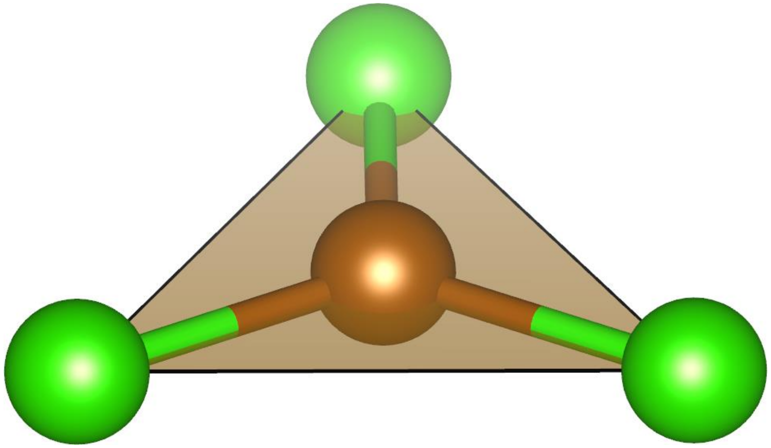
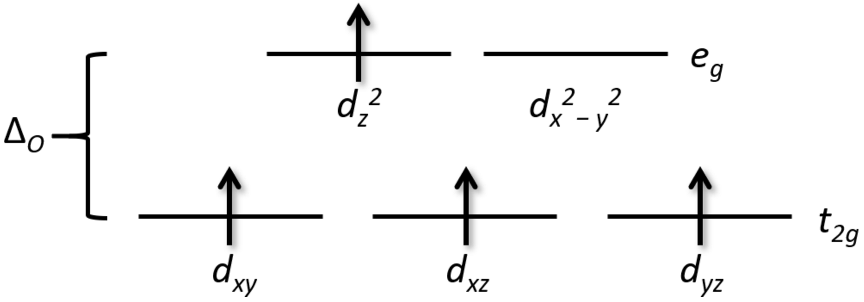
Lecture 11:
d-electrons and Ligand Field Theory

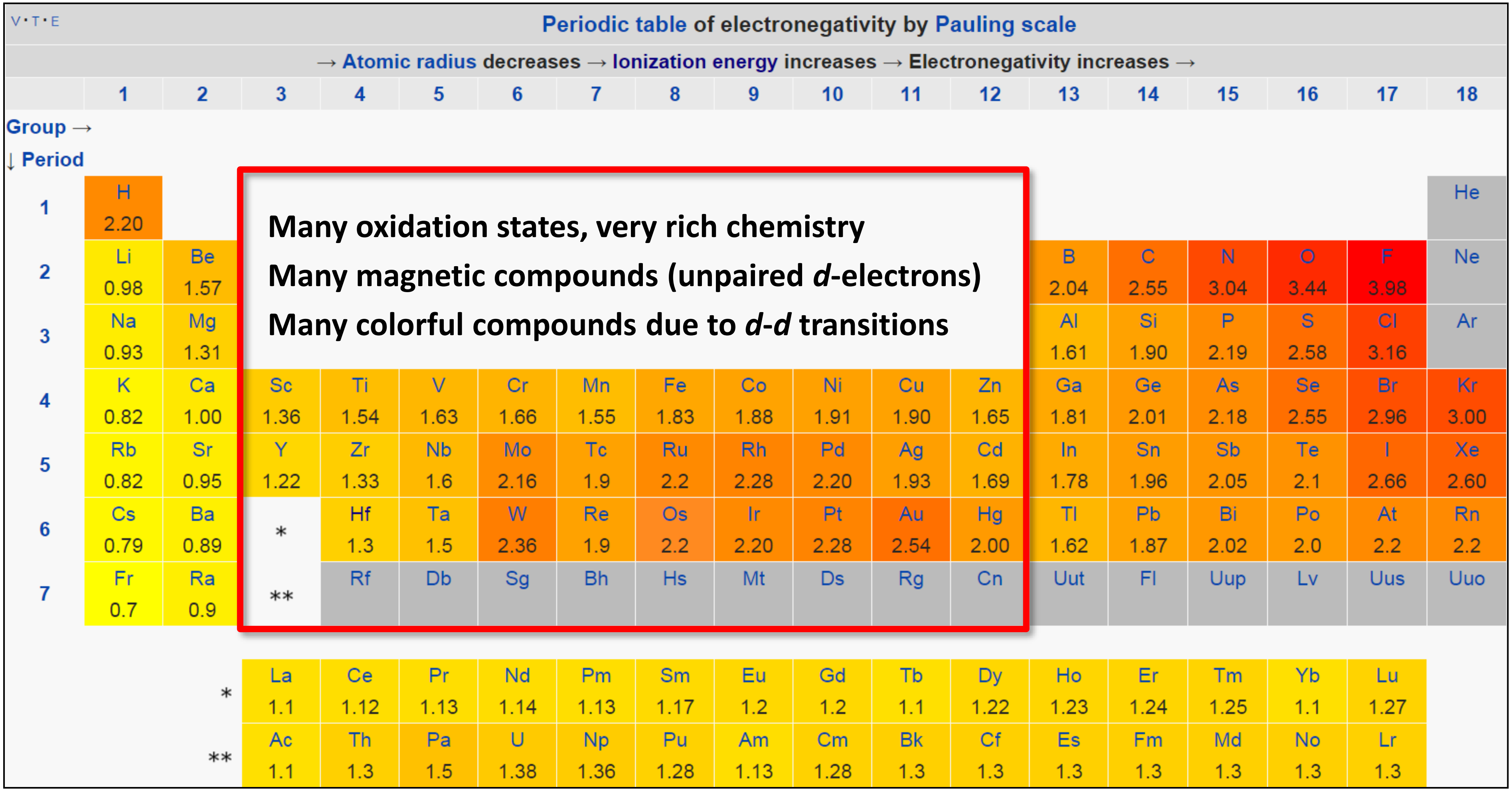
- Concept of oxidation state
- Oxidation states in *d*-block metal compounds
- Crystal field theory
- Ligand field theory
  - Jahn-Teller distortion
- Magnetic moments due to unpaired *d*-electrons





Figures: AJK

d-block metals



Many oxidation states, very rich chemistry

Many magnetic compounds (unpaired *d*-electrons)

