Imperfect Geometries……
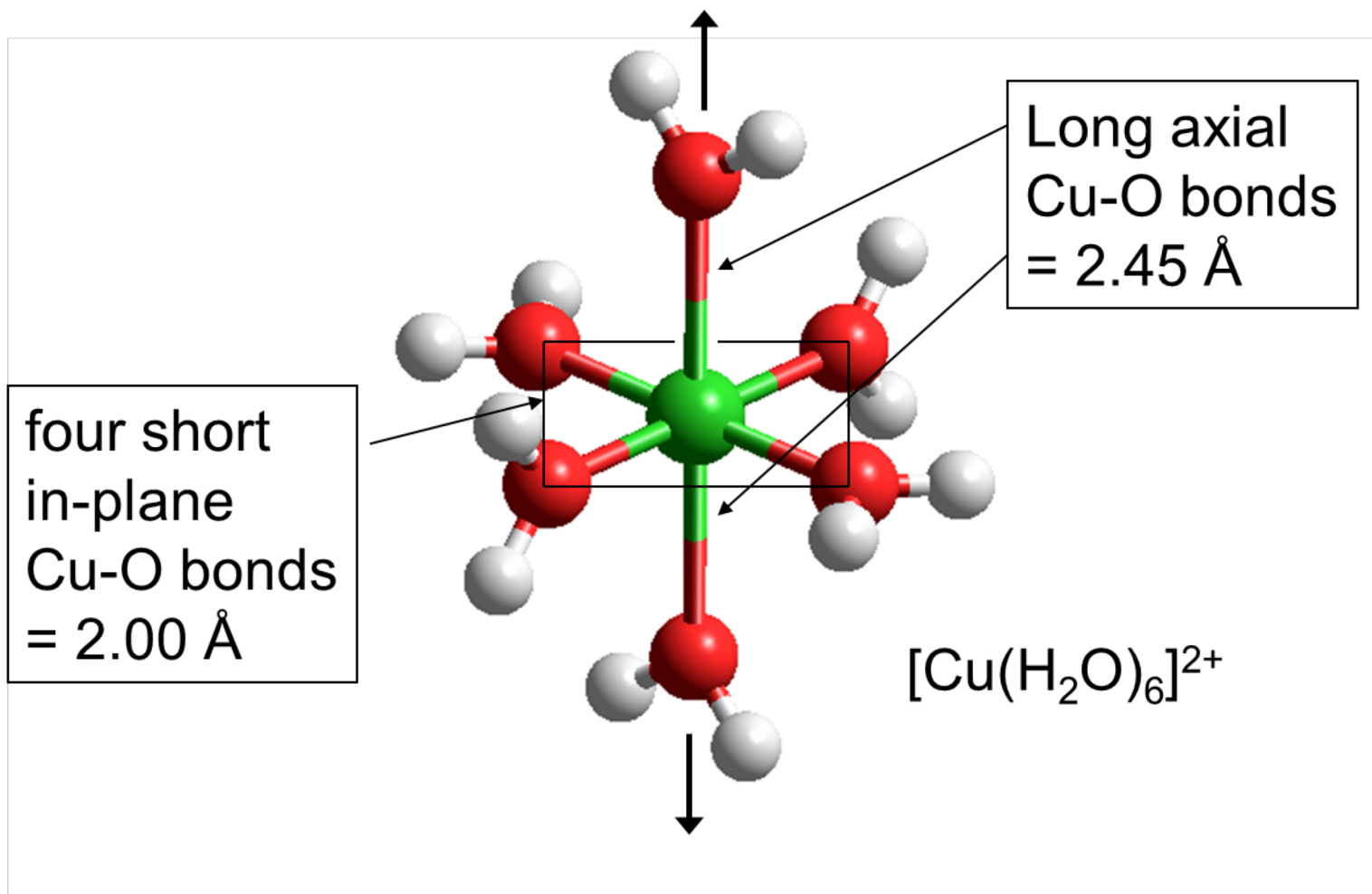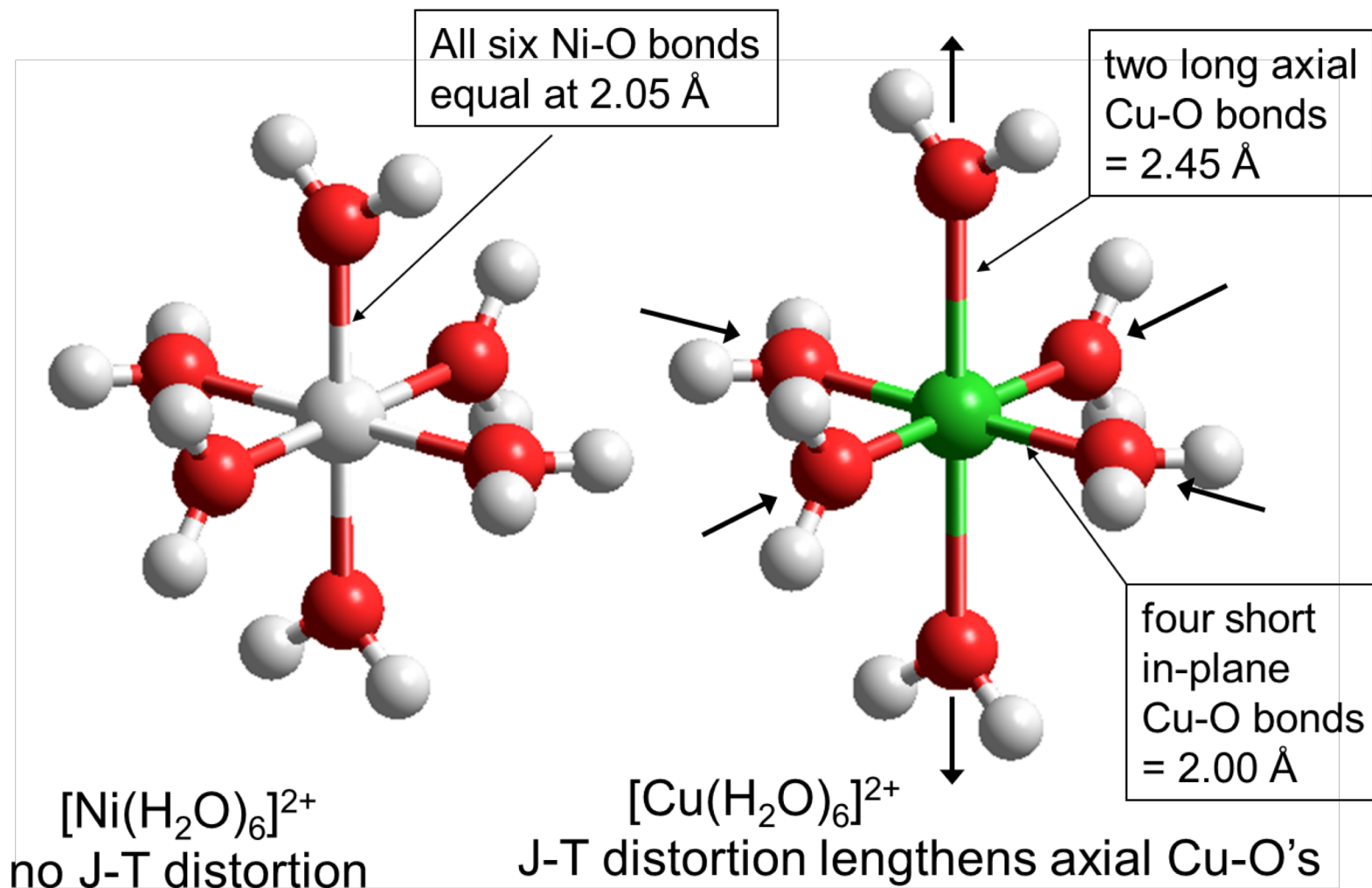
❑ **So far we have considered "perfect" geometries, i.e., we expect a complex of the type ML_6 to have all bonds equivalent. But….**

