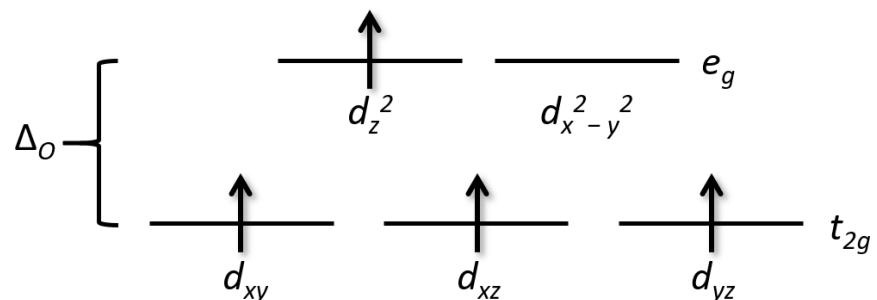
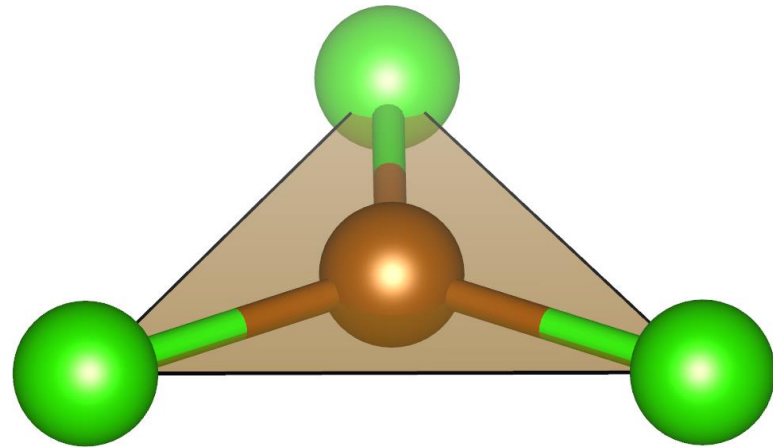


Lecture 11:

d-electrons and Ligand Field Theory

- Concept of oxidation state
- Oxidation states in *d*-block metal compounds
- Crystal field theory
- Ligand field theory
 - Jahn-Teller distortion
- Magnetic moments due to unpaired *d*-electrons



Figures: AJK

d-block metals

V·T·E

Periodic table of electronegativity by Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

| Group → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| ↓ Period | | | | | | | | | | | | | | | | | | |
| 1 | H 2.20 | | | | | | | | | | | | | | | | | He |
| 2 | Li 0.98 | Be 1.57 | | | | | | | | | | | B 2.04 | C 2.55 | N 3.04 | O 3.44 | F 3.98 | Ne |
| 3 | Na 0.93 | Mg 1.31 | | | | | | | | | | | Al 1.61 | Si 1.90 | P 2.19 | S 2.58 | Cl 3.16 | Ar |
| 4 | K 0.82 | Ca 1.00 | Sc 1.36 | Ti 1.54 | V 1.63 | Cr 1.66 | Mn 1.55 | Fe 1.83 | Co 1.88 | Ni 1.91 | Cu 1.90 | Zn 1.65 | Ga 1.81 | Ge 2.01 | As 2.18 | Se 2.55 | Br 2.96 | Kr 3.00 |
| 5 | Rb 0.82 | Sr 0.95 | Y 1.22 | Zr 1.33 | Nb 1.6 | Mo 2.16 | Tc 1.9 | Ru 2.2 | Rh 2.28 | Pd 2.20 | Ag 1.93 | Cd 1.69 | In 1.78 | Sn 1.96 | Sb 2.05 | Te 2.1 | I 2.66 | Xe 2.60 |
| 6 | Cs 0.79 | Ba 0.89 | * | Hf 1.3 | Ta 1.5 | W 2.36 | Re 1.9 | Os 2.2 | Ir 2.20 | Pt 2.28 | Au 2.54 | Hg 2.00 | Tl 1.62 | Pb 1.87 | Bi 2.02 | Po 2.0 | At 2.2 | Rn 2.2 |
| 7 | Fr 0.7 | Ra 0.9 | ** | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn | Uut | Fl | Uup | Lv | Uus | Uuo |
| | | | * | La 1.1 | Ce 1.12 | Pr 1.13 | Nd 1.14 | Pm 1.13 | Sm 1.17 | Eu 1.2 | Gd 1.2 | Tb 1.1 | Dy 1.22 | Ho 1.23 | Er 1.24 | Tm 1.25 | Yb 1.1 | Lu 1.27 |
| | | | ** | Ac 1.1 | Th 1.3 | Pa 1.5 | U 1.38 | Np 1.36 | Pu 1.28 | Am 1.13 | Cm 1.28 | Bk 1.3 | Cf 1.3 | Es 1.3 | Fm 1.3 | Md 1.3 | No 1.3 | Lr 1.3 |

Many oxidation states, very rich chemistry

Many magnetic compounds (unpaired *d*-electrons)

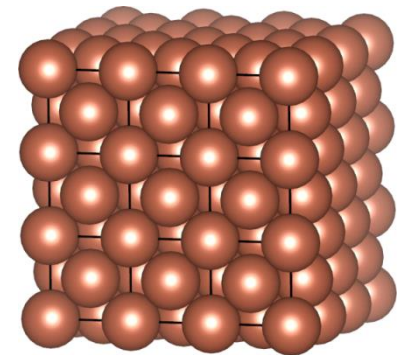
Many colorful compounds due to *d-d* transitions

Figure: [Wikipedia](#)

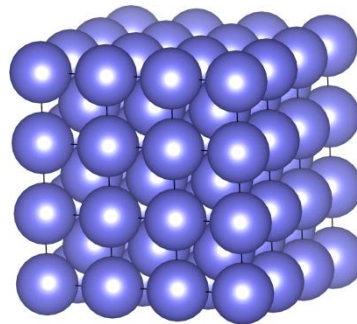
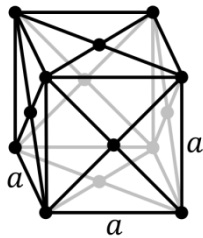
Elemental *d*-block metals

| | | | | | | | | | |
|-----------------|--------------------|----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 21 Sc HCP | 22 Ti HCP | 23 V BCC | 24 Cr BCC | 25 Mn BCC | 26 Fe BCC | 27 Co HCP | 28 Ni FCC | 29 Cu FCC | 30 Zn HCP |
| 39 Y HCP | 40 Zr HCP | 41 Nb BCC | 42 Mo BCC | 43 Tc HCP | 44 Ru HCP | 45 Rh FCC | 46 Pd FCC | 47 Ag FCC | 48 Cd HCP |
| | 72 Hf HCP | 73 Ta BCC/TETR | 74 W BCC | 75 Re HCP | 76 Os HCP | 77 Ir FCC | 78 Pt FCC | 79 Au FCC | 80 Hg RHO |
| | 104 Rf [HCP] | 105 Db [BCC] | 106 Sg [BCC] | 107 Bh [HCP] | 108 Hs [HCP] | 109 Mt [FCC] | 110 Ds [BCC] | 111 Rg [BCC] | 112 Cn [HCP] |