Many colorful compounds due to *d*-*d* transitions

V·T·E

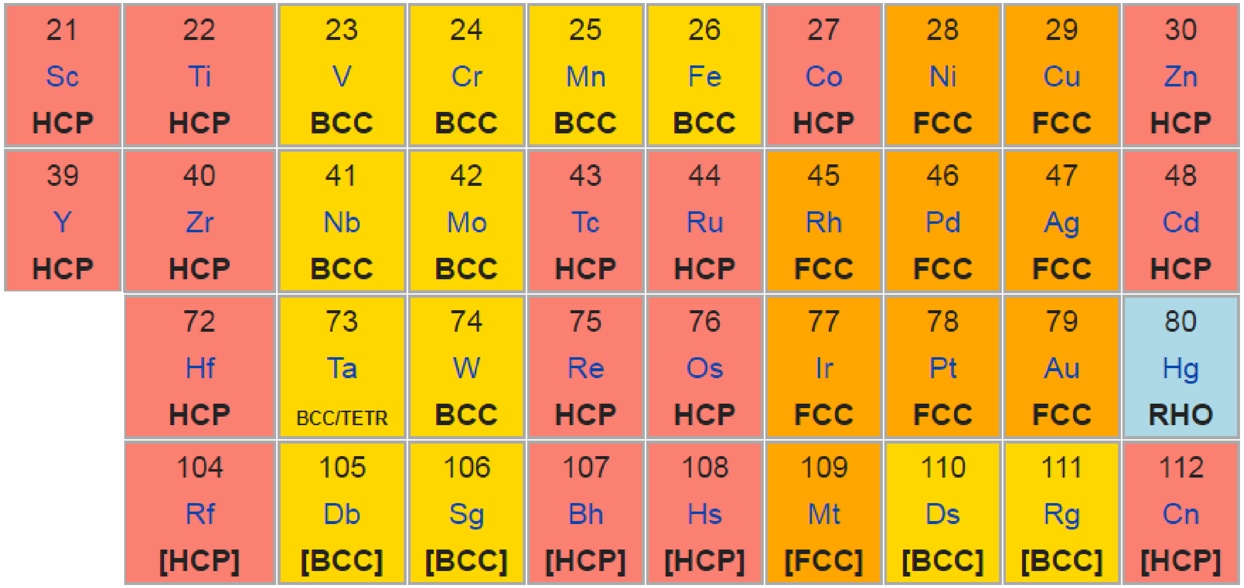
Periodic table of electronegativity by Pauling scale

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

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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	

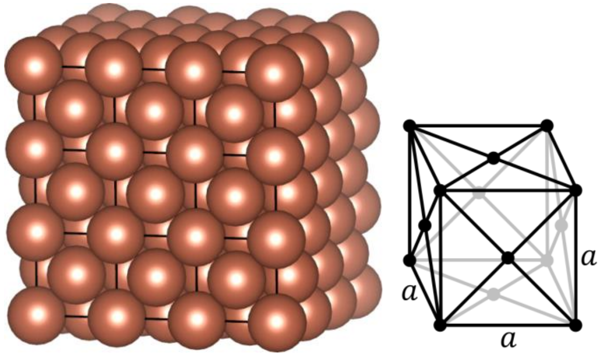
Figure: Wikipedia

Elemental *d*-block metals

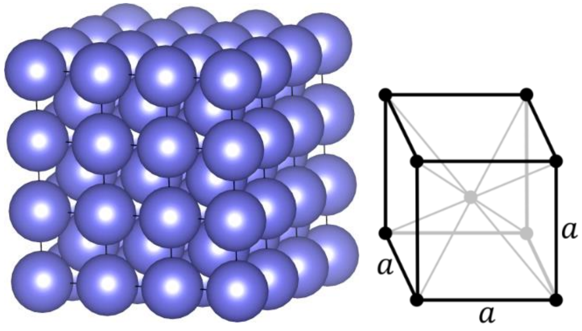


21 Sc **HCP**	22 Ti **HCP**	23 V **BCC**	24 Cr **BCC**	25 Mn **BCC**	26 Fe **BCC**	27 Co **HCP**	28 Ni **FCC**	29 Cu **FCC**	30 Zn **HCP**
39 Y **HCP**	40 Zr **HCP**	41 Nb **BCC**	42 Mo **BCC**	43 Tc **HCP**	44 Ru **HCP**	45 Rh **FCC**	46 Pd **FCC**	47 Ag **FCC**	48 Cd **HCP**
	72 Hf **HCP**	73 Ta BCC/TETR	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]**

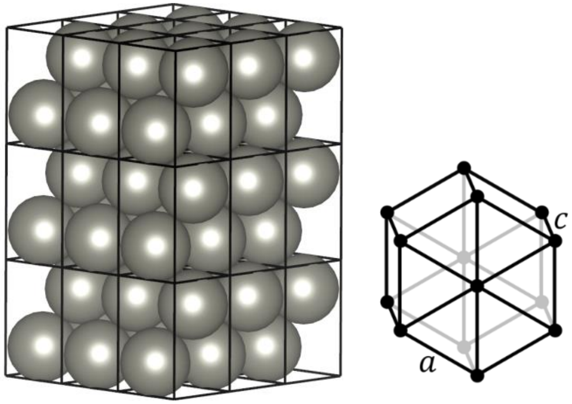
Figure: Wikipedia



Cu (fcc)



Fe (bcc)



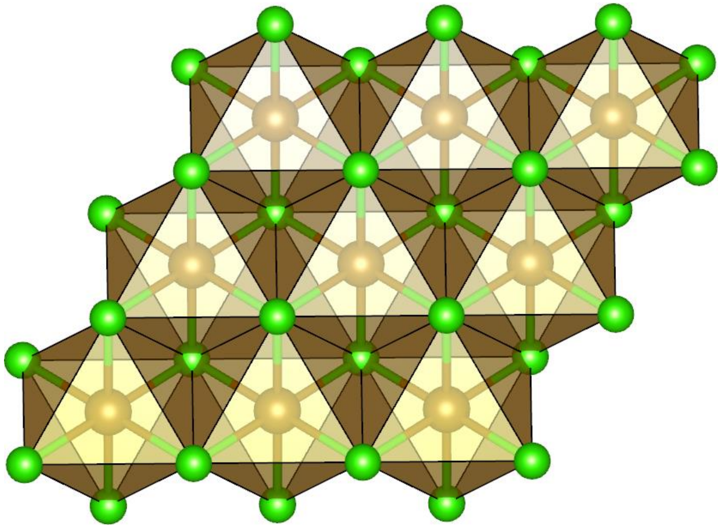
Zn (hcp)

Figures: AJK / Wikipedia

Oxidation state (1)

