Inorganic Chemistry III

C4010

Prof. RNDr. Jiří Příhoda, CSc.

Prof. RNDr. Jiří Pinkas, Ph.D.

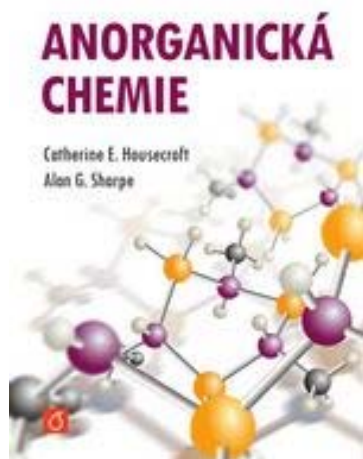# Syllabus

Část I. Prof. Příhoda

1. Koordinační chemie

2. Chelatující ligandy

3. Ionty v roztoku

4. Makroseparační metody kovů
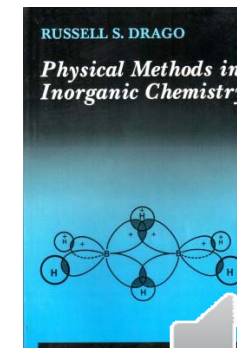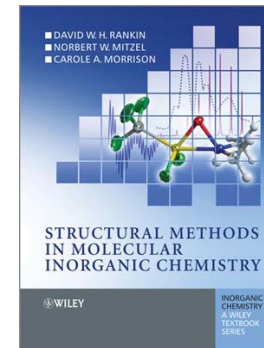
5. Transurany

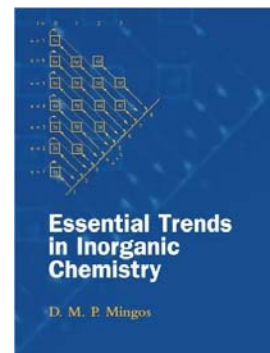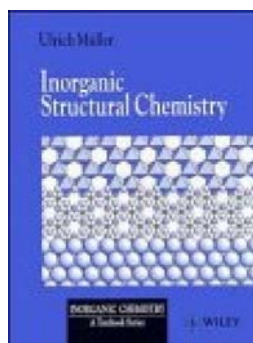***Část II. Prof. Pinkas***

6. Periodic Table

7. + 8. Chemical Bonding

9. Acid-base Chemistry

10. + 11. Rings and Polyhedra

12. Magnetochemistry

13. Moessbauer spectroscopy

Textbooks

Reading assignments = FIND ERRORS
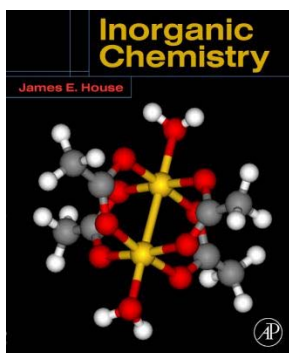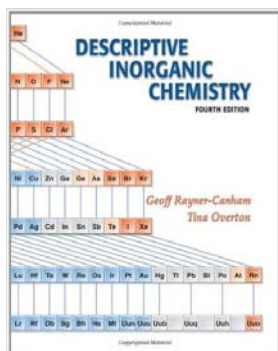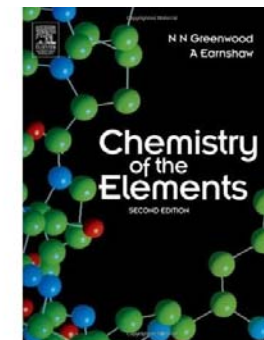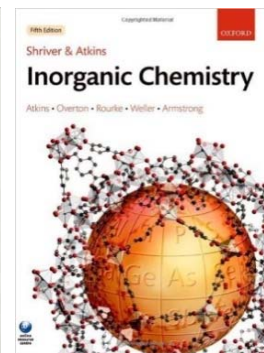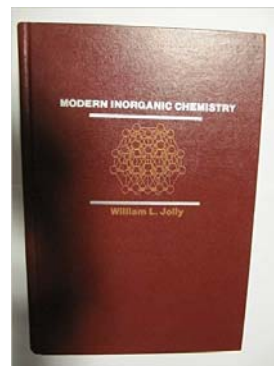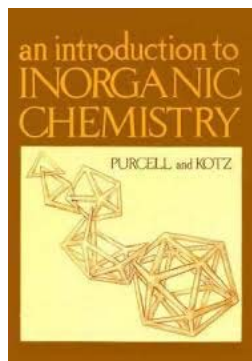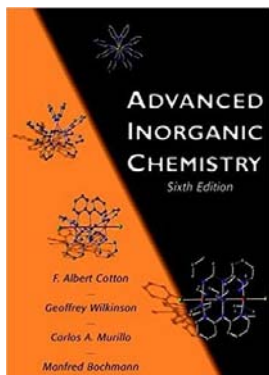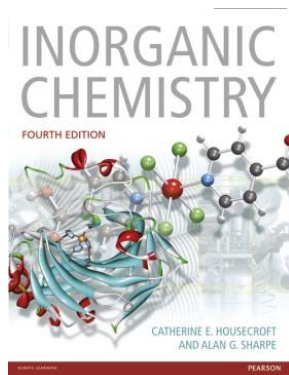
Journals

