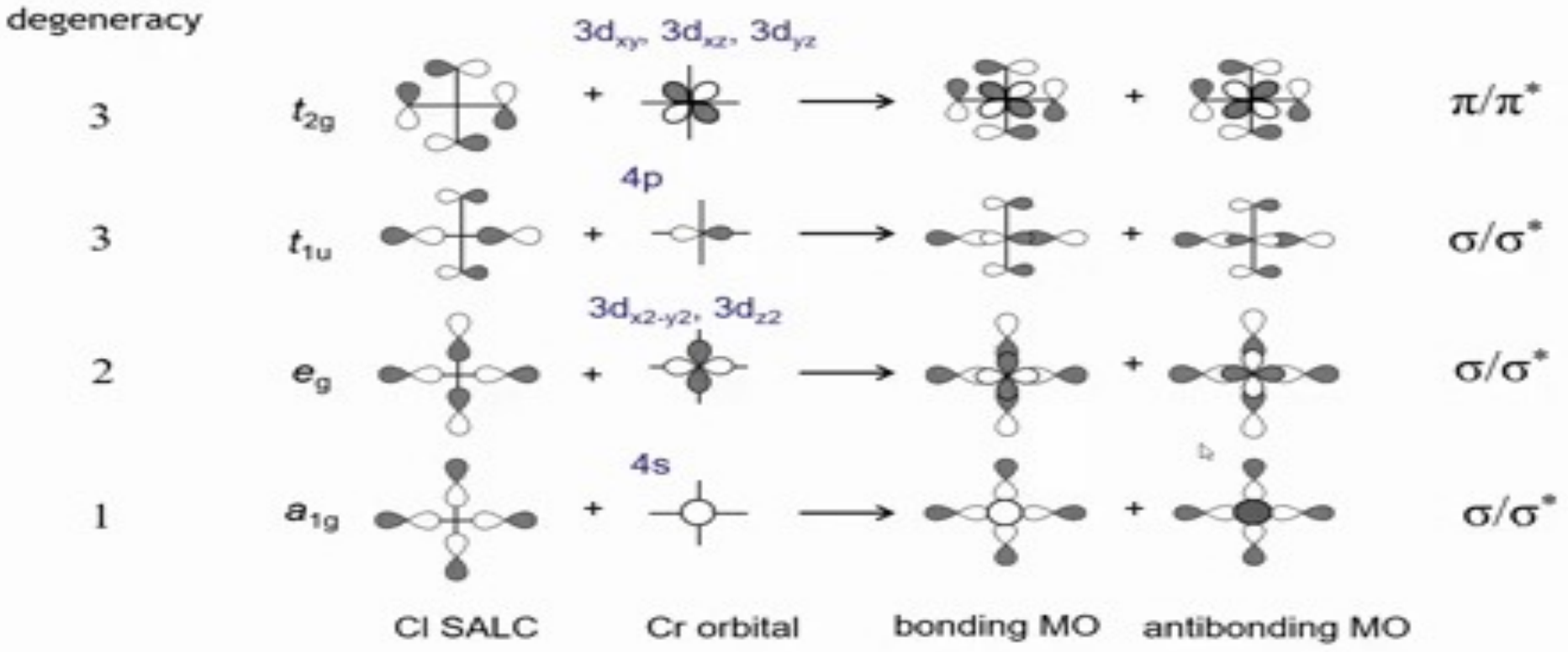


Cl [Ne] $3s^2 3p^5$ ⟶ 6×5 3p e^- = 30 e^-

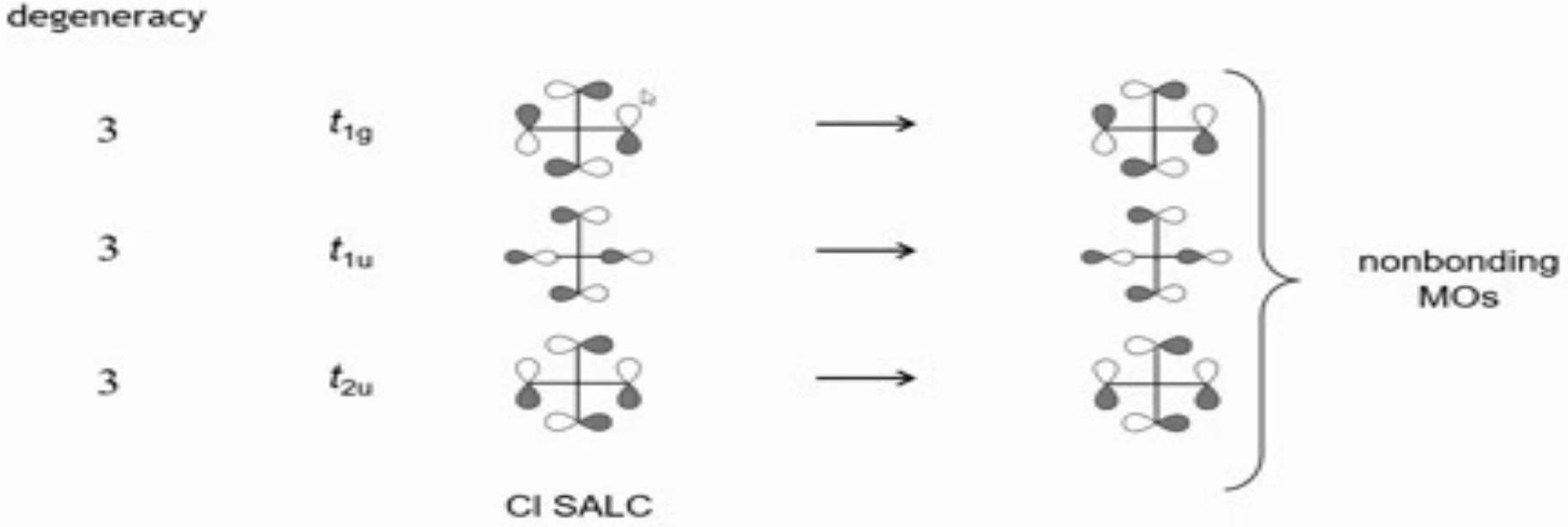
Cr [Ar] $4s^1 3d^5$ ⟶ 6 e^-

Total electrons = 30 + 6 + 3 = 39

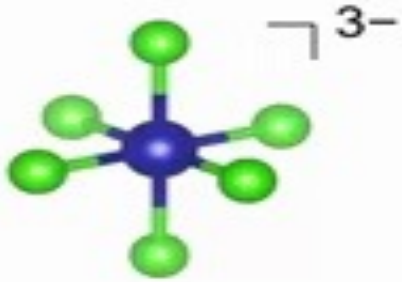
$CrCl_6^{3-}$ Bonding/Antibonding MOs



$CrCl_6^{3-}$ Nonbonding MOs



$CrCl_6^{3-}$



$t_{1u}(\sigma^*)$

$a_{1g}(\sigma^*)$

$e_g(\sigma^*)$

$t_{2g}(\pi^*)$

$4p_x, 4p_y, 4p_z\ (t_{1u})$

$4s\ (a_{1g})$

$3d_{xy}, 3d_{xz}, 3d_{yz}\ (t_{2g})$

$3d_{x2-y2}, 3d_{z2}\ (e_g)$

Cr orbitals

σ SALCs: a_{1g}, e_g, t_{1u}

π SALCs: t_{2g}, t_{1g}, t_{2u}, t_{1u}

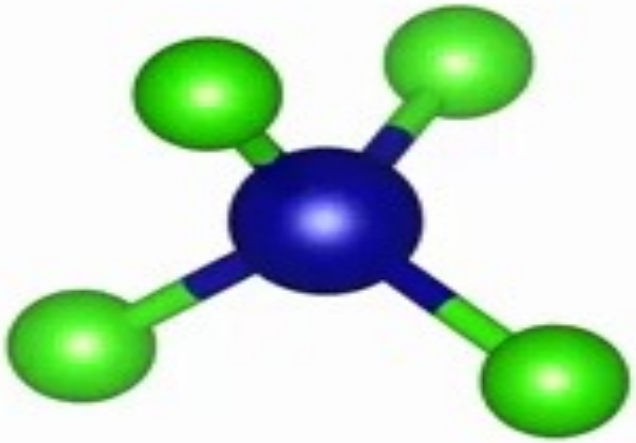
Cl 3*p* orbitals

t_{1g}
t_{1u}
t_{2u}

$t_{2g}(\pi)$

$t_{1u}(\sigma)$
$e_g(\sigma)$
$a_{1g}(\sigma)$

Tetrahedral complex, $CoCl_4^{2-}$



Cl
3s −29.1
3p −13.7
(in eV)

12 Cl 3p AOs

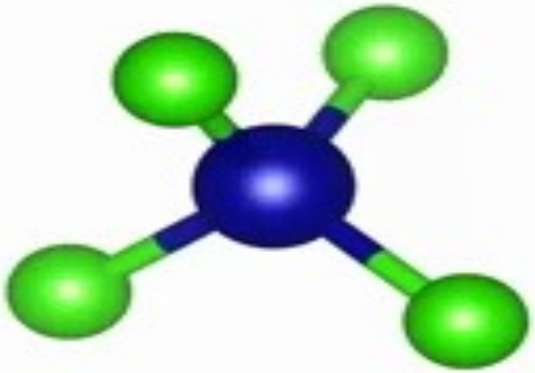
Ti
4s −6.0
4p ----
3d −10.7
(in eV)

• • •

Zn
4s −8.1
4p ----
3d −20.6
(in eV)