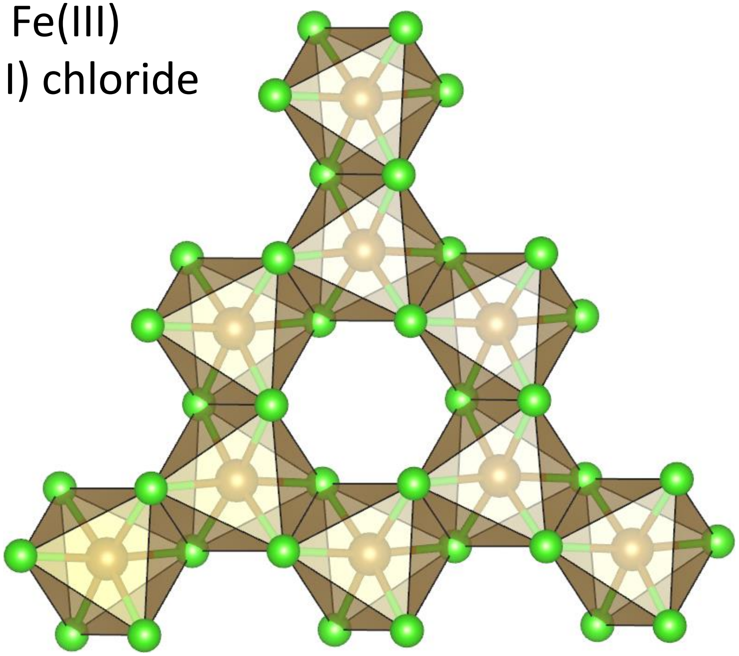
- ***Oxidation state*** is a key concept for understanding the chemistry of *d*-block metals
- Indicates the degree of oxidation (***loss of electrons***) of an atom in a compound
- Using $FeCl_2$ and $FeCl_3$ as examples (Pauling electronegativities: Fe = 1.83, Cl = 3.16):

$FeCl_2$
Formally Fe^{2+} and 2 Cl^{-}
Fe^{2+} = Fe(II)
Iron(II) chloride



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

$FeCl_3$
Formally Fe^{3+} and 3 Cl^{-}
Fe^{3+} = Fe(III)
Iron(III) chloride



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

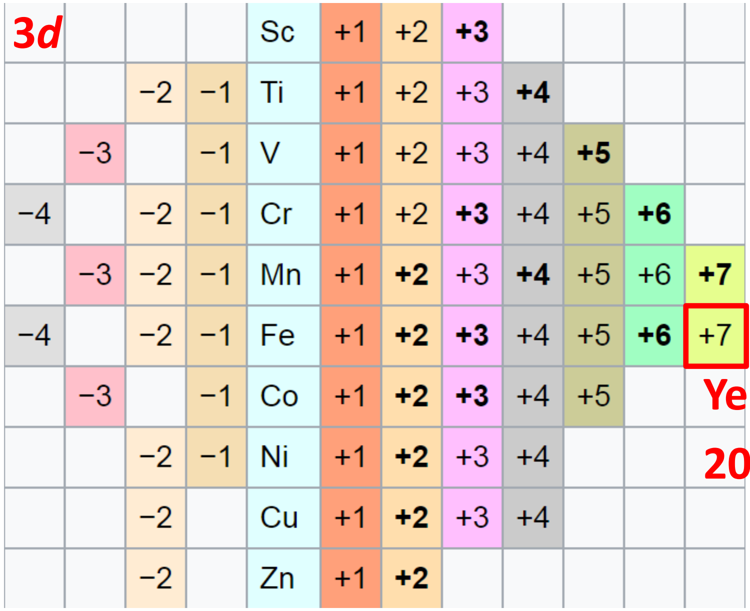
Both structures composed of 2D layers, top view along c-axis

Figures: AJK

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



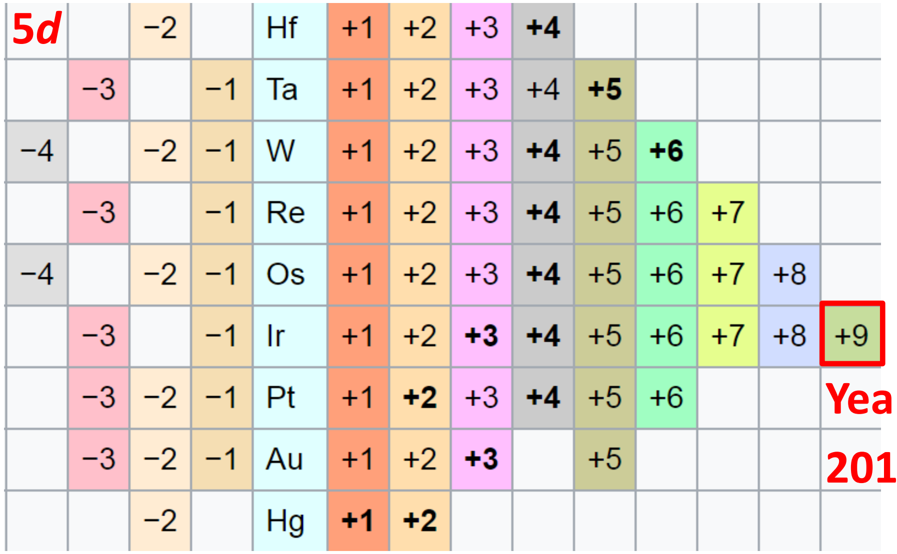
3d				Sc	+1	+2	**+3**					
		−2	−1	Ti	+1	+2	+3	**+4**				
	−3		−1	V	+1	+2	+3	+4	**+5**			
−4		−2	−1	Cr	+1	+2	**+3**	+4	+5	**+6**		
	−3	−2	−1	Mn	+1	**+2**	+3	**+4**	+5	+6	**+7**
−4		−2	−1	Fe	+1	**+2**	**+3**	+4	+5	**+6**	+7
	−3		−1	Co	+1	**+2**	**+3**	+4	+5		
		−2	−1	Ni	+1	**+2**	+3	+4			
		−2		Cu	+1	**+2**	+3	+4			
		−2		Zn	+1	**+2**					

Year 2016

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			
	−3	−2	−1	Au	+1	+2	**+3**		+5				
		−2		Hg	**+1**	**+2**							

Year 2014

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

LETTER *Nature* **2014**, *514*, 475.