Reading assignments
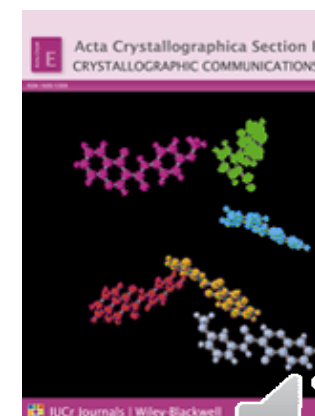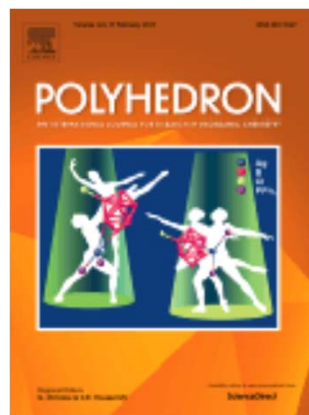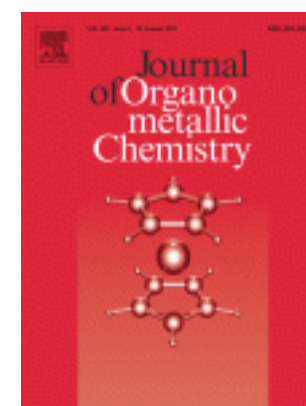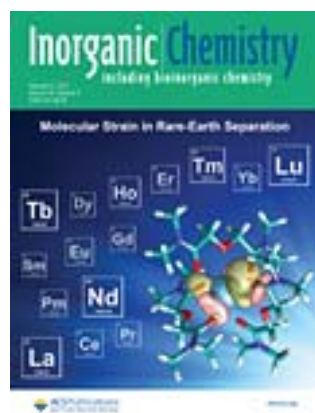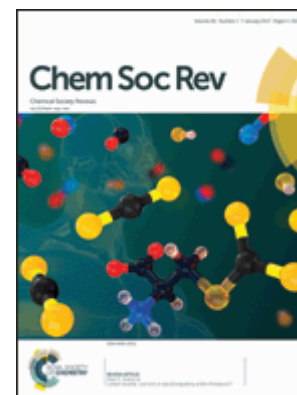
Periodic Table of the Elements

IUPAC Periodic Table of the Elements

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 28 N...
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Periodic Table of the Elements