Long axial Cu-O bonds = 2.45 Å

four short in-plane Cu-O bonds = 2.00 Å

$[Cu(H_2O)_6]^{2+}$

Distorted Octahedral Complex

❑ **Not all complexes exhibit such distortion.**
❑ **This phenomena is referred to as Jahn-Teller distortion**

All six Ni-O bonds equal at 2.05 Å

two long axial Cu-O bonds = 2.45 Å

four short in-plane Cu-O bonds = 2.00 Å

$[Ni(H_2O)_6]^{2+}$
no J-T distortion

$[Cu(H_2O)_6]^{2+}$
J-T distortion lengthens axial Cu-O's

The Jahn-Teller Theorem

❑ **The Jahn-Teller (J-T) theorem states that in molecules/ ions that have a degenerate ground-state, the molecule/ion will distort to remove the degeneracy.**

This is a fancy way of saying that when orbitals in the same level are occupied by different numbers of electrons, this will lead to distortion of the molecule.

For us, what is important is that if the two orbitals of the e_g level have different numbers of electrons, this will lead to J-T distortion.

High-spin Ni(II) – only one way of filling
the e_g level – not degenerate,
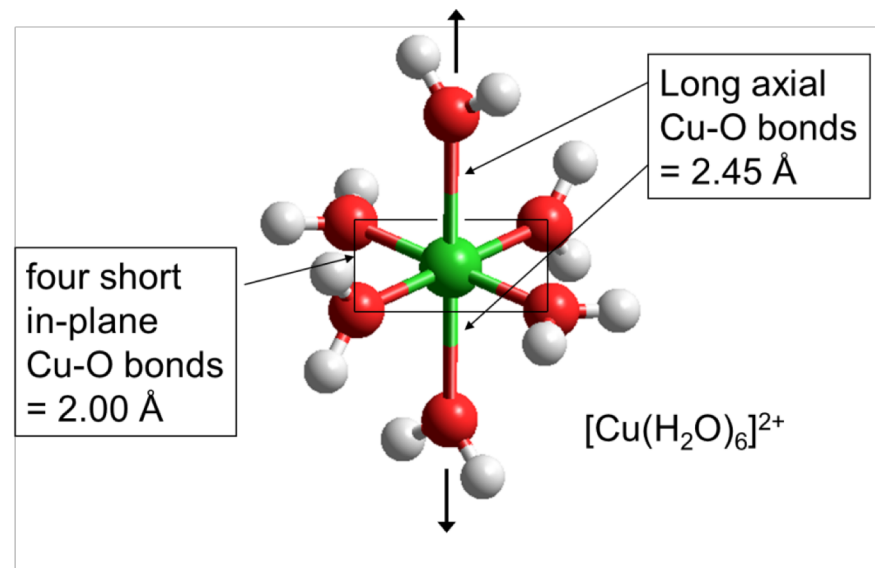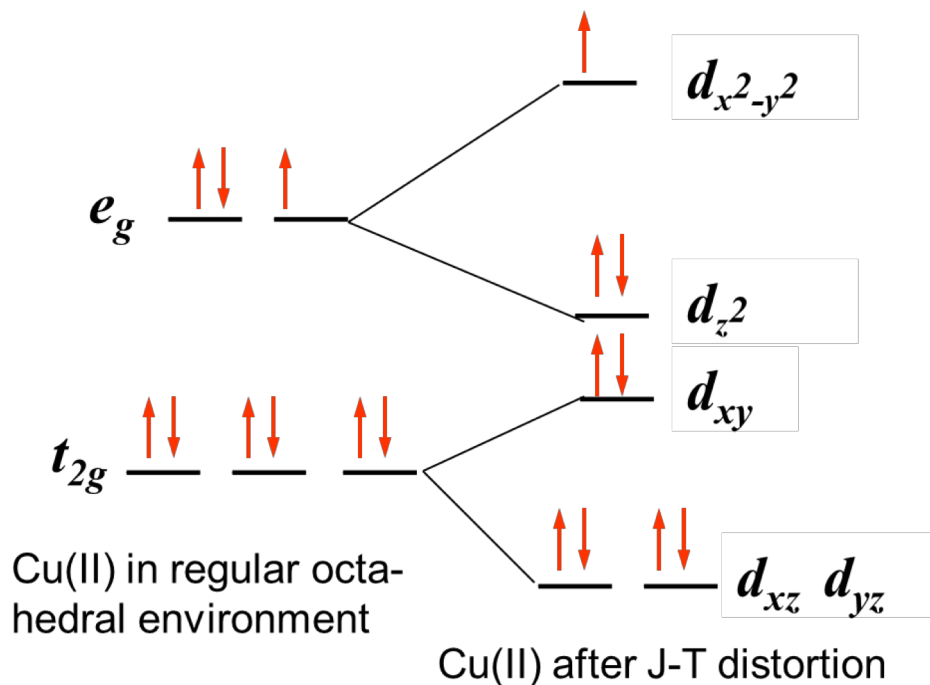no J-T distortion
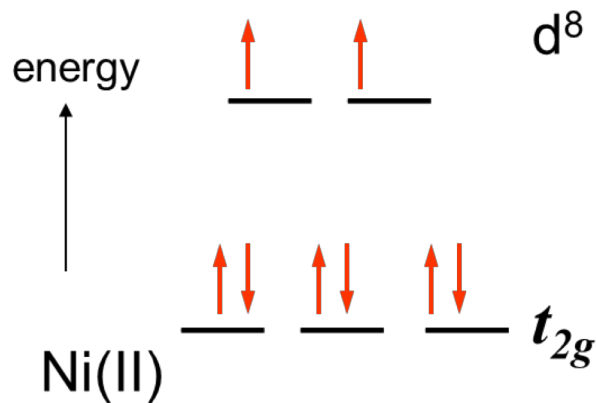
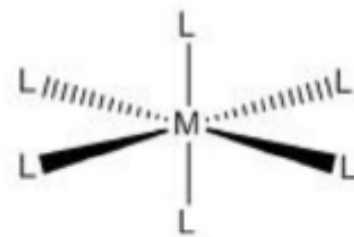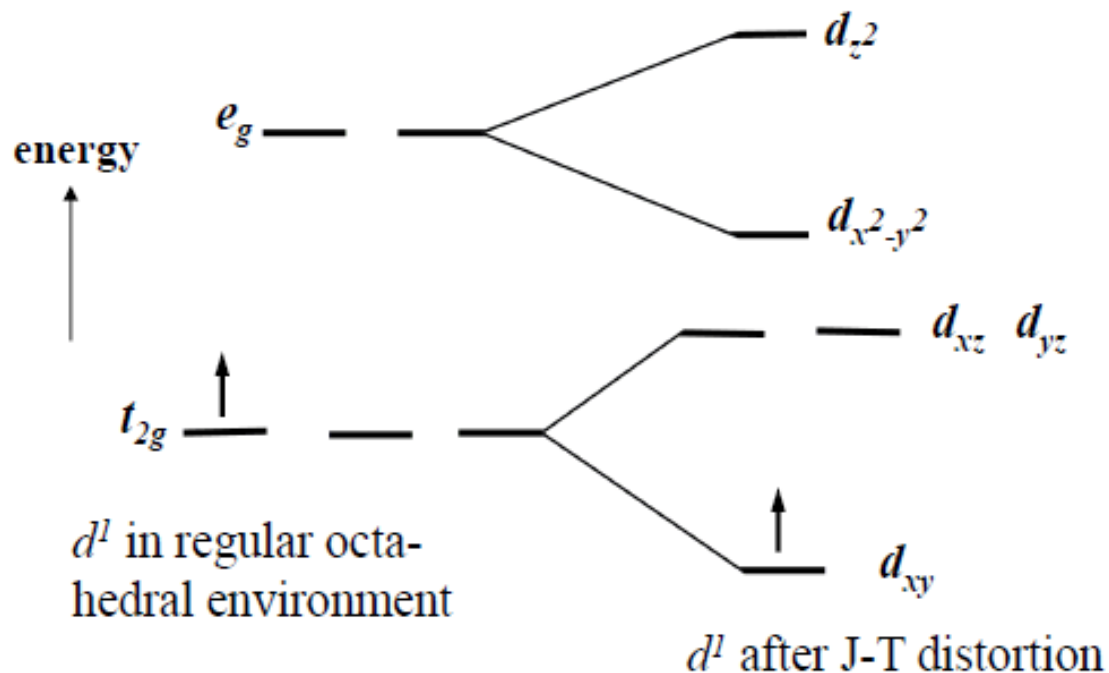Cu(II) – two ways of filling e_g level – it is degenerate, and has J-T distortion
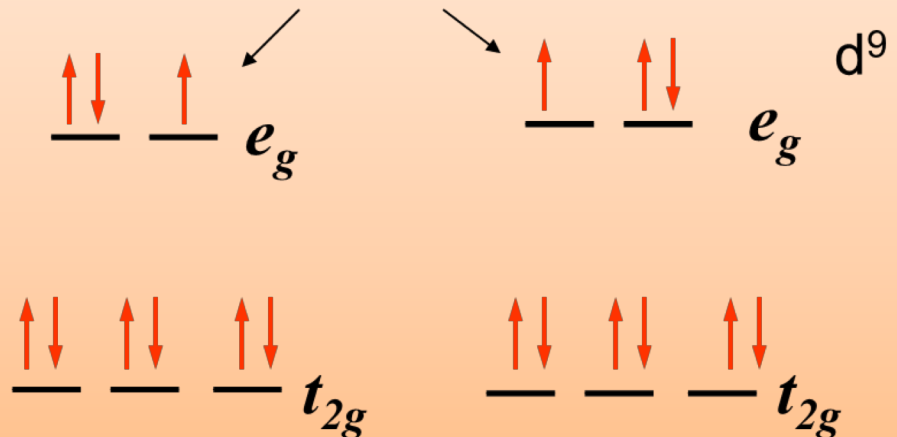
Further Splitting of the t_{2g} and e_g Levels

