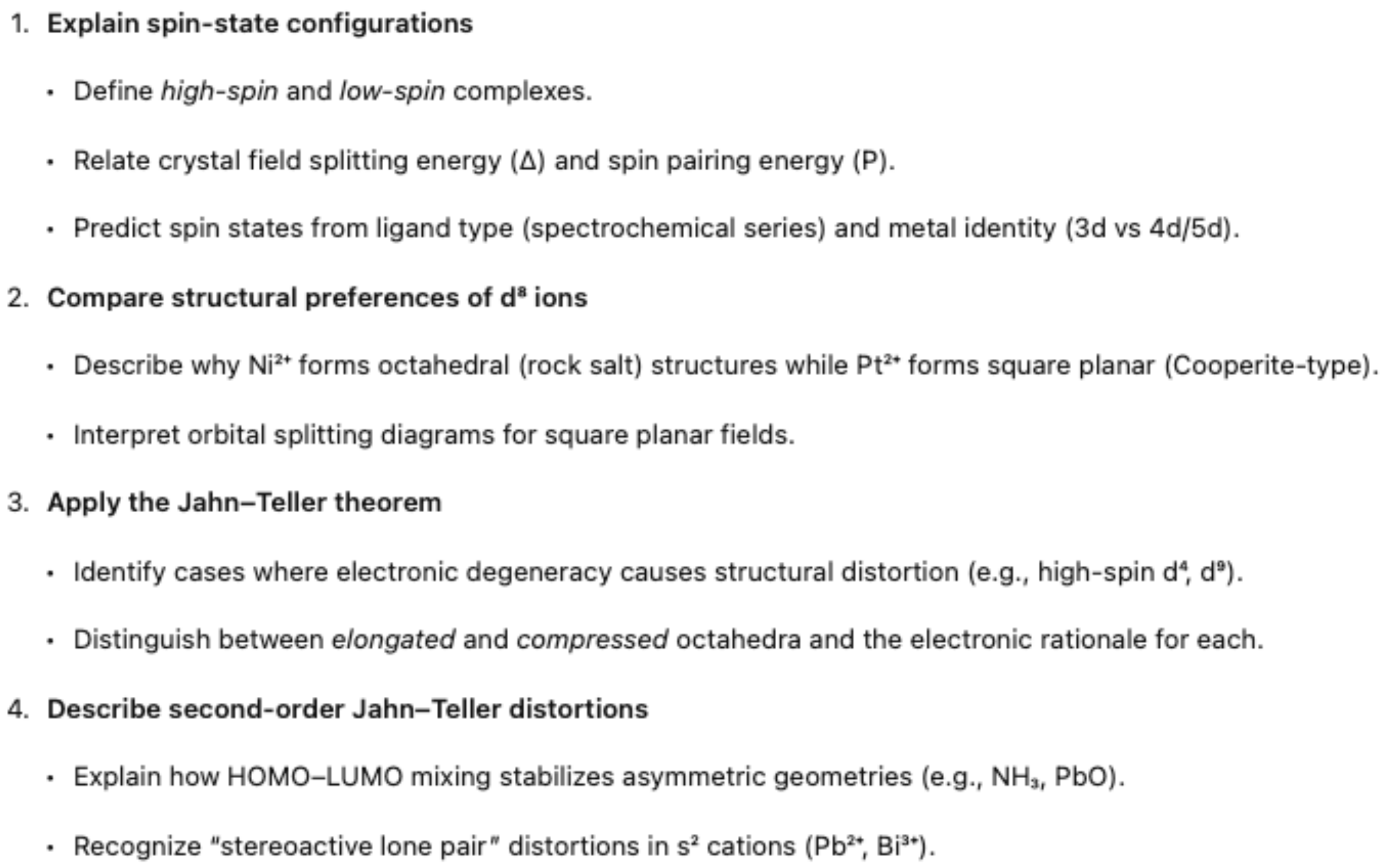
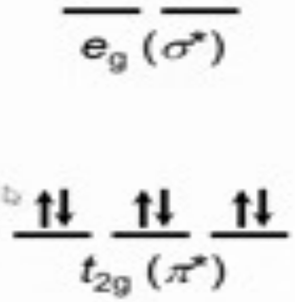
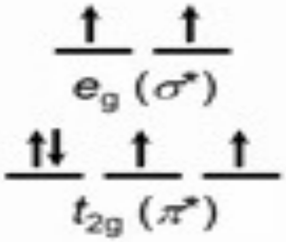
Spin States & Jahn–Teller Distortions



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 ($P < \Delta$)



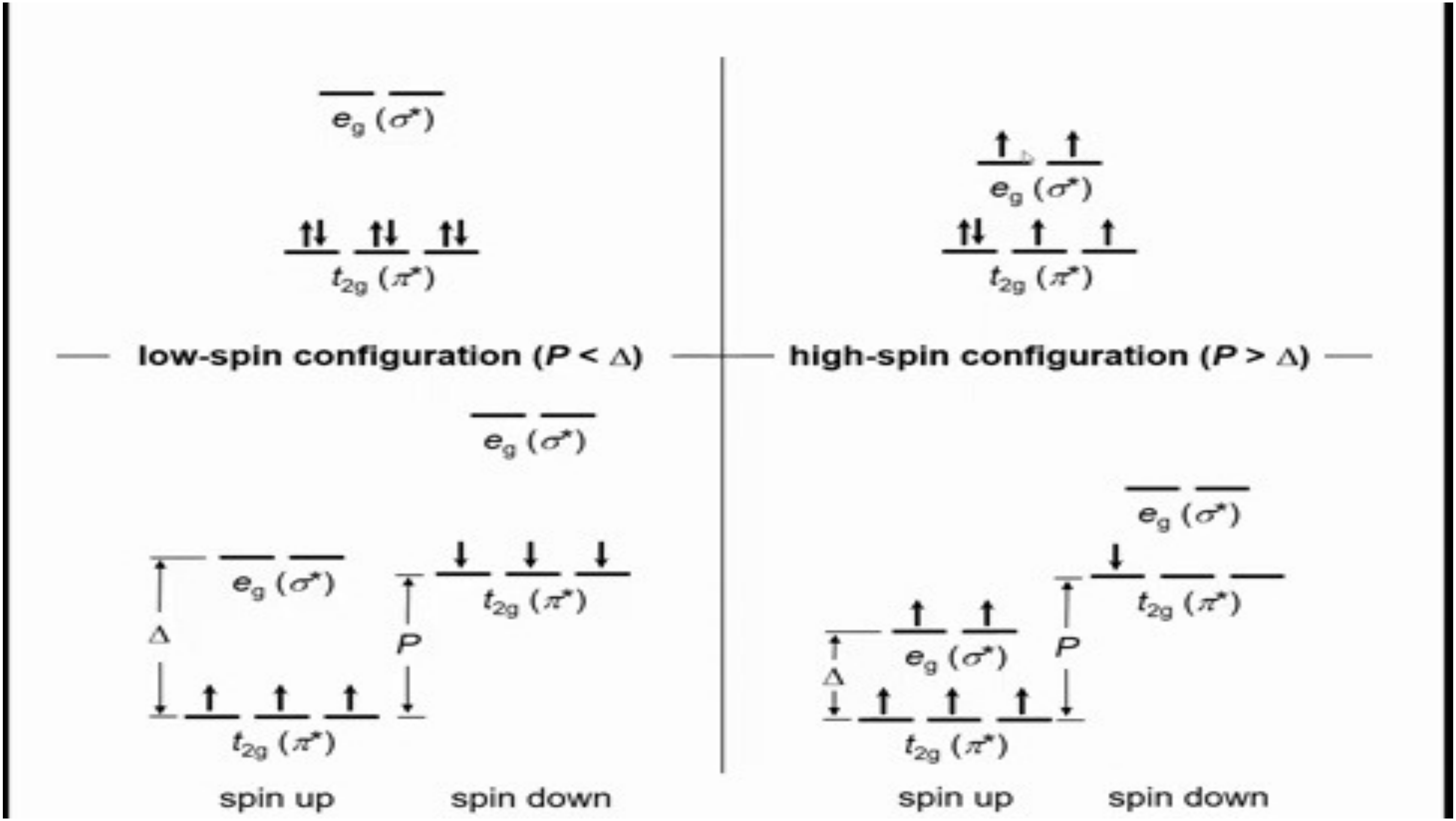
high-spin configuration ($P > \Delta$)

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

High spin vs. Low spin

- 2nd and 3rd row transition-metal ions adopt LS configurations
  - The 4*d* and 5*d* 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

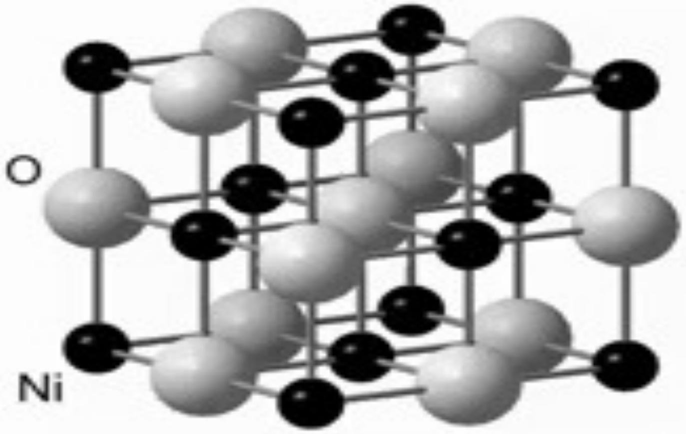
- Tetrahedrally coordinated ions are nearly always high spin
  - $\Delta_{tetr} < \Delta_{oct}$

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

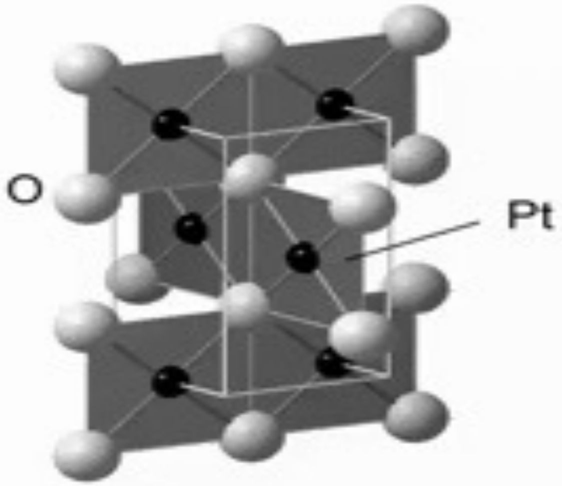
$$I^- < Br^- < S^{2-} < Cl^- < F^- < C_2O_4^{2-} < H_2O < NH_3 < CN^- < CO$$

weak field strong field

Crystal Chemistry of Group 10 Monoxides



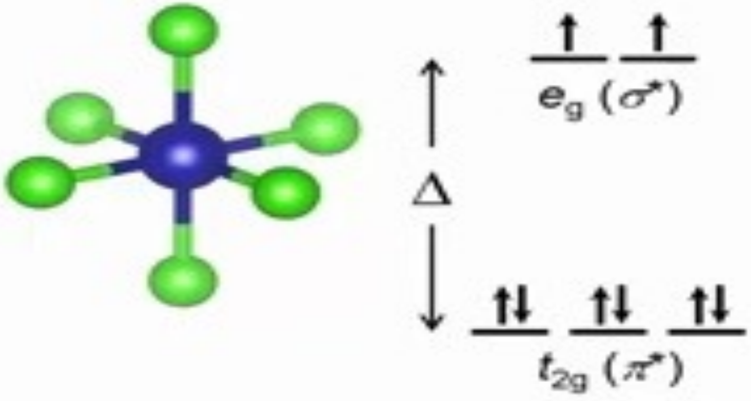
NiO (rock salt)



PtO (cooperite)

Why do NiO and PtO adopt different structure types?