Periodic Table of the Elements

Long form

Periodic Table of the Elements

Left-step form
Janet 1928
He – s^2 in Group 2

Periodic Table of the Elements

IUPAC 2017   **To be filled in the final exam**

Orbital Energies in Polyelectronic Atoms

Time-independent
Schroedinger equation

$$\hat{H}\,\Psi = E\,\Psi$$

Erwin Schroedinger

$$E_n = -\frac{N_A \mu e^4}{8\varepsilon_0^2 h^2}\frac{Z^2}{n^2}$$

(a) Hydrogen

(b) Multielectron atoms
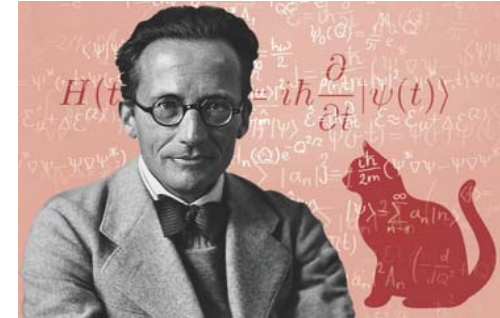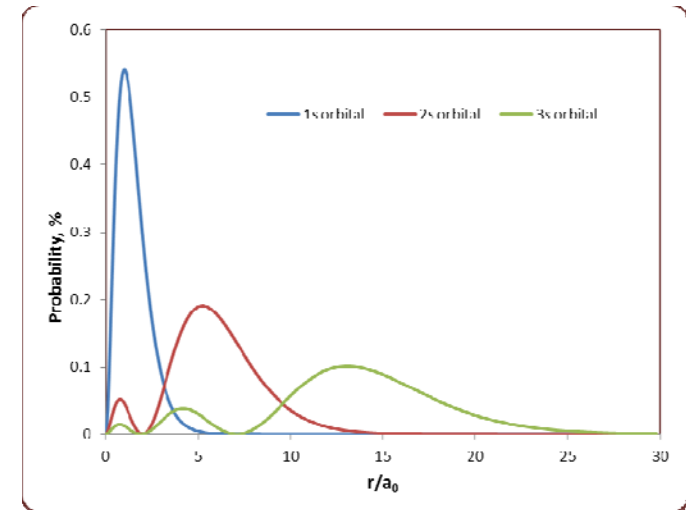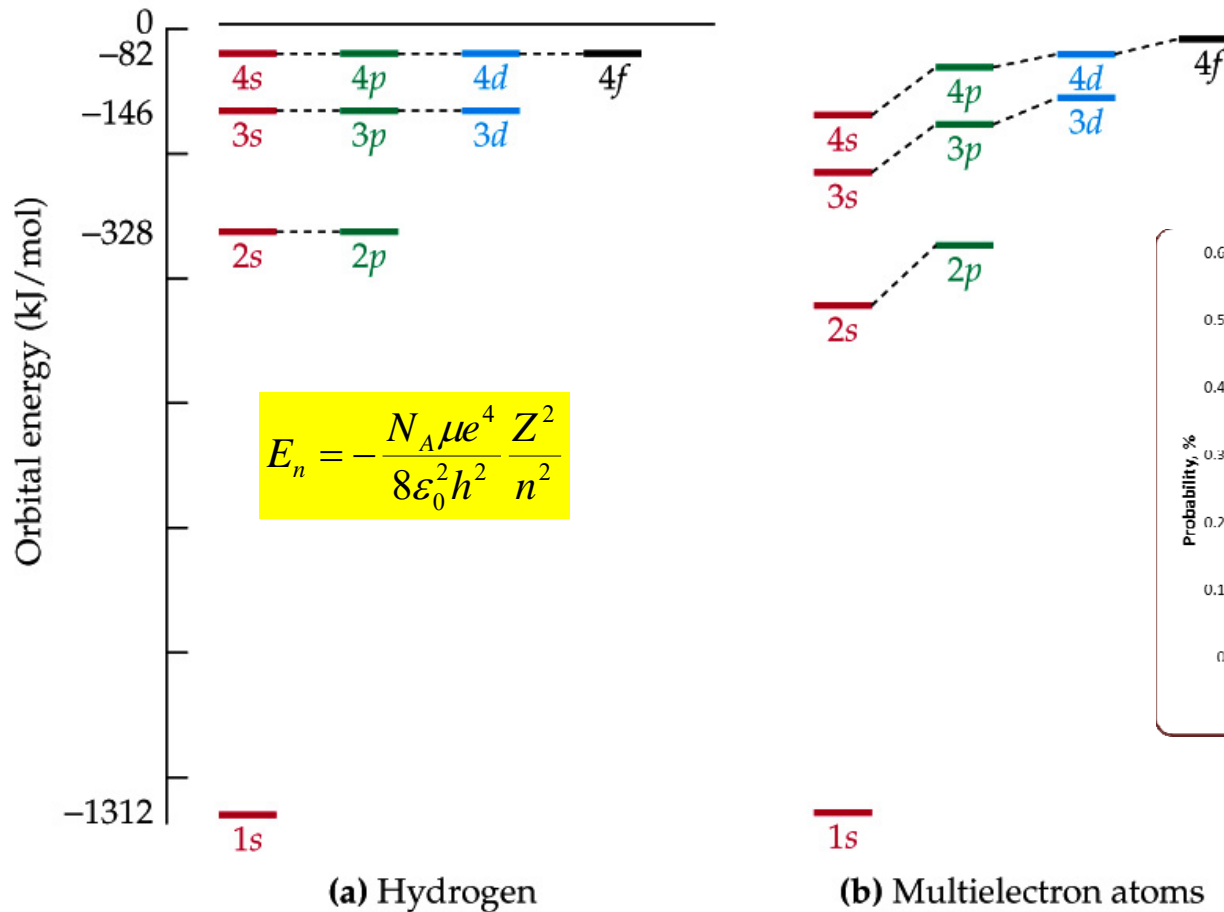
Radial Density Distribution Function

