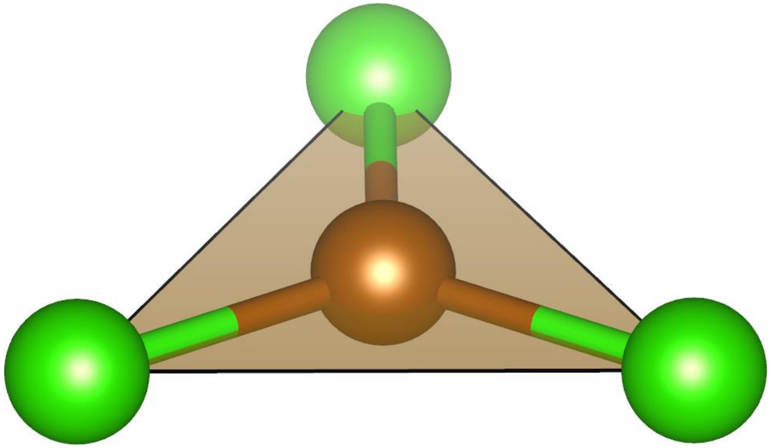
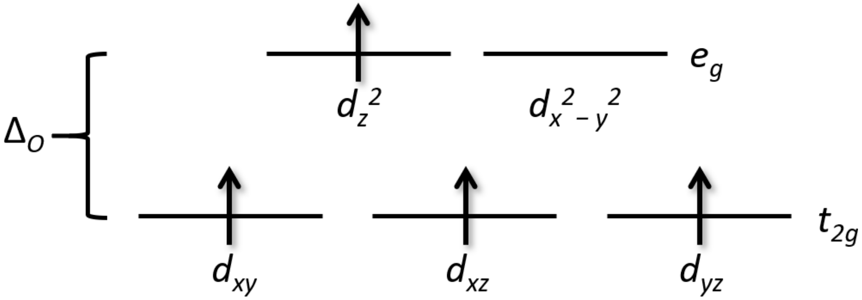
Lecture 11:

d-electrons and Ligand Field Theory

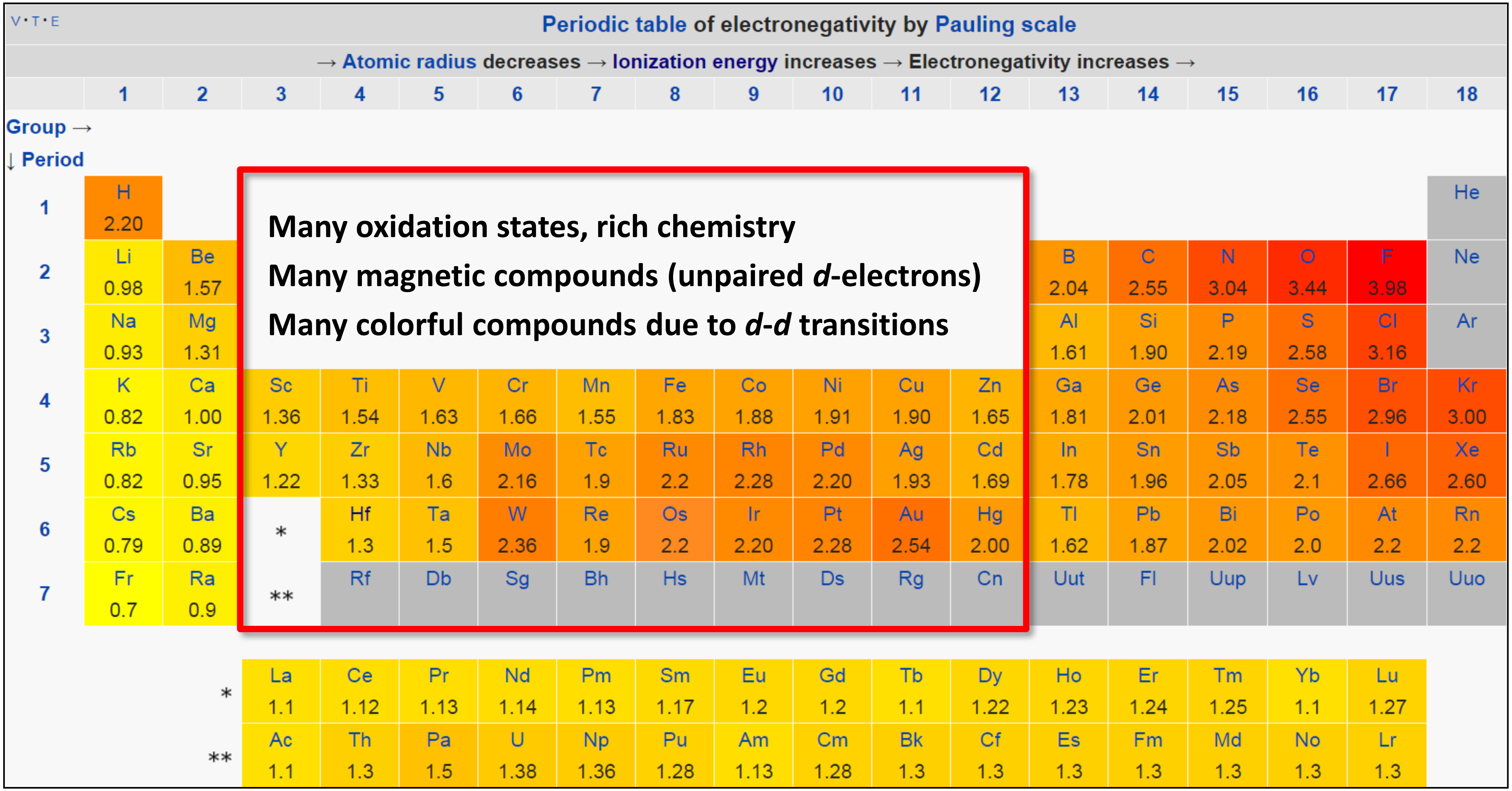
- Concept of oxidation state
- Oxidation states in *d*-block metal compounds
- Crystal field theory
- Ligand field theory
  - Jahn-Teller distortion
- Magnetic moments due to unpaired *d*-electrons





Figures: AJK

d-block metals



Many oxidation states, rich chemistry

Many magnetic compounds (unpaired *d*-electrons)