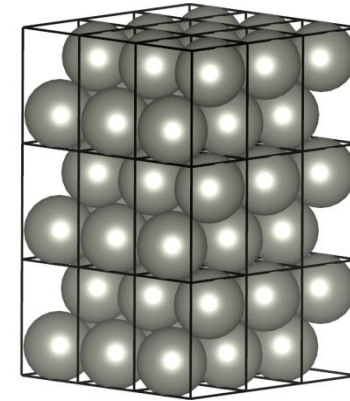
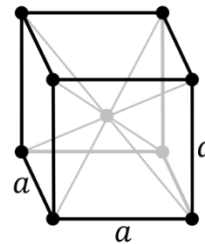
Figure: [Wikipedia](#)



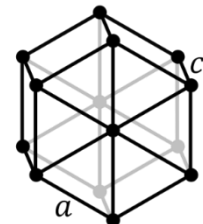
Cu (fcc)



Fe (bcc)



Zn (hcp)



Oxidation state (1)

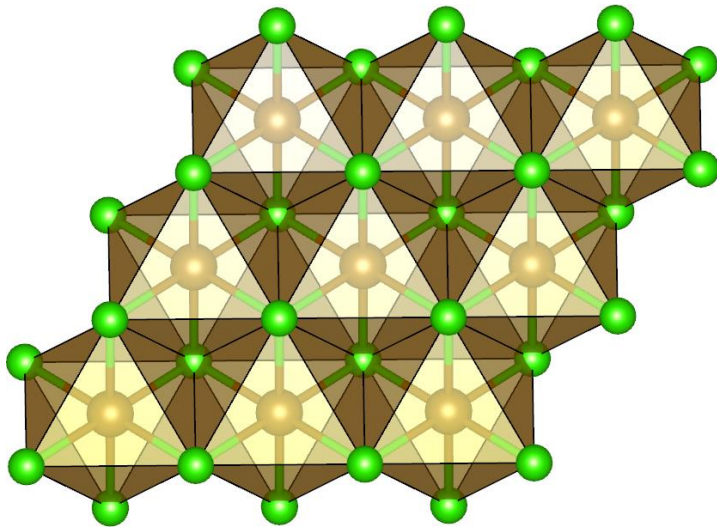
- **Oxidation state** is a key concept for understanding the chemistry of *d*-block metals
- Indicates the degree of oxidation (**loss of electrons**) of an atom in a compound
- Using FeCl_2 and FeCl_3 as examples (Pauling electronegativities: Fe = 1.83, Cl = 3.16):



Formally Fe^{2+} and 2 Cl^-

$\text{Fe}^{2+} = \text{Fe(II)}$

Iron(II) chloride



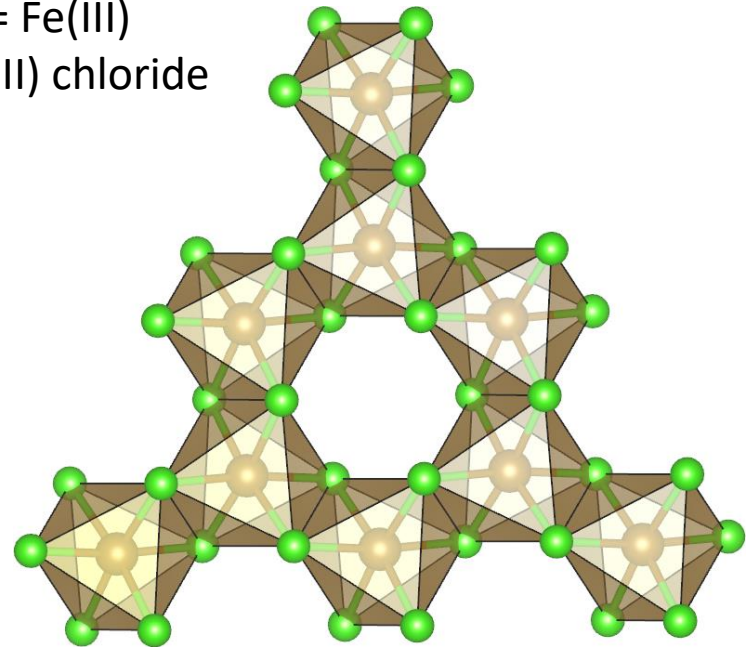
One layer in FeCl_2 ($R-3m$)
3-coordinate Cl



Formally Fe^{3+} and 3 Cl^-

$\text{Fe}^{3+} = \text{Fe(III)}$

Iron(III) chloride



One layer in FeCl_3 ($R-3$)
2-coordinate Cl

Both structures composed of 2D layers, top view along c-axis

Oxidation state (2)

- The exact definition of an oxidation state has been debated for a very long time
- IUPAC Technical Report *Toward a comprehensive definition of oxidation state*:
 - P. Karen et al. *Pure Appl. Chem.* **2014**, *86*, 1017–1081
 - “The oxidation state of a bonded atom equals its charge after ionic approximation”
 - “In the ionic approximation, the atom that contributes more to the bonding molecular orbital (MO) becomes negative”
- IUPAC Recommendation *Comprehensive definition of oxidation state*
 - P. Karen et al. *Pure Appl. Chem.* **2016**, *88*, 831–839
 - **The oxidation state of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds**
- The sum of oxidation states in a compound must be zero!
- The oxidation state of an atom is a useful concept, but it is really just a concept
- In particular, the formal charges such as Fe^{2+} and Cl^- in FeCl_2 **are not real!**

Known oxidation states for *d*-metals

3d

| | | | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|-----------|-----------|-----------|----|-----------|-----------|--|--|--|--|--|--|--|--|-------------|
| | | | Sc | +1 | +2 | +3 | | | | | | | | | | | | | | |
| | | -2 | -1 | Ti | +1 | +2 | +3 | +4 | | | | | | | | | | | | |
| | | -3 | | -1 | V | +1 | +2 | +3 | +4 | +5 | | | | | | | | | | |
| -4 | | -2 | -1 | Cr | +1 | +2 | +3 | +4 | +5 | +6 | | | | | | | | | | |
| | -3 | -2 | -1 | Mn | +1 | +2 | +3 | +4 | +5 | +6 | +7 | | | | | | | | | |
| -4 | | -2 | -1 | Fe | +1 | +2 | +3 | +4 | +5 | +6 | +7 | | | | | | | | | |
| | -3 | | -1 | Co | +1 | +2 | +3 | +4 | +5 | | | | | | | | | | | Year |
| | | -2 | -1 | Ni | +1 | +2 | +3 | +4 | | | | | | | | | | | | 2016 |
| | | -2 | | Cu | +1 | +2 | +3 | +4 | | | | | | | | | | | | |
| | | -2 | | Zn | +1 | +2 | | | | | | | | | | | | | | |