Name	Symbol	Orbital meaning	Range of values
Principal quantum number	n	energy level or shell (size)	$1 \leq n$ 1, 2, 3, 4 ...
Azimuthal quantum number	ℓ	sublevel or subshell (shape) (s = 0, p = 1, d = 2, f = 3)	Zero or integer less than n
Magnetic quantum number	m_ℓ	energy shift (orientation) (p_x, p_y or p_z)	$-\ell \leq m_\ell \leq \ell$
Spin projection quantum number	m_s	spin of the electron (-1/2 = counter-clockwise, +1/2 = clockwise)	+1/2 or -1/2

Penetration
Nuclear charge screening

$$n = 1$$
$$\ell = 0$$
$$m_\ell = 0$$
$$m_s = \pm \frac{1}{2}$$

Maximum
2
Electrons

Number of nodal surfaces = n - ℓ - 1

Radial Density Distributions

Farthest penetration extent

4s orbital   4p orbital

4d orbital   4f orbital

$a_0 r^2 R_{nl}^2(r)$ (Radial Probability Density)
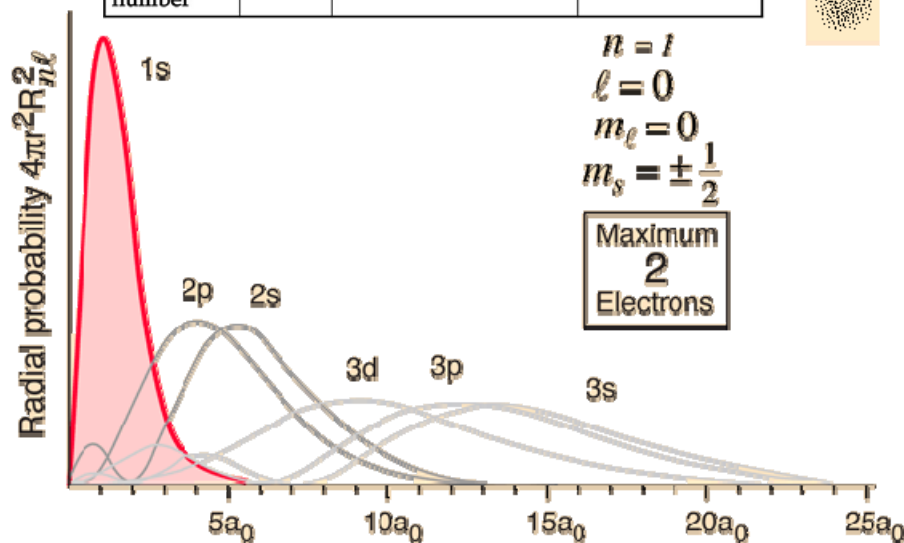
r/a$_0$ (a$_0$ in angstroms)
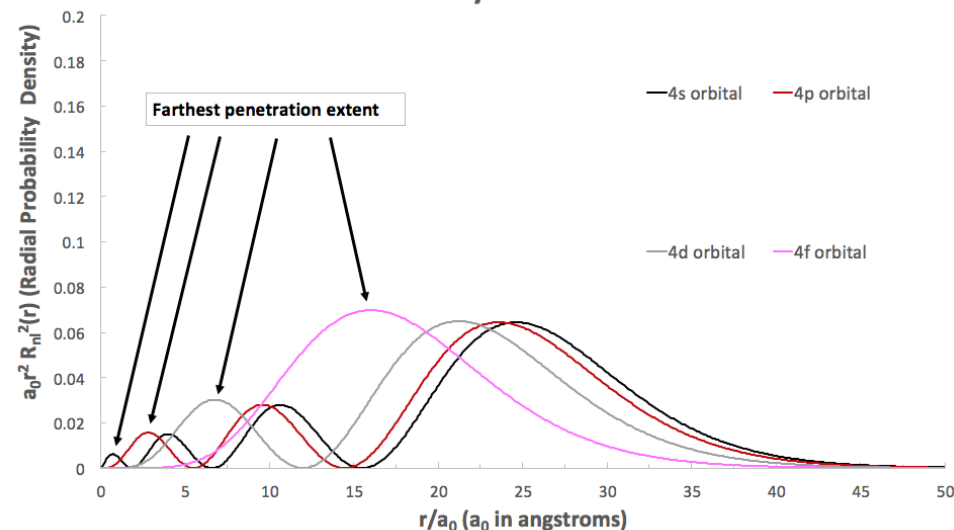
Angular Function