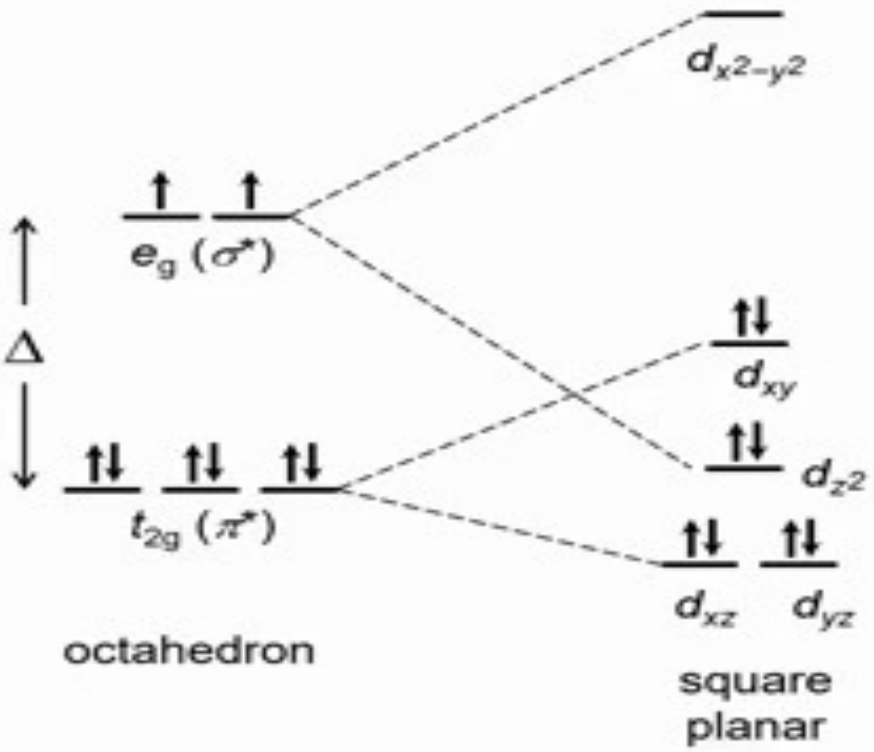
Octahedral vs Square Planar



octahedron

Octahedral vs Square Planar

NiO, 3d orbitals
Δ is small
High spin favored



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

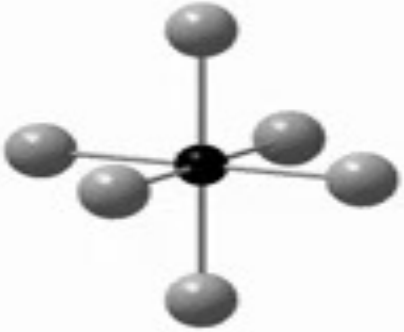
- Follows the letter of the JT theorem. A partially filled HOMO is needed