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

V·T·E

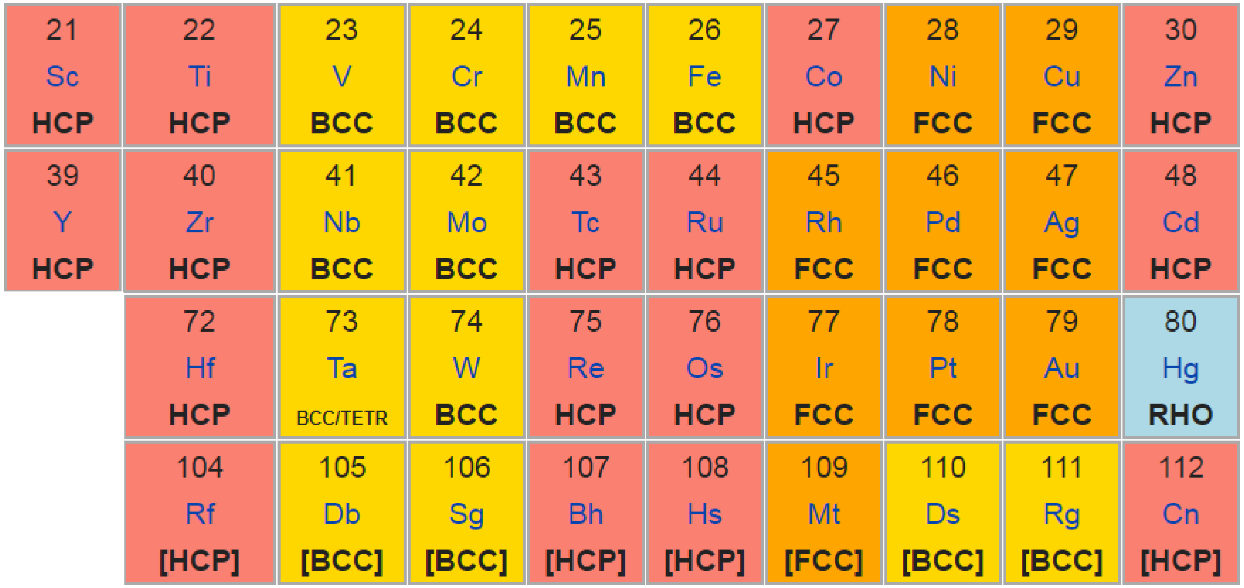
Periodic table of electronegativity by Pauling scale

→ 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	

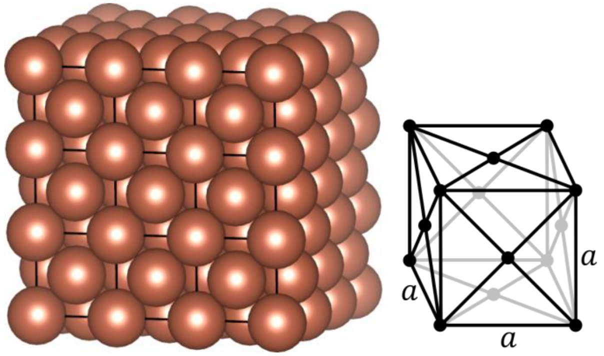
Figure: Wikipedia

Elemental *d*-block metals

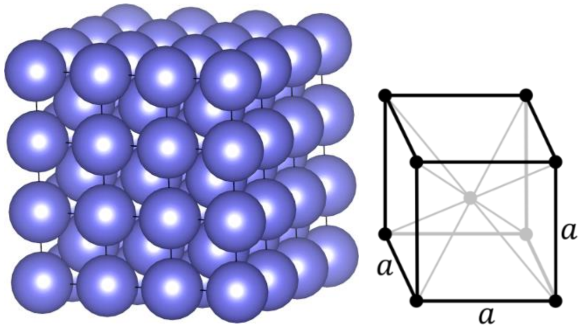


21 Sc HCP	22 Ti HCP	23 V BCC	24 Cr BCC	25 Mn BCC	26 Fe BCC	27 Co HCP	28 Ni FCC	29 Cu FCC	30 Zn HCP
39 Y HCP	40 Zr HCP	41 Nb BCC	42 Mo BCC	43 Tc HCP	44 Ru HCP	45 Rh FCC	46 Pd FCC	47 Ag FCC	48 Cd HCP
	72 Hf HCP	73 Ta BCC/TETR	74 W BCC	75 Re HCP	76 Os HCP	77 Ir FCC	78 Pt FCC	79 Au FCC	80 Hg RHO
	104 Rf [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]

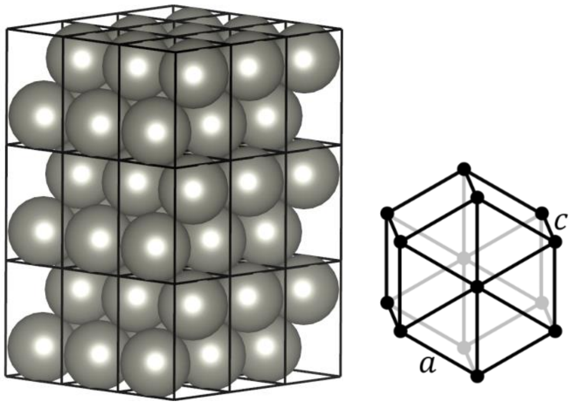
Figure: Wikipedia



Cu (fcc)



Fe (bcc)

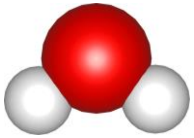


Zn (hcp)

Figures: AJK / Wikipedia

Oxidation state (1)

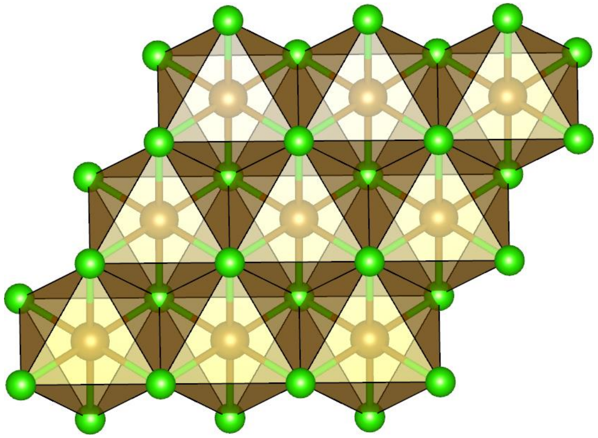
- The exact definition of an oxidation state has been debated for a very long time
- IUPAC recommendation ("Comprehensive definition of oxidation state")
  - ***The oxidation state of an atom is the <u>charge of this atom</u> after <u>ionic approximation of its heteronuclear bonds</u>***
- In other words:
  1. When a bond has two different atoms, for example O–H, all bonding electrons go to the more electronegative atom.
  2. When a bond has two similar atoms, for example F–F, all bonding electrons are divided equally between the atoms.
  3. When points (1) and (2) have been sorted out for all bonds, the number of electrons for each atom is calculated and compared to a neutral atom → oxidation state.
- In a neutral molecule, the sum of oxidation states must be zero!