5 Co 3d, **1** Co 4s, **3** Co 4p AOs

Electron counting $CoCl_4^{2-}$

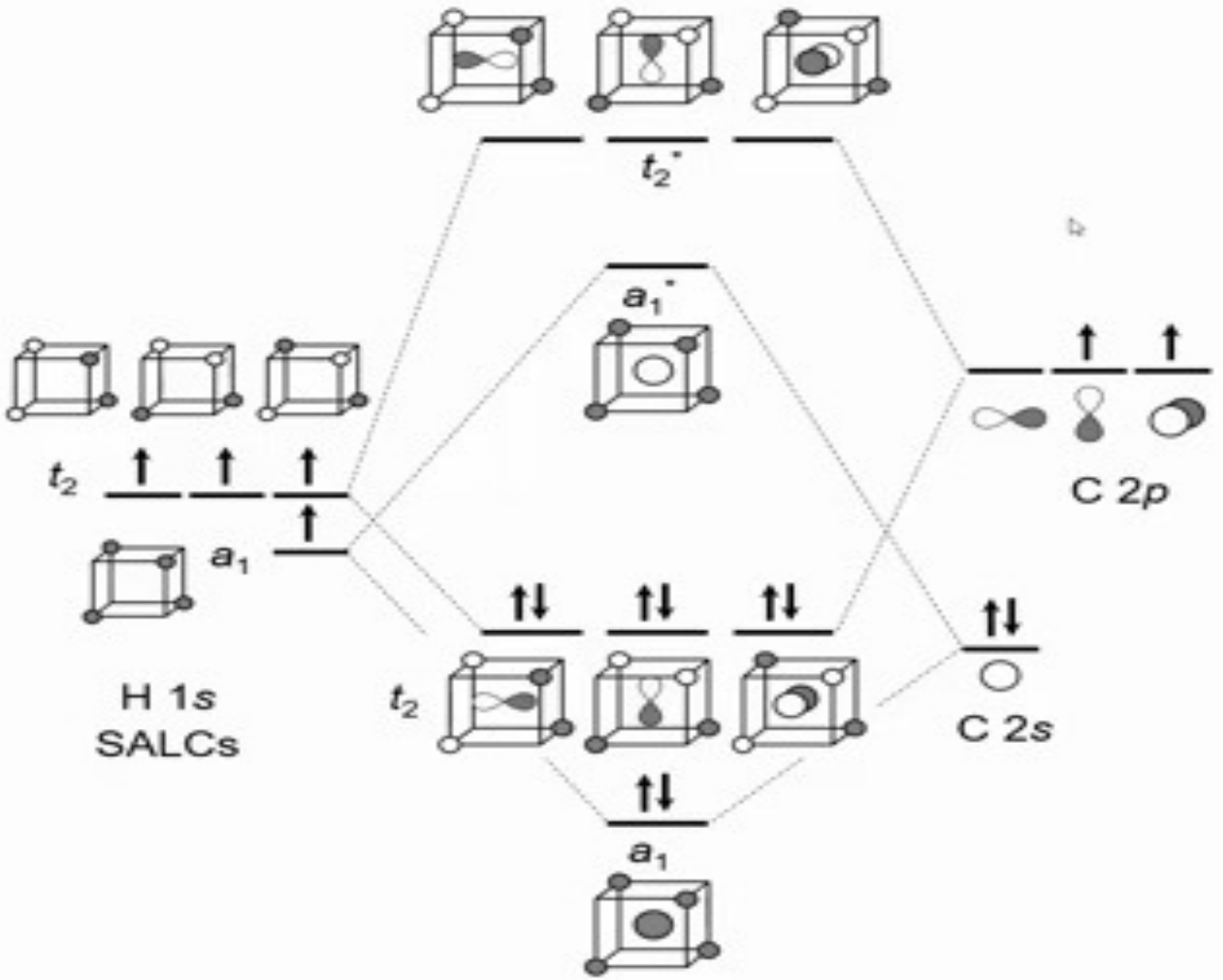


Cl [Ne] $3s^2 3p^5$ ⟶ 4×5 3p e^- = 20 e^-

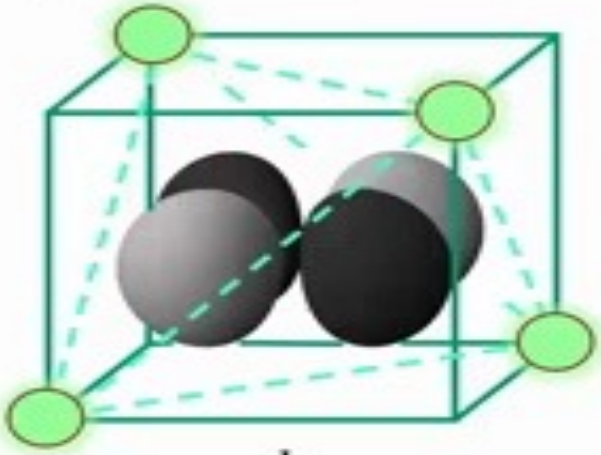
Co [Ar] $4s^2 3d^7$ ⟶ 9 e^-

Total electrons = 20 + 9 + 2 = 31 e^-

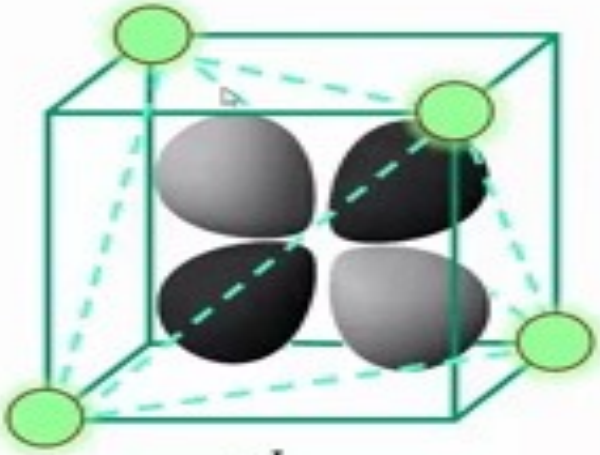
CH_4



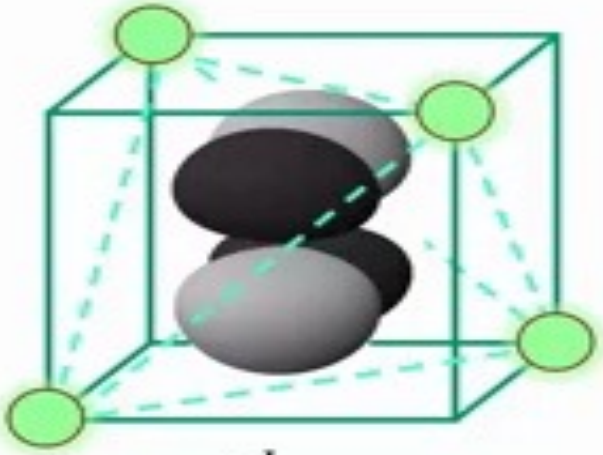
t_2 orbitals



d_{xy}

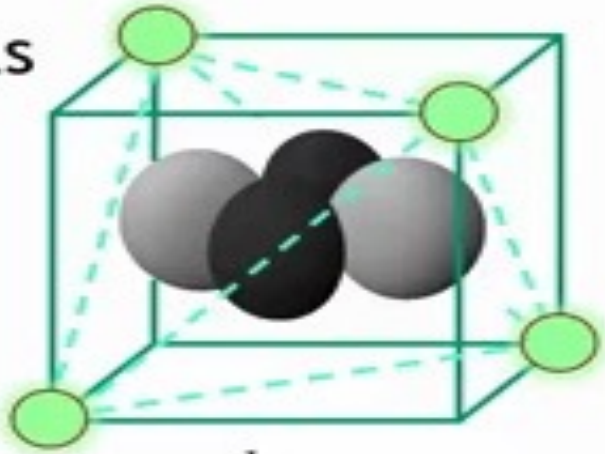


d_{xz}

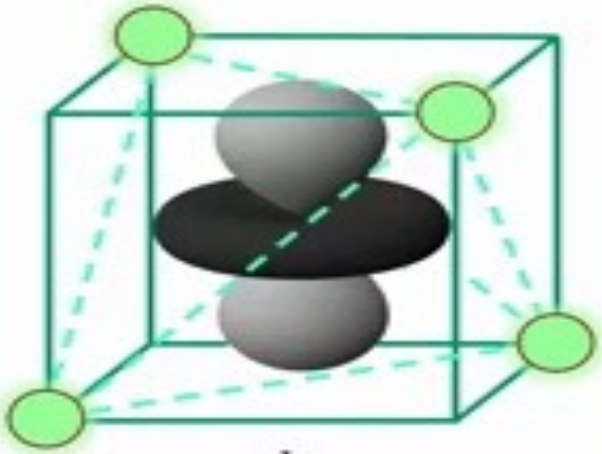


d_{yz}

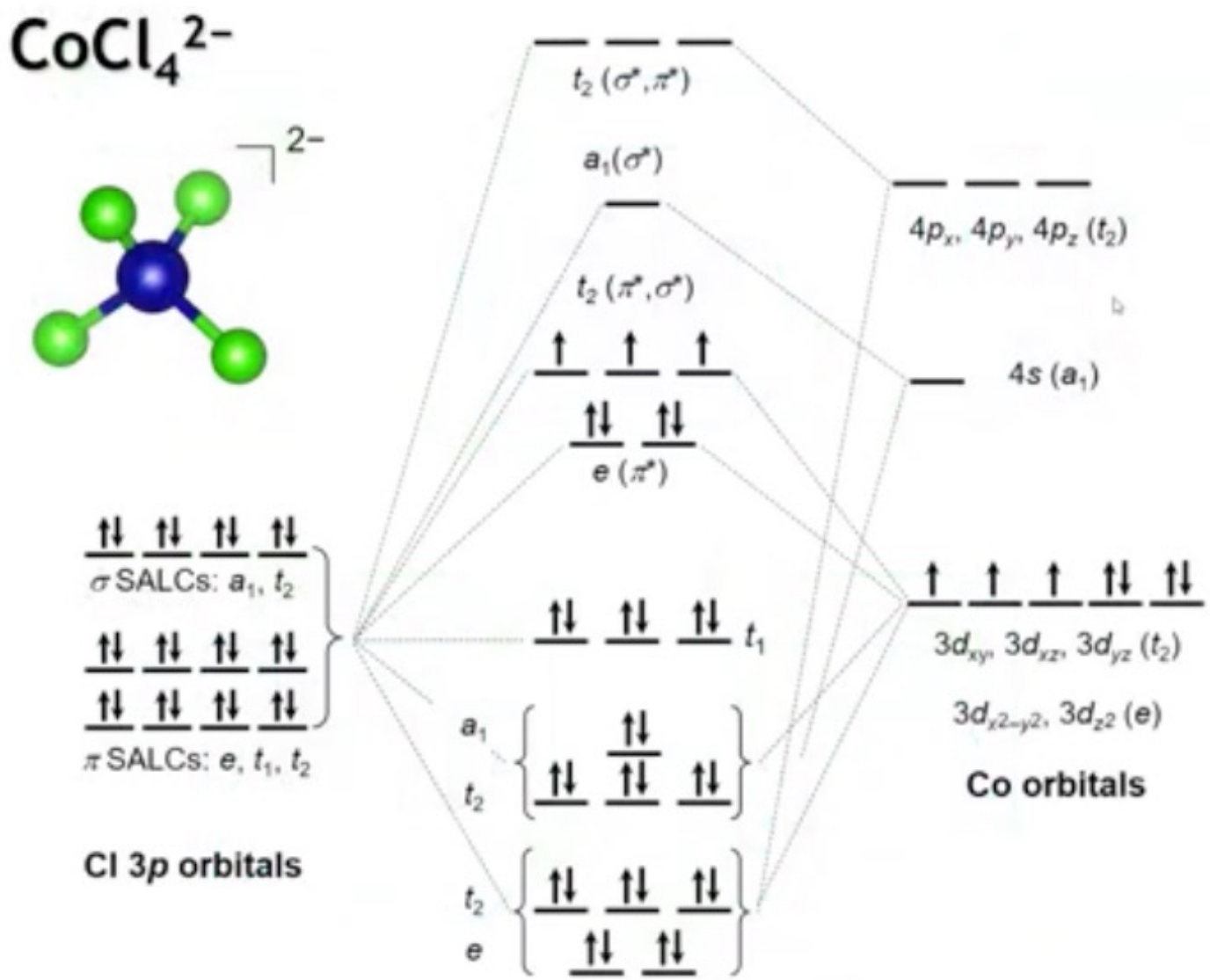
e orbitals



$d_{x^2-y^2}$



d_{z^2}


$CoCl_4^{2-}$
2−
t_2 (σ^*,π^*)
a_1(σ^*)
t_2 (π^*,σ^*)
e (π^*)
$4p_x$, $4p_y$, $4p_z$ (t_2)
4s (a_1)
$3d_{xy}$, $3d_{xz}$, $3d_{yz}$ (t_2)
$3d_{x2-y2}$, $3d_{z2}$ (e)
Co orbitals
σ SALCs: a_1, t_2
π SALCs: e, t_1, t_2
Cl 3p orbitals
t_1
a_1
t_2
t_2
e

Summary — MO Theory in Transition-Metal Complexes

$[CrCl_6]^{3-}$ (Octahedral)

- Orbitals: 9 metal (5 d, 1 s, 3 p) + 18 ligand (Cl 3p)
- 9 bonding, 9 antibonding, 9 non-bonding SALCs
- Frontier orbitals:
  t_{2g} (dxy, dyz, dxz) = π antibonding (lower E)
  e_g ($dx^2–y^2$, dz^2) = σ antibonding (higher E)

$[CoCl_4]^{2-}$ (Tetrahedral)

- 9 metal + 12 ligand orbitals → 9 bonding, 9 antibonding, 3 non-bonding
- Splitting reversed: e ($dx^2–y^2$, dz^2) lower E; t_2 (dxy, dxz, dyz) higher E
- $\Delta_t \approx \frac{1}{2} \Delta_o$ (no pure σ antibonding)

Takeaways

- Geometry → symmetry → Δ magnitude and order.
- Octahedral: t_{2g} below e_g | Tetrahedral: e below t_2
- Frontier d-orbitals govern color and reactivity.

Question:

For chloride ligands (weak field), compare **$[FeCl_6]^{4-}$ (octahedral)** and **$[FeCl_4]^{2-}$ (tetrahedral)**. Determine Fe oxidation state, d-electron count, orbital splitting pattern, and number of unpaired electrons. Identify which has the larger splitting and explain why.

Question:

For chloride ligands (weak field), compare **$[FeCl_6]^{4-}$ (octahedral)** and **$[FeCl_4]^{2-}$ (tetrahedral)**. Determine Fe oxidation state, d-electron count, orbital splitting pattern, and number of unpaired electrons. Identify which has the larger splitting and explain why.