doi:10.1038/nature13795

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

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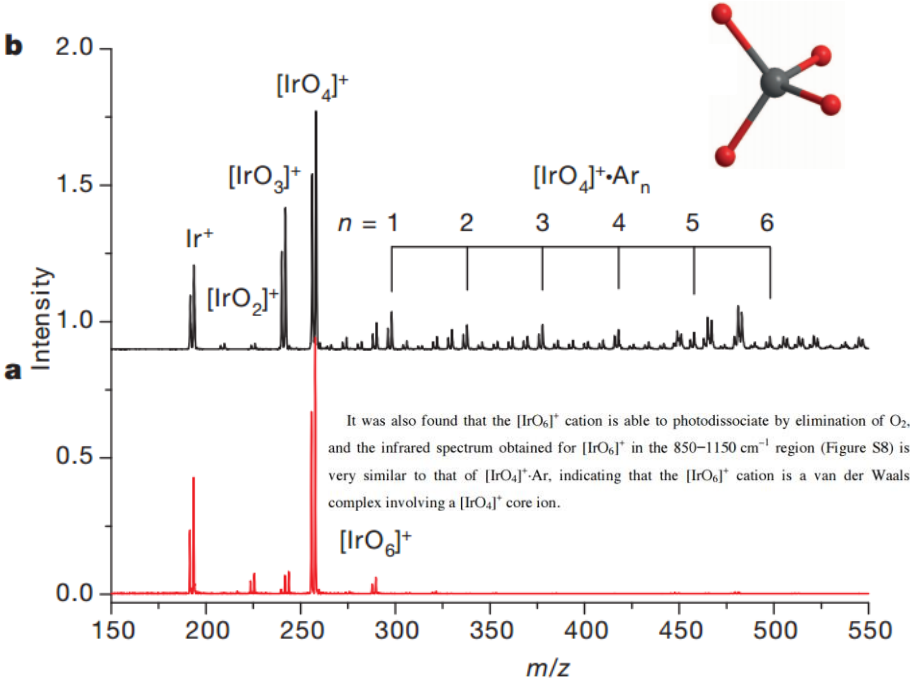
One of the most important classifications in chemistry and within the periodic table is the concept of formal oxidation states[1–4]. The preparation and characterization of compounds containing elements with unusual oxidation states is of great interest to chemists[5]. The highest experimentally known 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 compounds[8] (for example XeO_4 and XeO_3F_2) and the well-characterized species RuO_4 and OsO_4 (refs 2–4). Iridium, which has nine valence electrons, is predicted to have the greatest chance of being oxidized beyond the VIII oxidation state[1]. In recent matrix-isolation experiments, the IrO_4 molecule was characterized as an isolated molecule in rare-gas matrices[9]. The valence electron configuration of iridium in IrO_4 is $5d^1$, with a formal oxidation state of VIII. Removal of the remaining *d* electron from IrO_4 would lead to the iridium tetroxide cation ($[IrO_4]^+$), which was recently predicted to be stable[10] and in which iridium is in a formal oxidation state of IX. There has been some speculation about the formation of $[IrO_4]^+$ species[11,12], but these experimental observations have not been structurally confirmed. Here we report the formation of $[IrO_4]^+$ 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 d^0 electron configuration, is the most stable of all possible $[IrO_4]^+$ isomers.



It was also found that the $[IrO_6]^+$ cation is able to photodissociate by elimination of O_2, and the infrared spectrum obtained for $[IrO_6]^+$ in the 850–1150 cm^{-1} region (Figure S8) is very similar to that of $[IrO_4]^+{\cdot}Ar$, indicating that the $[IrO_6]^+$ cation is a van der Waals complex involving a $[IrO_4]^+$ core ion.

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 (^{191}Ir, 37.3%; ^{193}Ir, 62.7%). *m*/*z*, mass/charge ratio; intensity is shown in arbitrary units.

Electron configurations for 3*d* 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})

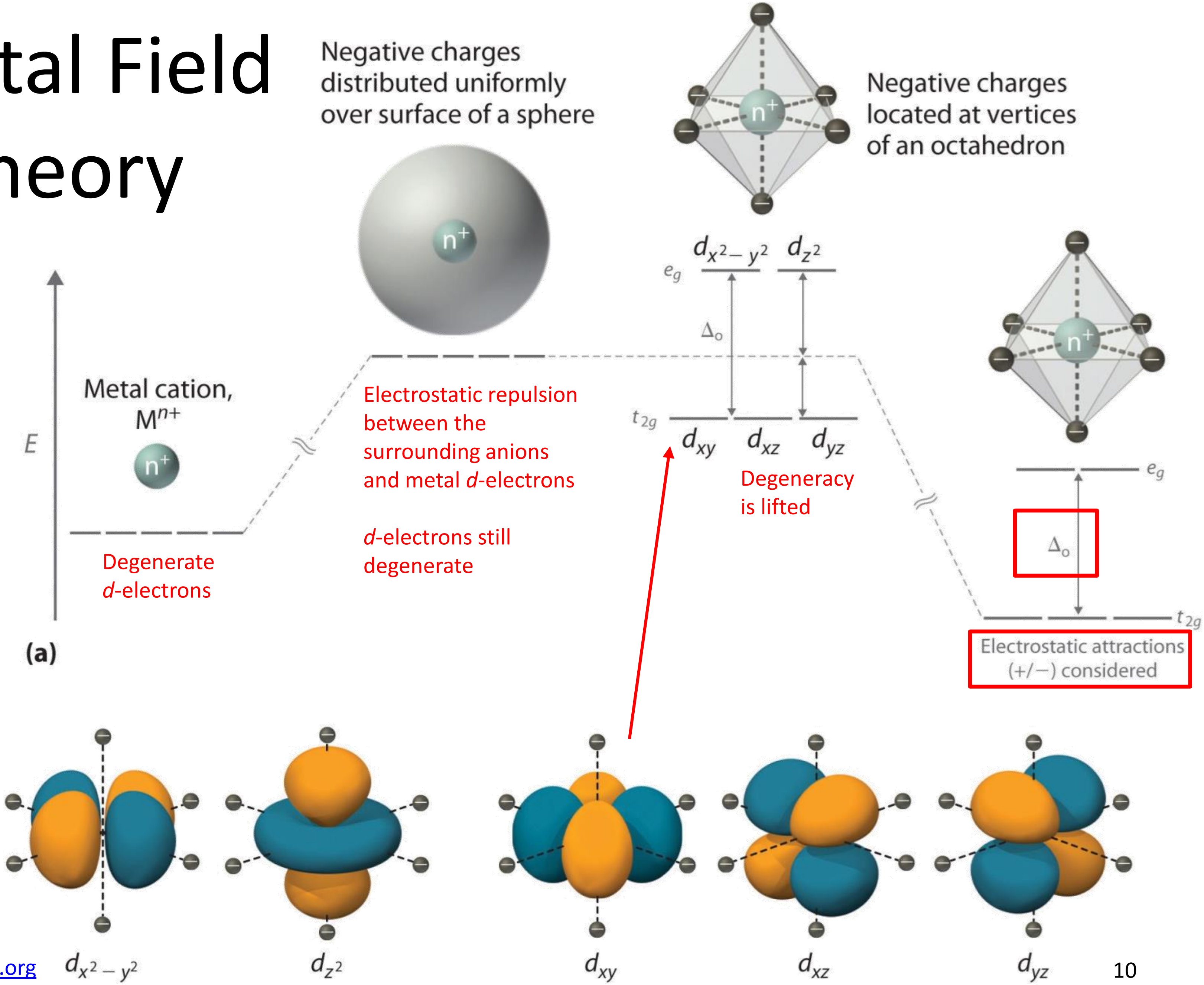
In compounds where the metal is oxidized, consider that it only has *d*-electrons left