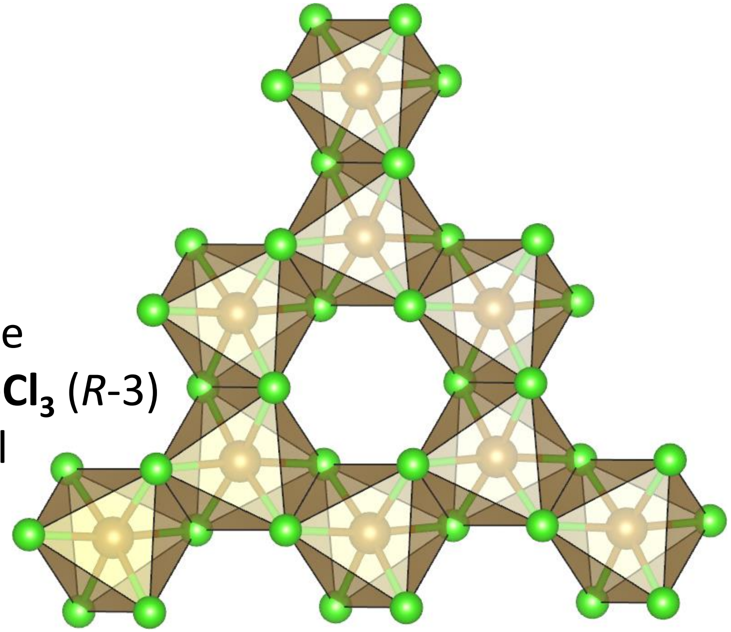
In H_2O, oxidation states are O(−II) and H(I). Oxidation states are **formal**, they do not correspond to real charges. H_2O is not $[H^+]_2[O^{2-}]$! The bonding is polar covalent.

Oxidation state (2)

- Oxidation state is a key concept for understanding the chemistry of *d*-block metals
- *d*-metals show more versatile oxidation states in comparison to main group elements.
- *d*-metals also show compounds where the same metal has different oxidation states in the compound. For example, iron(II,III) oxide Fe_3O_4 (mineral *magnetite*).
- In many cases it is crucial to know the **crystal structure** of the material to determine the oxidation states.
- Using $FeCl_2$ and $FeCl_3$ as examples (Pauling electronegativities: Fe = 1.83, Cl = 3.16):



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

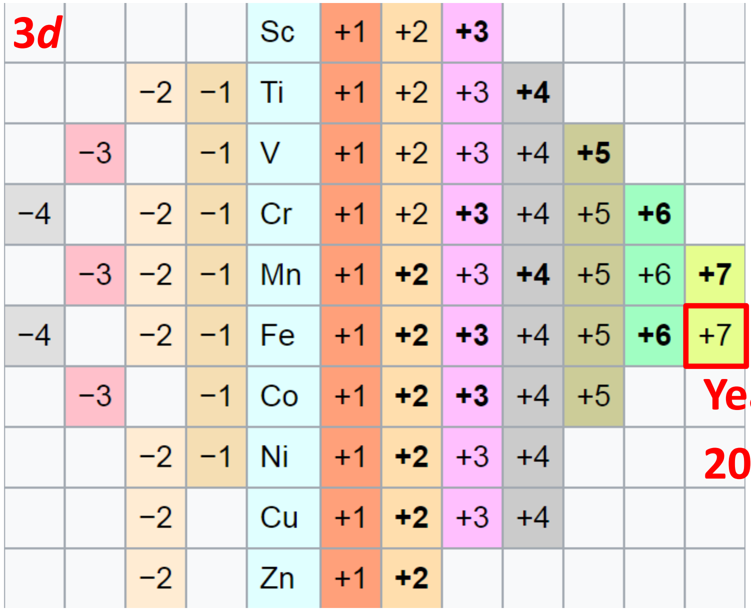


Iron(III) chloride
One layer in **$FeCl_3$** (*R*-3)
2-coordinate Cl

Fe–Cl bond orders are here less than 1.