Each Cl^- = −1.

- $[FeCl_6]^{4-}$: x − 6 = −4 → Fe^{2+} → $3d^6$
- $[FeCl_4]^{2-}$: x − 4 = −2 → Fe^{2+} → $3d^6$

Both complexes have Fe^{2+} (d^6).

- **Octahedral field:** t_2g (lower), e_g (higher).
  Weak field → high spin → t_2g^4 e_g^2 → **4 unpaired electrons.**
- **Tetrahedral field:** e (lower), t_2 (higher).
  Weak field → high spin → e^3 t_2^3 → **4 unpaired electrons.**
- **Splitting:** $\Delta_t \approx \frac{1}{2} \Delta_o$.
  Octahedral splitting larger because ligands point directly at metal orbitals (stronger σ interaction).

Answer:

Both are high-spin Fe^{2+} (d^6) with 4 unpaired electrons; $[FeCl_6]^{4-}$ has the larger splitting.

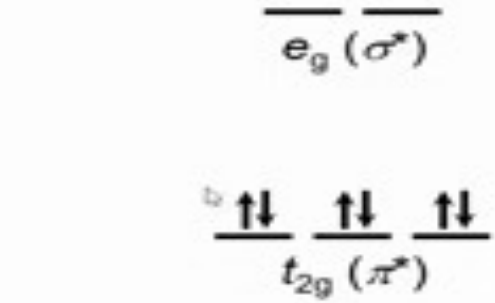
homework

→ Problem 5.10

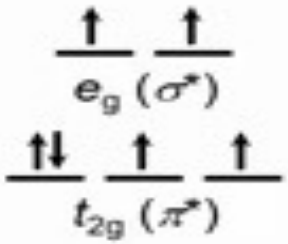
"Construct an MO diagram for trigonal-planar BH_3 by analogy with the MOs for trigonal-planar NH_3 in Figure 5.26. Use this diagram to determine the degeneracy and orbital character of the HOMO and LUMO."

Spin States & Jahn–Teller Distortions

1. **Explain spin-state configurations**
   - Define *high-spin* and *low-spin* complexes.
   - Relate crystal field splitting energy (Δ) and spin pairing energy (P).
   - Predict spin states from ligand type (spectrochemical series) and metal identity (3d vs 4d/5d).
2. **Compare structural preferences of d^8 ions**
   - Describe why Ni^{2+} forms octahedral (rock salt) structures while Pt^{2+} forms square planar (Cooperite-type).
   - Interpret orbital splitting diagrams for square planar fields.
3. **Apply the Jahn–Teller theorem**
   - Identify cases where electronic degeneracy causes structural distortion (e.g., high-spin d^4, d^9).
   - Distinguish between *elongated* and *compressed* octahedra and the electronic rationale for each.
4. **Describe second-order Jahn–Teller distortions**
   - Explain how HOMO–LUMO mixing stabilizes asymmetric geometries (e.g., NH_3, PbO).
   - Recognize "stereoactive lone pair" distortions in s^2 cations (Pb^{2+}, Bi^{3+}).



low-spin configuration ($P < \Delta$)