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

Ref: Müller p. 73

Crystal Field Theory



Degenerate *d*-electrons

Electrostatic repulsion between the surrounding anions and metal *d*-electrons

d-electrons still degenerate

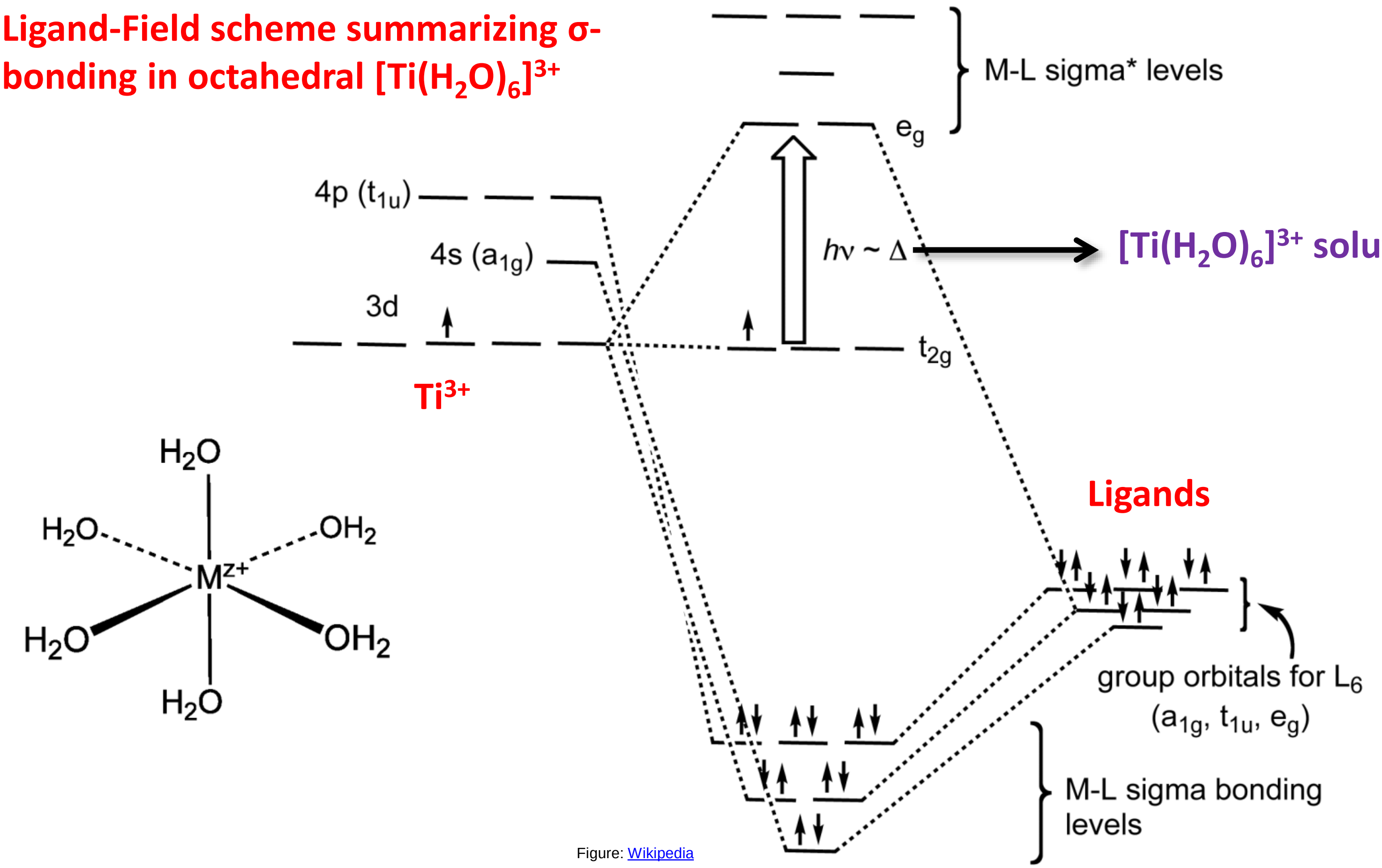
Degeneracy is lifted

Figures: libretexts.org

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 $[Ti(H_2O)_6]^{3+}$



Ti^{3+}

$[Ti(H_2O)_6]^{3+}$ solution is violet

Ligands

Figure: Wikipedia

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 > **N**CS^- > H_2O > RCO_2^- ≈ OH^- > F^- > NO_3^- > Cl^- ≈ **S**CN^- > S_2^- > Br^- > I^- (weak field, small Δ_O)
- 4*d* and 5*d* orbitals have larger overlap with ligand orbitals and larger Δ_O than 3*d*

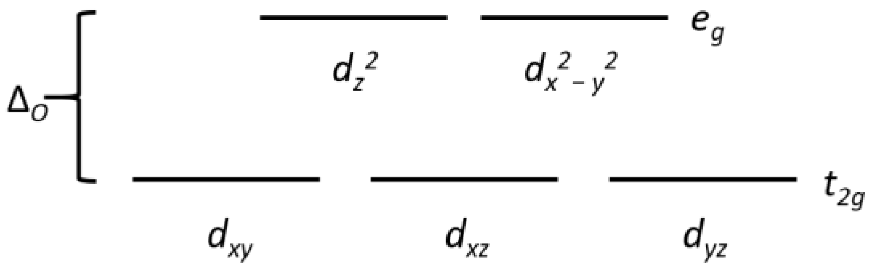
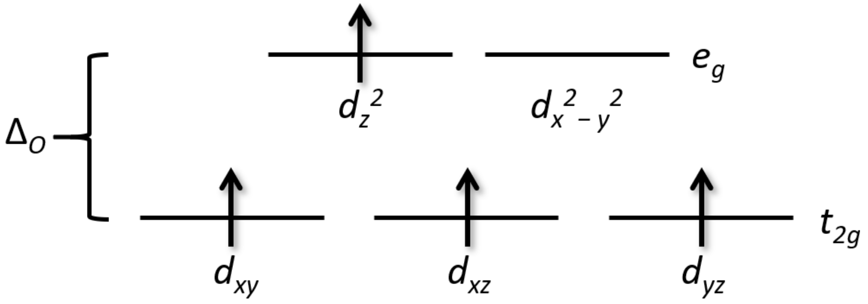


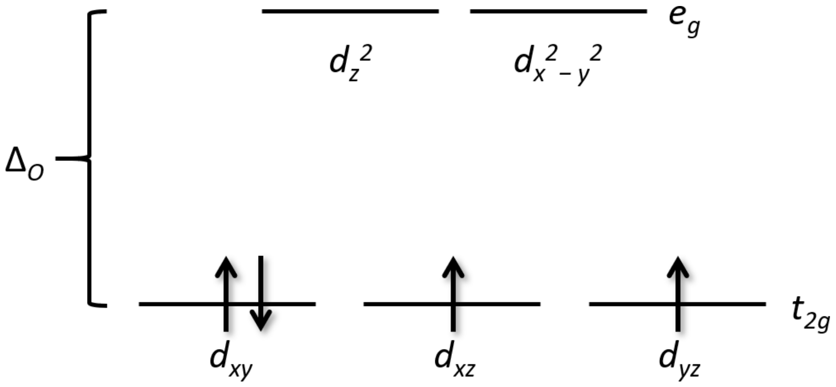
Figure: AJK

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)