❑ **The CF view of the splitting of the d-orbitals is that those aligned with the two more distant donor atoms along the z-coordinate experience less repulsion and so drop in energy (d_{xz}, d_{yz}, and d_{z2}), while those closer to the in-plane donor atoms (d_{xy}, d_{x2-y2}) rise in energy.**

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

e_g

d_{z^2}

d_{xy}

t_{2g}

Cu(II) in regular octa-hedral environment

d_{xz} d_{yz}

Cu(II) after J-T distortion

Long axial Cu-O bonds = 2.45 Å

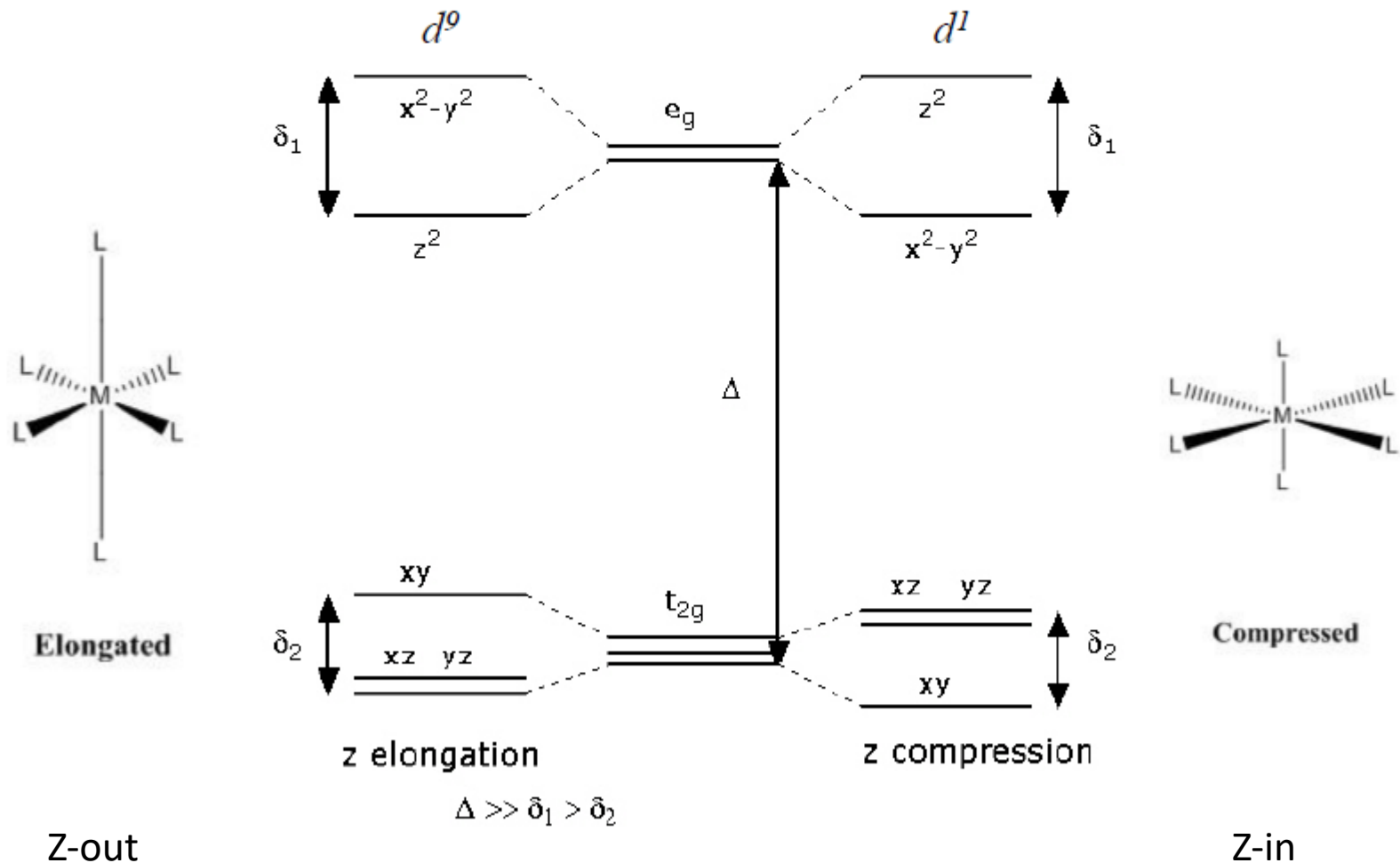four short in-plane Cu-O bonds = 2.00 Å