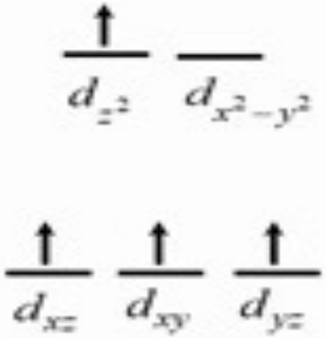
2nd Order Jahn-Teller distortion

- 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

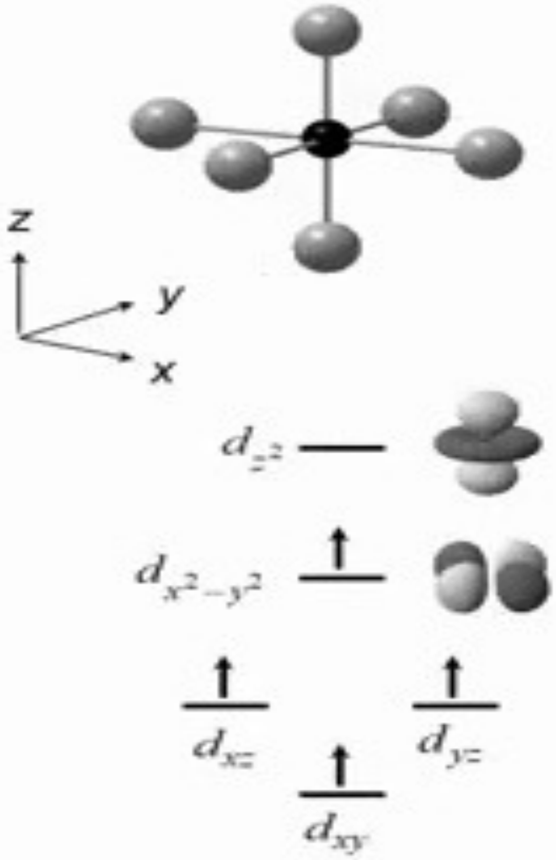
octahedron



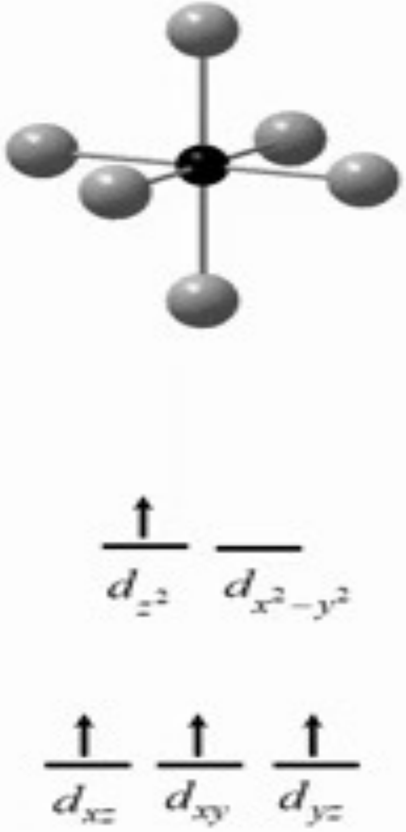


1st order Jahn-Teller Distortion

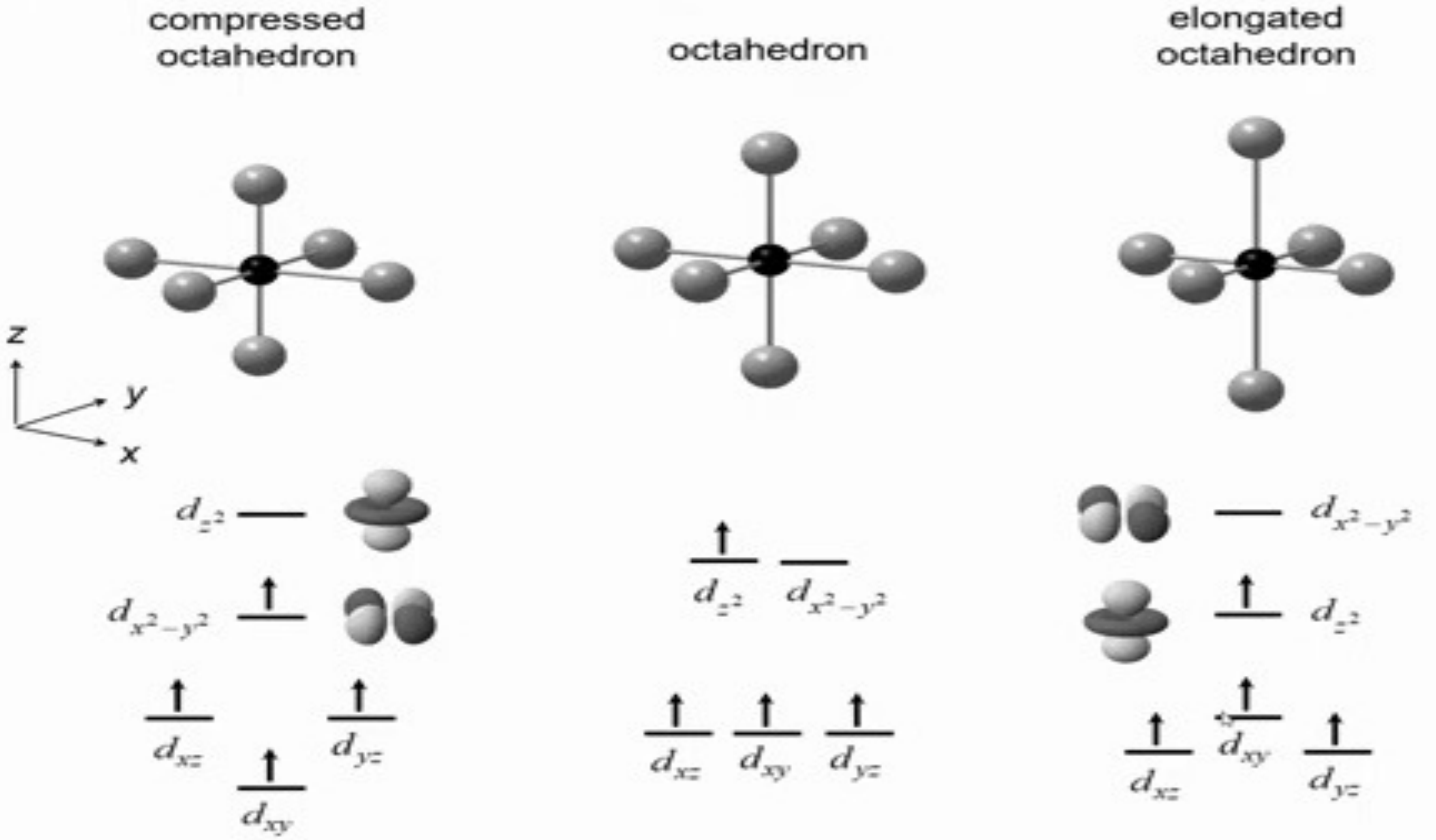
compressed octahedron

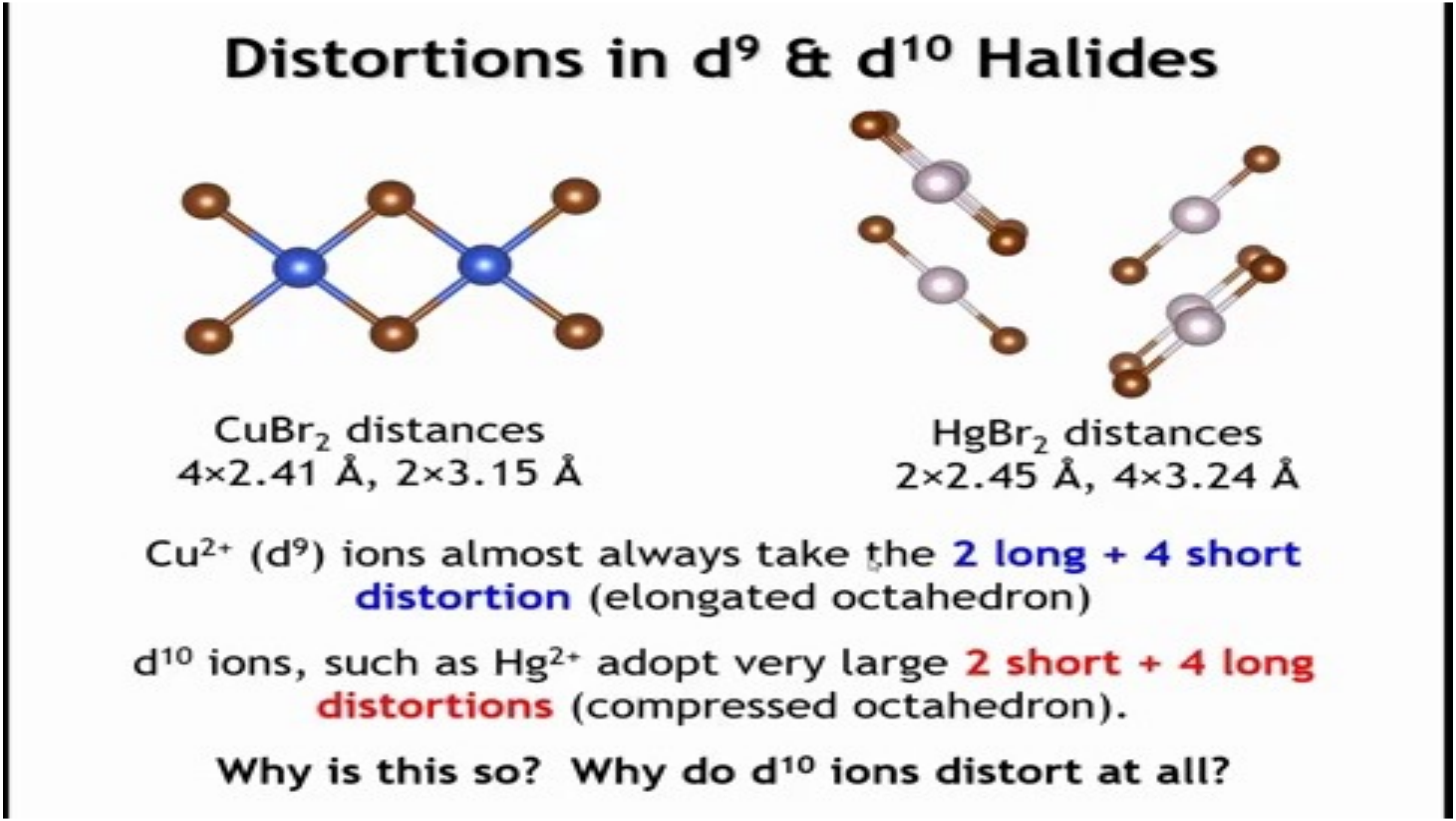


octahedron



1st order Jahn-Teller Distortion





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

$CuBr_2$ distances
4×2.41 Å, 2×3.15 Å

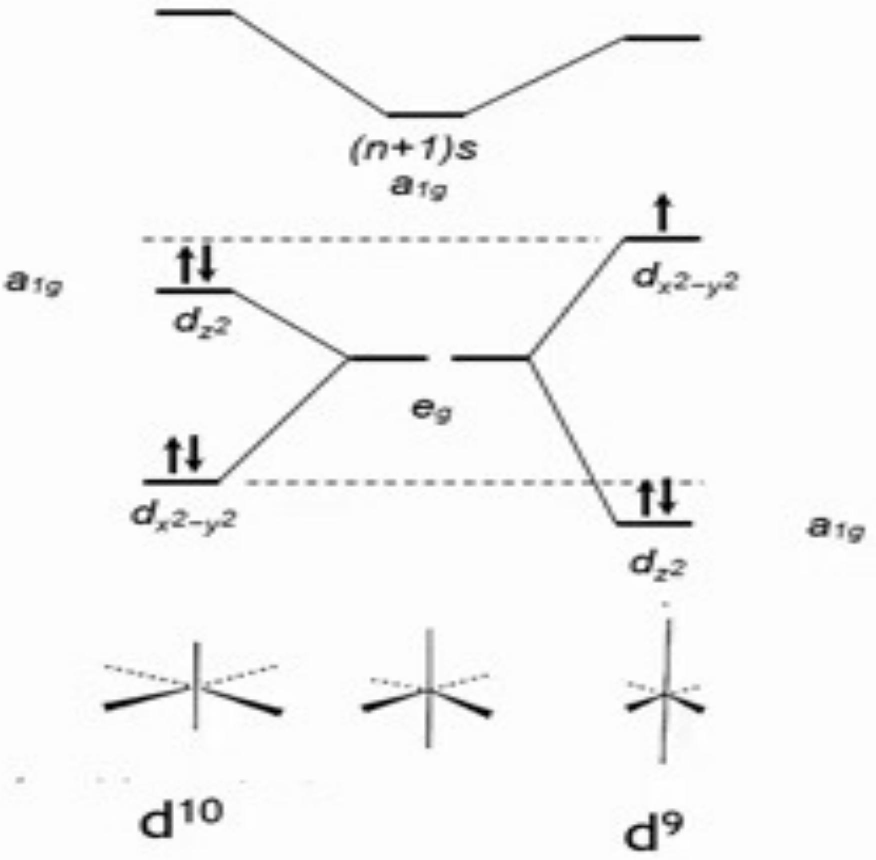
$HgBr_2$ distances
2×2.45 Å, 4×3.24 Å

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).

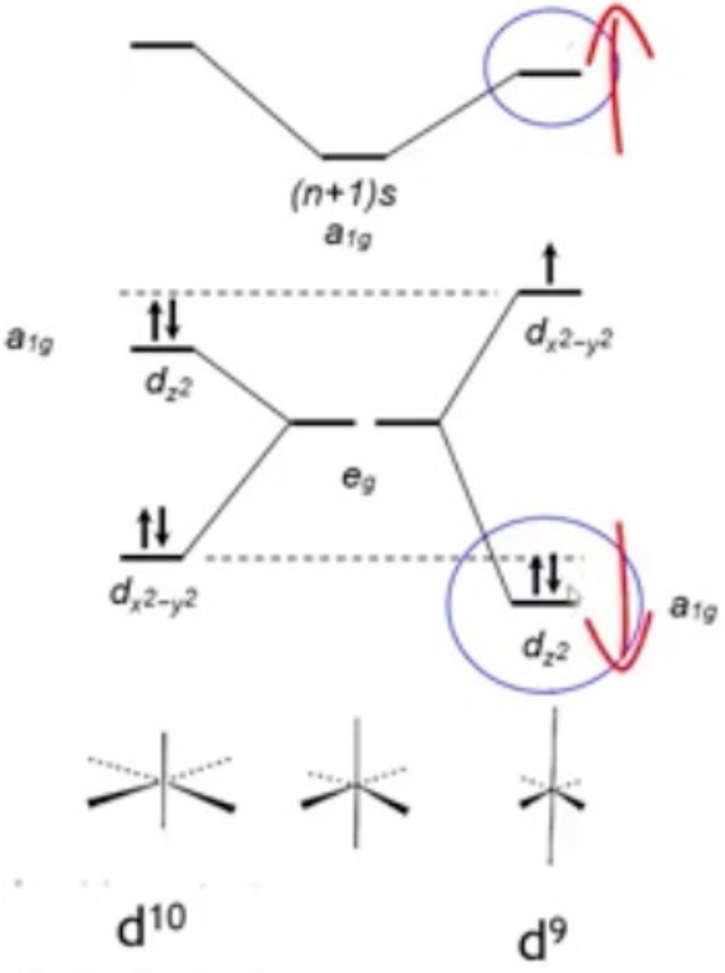
Why is this so? Why do d^{10} ions distort at all?

Jahn-Teller Distortions s-d_{z2} Mixing



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

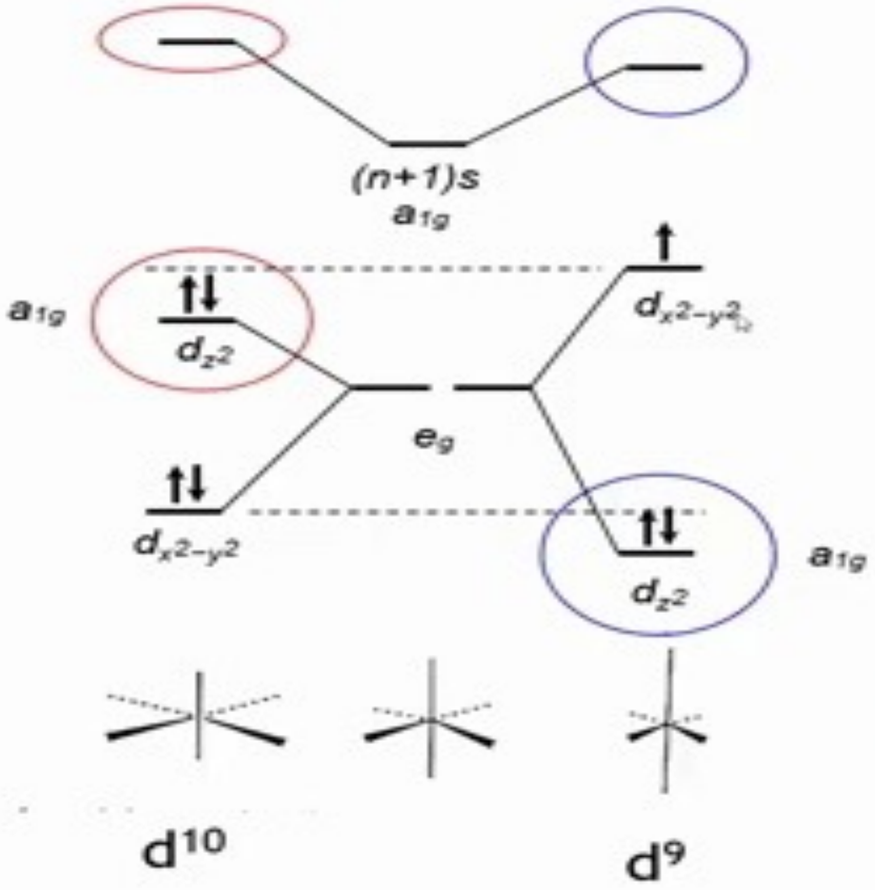
Jahn-Teller Distortions s-d_{z2} Mixing



The empty *n*s orbital is of appropriate symmetry (a_{1g}) to mix with the (*n-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)

Jahn-Teller Distortions s-d_{z2} Mixing



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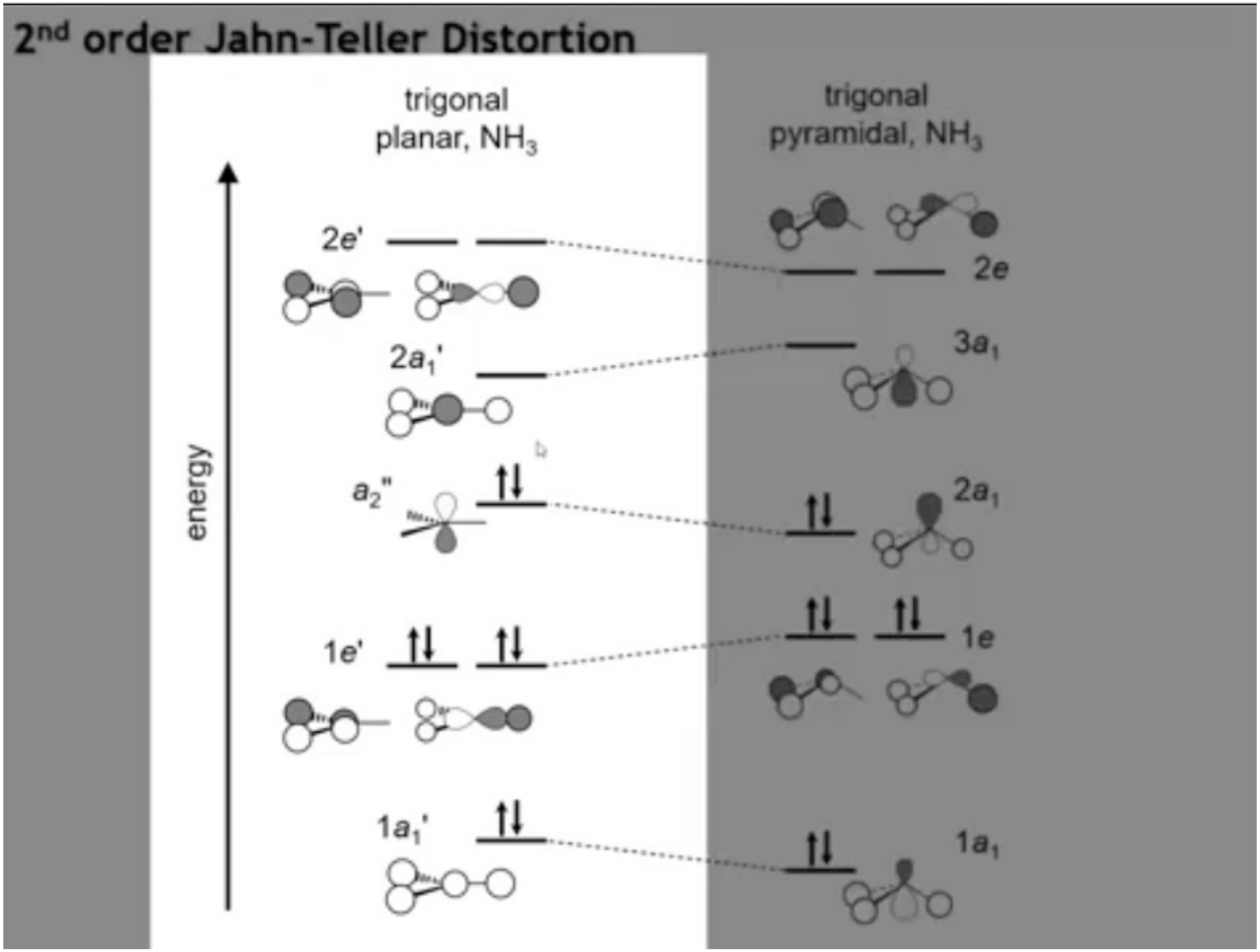
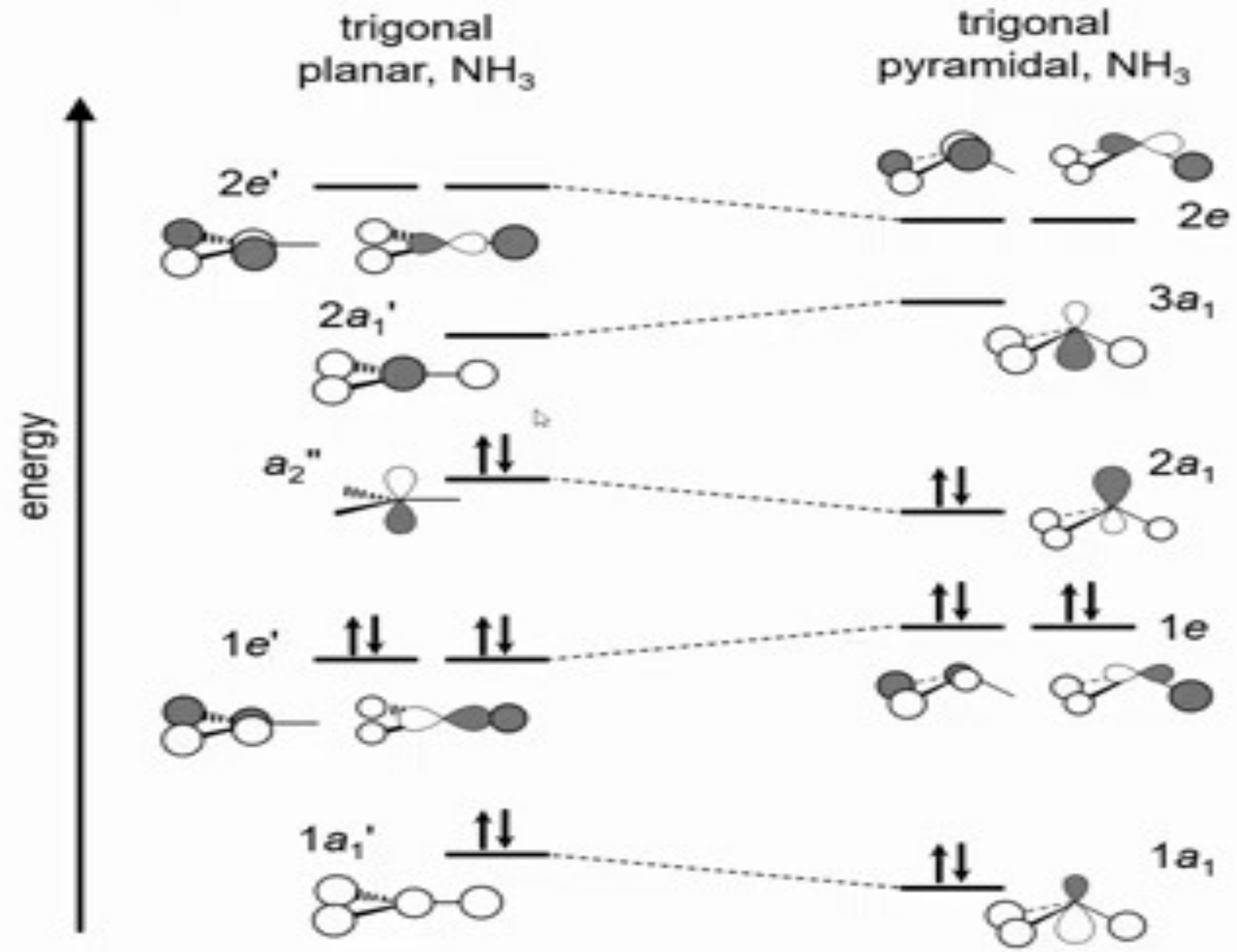
d^9 case (Cu^{2+}): The s-d_{z2} mixing favors preferential occupation of the d_{z2} orbital (2 long + 4 short favored)