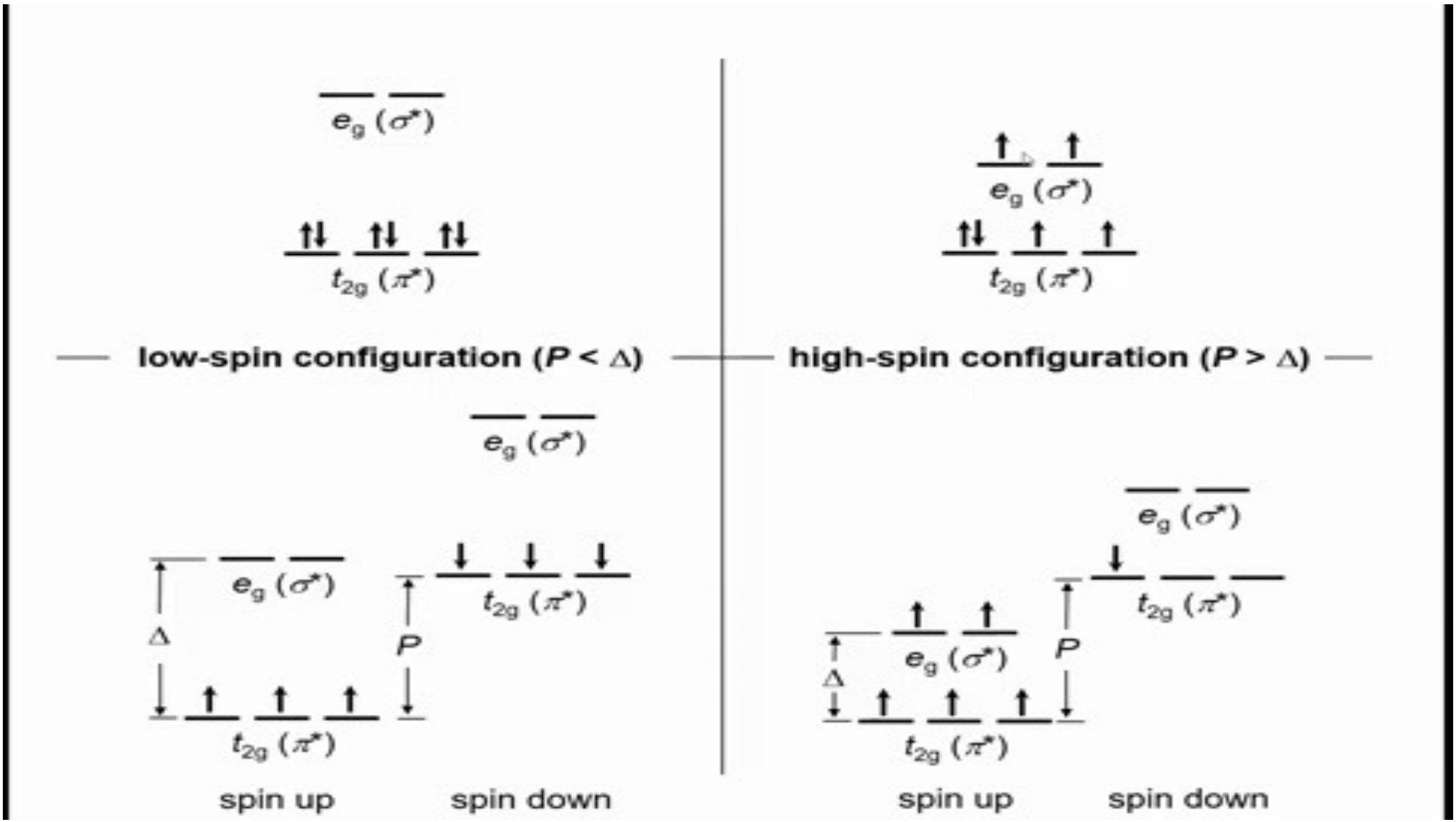
high-spin configuration ($P > \Delta$)

Δ = Crystal field splitting energy

Favors filling lower energy set (t_{2g}) of orbitals completely before adding electrons to higher energy set (e_g)

P = Spin pairing energy

Favors spreading the electrons out across all five d-orbitals before placing two electrons in the same orbital (strong Hunds rule coupling)


$e_g(\sigma^*)$
$t_{2g}(\pi^*)$
low-spin configuration ($P < \Delta$)
high-spin configuration ($P > \Delta$)
Δ
P
spin up
spin down

High spin vs. Low spin

- **2nd and 3rd row transition-metal ions adopt LS configurations**
  - The *4d* and *5d* orbitals interact more strongly with the ligands, increasing Δ, plus their larger size decreases P.

- **Increasing the covalency of the metal–ligand bonds increases Δ thereby favoring LS configurations**
  - Either by increasing the metal oxidation state or by moving from left to right across the transition-metal series

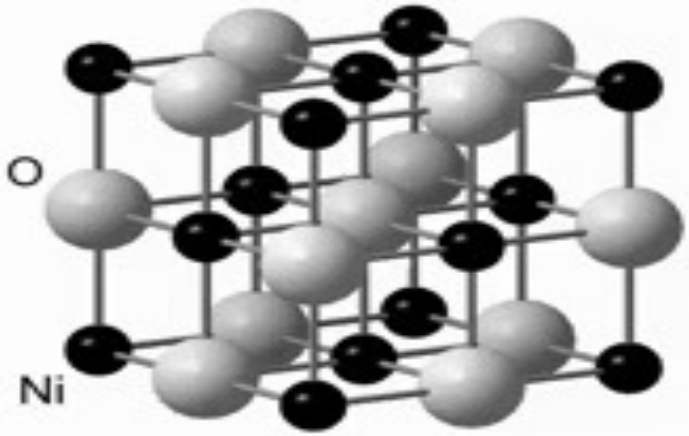
- **Tetrahedrally coordinated ions are nearly always high spin**
  - $\Delta_{tetr} < \Delta_{oct}$

- **High field ligands (see spectrochemical series) favor LS configurations**

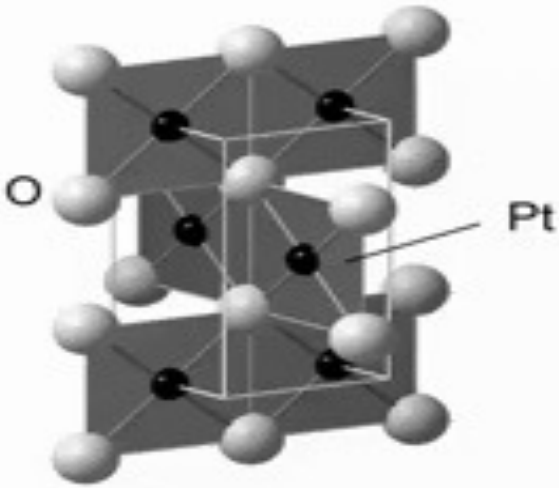
$$I^- < Br^- < S^{2-} < Cl^- < F^- < C_2O_4^{2-} < H_2O < NH_3 < CN^- < CO$$

weak field — strong field

Crystal Chemistry of Group 10 Monoxides



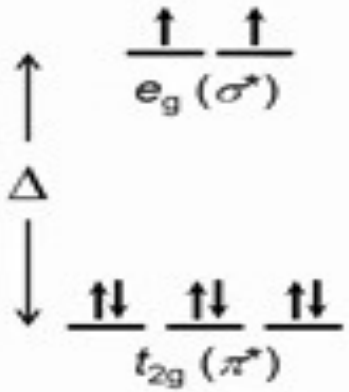
NiO (rock salt)



PtO (cooperite)

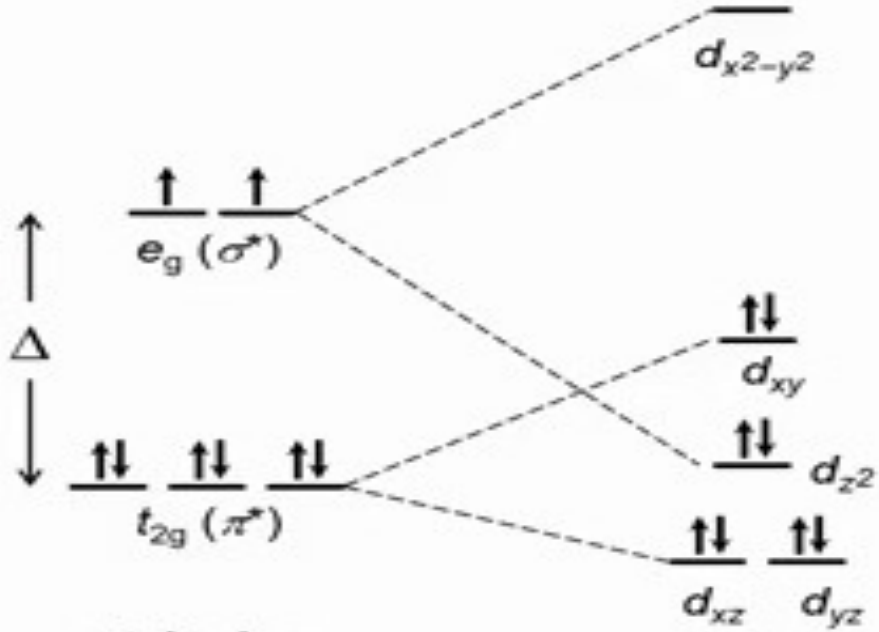
Why do NiO and PtO adopt different structure types?