4d

| | | | | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|-----------|-----------|-----------|-----------|----|-----------|-----------|-----------|--|--|--|--|--|--|--|--|--|
| | | | | Y | +1 | +2 | +3 | | | | | | | | | | | | | | |
| | | -2 | | Zr | +1 | +2 | +3 | +4 | | | | | | | | | | | | | |
| | | -3 | | -1 | Nb | +1 | +2 | +3 | +4 | +5 | | | | | | | | | | | |
| -4 | | -2 | -1 | Mo | +1 | +2 | +3 | +4 | +5 | +6 | | | | | | | | | | | |
| | -3 | | -1 | Tc | +1 | +2 | +3 | +4 | +5 | +6 | +7 | | | | | | | | | | |
| -4 | | -2 | | Ru | +1 | +2 | +3 | +4 | +5 | +6 | +7 | +8 | | | | | | | | | |
| | -3 | | -1 | Rh | +1 | +2 | +3 | +4 | +5 | +6 | | | | | | | | | | | |
| | | | | Pd | +1 | +2 | +3 | +4 | +5 | +6 | | | | | | | | | | | |
| | | -2 | -1 | Ag | +1 | +2 | +3 | +4 | | | | | | | | | | | | | |
| | | -2 | | Cd | +1 | +2 | | | | | | | | | | | | | | | |

d-block metals show a larger number of oxidation states in comparison to main group elements or *f*-block elements

The most common oxidation states are shown in bold

5d

| | | | | | | | | | | | | | | | | | | | | | |
|----|--|----|----|----|-----------|-----------|-----------|-----------|-----------|-----------|----|----|----|-----------|--|--|--|--|--|--|-------------|
| | | -2 | | Hf | +1 | +2 | +3 | +4 | | | | | | | | | | | | | |
| | | -3 | | -1 | Ta | +1 | +2 | +3 | +4 | +5 | | | | | | | | | | | |
| -4 | | -2 | -1 | W | +1 | +2 | +3 | +4 | +5 | +6 | | | | | | | | | | | |
| | | -3 | | -1 | Re | +1 | +2 | +3 | +4 | +5 | +6 | +7 | | | | | | | | | |
| -4 | | -2 | -1 | Os | +1 | +2 | +3 | +4 | +5 | +6 | +7 | +8 | | | | | | | | | |
| | | -3 | | -1 | Ir | +1 | +2 | +3 | +4 | +5 | +6 | +7 | +8 | +9 | | | | | | | |
| | | -3 | -2 | -1 | Pt | +1 | +2 | +3 | +4 | +5 | +6 | | | | | | | | | | Year |
| | | -3 | -2 | -1 | Au | +1 | +2 | +3 | | +5 | | | | | | | | | | | 2014 |
| | | -2 | | Hg | +1 | +2 | | | | | | | | | | | | | | | |

Ref: https://en.wikipedia.org/wiki/List_of_oxidation_states_of_the_elements (based on Greenwood and Earnshaw + recent literature)

Identification of an iridium-containing compound with a formal oxidation state of IX

Guanjun Wang¹, Mingfei Zhou¹, James T. Goettel², Gary J. Schrobilgen², Jing Su³, Jun Li³, Tobias Schlöder⁴ & Sebastian Riedel^{4,5}

One of the most important classifications in chemistry and within the periodic table is the concept of formal oxidation states^{1–4}. The preparation and characterization of compounds containing elements with unusual oxidation states is of great interest to chemists⁵. The highest experimentally known formal oxidation state of any chemical element is at present VIII^{2–4}, although higher oxidation states have been postulated^{6,7}. Compounds with oxidation state VIII include several xenon compounds⁸ (for example XeO₄ and XeO₃F₂) and the well-characterized species RuO₄ and OsO₄ (refs 2–4). Iridium, which has nine valence electrons, is predicted to have the greatest chance of being oxidized beyond the VIII oxidation state¹. In recent matrix-isolation experiments, the IrO₄ molecule was characterized as an isolated molecule in rare-gas matrices⁹. The valence electron configuration of iridium in IrO₄ is 5d¹, with a formal oxidation state of VIII. Removal of the remaining *d* electron from IrO₄ would lead to the iridium tetroxide cation ([IrO₄]⁺), which was recently predicted to be stable¹⁰ and in which iridium is in a formal oxidation state of IX. There has been some speculation about the formation of [IrO₄]⁺ species^{11,12}, but these experimental observations have not been structurally confirmed. Here we report the formation of [IrO₄]⁺ and its identification by infrared photodissociation spectroscopy. Quantum-chemical calculations were carried out at the highest level of theory that is available today, and predict that the iridium tetroxide cation, with a T_d-symmetrical structure and a d⁰ electron configuration, is the most stable of all possible [IrO₄]⁺ isomers.