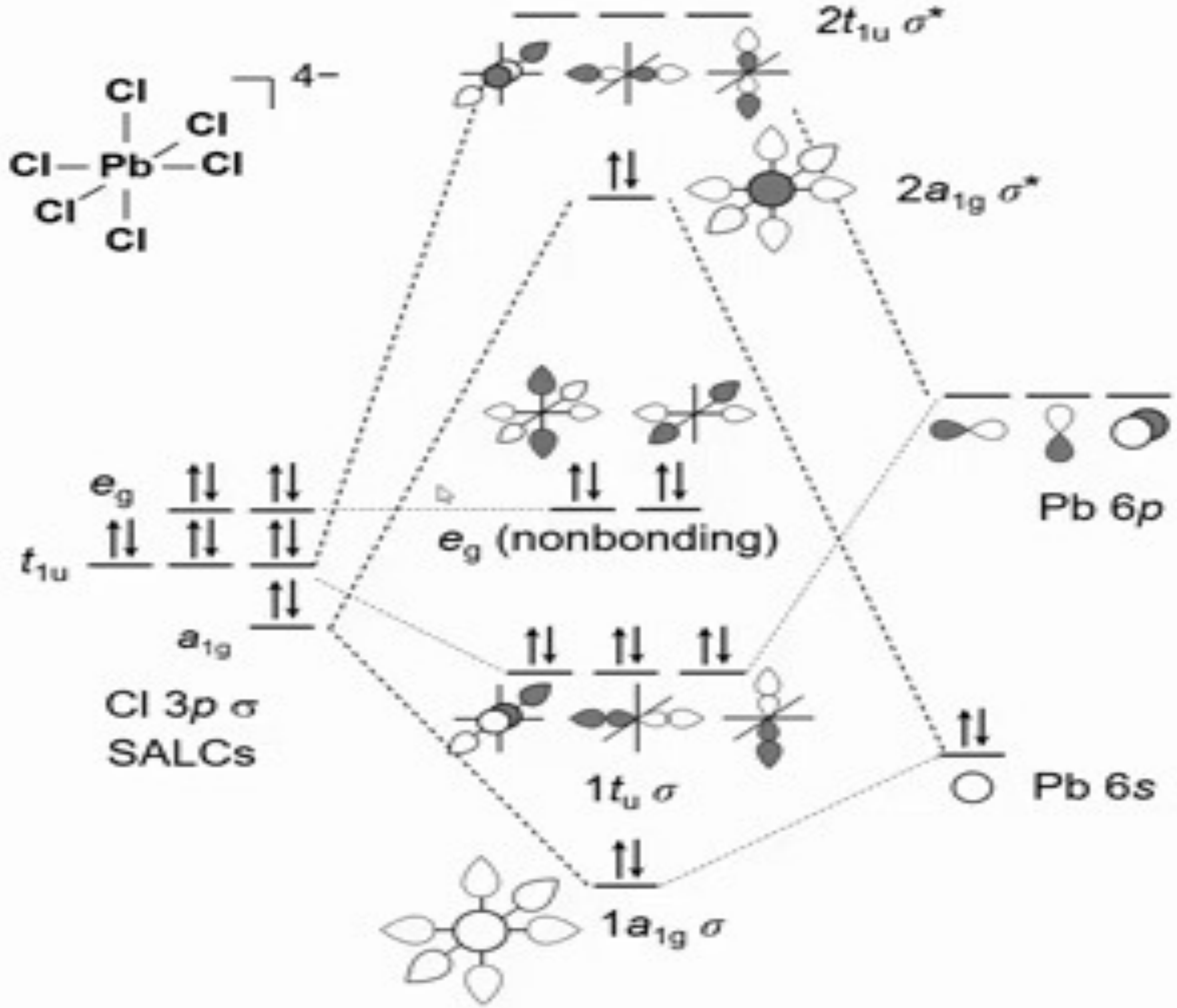
d^{10} case (Hg^{2+}): The s-d_{z2} mixing is largest when the energy separation between the two is minimized (2 short + 4 long favored)



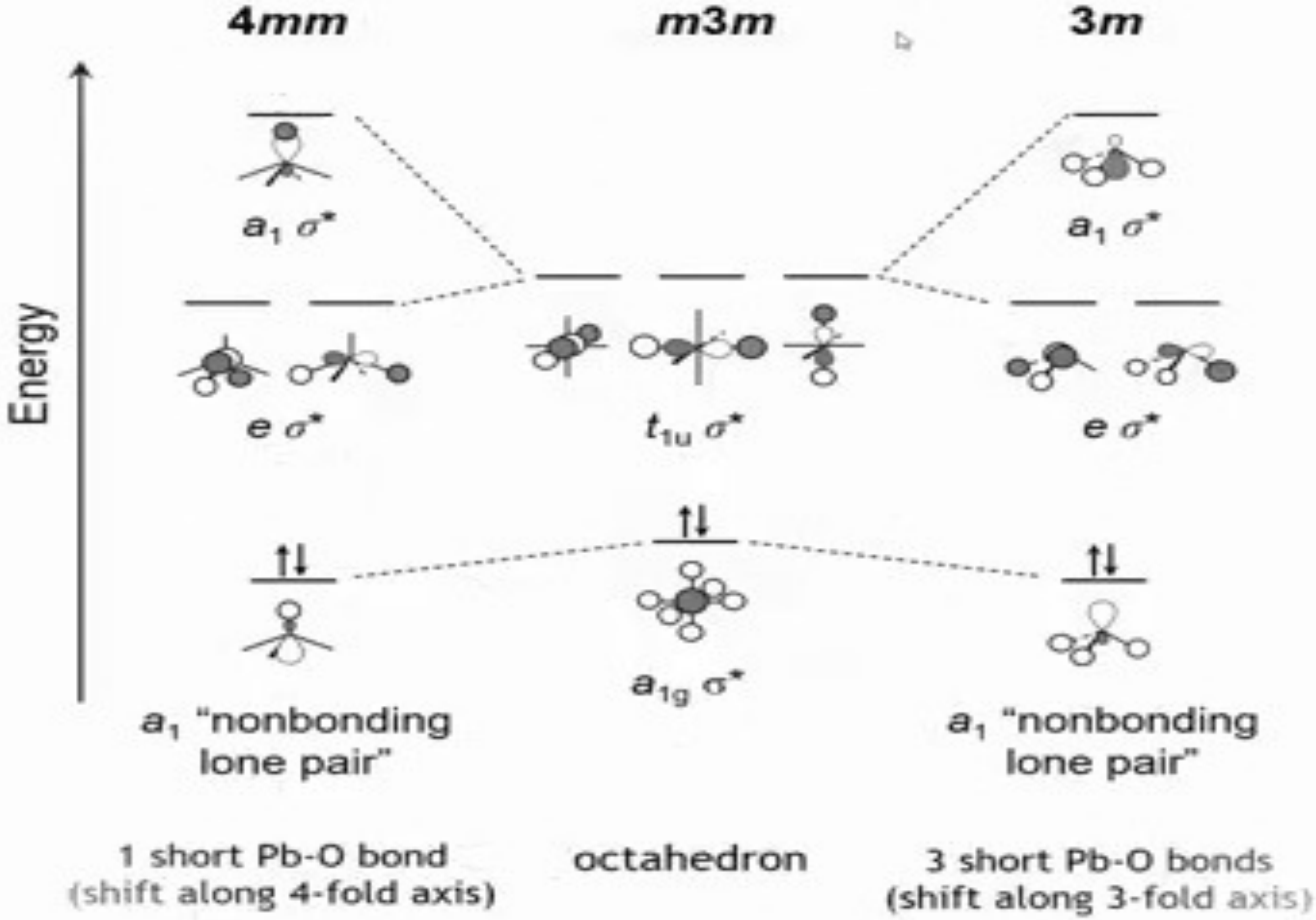
2nd order Jahn-Teller Distortion

2nd order Jahn-Teller Distortion

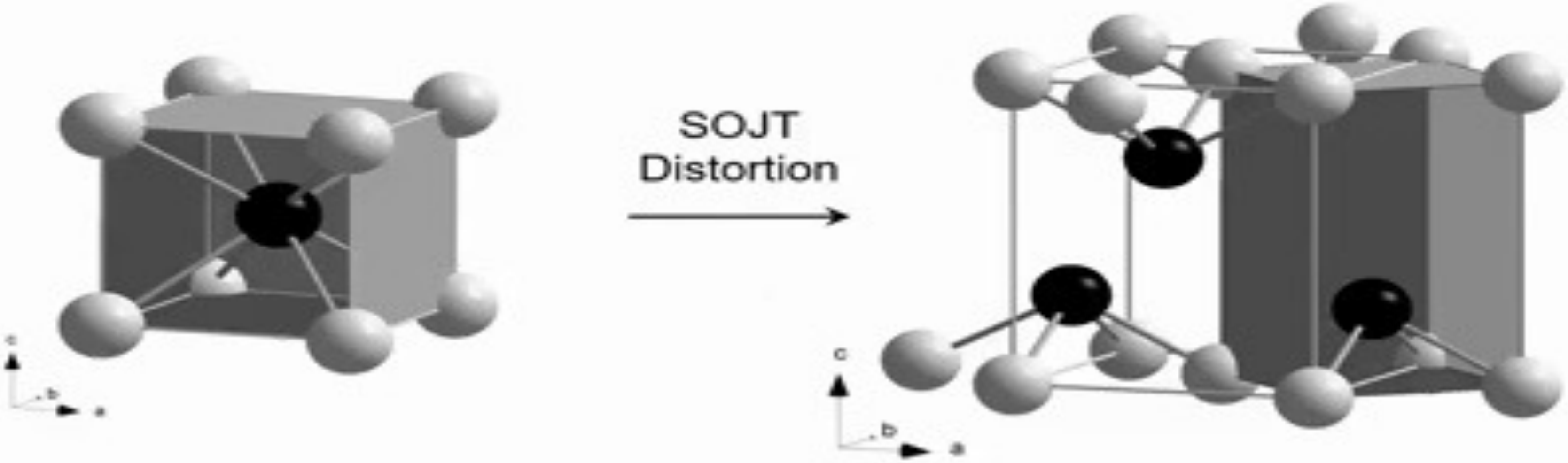




Cl
Cl
Cl
Pb
Cl
Cl
Cl
4−
2t1u σ*
2a1g σ*
eg
t1u
a1g
Cl 3p σ
SALCs
eg (nonbonding)
Pb 6p
1tu σ
Pb 6s
1a1g σ