Octahedral vs Square Planar



octahedron

Octahedral vs Square Planar



NiO, 3d orbitals
Δ is small
High spin favored

octahedron

square planar

PtO, 5d orbitals
Δ is large
Low spin favored

Jahn-Teller Distortions

Jahn–Teller theorem

- An incompletely filled set of otherwise degenerate MOs will undergo a structural distortion that removes the degeneracy and lowers the energy of the occupied orbital

1st Order Jahn-Teller distortion

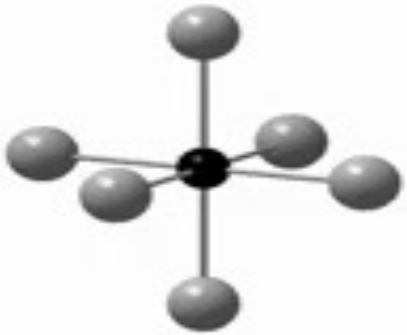
- Follows the letter of the JT theorem. A partially filled HOMO is needed

2nd Order Jahn-Teller distortion

- Involves mixing between filled and empty orbitals (that should be close in energy) that lowers the energy of the filled orbitals

1st order Jahn-Teller Distortion

octahedron

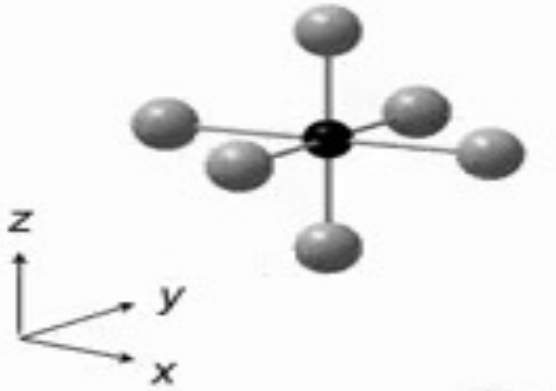


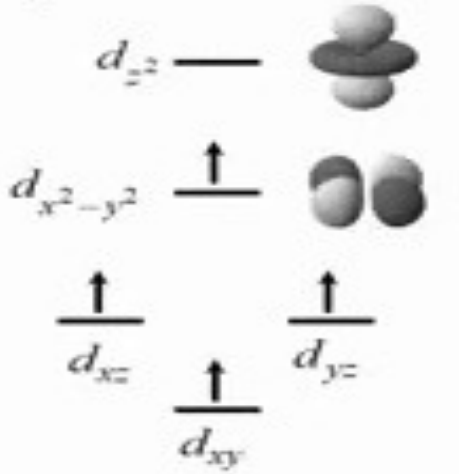
$\uparrow$ d_{z^2} $\quad$ $\_\_$ $d_{x^2-y^2}$

$\uparrow$ d_{xz} $\quad$ $\uparrow$ d_{xy} $\quad$ $\uparrow$ d_{yz}

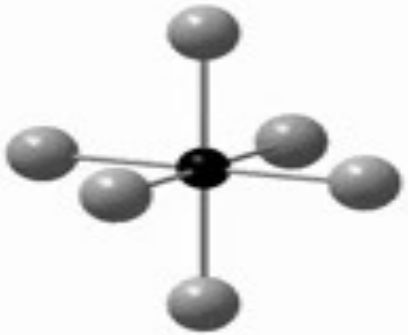
1st order Jahn-Teller Distortion

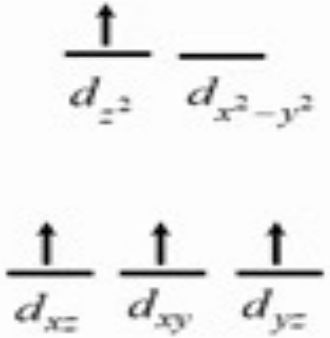
compressed octahedron





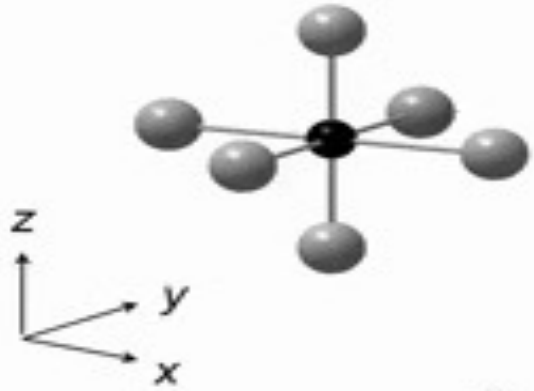
octahedron

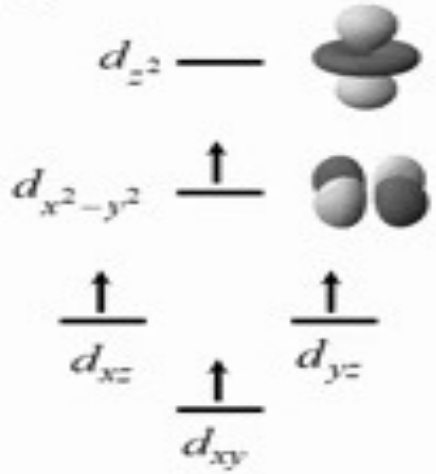




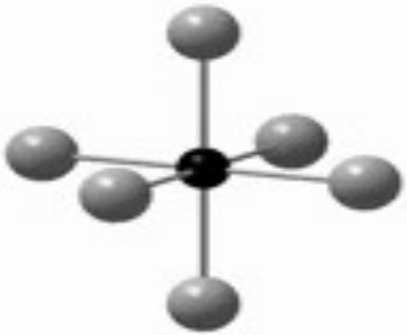
1st order Jahn-Teller Distortion

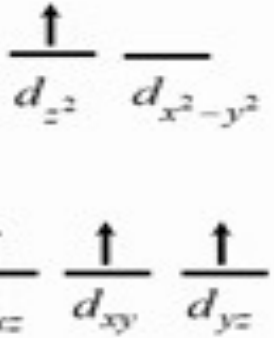
compressed octahedron



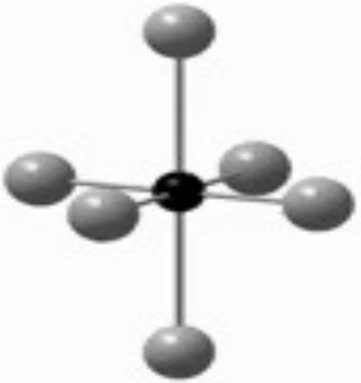


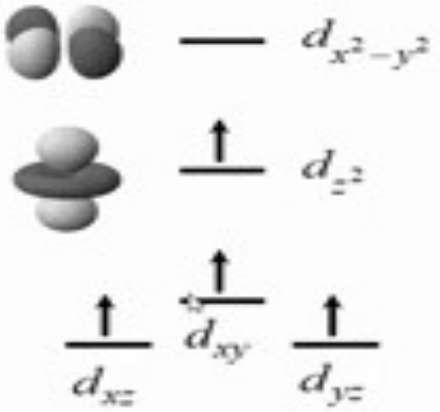
octahedron



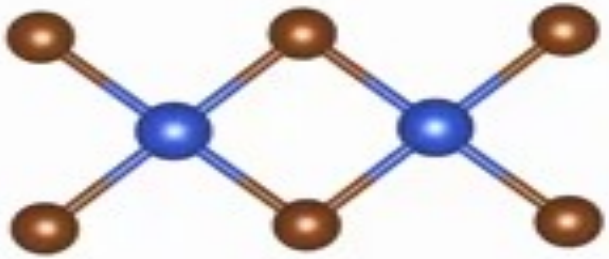


elongated octahedron

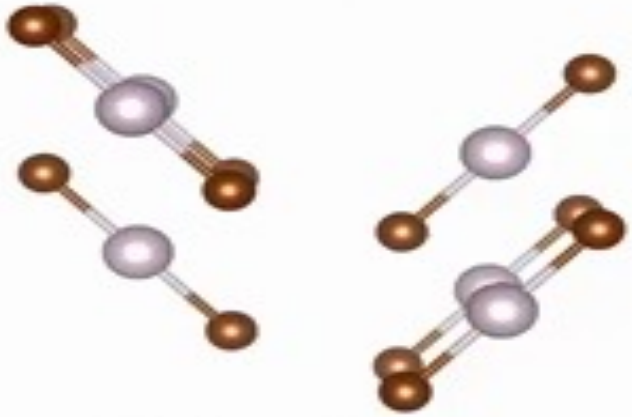




Distortions in d^9 & d^{10} Halides



$CuBr_2$ distances
4×2.41 Å, 2×3.15 Å



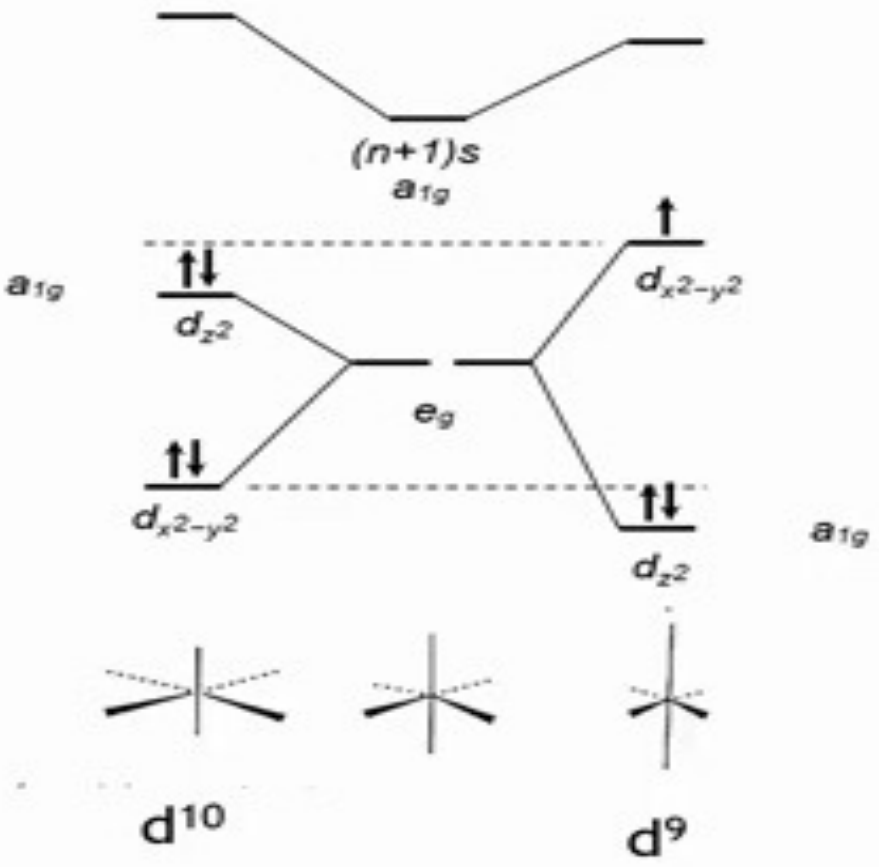
$HgBr_2$ distances
2×2.45 Å, 4×3.24 Å

Cu^{2+} (d^9) ions almost always take the **2 long + 4 short distortion** (elongated octahedron)

d^{10} ions, such as Hg^{2+} adopt very large **2 short + 4 long distortions** (compressed octahedron).