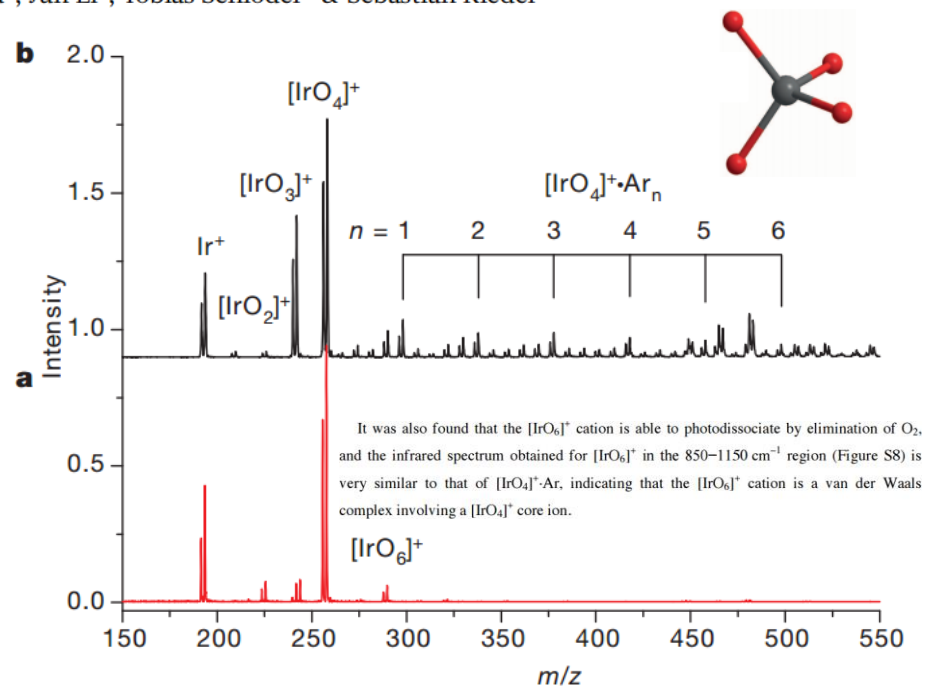


Figure 1 | Mass spectra of the iridium oxide cations. The cations are produced by pulsed-laser vaporization of an iridium metal target in an expansion of helium (a) or argon (b) seeded by dioxygen. The isotopic splitting of iridium can clearly be resolved with the relative peak areas matching the natural abundance isotopic distribution (¹⁹¹Ir, 37.3%; ¹⁹³Ir, 62.7%). *m/z*, mass/charge ratio; intensity is shown in arbitrary units.

Electron configurations for 3d metals

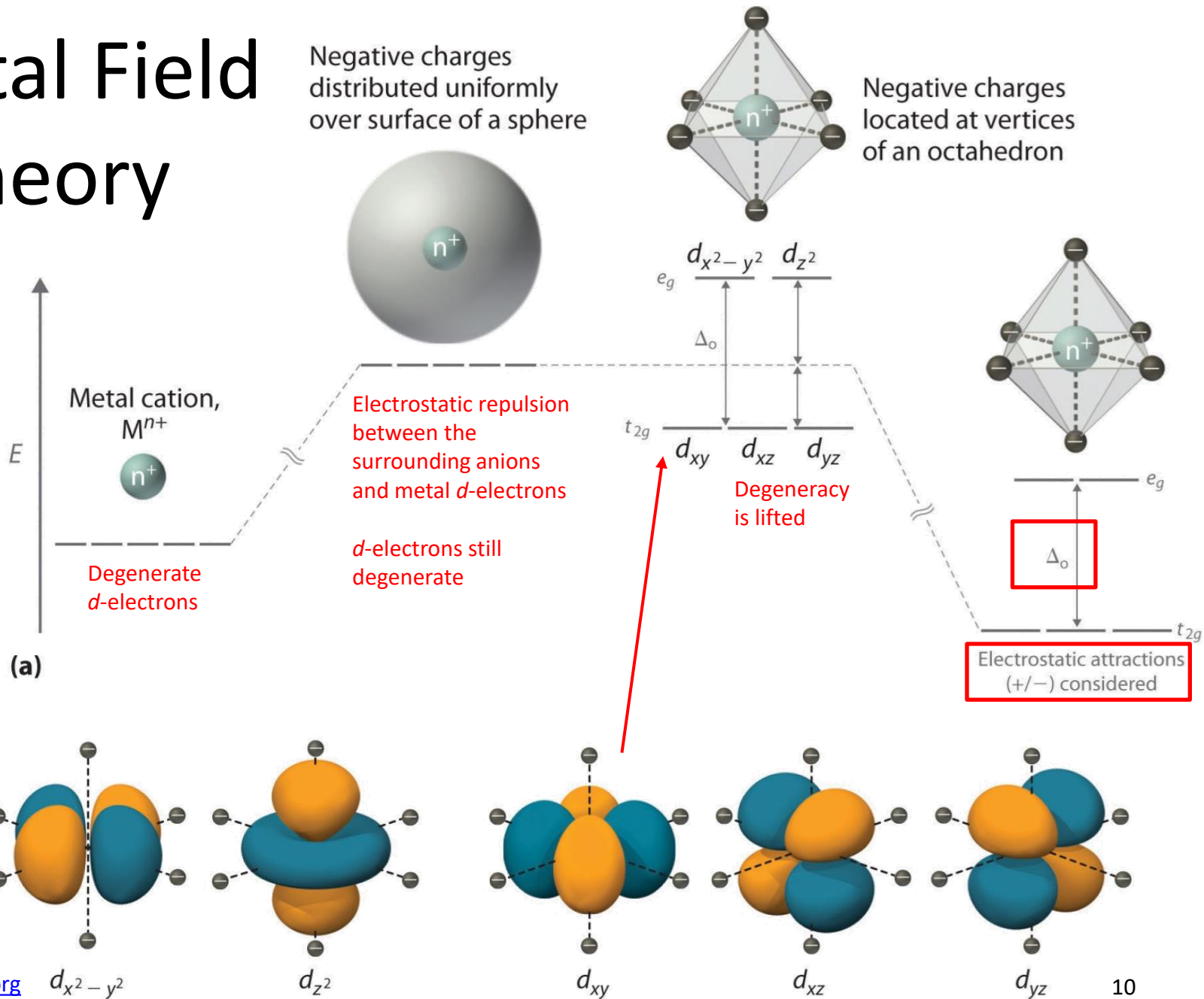
| Metal | Z | Group | The most common oxidation states |
|-------|----|-------|--|
| Sc | 21 | 3 | +3 (d^0) |
| Ti | 22 | 4 | +4 (d^0) |
| V | 23 | 5 | +2 (d^3), +3 (d^2), +4 (d^1), +5 (d^0) |
| Cr | 24 | 6 | +3 (d^3), +6 (d^0) |
| Mn | 25 | 7 | +2 (d^5), +4 (d^3), +7 (d^0) |
| Fe | 26 | 8 | +2 (d^6), +3 (d^5) |
| Co | 27 | 9 | +2 (d^7), +3 (d^6) |
| Ni | 28 | 10 | +2 (d^8) |
| Cu | 29 | 11 | +1 (d^{10}), +2 (d^9) |
| Zn | 30 | 12 | +2 (d^{10}) |

In compounds where the metal is oxidized, consider that it only has *d*-electrons left

Non-bonding *d*-electrons

- The mutual interaction between *bonding* electron pairs is similar in *d*-block metal compounds and main group compounds
- However, *d*-metals can possess *nonbonding d*-electrons in their five *d* orbitals.
- *d* electron configurations can be determined with ***ligand field theory*** (LFT)
 1. Attain a minimum repulsion with other *d*-electrons
 2. Attain a minimum repulsion with the bonding electron pairs (ligands)
- In its original version by Hans Bethe, it was formulated as ***crystal field theory (CFT)***
 - Ligands are treated as point-like ions
 - Only consider electrostatic repulsion between the *d*-electrons and the ligands
- LFT is in principle superseded by the ***molecular orbital theory***
 - LFT is still is a convenient and simple tool to understand the bonding and magnetism of *d*-metal compounds