4mm
m3m
3m
Energy
a_1 σ*
a_1 σ*
e σ*
t_{1u} 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)

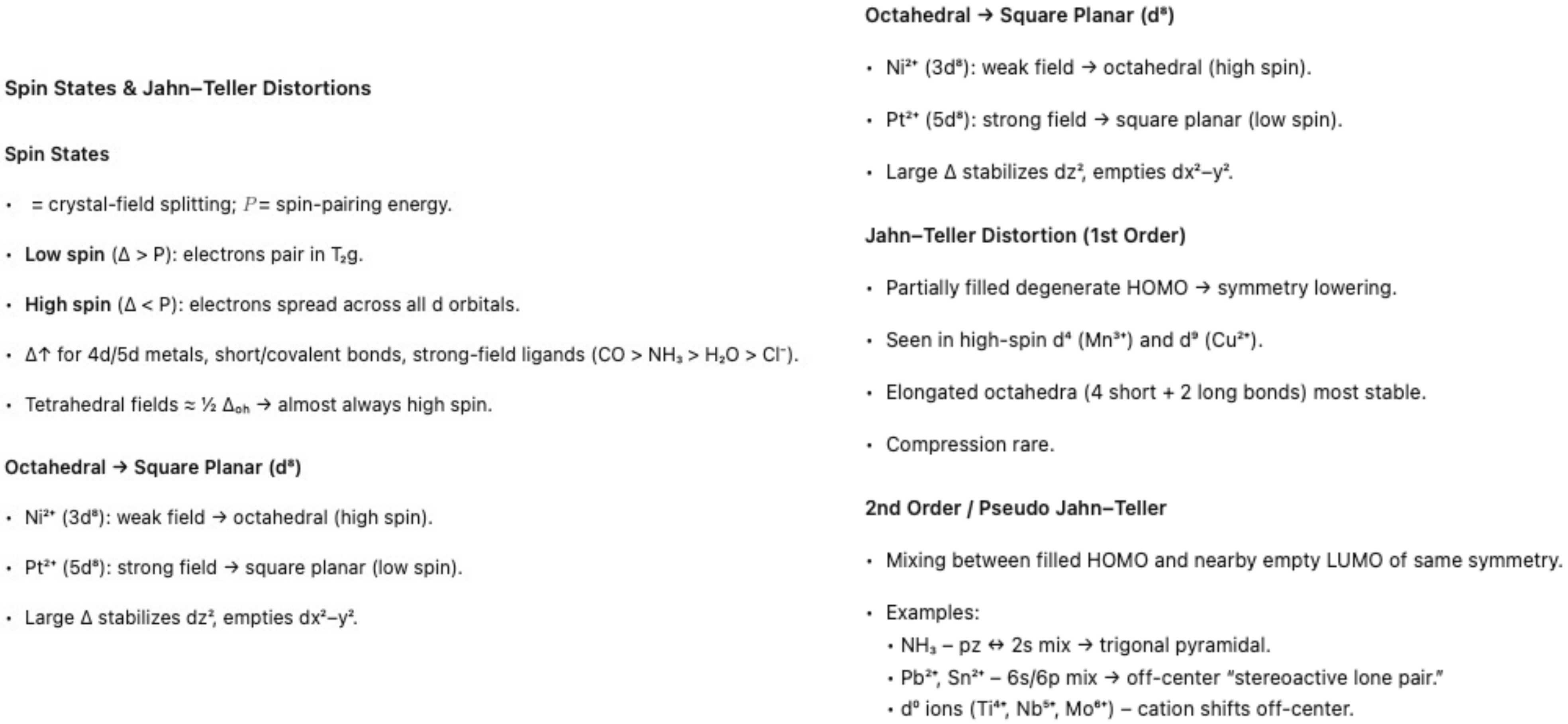
PbO



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** ($\Delta > P$): electrons pair in T_2g.
- **High spin** ($\Delta < P$): 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 $dx^2{-}y^2$.

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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

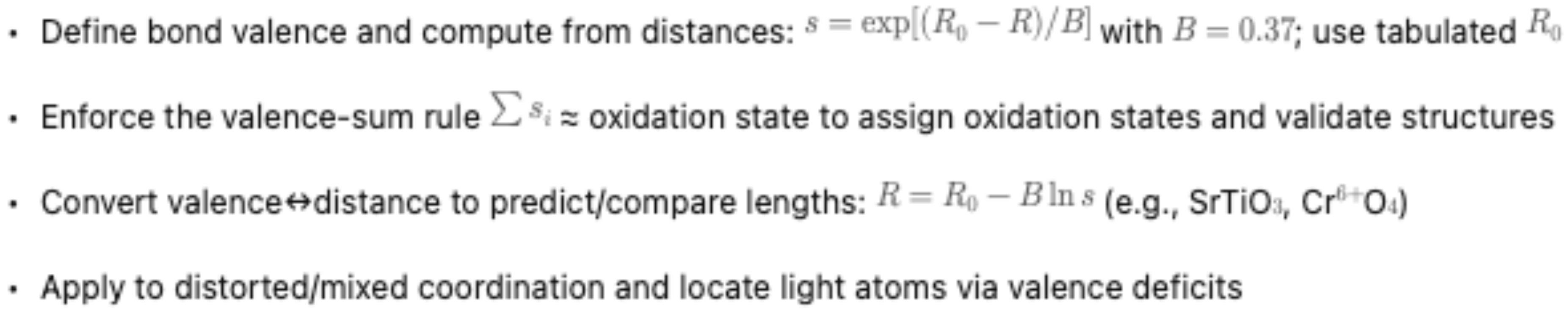
Why do Cu^{2+} (d^9) complexes typically show elongated octahedral geometry rather than compressed?

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.

Learning Objectives



- Define bond valence and compute from distances: $s = \exp[(R_0 - R)/B]$ with $B = 0.37$; use tabulated R_0
- Enforce the valence-sum rule $\sum s_i \approx$ oxidation state to assign oxidation states and validate structures
- Convert valence↔distance to predict/compare lengths: $R = R_0 - B \ln s$ (e.g., $SrTiO_3$, $Cr^{6+}O_4$)
- Apply to distorted/mixed coordination and locate light atoms via valence deficits

Electrostatic Bond Valence

(Pauling 1929 JACS)

$$C_m^{c+[N;]}A_n^{a-[M;]}$$

electroneutrality balance

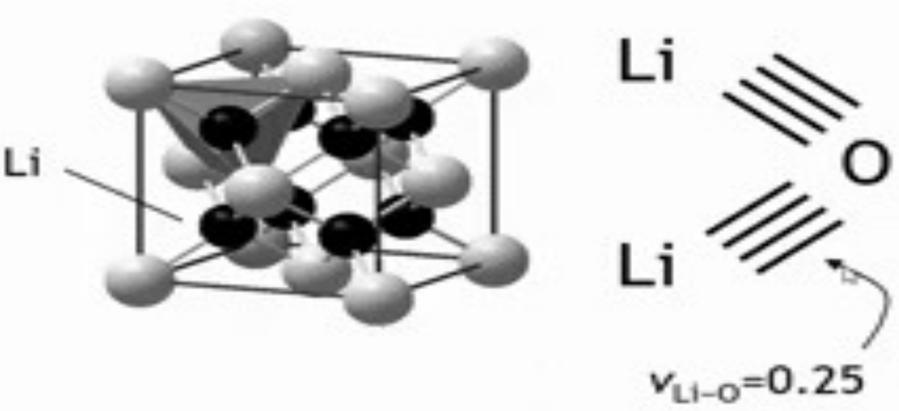
$m \times c = n \times a$

connectivity balance

$m \times N = n \times M$

bond valence balance

$c/N = a/M$



Electrostatic Bond Valence

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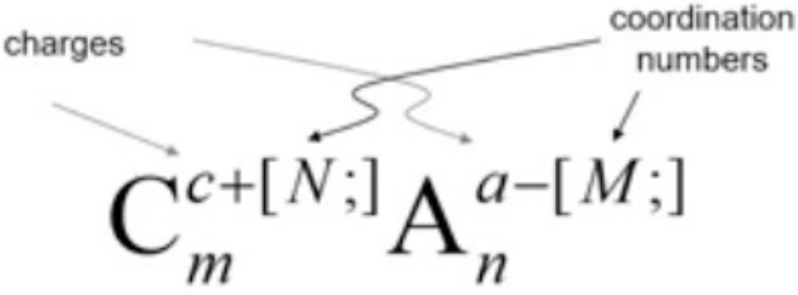

charges

coordination numbers

$$C_m^{c+[N;]}A_n^{a-[M;]}$$

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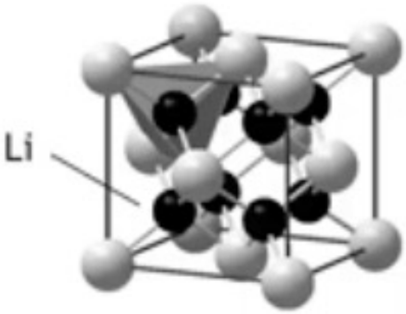