$[Cu(H_2O)_6]^{2+}$

J-T Distortion for d^1 System

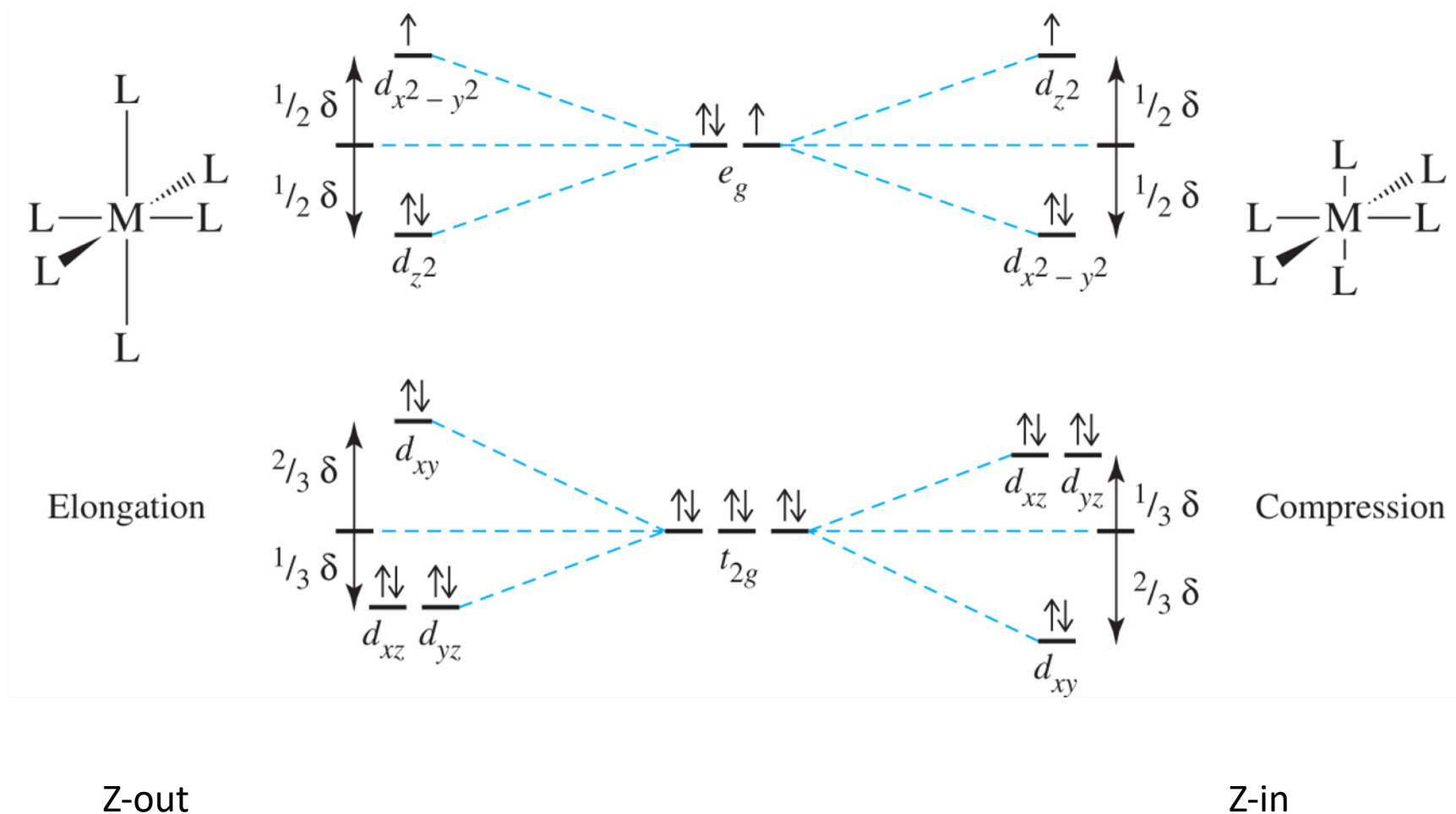❑ **in molecules/ ions that have a degenerate ground-state, the molecule/ion will distort to remove the degeneracy.**

energy

e_g — — d_{z^2}

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

t_{2g} — — d_{xz} d_{yz}

d_{xy}

d^1 in regular octa-hedral environment

d^1 after J-T distortion

Compressed

Comparison of d⁹ and d¹ Systems

Distortions are more pronounced if degeneracy occurs in an e_g orbital.
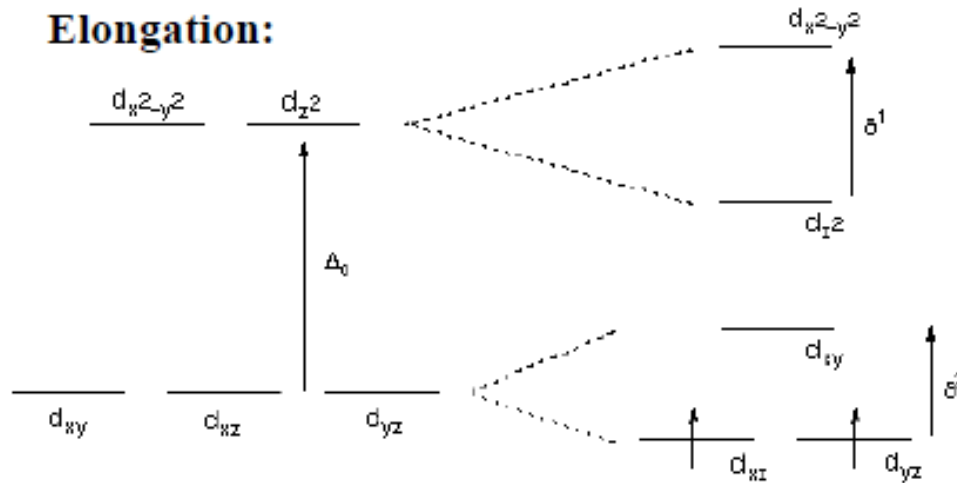
General Picture