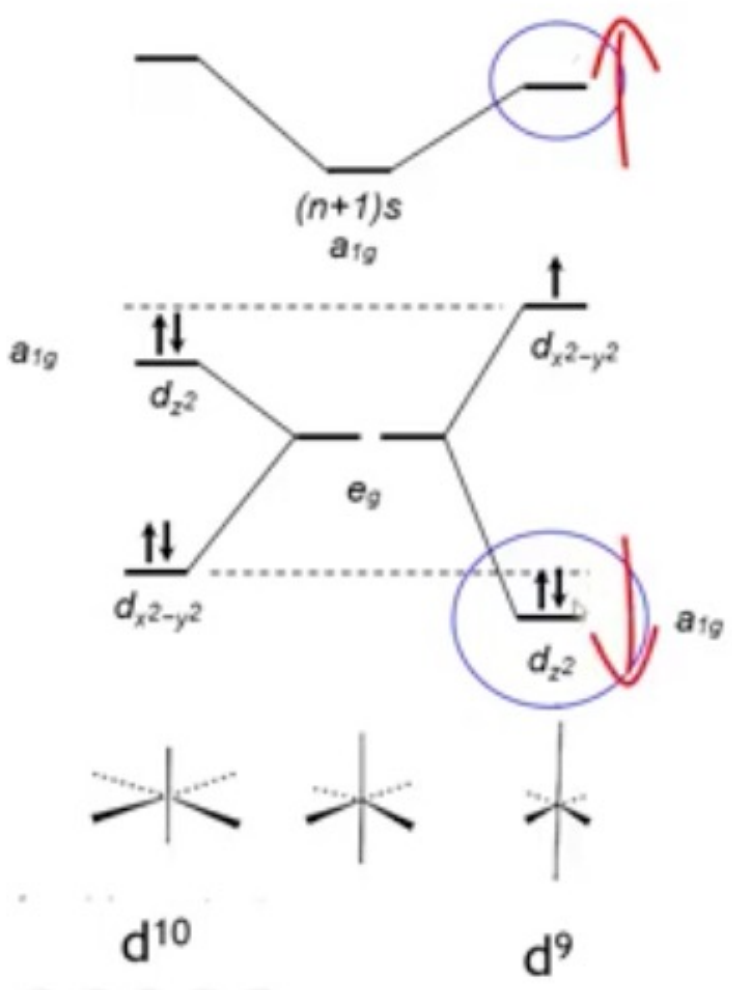
Why is this so? Why do d^{10} ions distort at all?

Jahn-Teller Distortions s-d_{z2} Mixing



The empty *n*s orbital is of appropriate symmetry (a_{1g}) to mix with the $(n\text{-}1)d_{z2}$ orbital, but not with the $(n\text{-}1)d_{x2\text{-}y2}$ orbital.

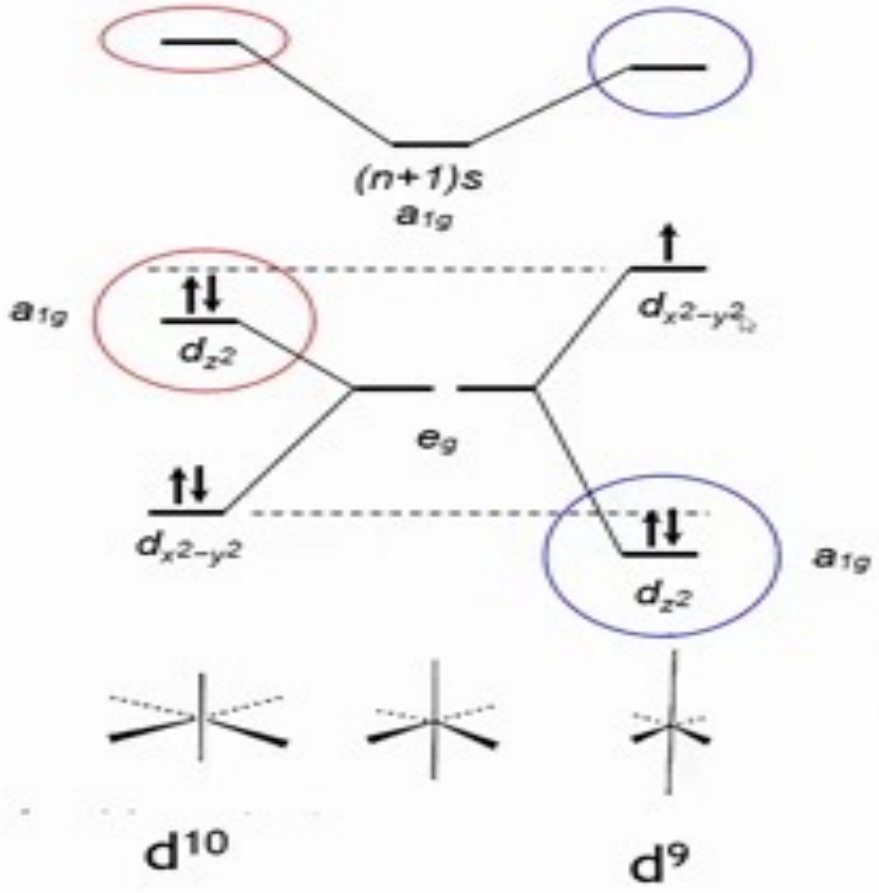
Jahn-Teller Distortions s-d_{z2} Mixing



The empty *n*s orbital is of appropriate symmetry (a_{1g}) to mix with the $(n\text{-}1)d_{z2}$ orbital, but not with the $(n\text{-}1)d_{x2\text{-}y2}$ orbital.

d^9 case (Cu^{2+}): The s-d_{z2} mixing favors preferential occupation of the d_{z2} orbital (2 long + 4 short favored)