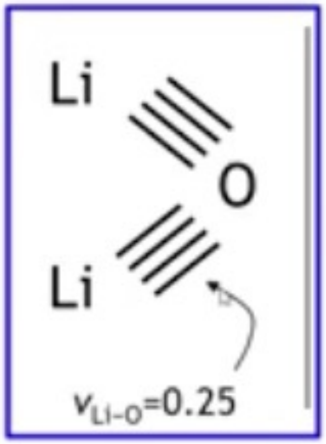

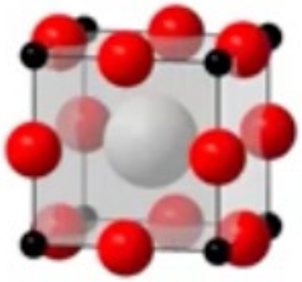

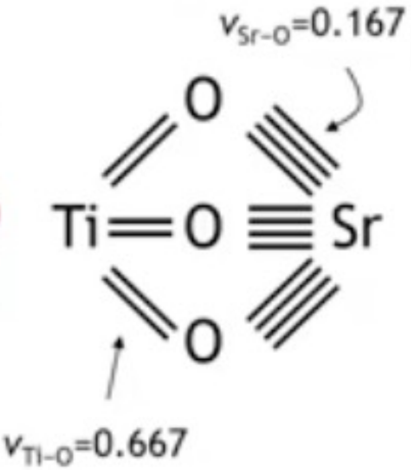

Electrostatic Bond Valence

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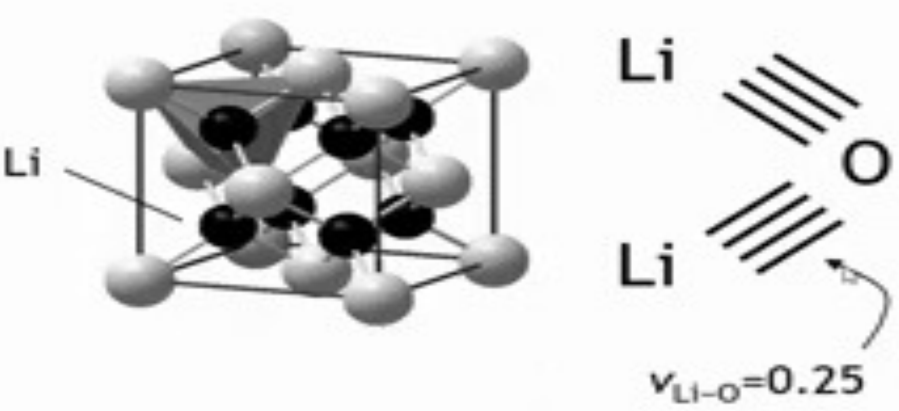
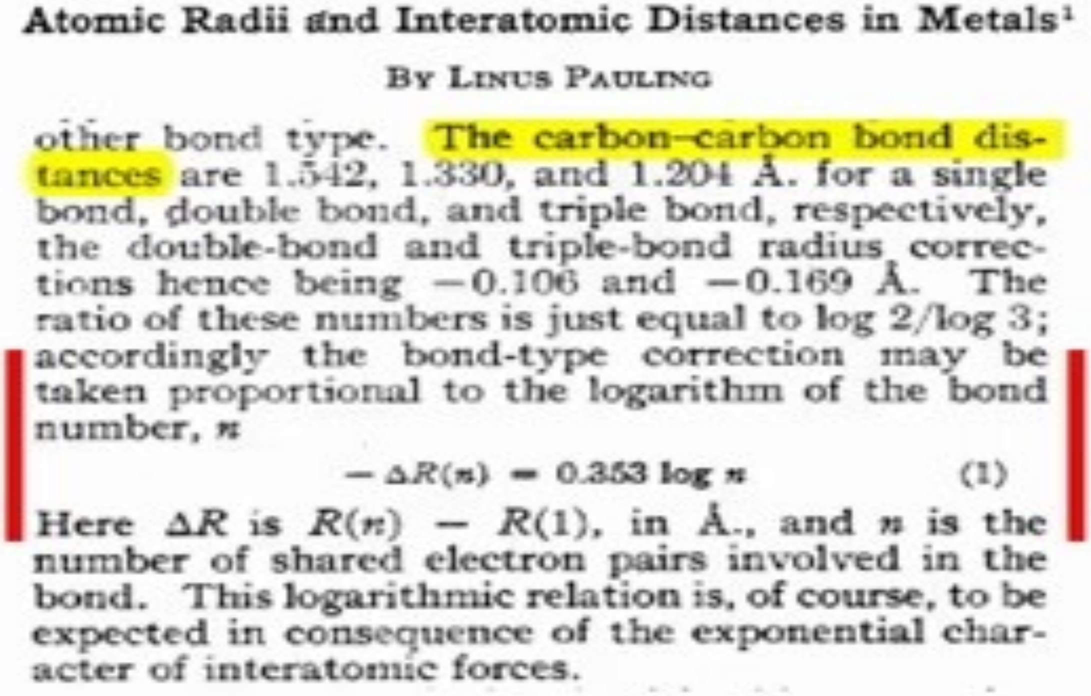


Bond Order in Organic Molecules



Atomic Radii and Interatomic Distances in Metals[1]

By Linus Pauling

other bond type. The carbon–carbon bond distances are 1.542, 1.330, and 1.204 Å. for a single bond, double bond, and triple bond, respectively, the double-bond and triple-bond radius corrections hence being −0.106 and −0.169 Å. The ratio of these numbers is just equal to log 2/log 3; accordingly the bond-type correction may be taken proportional to the logarithm of the bond number, n

$$-\Delta R(n) = 0.353 \log n \qquad (1)$$

Here ΔR is $R(n) - R(1)$, in Å., and n is the number of shared electron pairs involved in the bond. This logarithmic relation is, of course, to be expected in consequence of the exponential character of interatomic forces.

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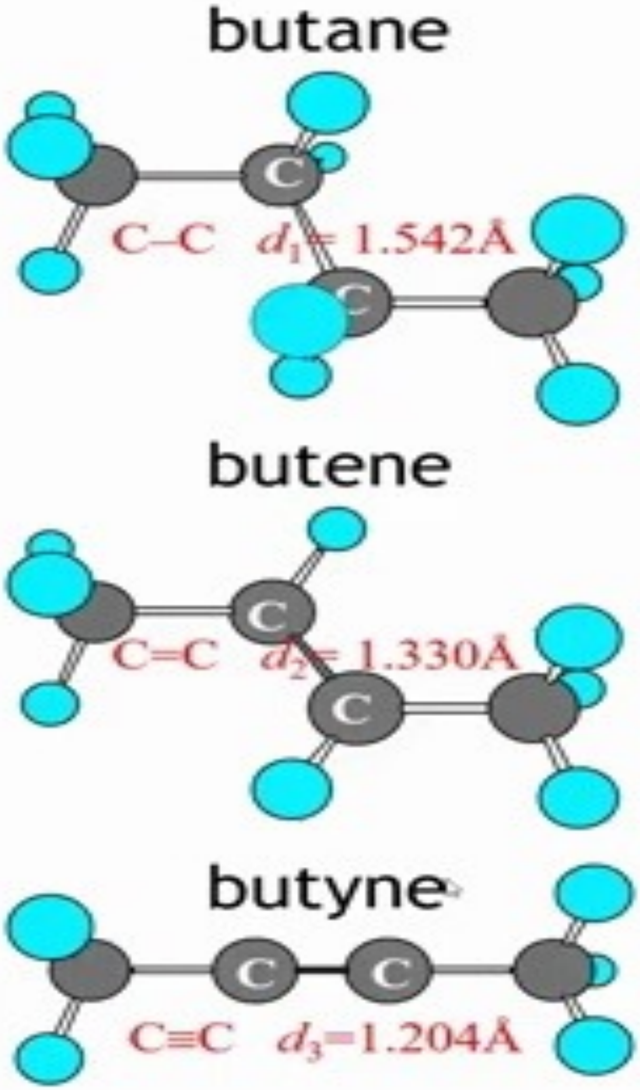


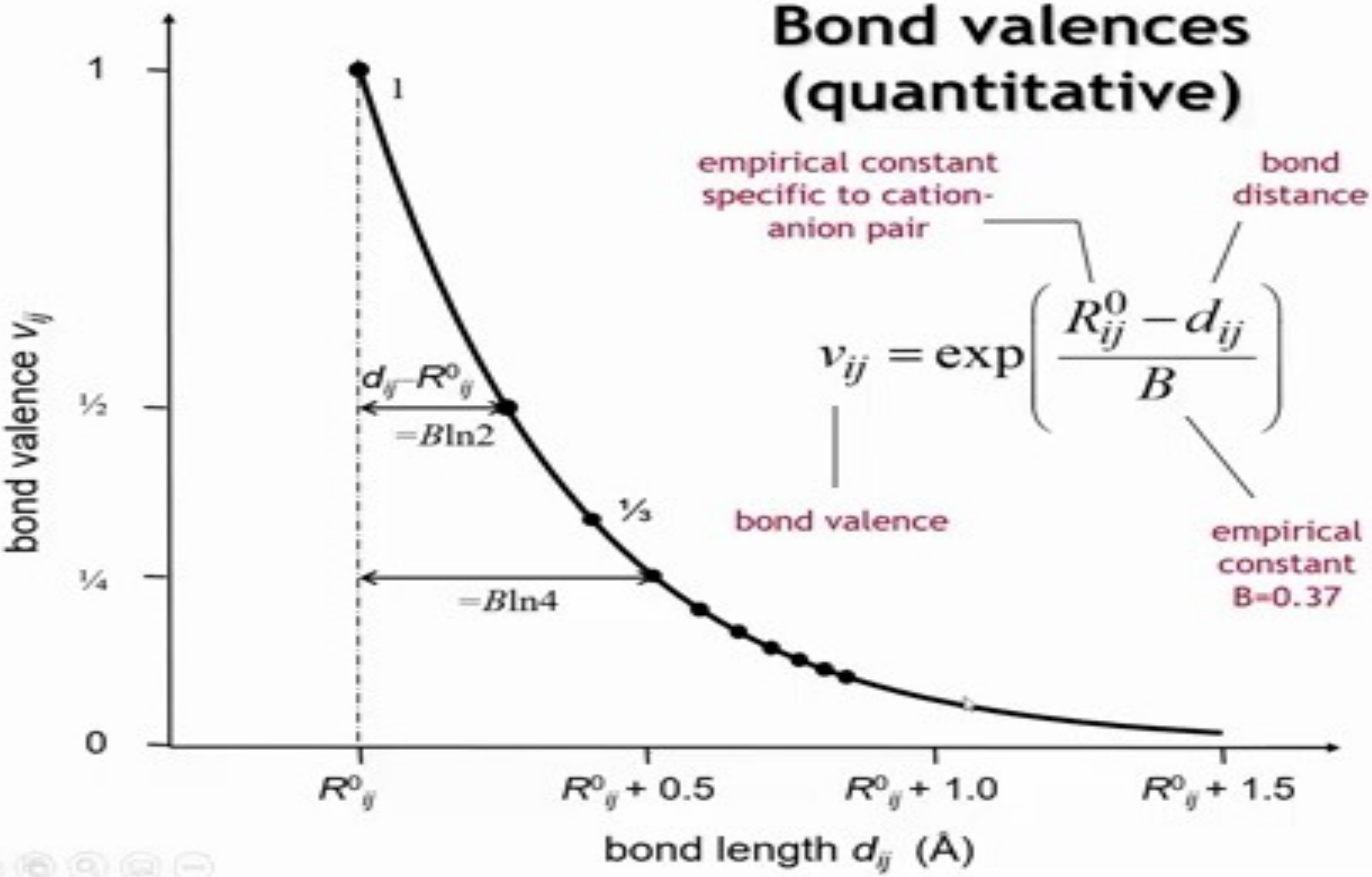
Bond order and bond distance

$$-\Delta R(n) = 0.353 \log n$$

$$-\big(\underset{\substack{\uparrow \\ \text{length of} \\ \text{the bond}}}{d(n)} - \underset{\substack{\uparrow \\ \text{length of a} \\ \text{single bond}}}{d(1)}\big) = 0.353 \log \underset{\substack{\uparrow \\ \text{bond order}}}{n}$$

$$n = 10^{[d(1)-d(n)]/0.353}$$

Bond valences (quantitative)



empirical constant specific to cation-anion pair

bond distance

$$v_{ij} = \exp\left(\frac{R^0_{ij} - d_{ij}}{B}\right)$$

bond valence

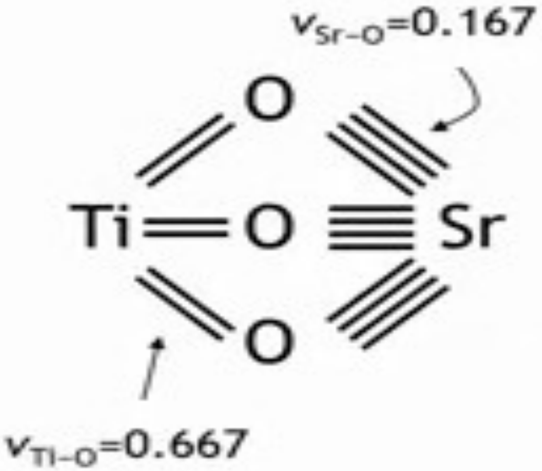
empirical constant B=0.37

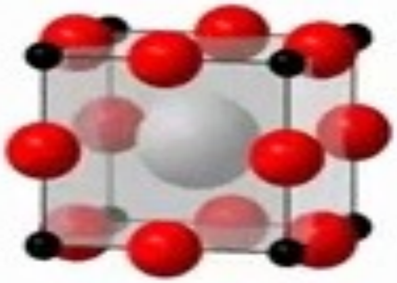
Valence sum rule

$$v_i = \sum_j v_{ij}$$

The valence sum v_i of an atom is equal to the sum of bond valences v_{ii} around it

The valence sum of each atom, v_i, should be equal to the oxidation state of the atom