Z-out

Z-in

❑ **Distortions are more pronounced if degeneracy occurs in an e$_g$ orbital.**
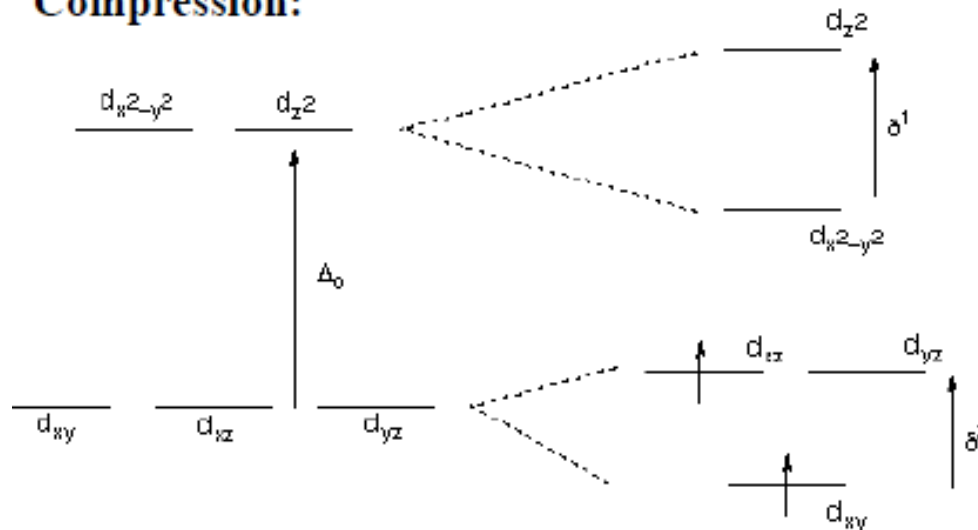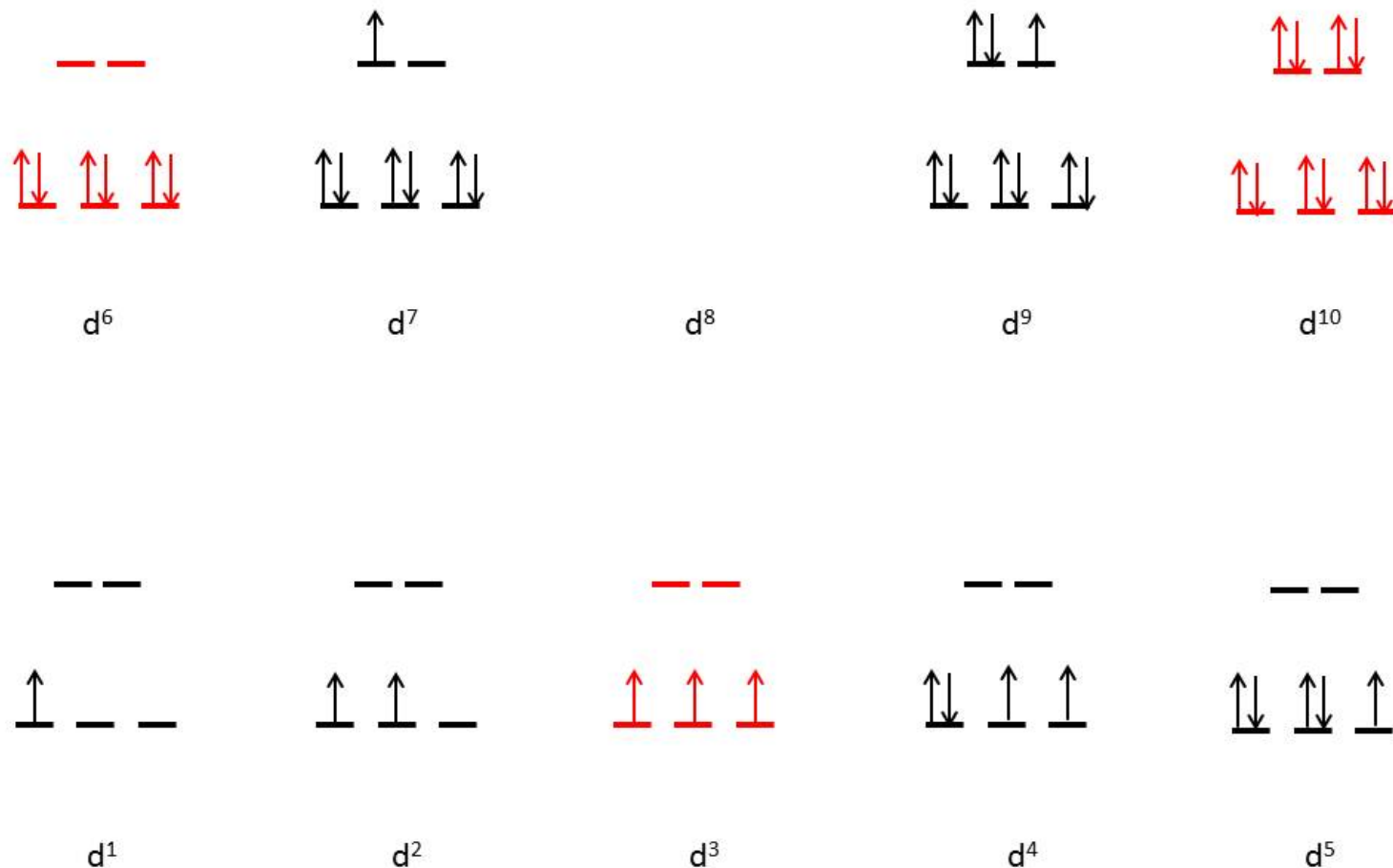
Will a d² system Exhibit Compression or Elongation?