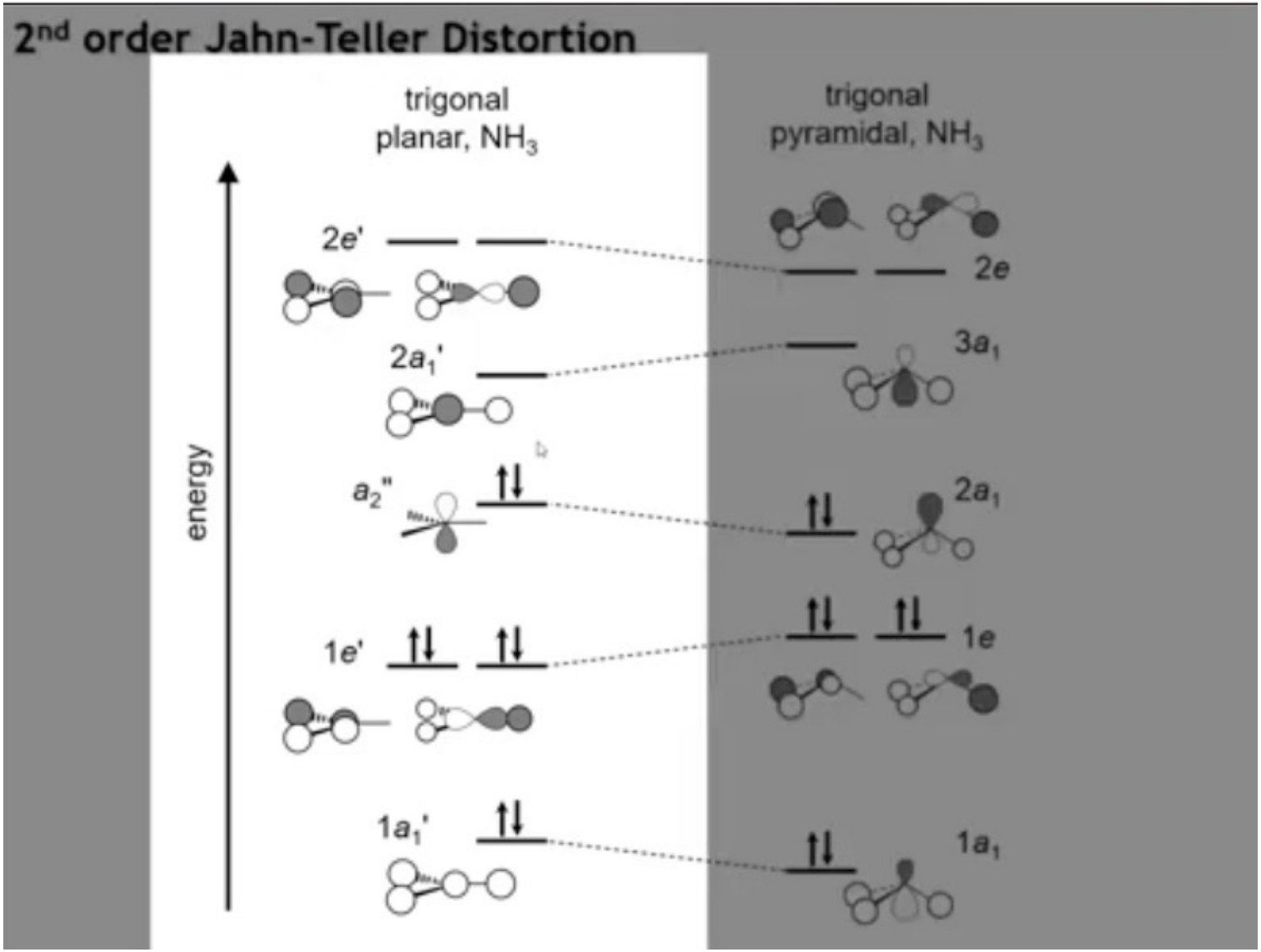
Jahn-Teller Distortions s-d_{z2} Mixing



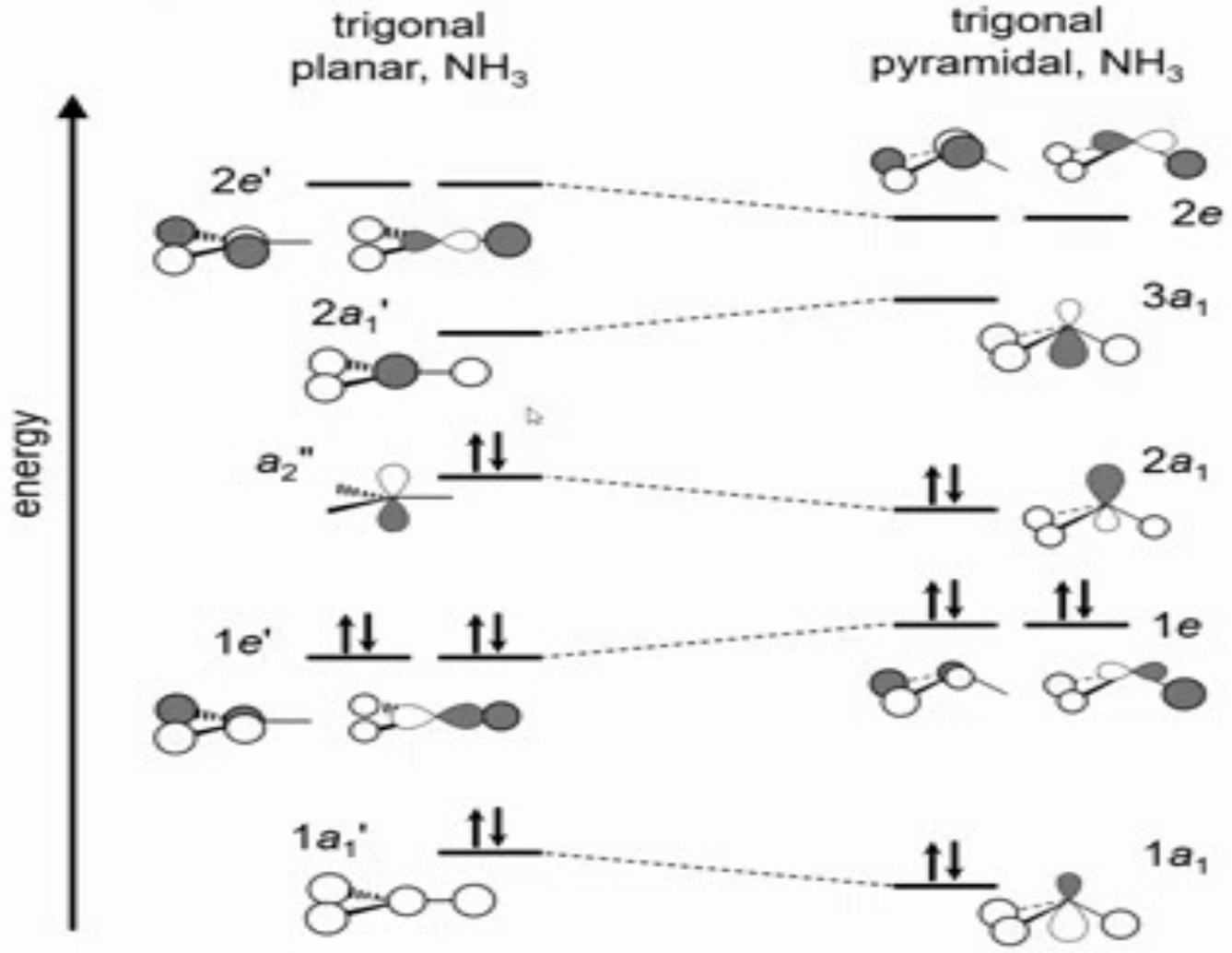
The empty *n*s orbital is of appropriate symmetry (a_{1g}) to mix with the $(n-1)d_{z2}$ orbital, but not with the $(n-1)d_{x2-y2}$ orbital.

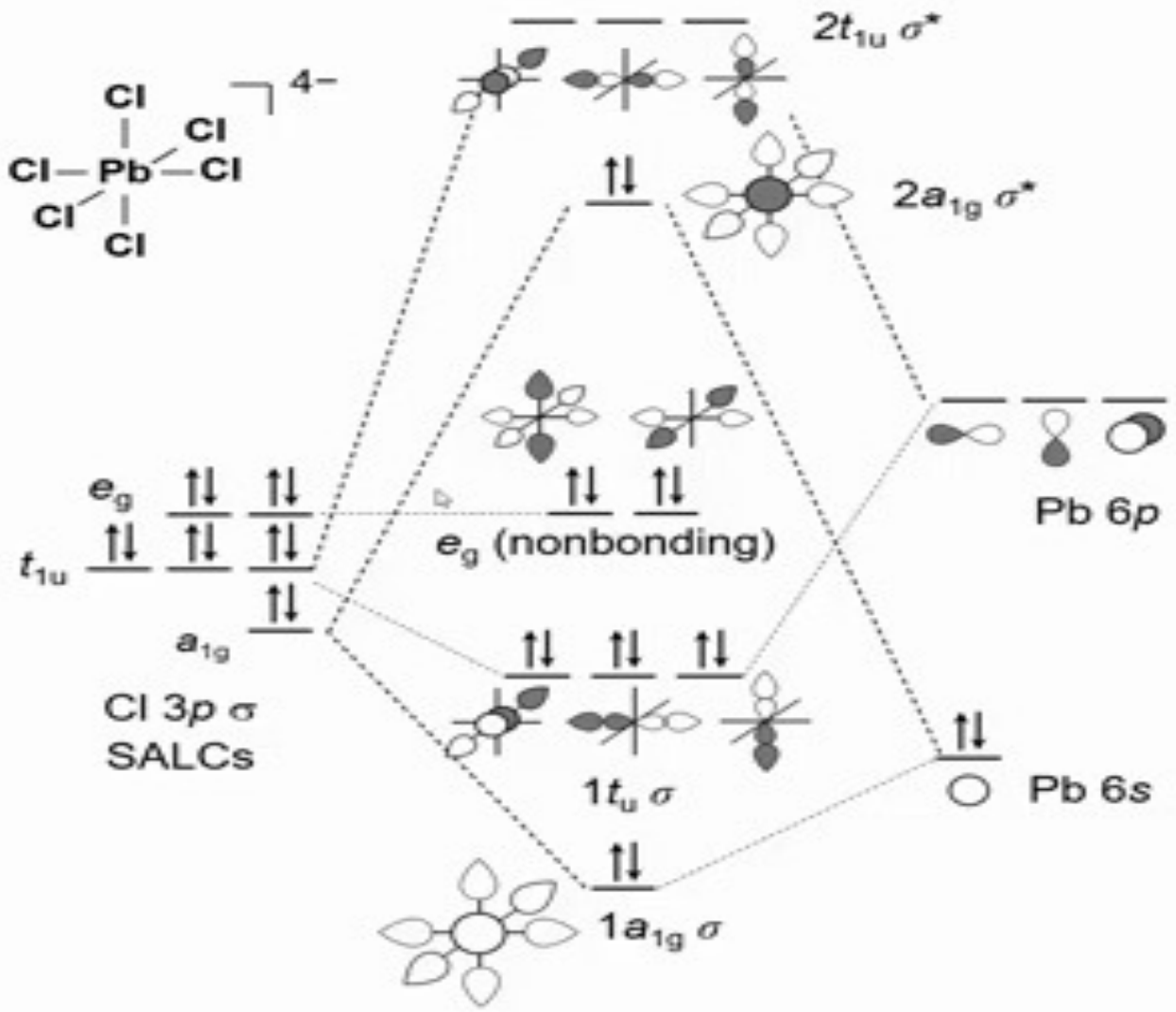
d^9 case (Cu^{2+}): The s-d_{z2} mixing favors preferential occupation of the d_{z2} orbital (2 long + 4 short favored)