High-spin d^4



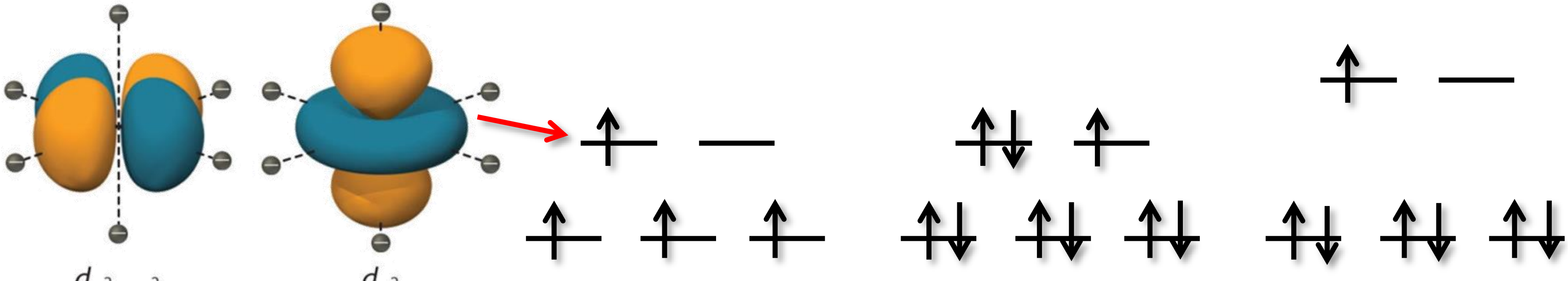
Low-spin d^4

Figure: AJK

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 -> 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 can be observed for the following electronic configurations:



d^4 high-spin
Cr(II), Mn(III)

d^9
Cu(II)

d^7 low-spin
Ni(III)

Figure: libretexts.org

Figure: AJK

Jahn-Teller effect (2)

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

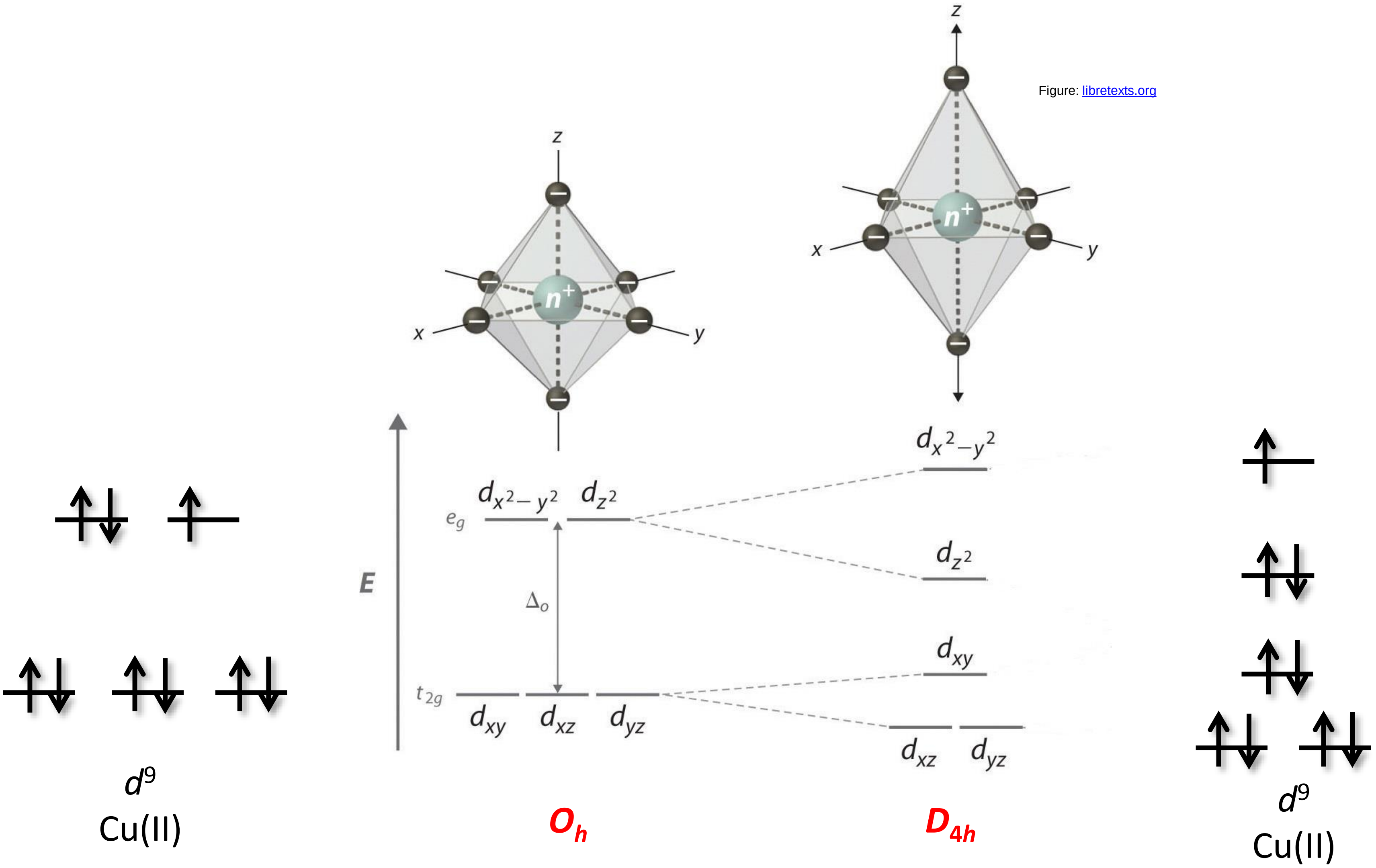
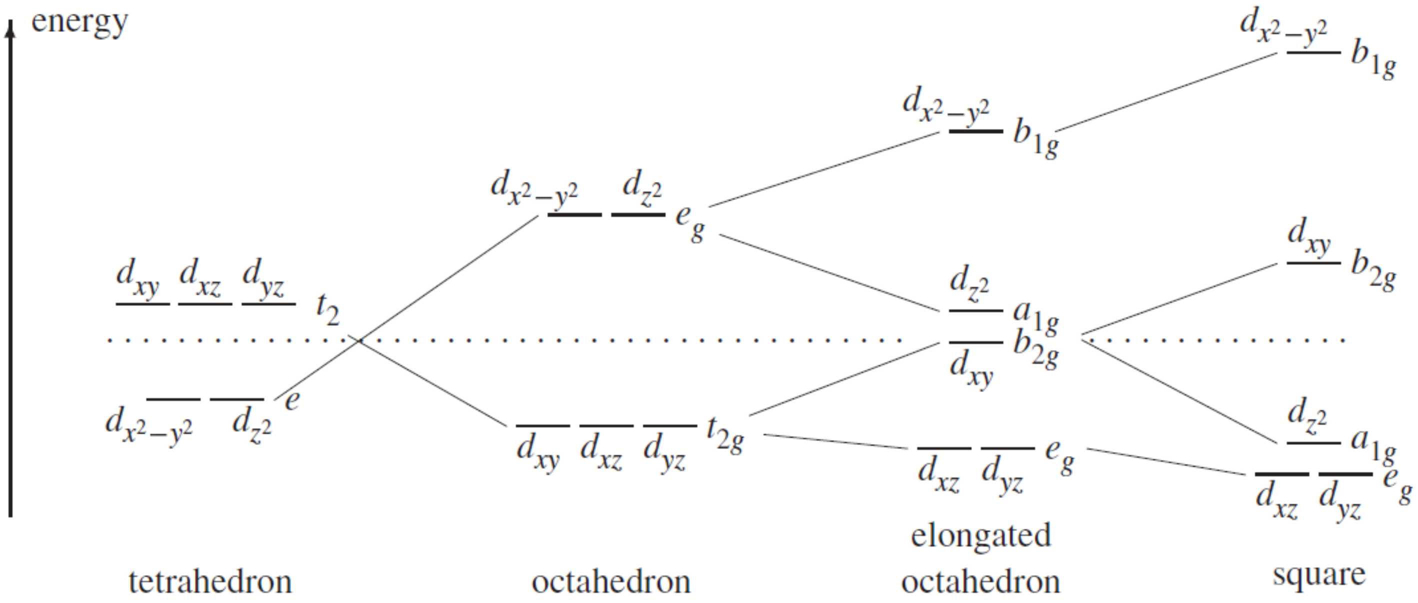