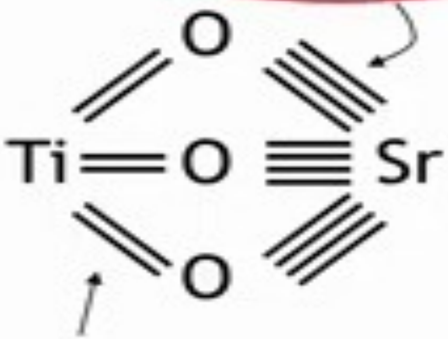


Sr = 12(0.167) = 2

Ti = 6(0.667) = 4

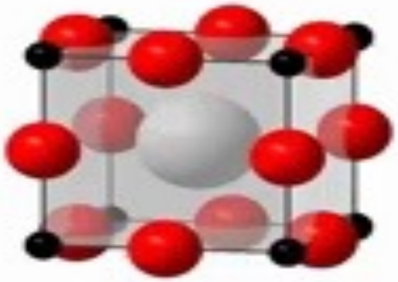
O = 2(0.667)+4(0.167) = 2

Fractional Bond Valences



v_{Sr-O}=0.167

v_{Ti-O}=0.667



Sr = 12(0.167) = 2

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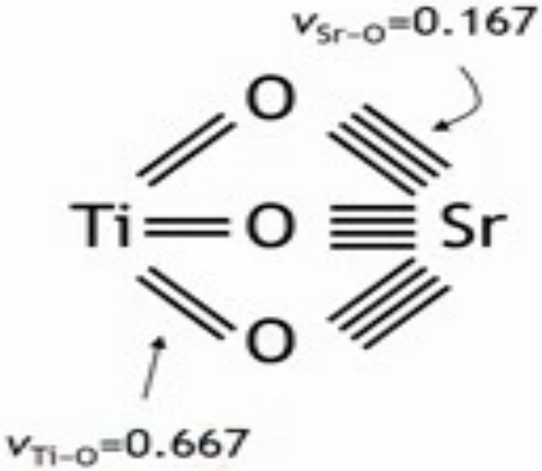
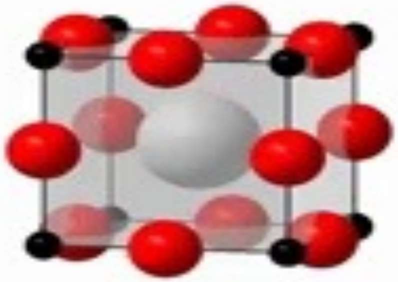
Sr—O bond length = 2.761 Å

$$v = e^{(R^0-d)/0.37}$$

$$v = e^{(2.118-2.761)/0.37} = 0.176$$

Fractional Bond Valences





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$$v = e^{(R^0-d)/0.37}$$

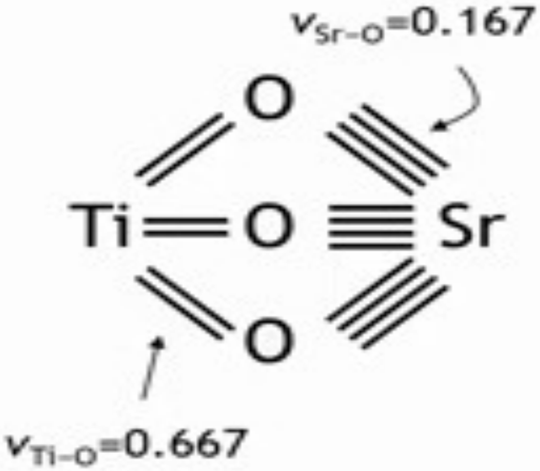
$$v = e^{(2.118-2.761)/0.37} = 0.176$$

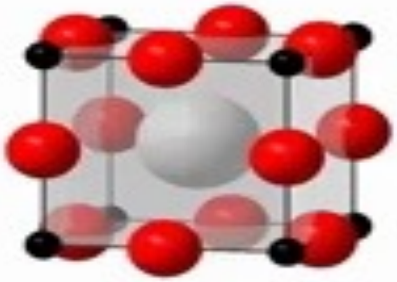
Ti—O bond length = 1.953 Å

$$v = e^{(R^0-d)/0.37}$$

$$v = e^{(1.813-1.953)/0.37} = 0.685$$

Fractional Bond Valences





Sr = 12(0.167) = 2

Ti = 6(0.667) = 4

O = 2(0.667)+4(0.167) = 2

Sr—O bond length = 2.761 Å

$$v = e^{(R^0-d)/0.37}$$

$$v = e^{(2.118-2.761)/0.37} = 0.176$$

Ti—O bond length = 1.953 Å

$$v = e^{(R^0-d)/0.37}$$

$$v = e^{(1.813-1.953)/0.37} = 0.685$$

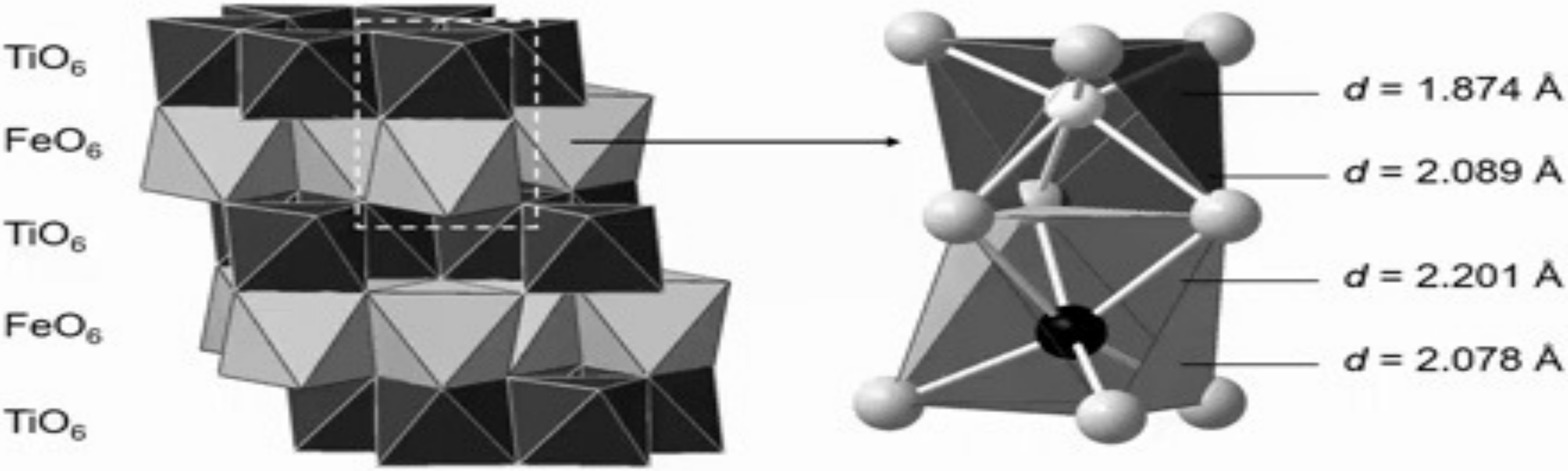
bond valence sums

$$\mathrm{Sr} = 12 \times 0.176 = 2.112$$

$$\mathrm{Ti} = 6 \times 0.685 = 4.110$$

$$\mathrm{O} = 4 \times 0.176 + 2 \times 0.685 = 2.074$$

Bond valences in $FeTiO_3$



What are the correct oxidation state assignments in this compound, $Fe^{2+}Ti^{4+}O_3$ or $Fe^{3+}Ti^{3+}O_3$?

Bond valence sums $FeTiO_3$

$$v_{\mathrm{Fe-O}}(1) = \exp\left(\frac{R^0_{\mathrm{Fe-O}} - d_{\mathrm{Fe-O}}}{B}\right) = \exp\left(\frac{1.734 - 2.078}{0.37}\right) = 0.395$$

$$v_{\mathrm{Fe-O}}(2) = \exp\left(\frac{R^0_{\mathrm{Fe-O}} - d_{\mathrm{Fe-O}}}{B}\right) = \exp\left(\frac{1.734 - 2.201}{0.37}\right) = 0.283$$

$$v_{\mathrm{Fe}} = 3v_{\mathrm{Fe-O}}(1) + 3v_{\mathrm{Fe-O}}(2) = 3(0.395) + 3(0.283) = 2.03$$

Bond valence sums $FeTiO_3$

$$v_{\text{Fe-O}}(1) = \exp\left(\frac{R^0_{\text{Fe-O}} - d_{\text{Fe-O}}}{B}\right) = \exp\left(\frac{1.734 - 2.078}{0.37}\right) = 0.395$$

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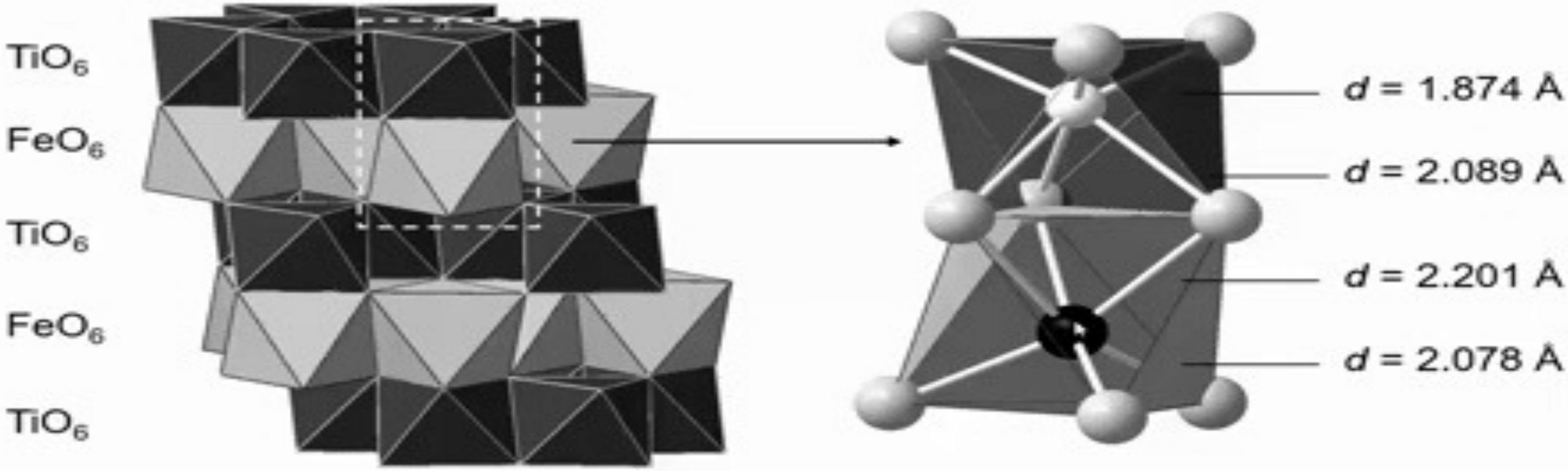
$$v_{\text{Fe}} = 3v_{\text{Fe-O}}(1) + 3v_{\text{Fe-O}}(2) = 3(0.395) + 3(0.283) = 2.03$$

$$v_{\text{Ti-O}}(1) = \exp\left(\frac{R^0_{\text{Ti-O}} - d_{\text{Ti-O}}}{B}\right) = \exp\left(\frac{1.815 - 2.089}{0.37}\right) = 0.477$$

$$v_{\text{Ti-O}}(2) = \exp\left(\frac{R^0_{\text{Ti-O}} - d_{\text{Ti-O}}}{B}\right) = \exp\left(\frac{1.815 - 1.874}{0.37}\right) = 0.853$$

$$v_{\text{Ti}} = 3v_{\text{Ti-O}}(1) + 3v_{\text{Ti-O}}(2) = 3(0.477) + 3(0.853) = 3.99$$

Bond valences in $FeTiO_3$



bond valence Fe = 2.03

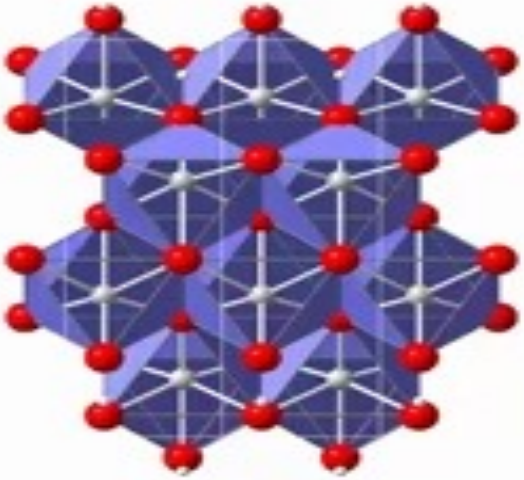
bond valence Ti = 3.99

bond valence O = 0.395 + 0.283 + 0.477 + 0.853 = 2.008

$Fe^{2+}Ti^{4+}O_3$

Using Bond Valences to Find H atoms

AlOOH (Diaspore)