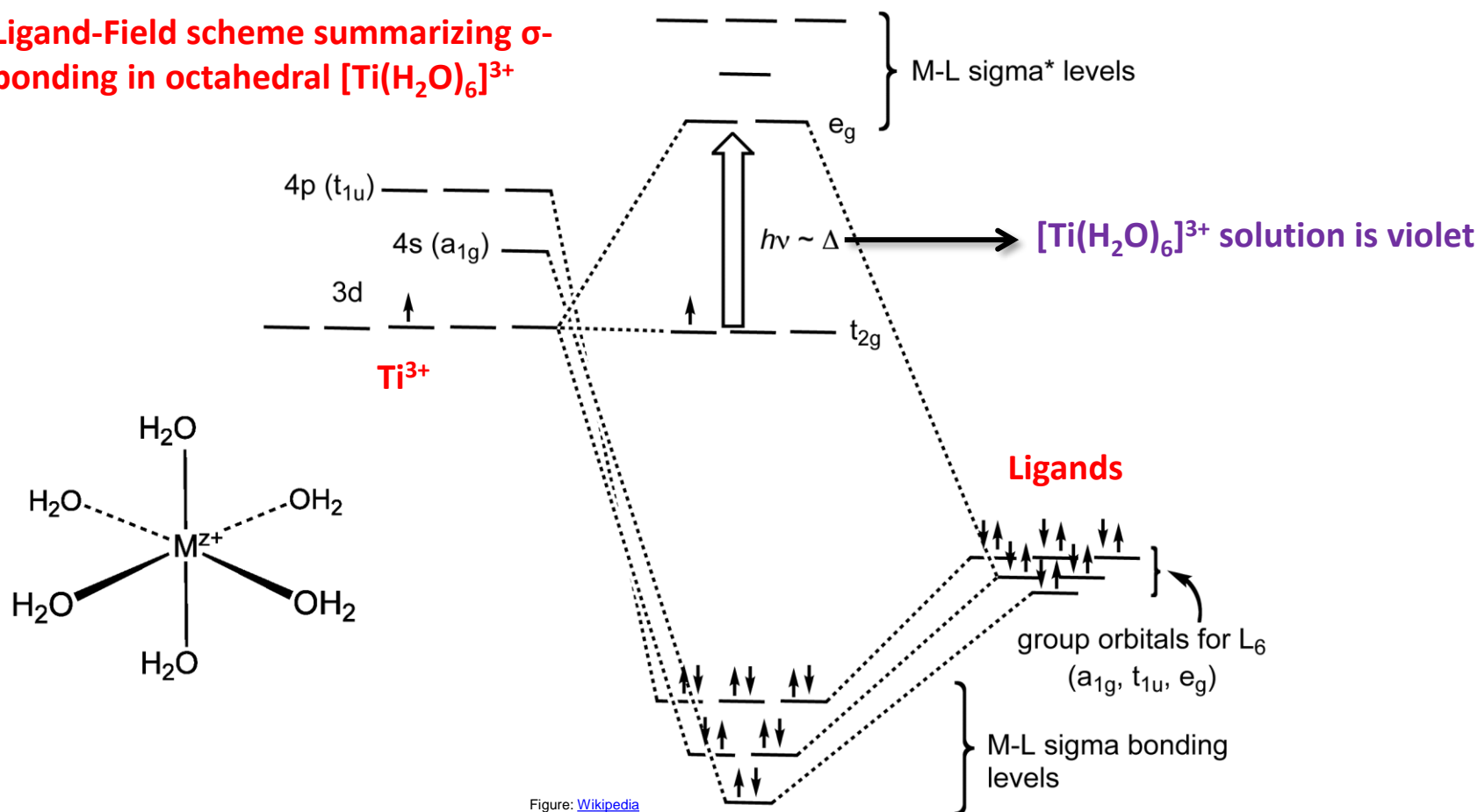
Crystal Field Theory



Ligand field theory (1)

- In ligand field theory, the ligands are not just considered as negative point charges, but the covalent nature of the σ -bonding is also taken into account
- The basic concept of the d -orbital splitting remains

Ligand-Field scheme summarizing σ -bonding in octahedral $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Ligand field theory (2)

Ref: Müller p. 74

- In an octahedral geometry, the t_{2g} and e_g orbitals are separated by energy Δ_o
 - Δ_o depends on the repulsion between the bonding electron pairs and d electrons
- Δ_o decreases when the ligand electronegativity increases
 - Bonding electrons are pulled further from the metal d electrons -> less repulsion
- Δ_o decreases when the size of the ligand atom increases
 - Bonding electrons are distributed over a larger space -> less repulsion
- Δ_o is large for ligands that form multiple bonds with the metal atom (e.g. CO, CN^-)
 - More bonding electrons -> more repulsion with the d electrons
- Δ_o can be measured with spectroscopic methods and the *spectrochemical series* is obtained by ordering different ligands according to decreasing Δ_o :
 - CO (strong field, large Δ_o) > CN^- > PR_3 > NO_2^- > NH_3 > NCS^- > H_2O > $\text{RCO}_2^- \approx \text{OH}^-$ > F^- > NO_3^- > $\text{Cl}^- \approx \text{SCN}^-$ > S_2^{2-} > Br^- > I^- (weak field, small Δ_o)
- $4d$ and $5d$ orbitals have larger overlap with ligand orbitals and larger Δ_o than $3d$