Figure: libretexts.org

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

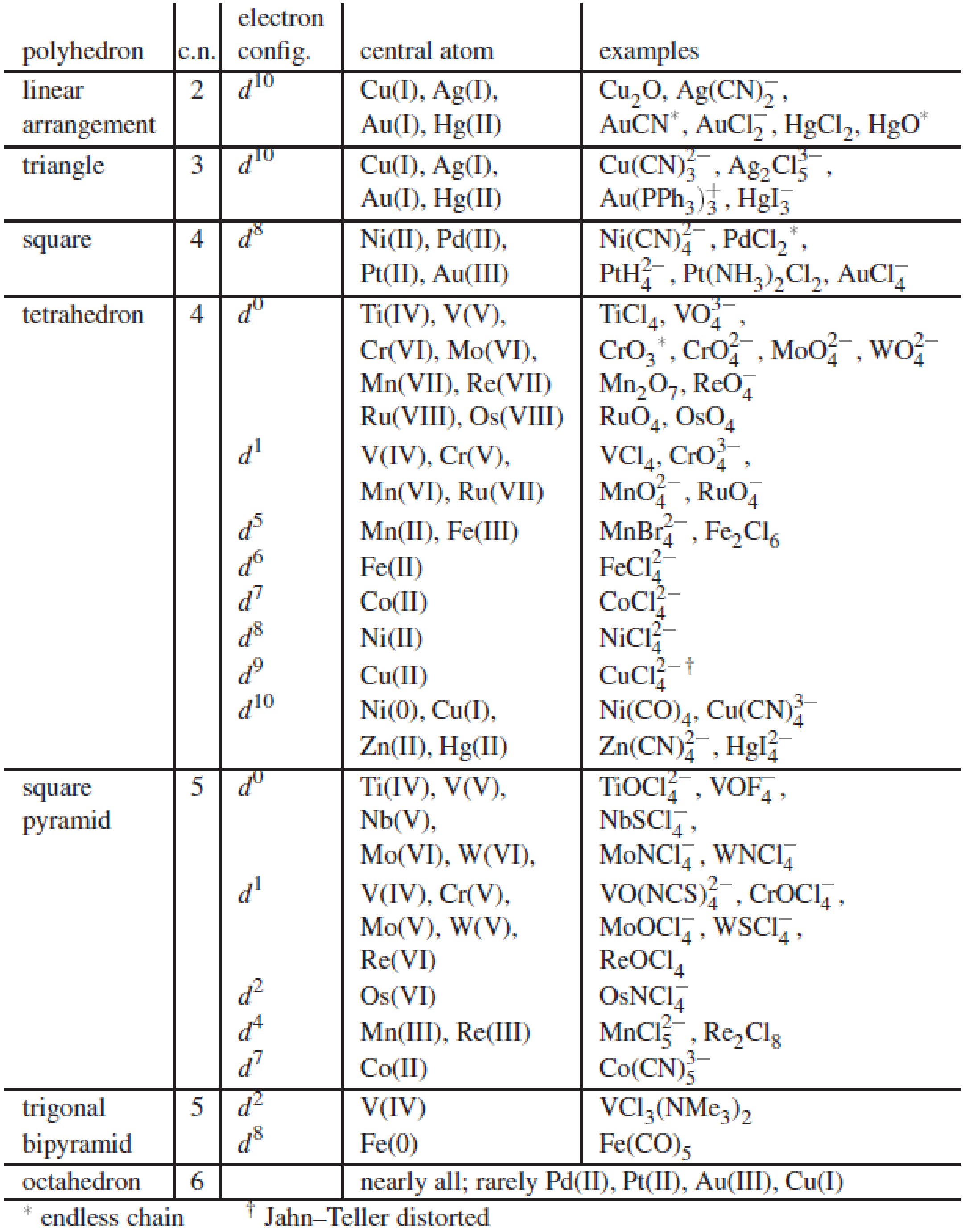


T_d O_h D_{4h} D_{4h}

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

Ref: Müller p. 77

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, $Ag(CN)_2^-$, $AuCN^*$, $AuCl_2^-$, $HgCl_2$, HgO^*
triangle	3	d^{10}	Cu(I), Ag(I), Au(I), Hg(II)	$Cu(CN)_3^{2-}$, $Ag_2Cl_5^{3-}$, $Au(PPh_3)_3^+$, HgI_3^-
square	4	d^8	Ni(II), Pd(II), Pt(II), Au(III)	$Ni(CN)_4^{2-}$, $PdCl_2{}^*$, PtH_4^{2-}, $Pt(NH_3)_2Cl_2$, $AuCl_4^-$
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)	$CuCl_4^{2-\dagger}$
		d^{10}	Ni(0), Cu(I), Zn(II), Hg(II)	$Ni(CO)_4$, $Cu(CN)_4^{3-}$ $Zn(CN)_4^{2-}$, 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)	$VO(NCS)_4^{2-}$, $CrOCl_4^-$, $MoOCl_4^-$, $WSCl_4^-$, $ReOCl_4$
		d^2	Os(VI)	$OsNCl_4^-$
		d^4	Mn(III), Re(III)	$MnCl_5^{2-}$, Re_2Cl_8
		d^7	Co(II)	$Co(CN)_5^{3-}$
trigonal bipyramid	5	d^2	V(IV)	$VCl_3(NMe_3)_2$
		d^8	Fe(0)	$Fe(CO)_5$
octahedron	6		nearly all; rarely Pd(II), Pt(II), Au(III), Cu(I)	

* endless chain † Jahn–Teller distorted

Ref: Müller p. 81

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, ½, and g is the gyromagnetic ratio (~2.00). Substituting for s and g gives μ_S = 1.73 BM for one electron.