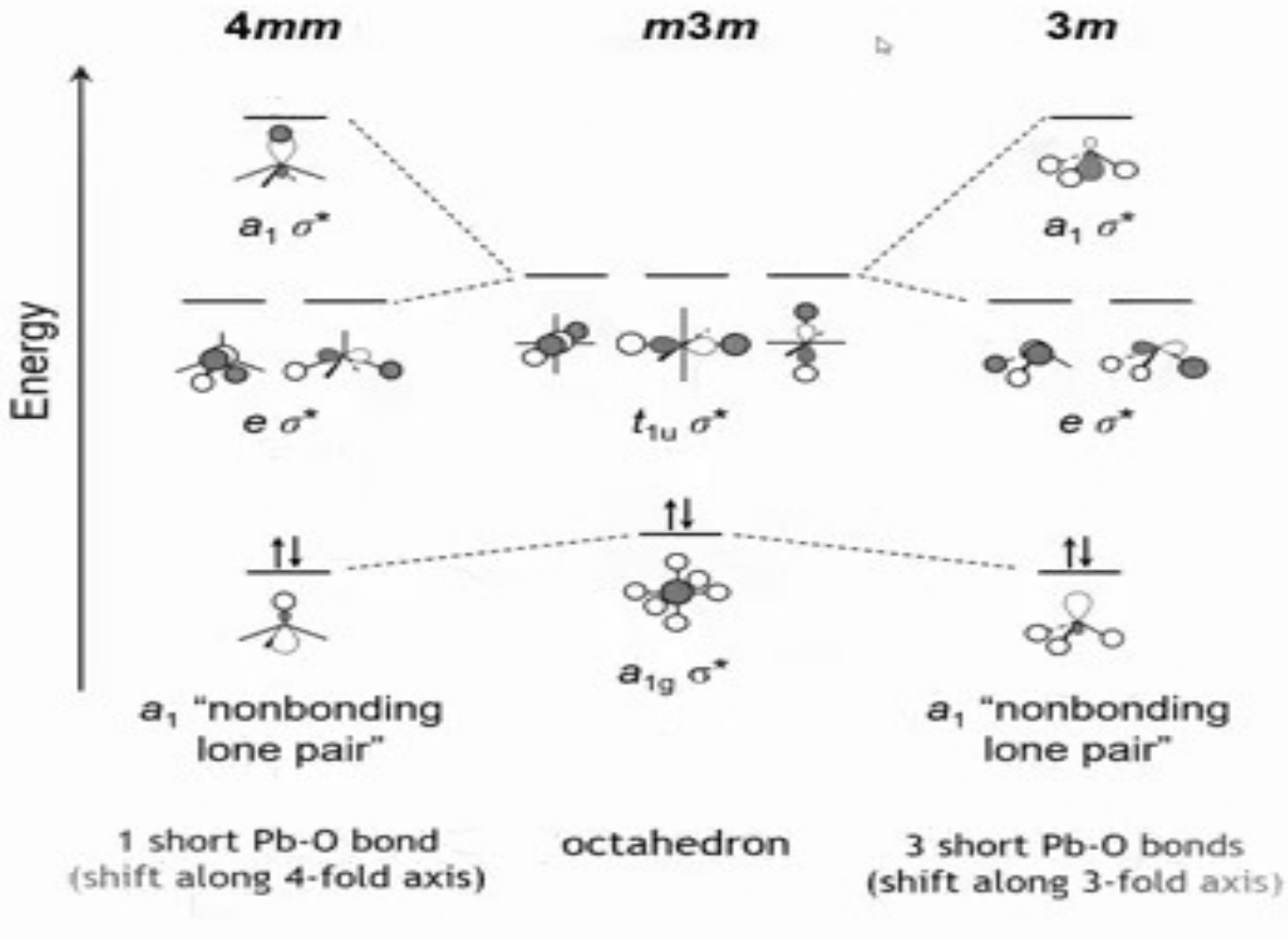
d^{10} case (Hg^{2+}): The s-d_{z2} mixing is largest when the energy separation between the two is minimized (2 short + 4 long favored)


2nd order Jahn-Teller Distortion
trigonal planar, NH3
trigonal pyramidal, NH3
energy
2e'
2a1'
a2"
1e'
1a1'
2e
3a1
2a1
1e
1a1

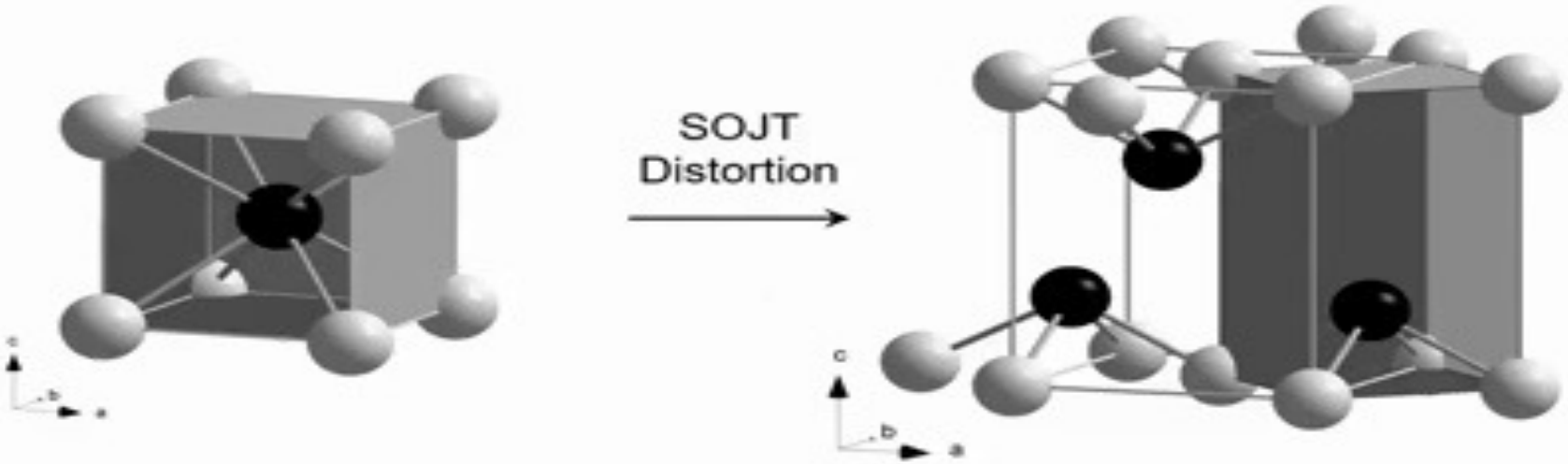
2nd order Jahn-Teller Distortion




Cl
Cl
Cl
Pb
Cl
Cl
Cl
4−
$2t_{1u}$ σ^*
$2a_{1g}$ σ^*
e_g
t_{1u}
a_{1g}
e_g (nonbonding)
Pb 6p
Cl 3p σ
SALCs
$1t_u$ σ
Pb 6s
$1a_{1g}$ σ


4mm
m3m
3m
Energy
a_1 σ*
e σ*
t_{1u} σ*
a_1 σ*
e σ*
a_{1g} σ*
a_1 "nonbonding lone pair"
a_1 "nonbonding lone pair"
1 short Pb-O bond (shift along 4-fold axis)
octahedron
3 short Pb-O bonds (shift along 3-fold axis)

PbO



CsCl structure

Litharge structure

The PbO structure is distorted from the high symmetry CsCl structure by a 2nd order Jahn-Teller distortion leading to a stereoactive lone pair on Pb^{2+}

Spin States & Jahn–Teller Distortions

Spin States

- = crystal-field splitting; P= spin-pairing energy.
- **Low spin** (Δ > P): electrons pair in T_2g.
- **High spin** (Δ < P): electrons spread across all d orbitals.
- Δ↑ for 4d/5d metals, short/covalent bonds, strong-field ligands (CO > NH_3 > H_2O > Cl^-).
- Tetrahedral fields ≈ ½ Δ_{oh} → almost always high spin.

Octahedral → Square Planar (d^8)

- Ni^{2+} ($3d^8$): weak field → octahedral (high spin).
- Pt^{2+} ($5d^8$): strong field → square planar (low spin).
- Large Δ stabilizes dz^2, empties $dx^2–y^2$.

Octahedral → Square Planar (d^8)

- Ni^{2+} ($3d^8$): weak field → octahedral (high spin).
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- Large Δ stabilizes dz^2, empties $dx^2–y^2$.

Jahn–Teller Distortion (1st Order)

- Partially filled degenerate HOMO → symmetry lowering.
- Seen in high-spin d^4 (Mn^{3+}) and d^9 (Cu^{2+}).
- Elongated octahedra (4 short + 2 long bonds) most stable.
- Compression rare.

2nd Order / Pseudo Jahn–Teller

- Mixing between filled HOMO and nearby empty LUMO of same symmetry.
- Examples:
  - NH_3 – pz ↔ 2s mix → trigonal pyramidal.
  - Pb^{2+}, Sn^{2+} – 6s/6p mix → off-center "stereoactive lone pair."
  - d^0 ions (Ti^{4+}, Nb^{5+}, Mo^{6+}) – cation shifts off-center.

Core Idea: Electronic degeneracy and Δ vs P competition drive spin state and geometry distortions.

Question 1 – Spin States

For an Fe^{2+} ion (d^6) in an octahedral field, how would the spin state differ between $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$, and why?

Question 1 – Spin States

For an Fe^{2+} ion (d^6) in an octahedral field, how would the spin state differ between $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$, and why?

→ **Answer:** H_2O is a weak-field ligand → small Δ → high-spin d^6 (four unpaired). CN^- is strong-field → large Δ → low-spin d^6 (no unpaired).

Question 2 – Jahn–Teller Distortion

Why do Cu^{2+} (d^9) complexes typically show elongated octahedral geometry rather than compressed?

Question 2 – Jahn–Teller Distortion

Why do Cu^{2+} (d^9) complexes typically show elongated octahedral geometry rather than compressed?

→ **Answer:** In d^9, the eg orbitals are unevenly filled. Elongation lowers the energy of dz^2 and reduces antibonding along the z-axis, giving net stabilization; compression would raise energy of the filled orbital, so elongation wins energetically.