Figures: AJK

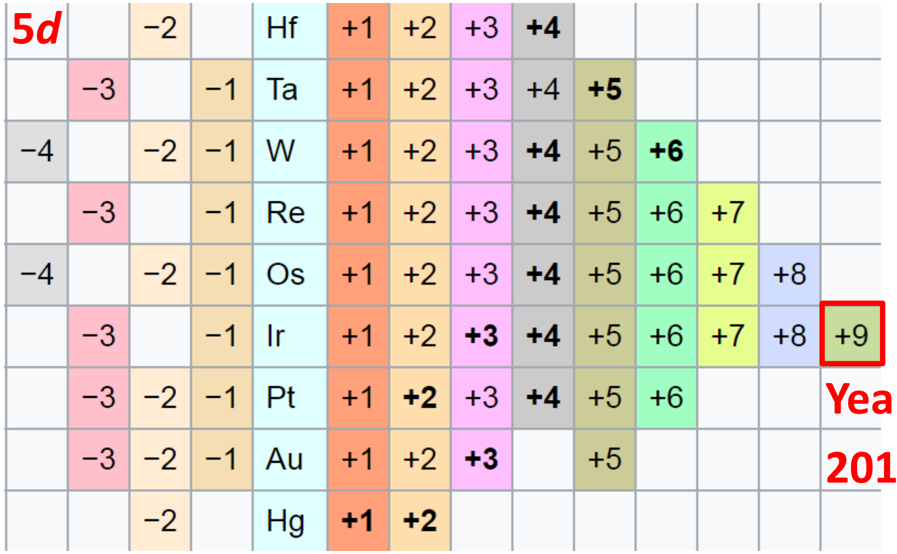
Known oxidation states for *d*-metals



3*d*				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

4*d*				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**						



5*d*		−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

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

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

LETTER

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

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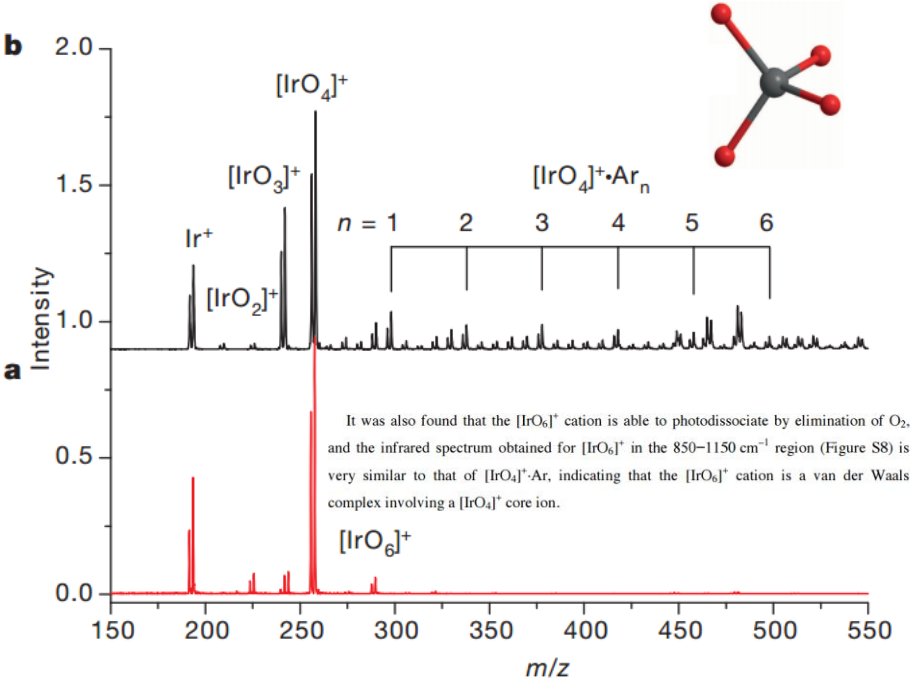
One of the most important classifications in chemistry and within the periodic table is the concept of formal oxidation states[1–4]. The preparation and characterization of compounds containing elements with unusual oxidation states is of great interest to chemists[5]. The highest experimentally known 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})

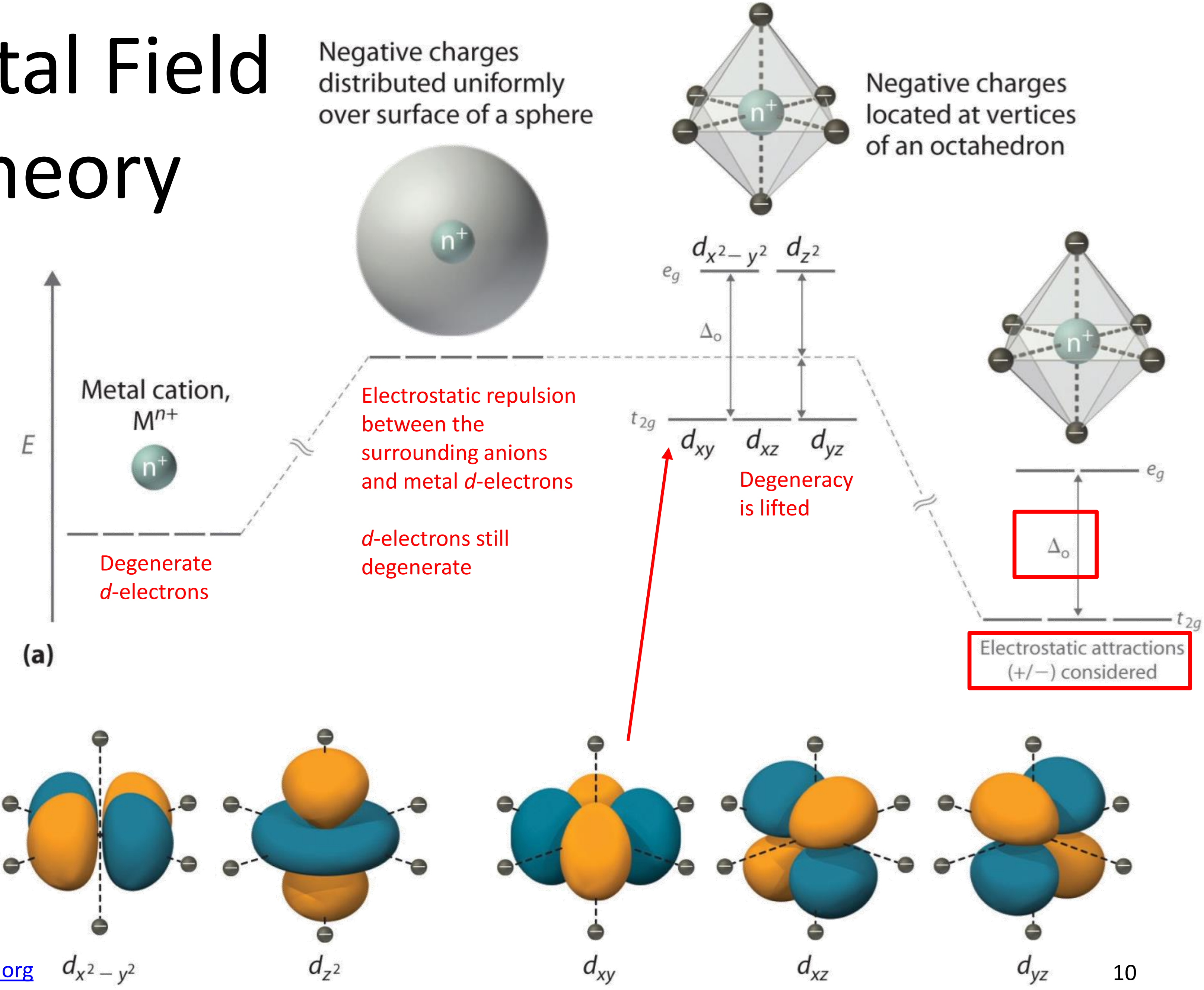
In compounds where the metal is oxidized, consider that it only has *d*-electrons left