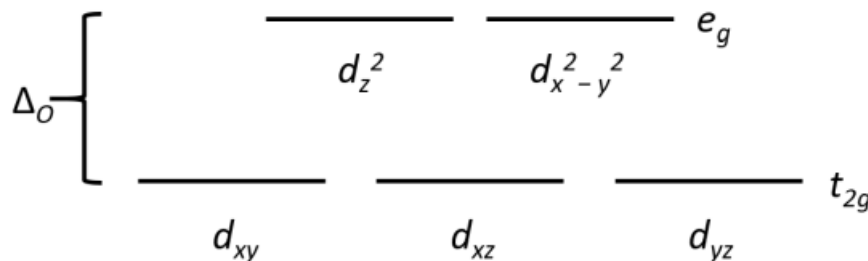
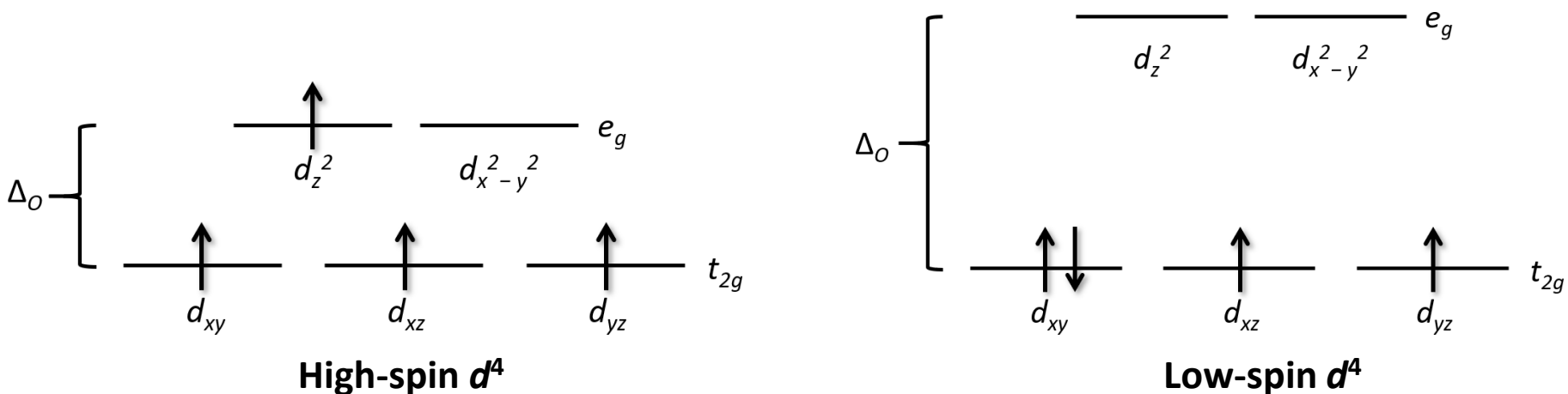


Figure: AJK

Ligand field theory (3)

- LFT can be used to explain the magnetism of transition metal compounds
- Because of the splitting of the d -orbitals, there is an energetical competition between **high-spin** and **low-spin** configuration of the d -orbitals
- The first three d electrons occupy the t_{2g} orbitals in accordance to **Hund's rule**
- When four d electrons are present, there are two alternatives for the fourth electron
 - The energy for putting a second electron in an already occupied orbital is called the electron pairing energy P
 - If $P > \Delta_O$, the fourth electron will occupy an e_g orbital (high-spin)
 - If $P < \Delta_O$, the fourth electron will occupy a t_{2g} orbital (low-spin)



Jahn-Teller effect (1)

Ref: Müller p. 76

- In a high-spin d^4 complex only one of the two e_g orbitals is occupied
- If d_z^2 is occupied \rightarrow repulsion on the bonding electrons of the ligands on the z axis
- The axial ligands are pushed back and the octahedron elongates along the z axis
 - This effect is known as the **Jahn-Teller effect**
- The $d_{x^2-y^2}$ orbital could have been occupied, elongating bonds along x and y axes
 - The energy cost of elongating four bonds is higher, and this is less common (but still possible!)
- The J-T effect occurs when degenerate orbitals are unevenly occupied
- **Strong** J-T effect is observed for the following electronic configurations:

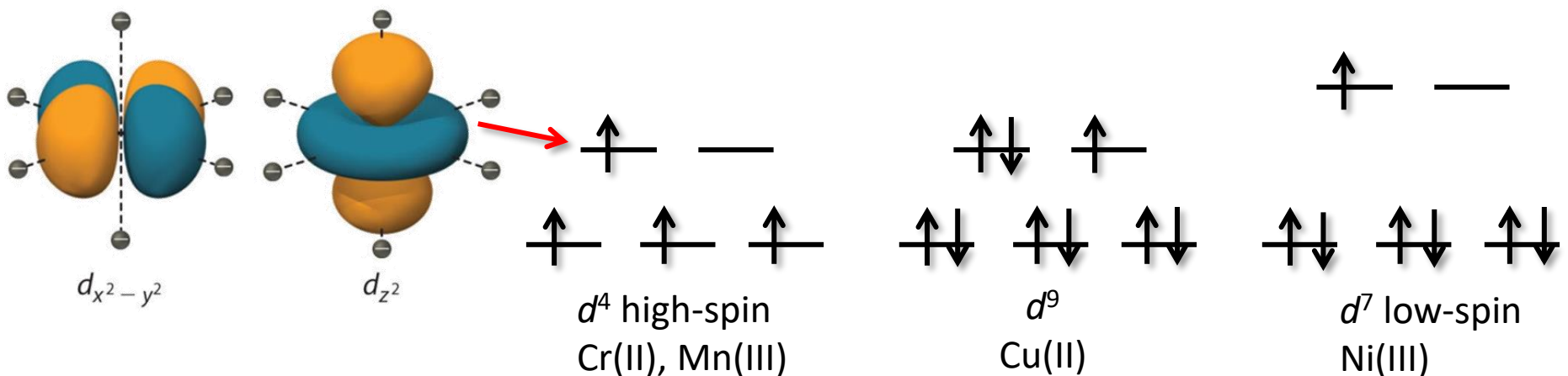
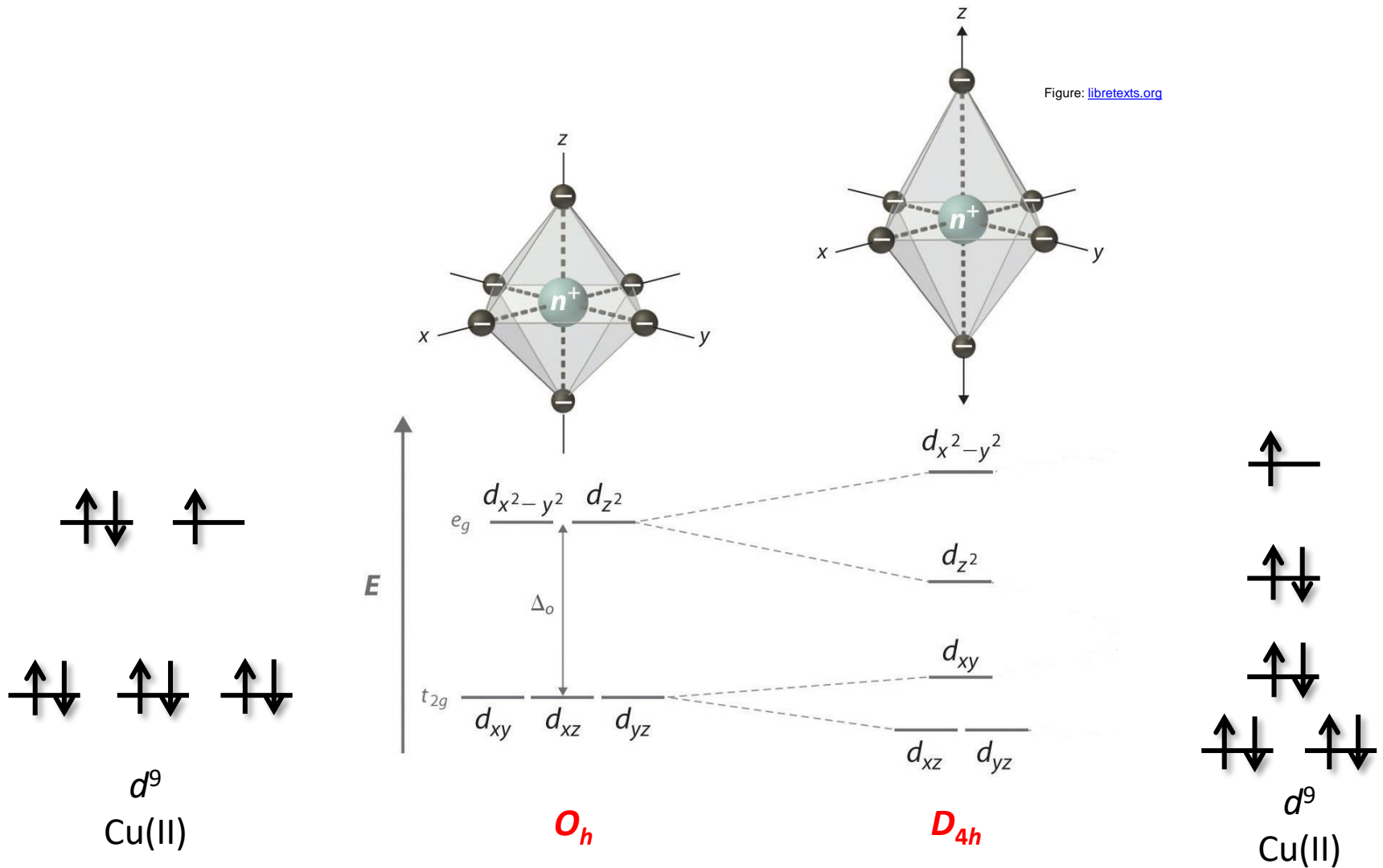