Bond Distances

O1-Al = 1.85, 1.85, 1.86

O2-Al = 1.97, 1.97, 1.98

Bond Valence Sums

Al = 2.75

O1 = 1.60

O2 = 1.16 ← OH group

Predicting Bond Lengths

$$d_{ij} = R_{ij}^{0} - B \ln v_{ij}$$

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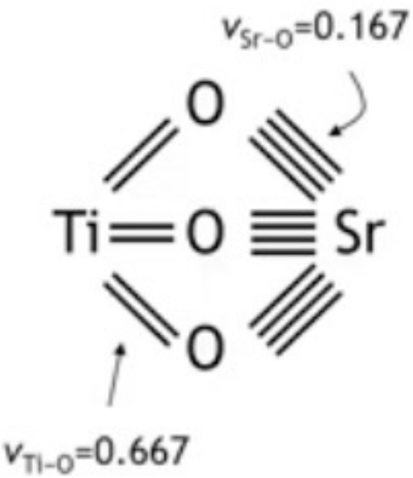
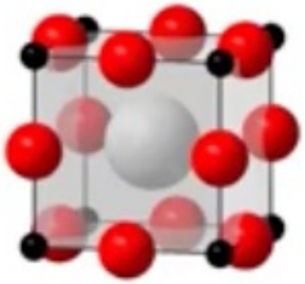
$$d_{ij} = R_{ij}^{0} - B \ln v_{ij}$$





$$d_{\mathrm{Sr-O}} = R_{\mathrm{Sr-O}}^{0} - B \ln v_{\mathrm{Sr-O}}$$

$$d_{\mathrm{Sr-O}} = 2.118 - 0.37 \ln(0.167)$$

$$d_{\mathrm{Sr-O}} = 2.78\ \text{Å}$$

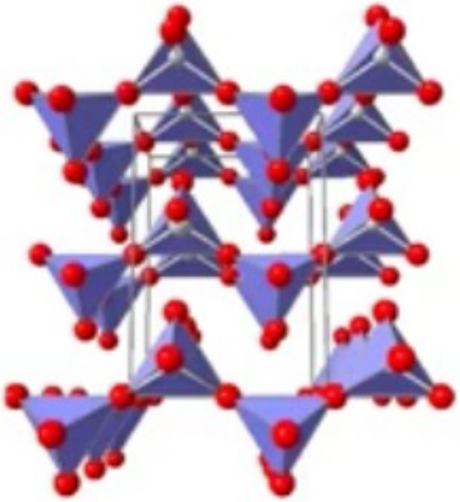
$$d_{\mathrm{Ti-O}} = R_{\mathrm{Ti-O}}^{0} - B \ln v_{\mathrm{Ti-O}}$$

$$d_{\mathrm{Ti-O}} = 1.815 - 0.37 \ln(0.667)$$

$$d_{\mathrm{Ti-O}} = 1.965\ \text{Å}$$

Bond Valences Predictively

CrO_3



The structure of CrO_3 consists of infinite chains of corner connected tetrahedra.

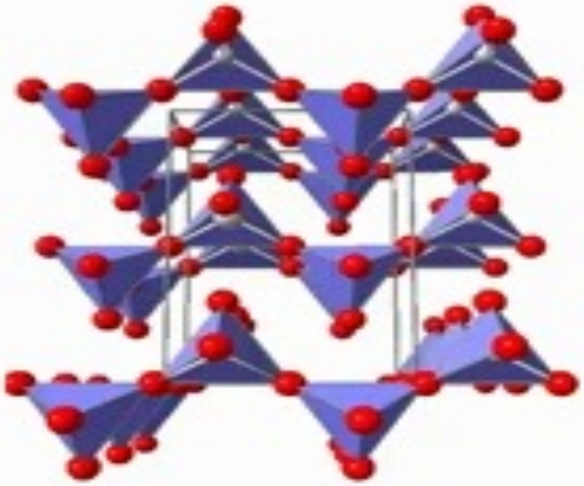
(a) Use either a bond graph or a Niggli formula to determine the number of bonds to each chemically distinct atom.

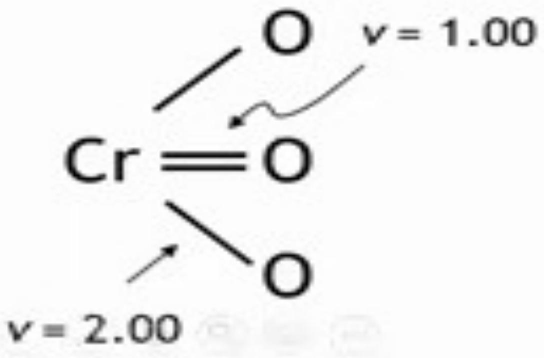
(b) Use the bond valence balance to assign ideal valences to each type of bond.

(c) Given the Cr(VI)–O bond valence parameters R_0 = 1.79 Å and b = 0.37 Å estimate the Cr –O bond lengths in this compound.

Bond Valences Predictively

CrO_3





Two types of Oxide ions -

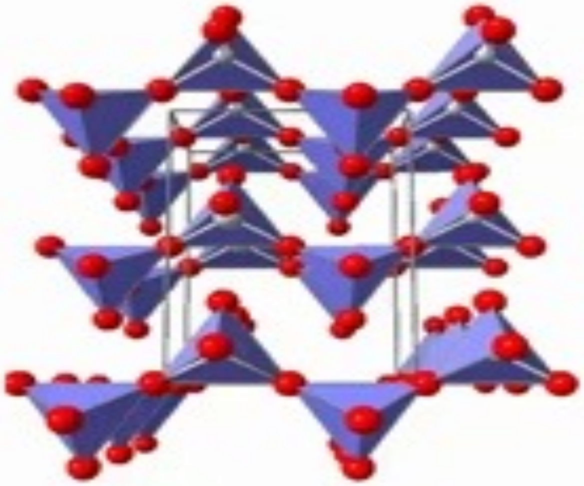
- Bridging - ^{II}O
- Terminal - ^{I}O

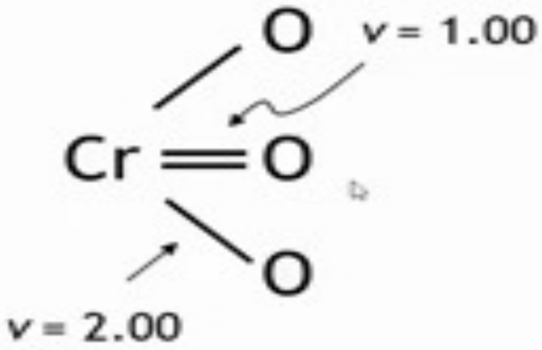
Pauling's 2nd rule gives the expected bond valences

- $Cr\text{-}^{II}O \rightarrow v_{ij} = 1.0$
- $Cr\text{-}^{I}O \rightarrow v_{ij} = 2.0$

Bond Valences Predictively

CrO_3





Two types of Oxide ions -

- Bridging - ^{II}O
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Pauling's 2nd rule gives the expected bond valences

- Cr-^{II}O → $v_{ij} = 1.0$
- Cr-^{I}O → $v_{ij} = 2.0$

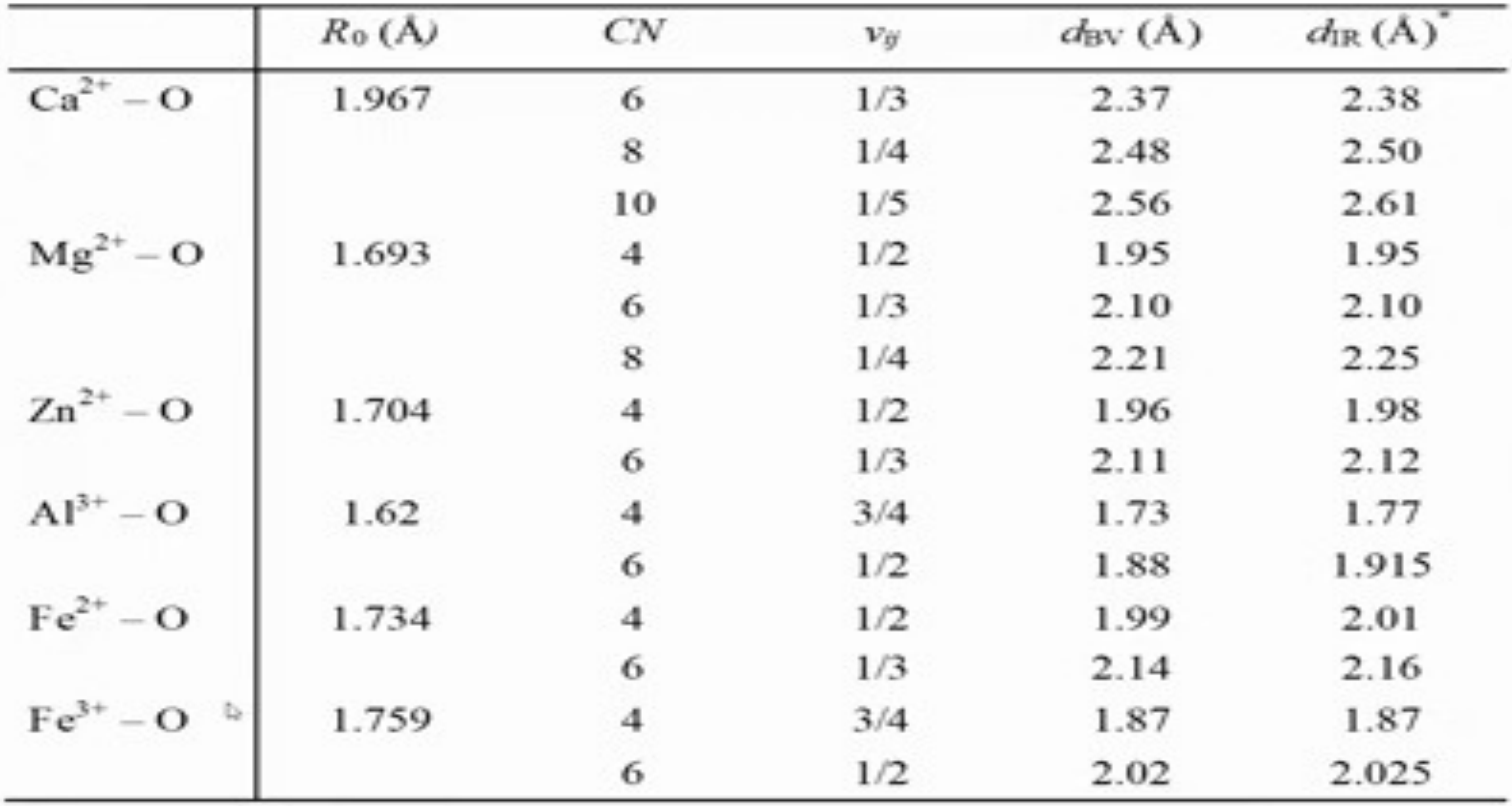
Inverting the bond valence calculation we can estimate distances

- Cr-^{II}O → 1.79 Å
- Cr-^{I}O → 1.54 Å

The observed bond distances are

- Cr-^{II}O → 1.75 Å
- Cr-^{I}O → 1.57 Å

Bond valences vs. Ionic Radii



	R_0 (Å)	CN	v_{ij}	d_{BV} (Å)	d_{IR} (Å)*
$Ca^{2+} - O$	1.967	6	1/3	2.37	2.38
		8	1/4	2.48	2.50
		10	1/5	2.56	2.61
$Mg^{2+} - O$	1.693	4	1/2	1.95	1.95
		6	1/3	2.10	2.10
		8	1/4	2.21	2.25
$Zn^{2+} - O$	1.704	4	1/2	1.96	1.98
		6	1/3	2.11	2.12
$Al^{3+} - O$	1.62	4	3/4	1.73	1.77
		6	1/2	1.88	1.915
$Fe^{2+} - O$	1.734	4	1/2	1.99	2.01
		6	1/3	2.14	2.16
$Fe^{3+} - O$	1.759	4	3/4	1.87	1.87
		6	1/2	2.02	2.025

Bond Valence Method — Summary

- **Core rule:**
$s_{ij} = \exp[(R_0 - d_{ij})/b]$, $\sum s_{ij} = V_i$
- **Purpose:**
  Links bond lengths ↔ oxidation states; works with distorted structures.
- **Advantages:**
  - One R_0 per atom pair covers all coordination numbers.
  - Handles mixed bond lengths; ionic radii cannot.
- **Uses:**
  - Verify oxidation states.
  - Predict reasonable bond distances.
  - Locate light atoms (e.g., H).

Homework

5.16 – 5.20