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

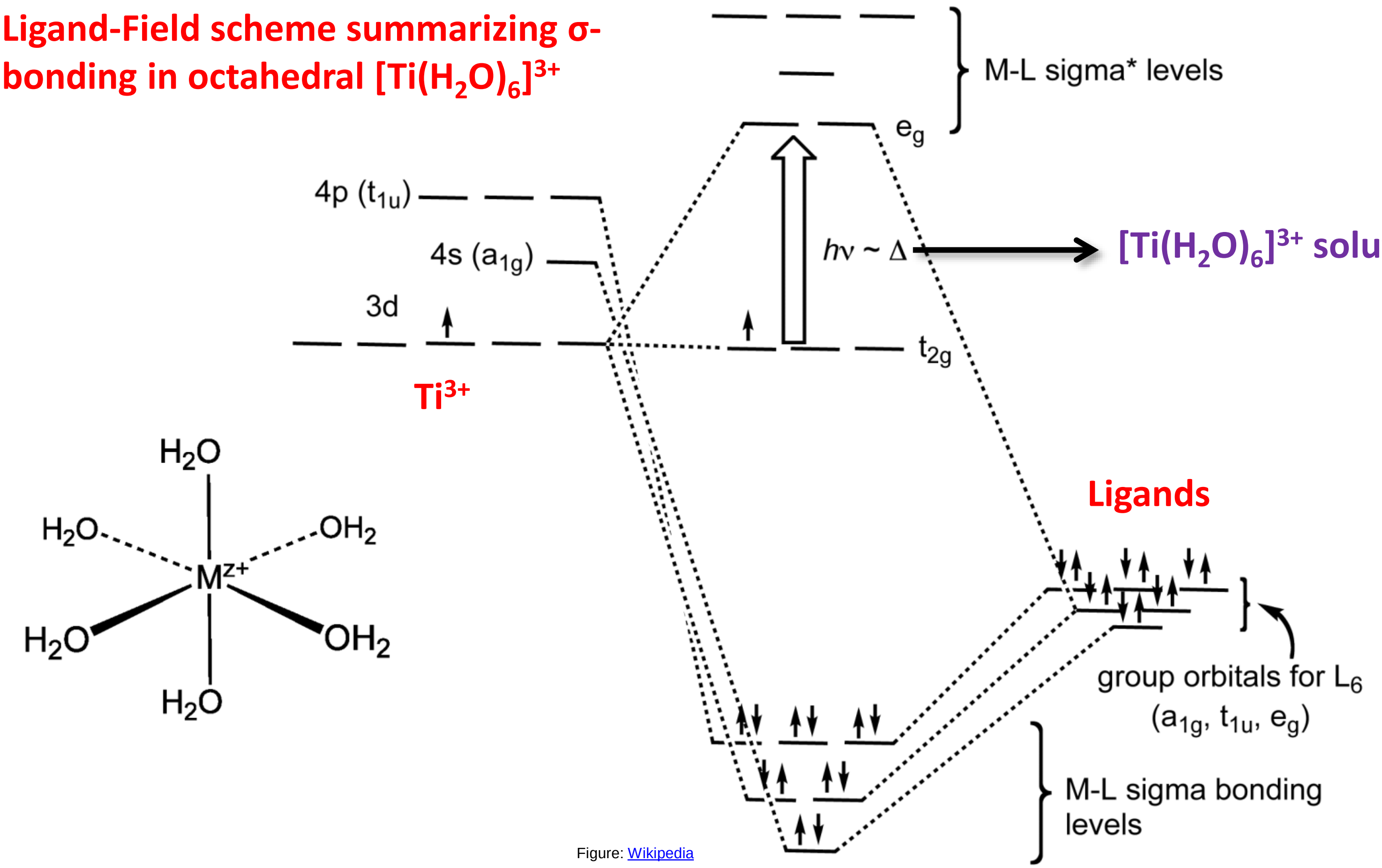
d-electrons still degenerate

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+}

Ligands

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

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*

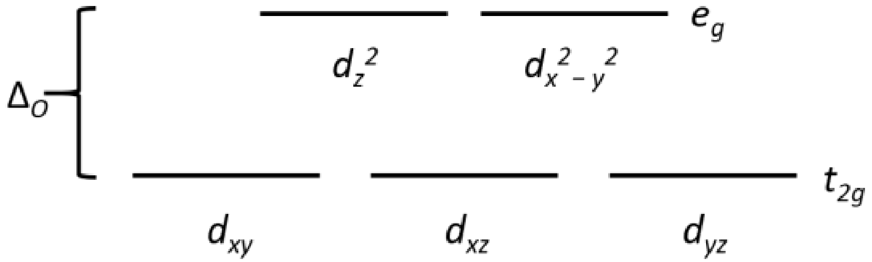
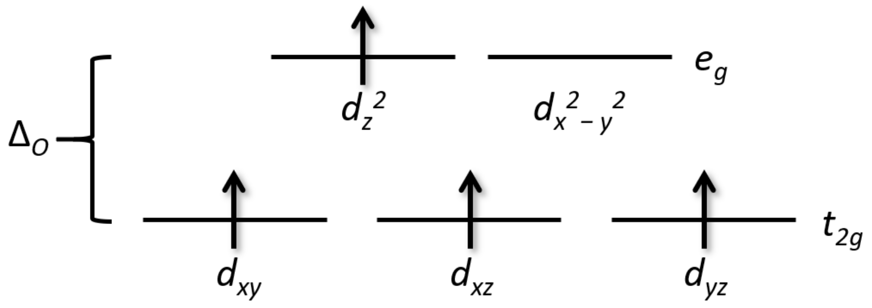


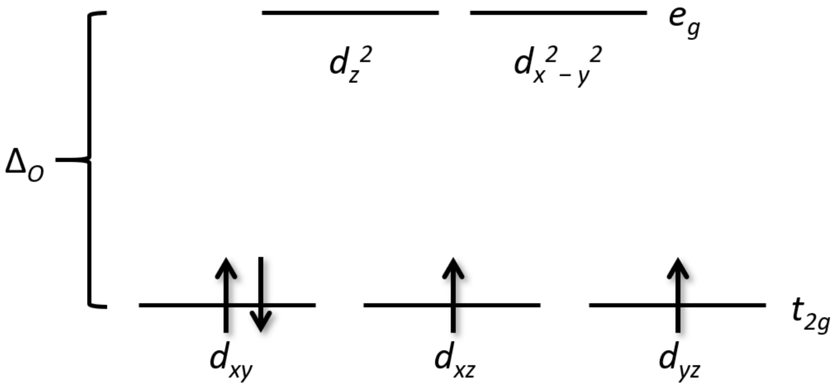
Figure: AJK

Ligand field theory (3)

- LFT can be used to explain the magnetism of *d*-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:

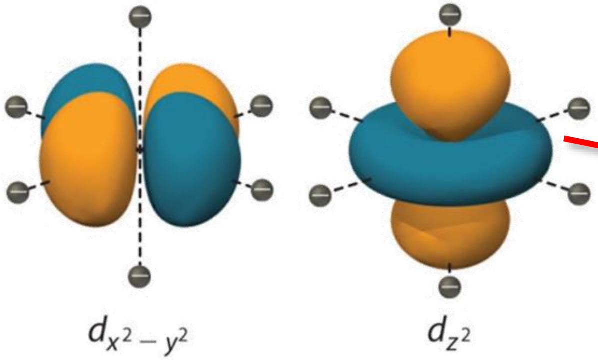


Figure: libretexts.org

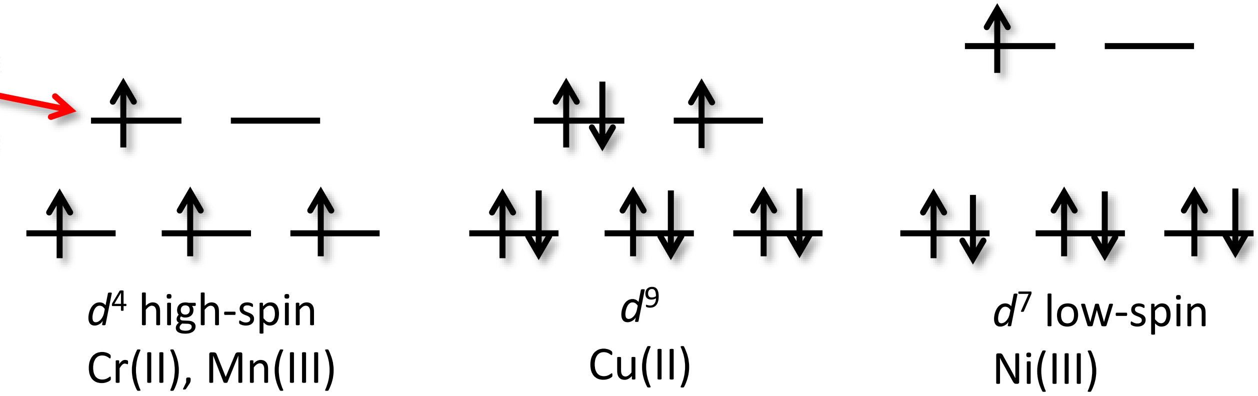


Figure: AJK

Jahn-Teller effect (2)

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

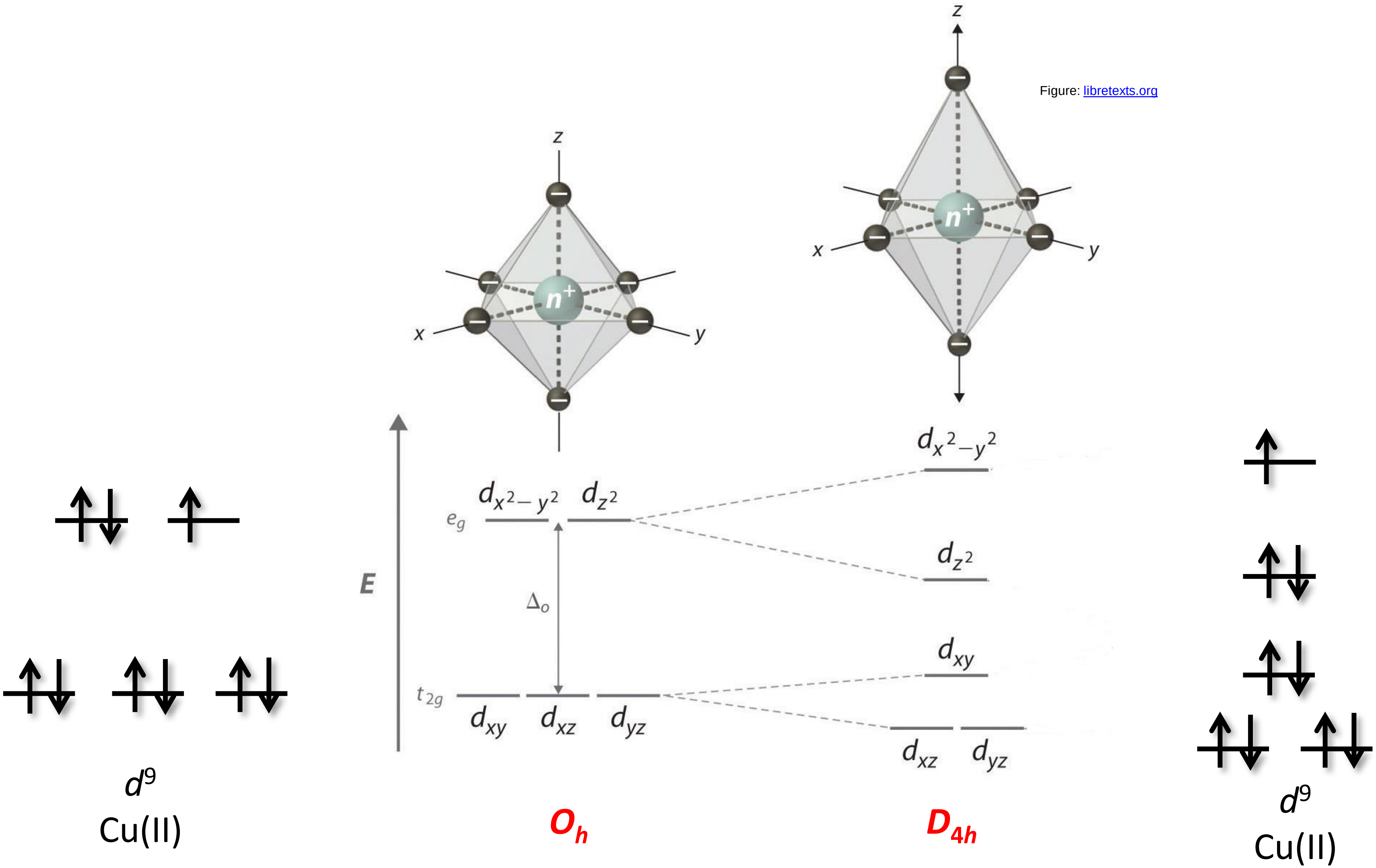
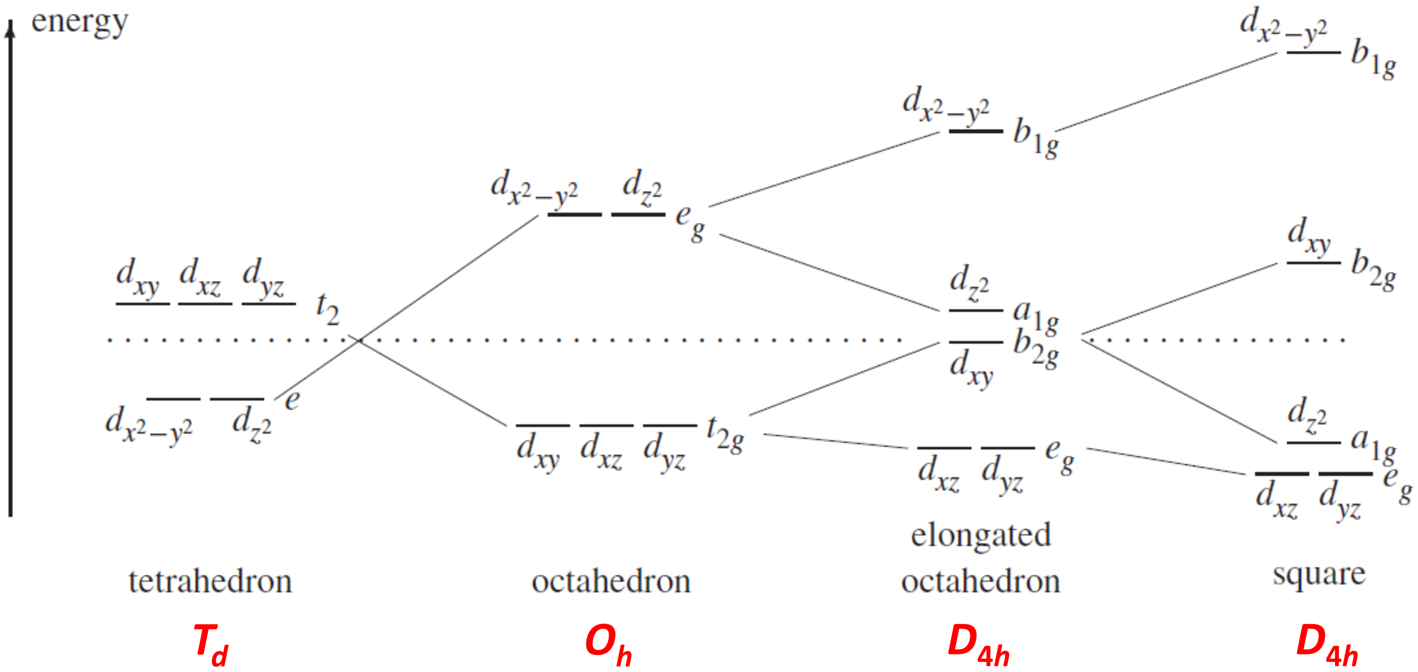