- BM = Bohr Magneton (SI units):

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

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

Ref: West p. 451

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:
  $S = 5 \times ½ = 5/2$ and $\mu_s = 5.92$ BM.

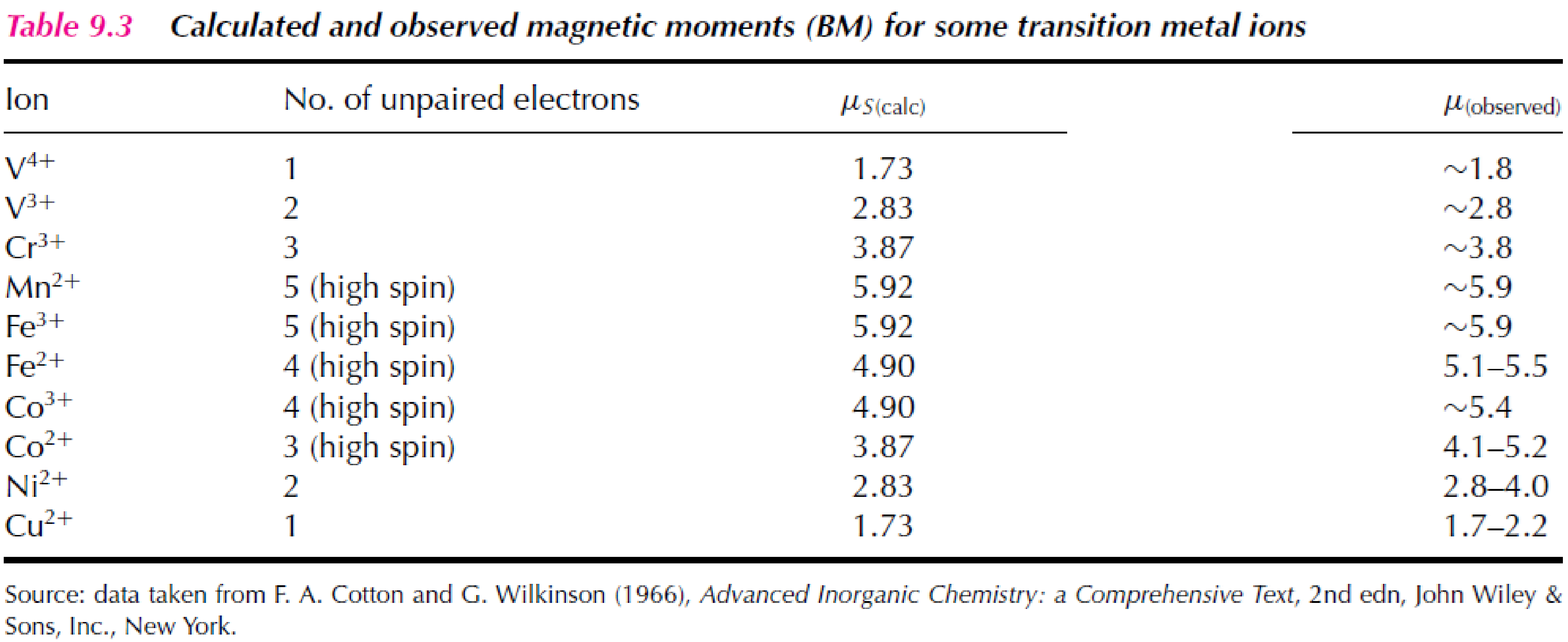


Table 9.3 ***Calculated and observed magnetic moments (BM) for some transition metal ions***

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* -> 0, *p* -> 1, *d* -> 2, *f* -> 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

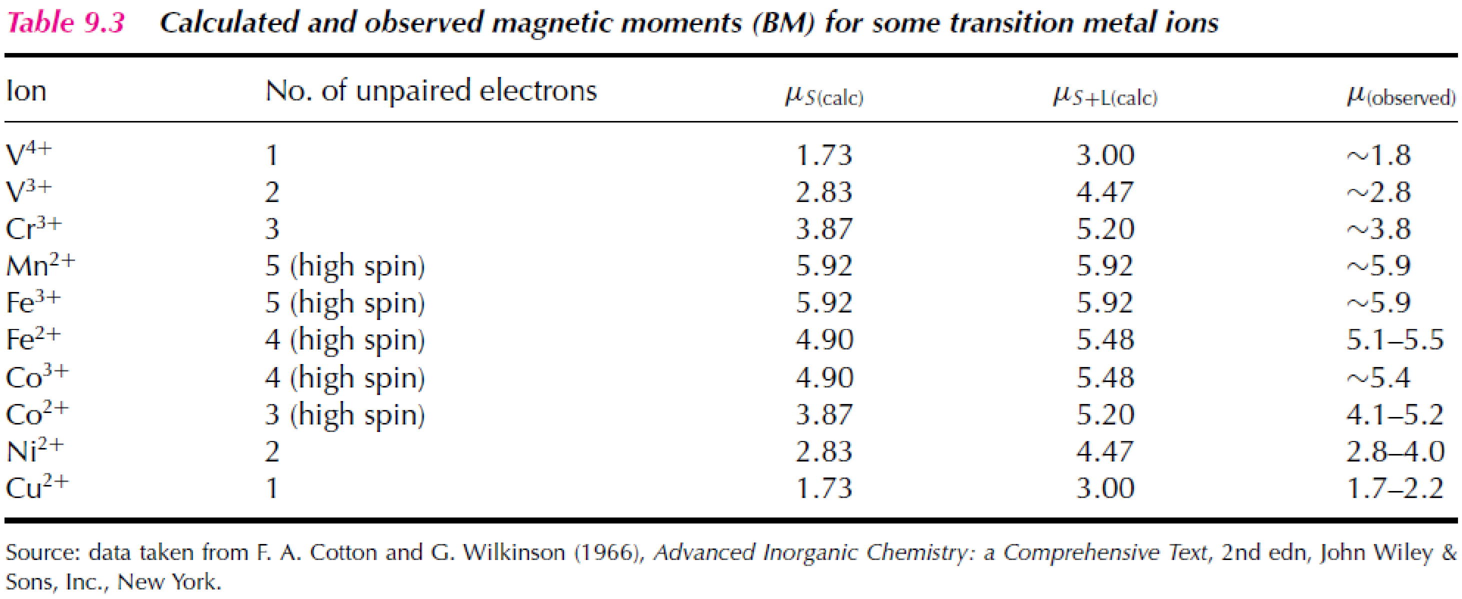


Table 9.3 *Calculated and observed magnetic moments (BM) for some transition metal ions*

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

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.