Figure: libretexts.org

Figure: AJK

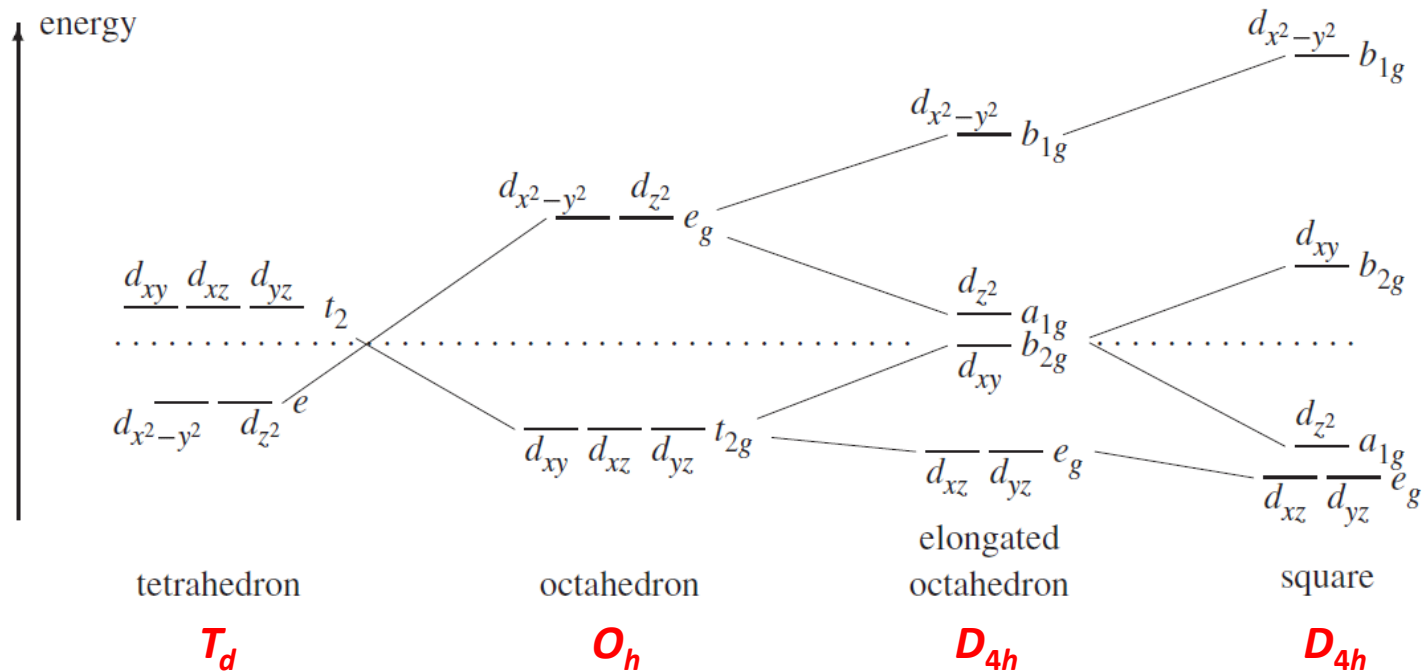
Jahn-Teller effect (2)

- Illustration of tetragonal distortion (elongation) for an octahedral d^9 complex



Other coordination geometries

- The splitting of the d -orbitals is different for other coordination geometries
- The figure below shows the most typical geometries for d -metals



Relative energies of electrons in d -orbitals for different coordination geometries