Figure: libretexts.org

Other coordination geometries

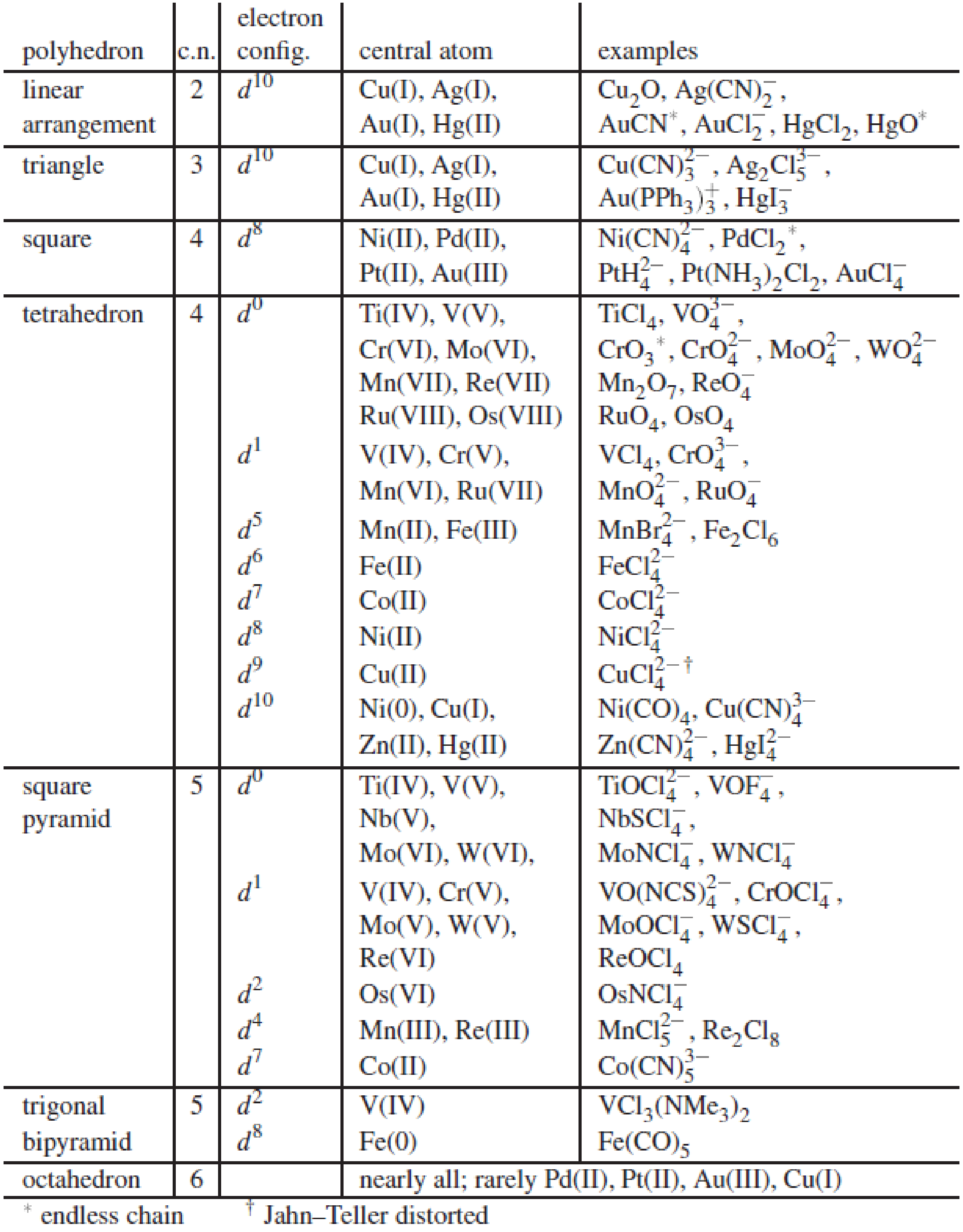
- The splitting of the *d*-orbitals is different for other coordination geometries
- The figure below shows the most typical geometries for *d*-metals



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.