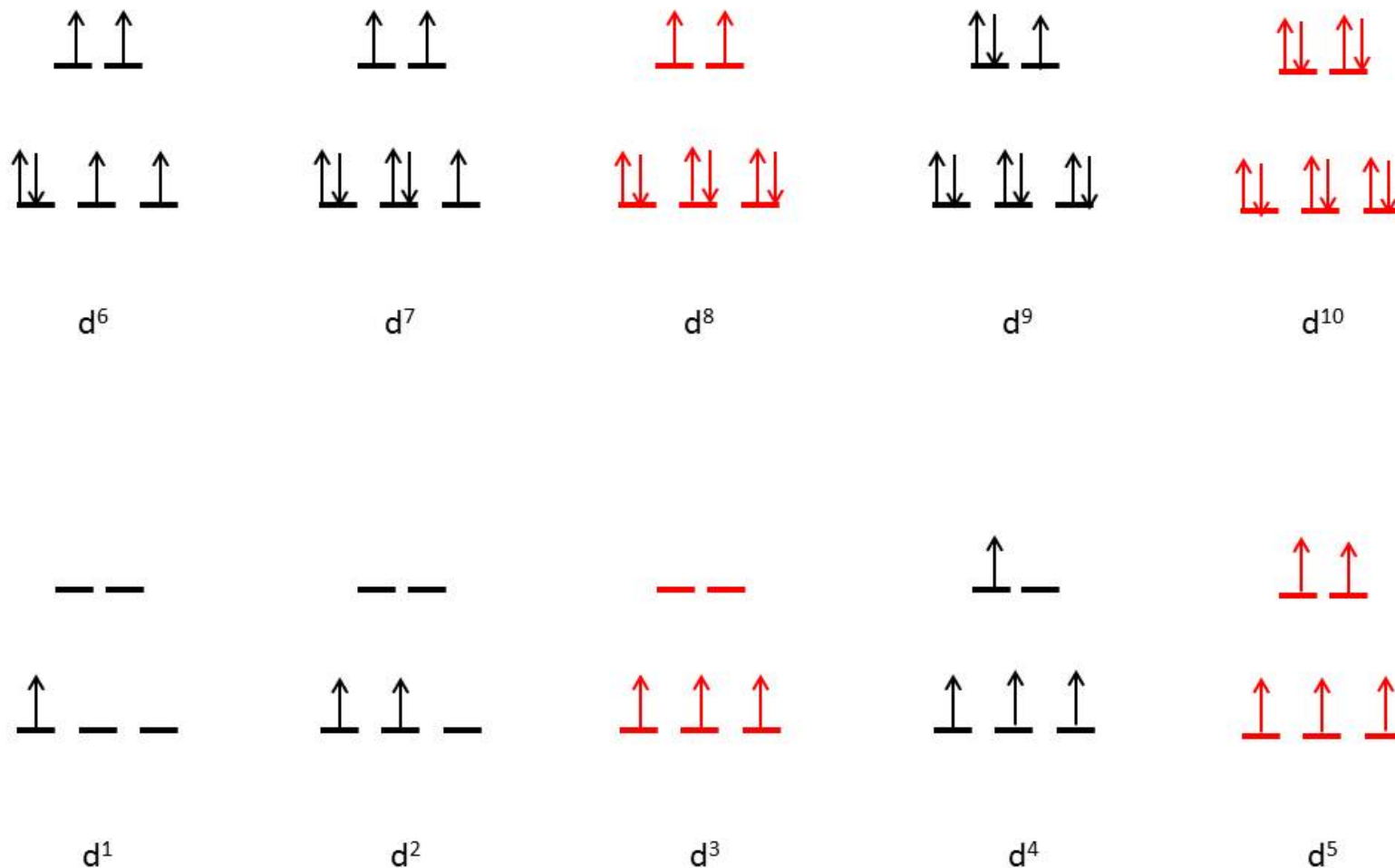Degeneracy removed

Degeneracy not removed

J-T Distortion Possibilities for Low-Spin Octahedral Complexes

According to Jahn-Teller theorem, low spin d^6 and d^{10} complexes wont exhibit distortion because there is no electronic degeneracy.

Low spin d^8 complexes are square planar in general.

J-T Distortion Possibilities for High-Spin Octahedral Complexes

According to Jahn-Teller theorem, high spin d^3, d^5, d^8, and d^{10} complexes wont exhibit distortion because there is no electronic degeneracy.