Most common coordination polyhedra for coordination numbers 2-6

| polyhedron | c.n. | electron config. | central atom | examples |
|--------------------|------|------------------|--|---|
| linear arrangement | 2 | d^{10} | Cu(I), Ag(I), Au(I), Hg(II) | Cu_2O , $\text{Ag}(\text{CN})_2^-$, AuCN^* , AuCl_2^- , HgCl_2 , HgO^* |
| triangle | 3 | d^{10} | Cu(I), Ag(I), Au(I), Hg(II) | $\text{Cu}(\text{CN})_3^{2-}$, $\text{Ag}_2\text{Cl}_3^{3-}$, $\text{Au}(\text{PPh}_3)_3^+$, HgI_3^- |
| square | 4 | d^8 | Ni(II), Pd(II), Pt(II), Au(III) | $\text{Ni}(\text{CN})_4^{2-}$, PdCl_2^* , PtH_4^{2-} , $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, AuCl_4^- |
| tetrahedron | 4 | d^0 | Ti(IV), V(V), Cr(VI), Mo(VI), Mn(VII), Re(VII), Ru(VIII), Os(VIII) | TiCl_4 , VO_4^{3-} , CrO_3^* , CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , Mn_2O_7 , ReO_4^- , RuO_4 , OsO_4 |
| | | d^1 | V(IV), Cr(V), Mn(VI), Ru(VII) | VCl_4 , CrO_4^{3-} , MnO_4^{2-} , RuO_4^- |
| | | d^5 | Mn(II), Fe(III) | MnBr_4^{2-} , Fe_2Cl_6 |
| | | d^6 | Fe(II) | FeCl_4^{2-} |
| | | d^7 | Co(II) | CoCl_4^{2-} |
| | | d^8 | Ni(II) | NiCl_4^{2-} |
| | | d^9 | Cu(II) | $\text{CuCl}_4^{2- \dagger}$ |
| | | d^{10} | Ni(0), Cu(I), Zn(II), Hg(II) | $\text{Ni}(\text{CO})_4$, $\text{Cu}(\text{CN})_4^{3-}$, $\text{Zn}(\text{CN})_4^{2-}$, HgI_4^{2-} |
| square pyramid | 5 | d^0 | Ti(IV), V(V), Nb(V), Mo(VI), W(VI) | TiOCl_4^{2-} , VOF_4^- , NbSCl_4^- , MoNCl_4^- , WNCl_4^- |
| | | d^1 | V(IV), Cr(V), Mo(V), W(V), Re(VI) | $\text{VO}(\text{NCS})_4^{2-}$, CrOCl_4^- , MoOCl_4^- , WCl_4^- , ReOCl_4 |
| | | d^2 | Os(VI) | OsNCl_4^- |
| | | d^4 | Mn(III), Re(III) | MnCl_5^{2-} , Re_2Cl_8 |
| | | d^7 | Co(II) | $\text{Co}(\text{CN})_5^{3-}$ |
| trigonal bipyramid | 5 | d^2 | V(IV) | $\text{VCl}_3(\text{NMe}_3)_2$ |
| | | d^8 | Fe(0) | $\text{Fe}(\text{CO})_5$ |
| octahedron | 6 | | nearly all; rarely Pd(II), Pt(II), Au(III), Cu(I) | |

* endless chain

† Jahn–Teller distorted

Magnetic moments (1)

- Unpaired electrons of *d*-block metal complexes give rise to magnetic properties
- Magnetic properties are often expressed in terms of the **magnetic moment** μ , which is directly related to the number of unpaired electrons
- μ arises from electron spin (μ_s) and electron orbital motion (μ_L)
- Electron may be considered as a bundle of negative charge spinning on its axis.

- Spin magnetic moment μ_s for a single electron can be calculated with

$$\mu_s = g\sqrt{s(s+1)}$$

where s is the spin quantum number, $\frac{1}{2}$, and g is the gyromagnetic ratio (~ 2.00).
Substituting for s and g gives $\mu_s = 1.73$ BM for one electron.

- BM = Bohr Magneton (SI units):

$$1 \text{ BM} = \frac{e\hbar}{2m_e}$$

where e is the charge, \hbar is the reduced Planck constant, m_e is the electron rest mass.

Magnetic moments (2)

- In atoms or ions with more than one unpaired electron, the overall spin moment is

$$\mu_S = g\sqrt{S(S+1)}$$

where S is the sum of the spin quantum numbers of the individual unpaired electrons.

- For high-spin Fe^{3+} with five unpaired electrons:

$$S = 5 \times \frac{1}{2} = 5/2 \text{ and } \mu_S = 5.92 \text{ BM.}$$

Table 9.3 Calculated and observed magnetic moments (BM) for some transition metal ions

| Ion | No. of unpaired electrons | $\mu_{S(\text{calc})}$ | $\mu_{(\text{observed})}$ |
|------------------|---------------------------|------------------------|---------------------------|
| V^{4+} | 1 | 1.73 | ~1.8 |
| V^{3+} | 2 | 2.83 | ~2.8 |
| Cr^{3+} | 3 | 3.87 | ~3.8 |
| Mn^{2+} | 5 (high spin) | 5.92 | ~5.9 |
| Fe^{3+} | 5 (high spin) | 5.92 | ~5.9 |
| Fe^{2+} | 4 (high spin) | 4.90 | 5.1–5.5 |
| Co^{3+} | 4 (high spin) | 4.90 | ~5.4 |
| Co^{2+} | 3 (high spin) | 3.87 | 4.1–5.2 |
| Ni^{2+} | 2 | 2.83 | 2.8–4.0 |
| Cu^{2+} | 1 | 1.73 | 1.7–2.2 |

Source: data taken from F. A. Cotton and G. Wilkinson (1966), *Advanced Inorganic Chemistry: a Comprehensive Text*, 2nd edn, John Wiley & Sons, Inc., New York.

Magnetic moments (3)

- The motion of an electron around the nucleus may give rise to an orbital moment (the expression is applicable to free atoms or ions):

$$\mu_{S+L} = g\sqrt{4S(S+1) + L(L+1)}$$

- L is the orbital angular momentum quantum number for the metal ion:

$$L = \hbar\sqrt{l(l+1)}$$

where l is the azimuthal quantum number ($s \rightarrow 0$, $p \rightarrow 1$, $d \rightarrow 2$, $f \rightarrow 3$, ...)

- In practice, L is often completely or partially quenched in cases where the electric fields on the surrounding atoms or ions restrict the orbital motion
 - In such cases, the observed moments are similar to predicted spin-only values

Table 9.3 Calculated and observed magnetic moments (BM) for some transition metal ions

| Ion | No. of unpaired electrons | $\mu_{S(\text{calc})}$ | $\mu_{S+L(\text{calc})}$ | $\mu_{(\text{observed})}$ |
|------------------|---------------------------|------------------------|--------------------------|---------------------------|
| V ⁴⁺ | 1 | 1.73 | 3.00 | ~1.8 |
| V ³⁺ | 2 | 2.83 | 4.47 | ~2.8 |
| Cr ³⁺ | 3 | 3.87 | 5.20 | ~3.8 |
| Mn ²⁺ | 5 (high spin) | 5.92 | 5.92 | ~5.9 |
| Fe ³⁺ | 5 (high spin) | 5.92 | 5.92 | ~5.9 |
| Fe ²⁺ | 4 (high spin) | 4.90 | 5.48 | 5.1–5.5 |
| Co ³⁺ | 4 (high spin) | 4.90 | 5.48 | ~5.4 |
| Co ²⁺ | 3 (high spin) | 3.87 | 5.20 | 4.1–5.2 |
| Ni ²⁺ | 2 | 2.83 | 4.47 | 2.8–4.0 |
| Cu ²⁺ | 1 | 1.73 | 3.00 | 1.7–2.2 |