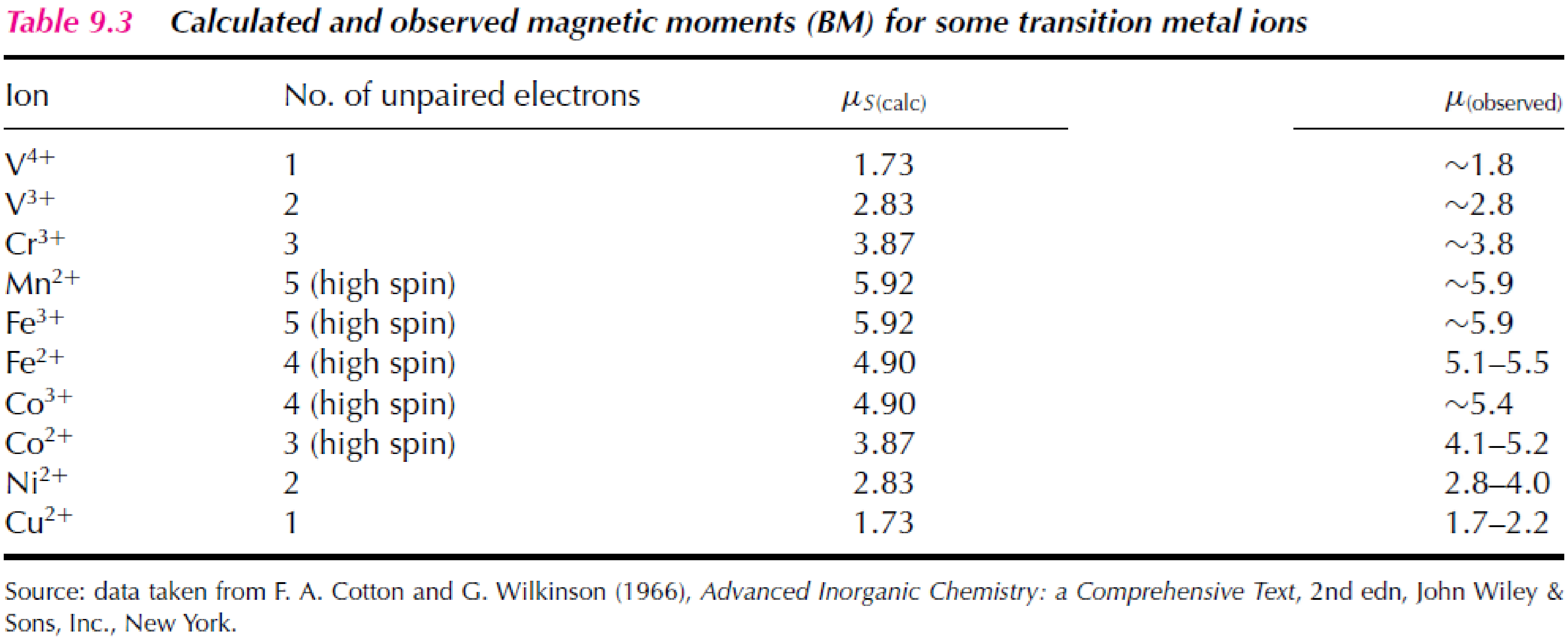


Table 9.3 ***Calculated and observed magnetic moments (BM) for some transition metal ions***

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

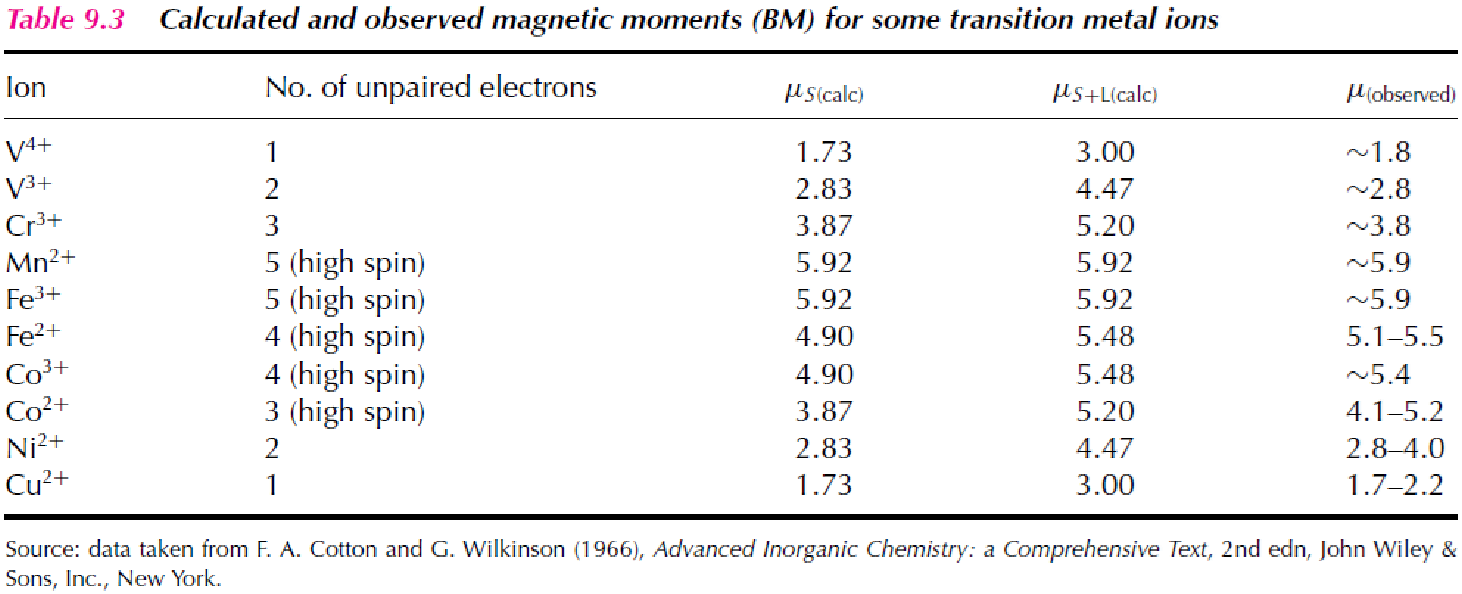


Table 9.3 *Calculated and observed magnetic moments (BM) for some transition metal ions*

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.