Name	Symbol	Orbital meaning	Range of values
Principal quantum number	n	energy level or shell (size)	$1 \leq n$ $1, 2, 3, 4 \ldots$
Azimuthal quantum number	ℓ	sublevel or subshell (shape) (s = 0, p =1, d = 2, f = 3)	Zero or integer less than n
Magnetic quantum number	m_ℓ	energy shift (orientation) (p_x, p_y or p_z)	$-\ell \leq m_\ell \leq \ell$
Spin projection quantum number	m_s	spin of the electron (-1/2 = counter-clockwise, +1/2 = clockwise)	+1/2 or −1/2

Aufbau Principle

The order of orbital filling – not the order of atomic energies
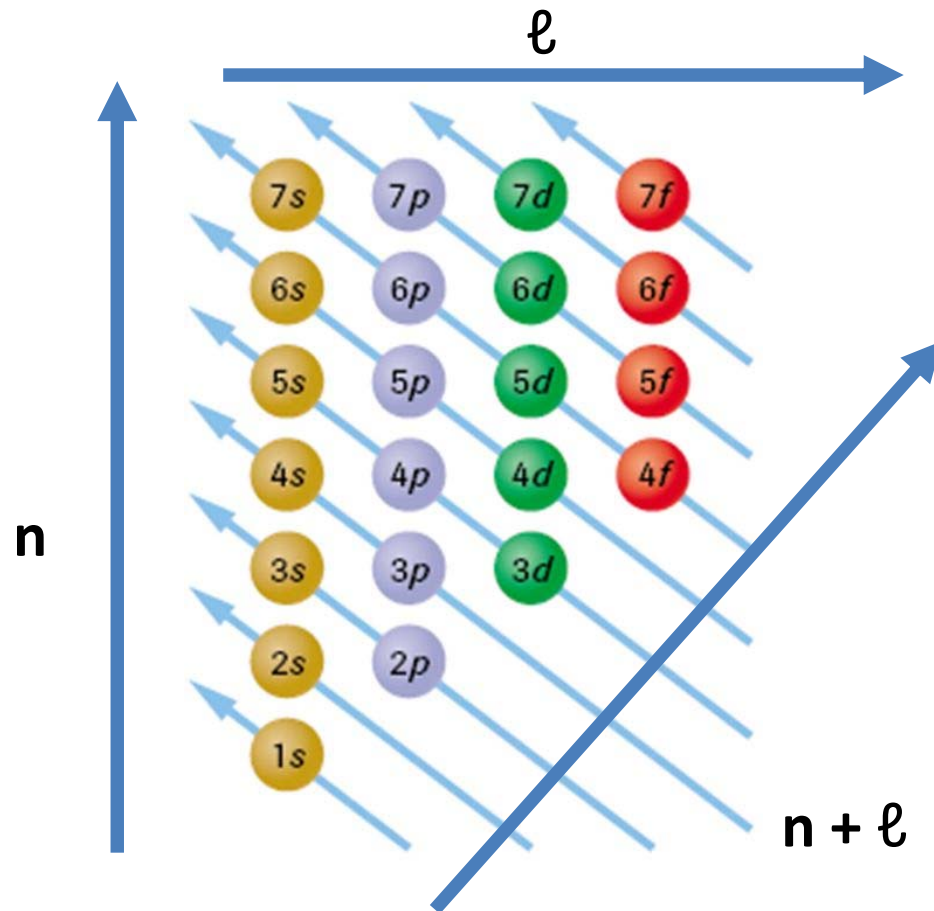
The Madelung rule:

Electrons (**e**) fill orbitals starting at the lowest available energy state before filling higher states

The higher the total number of nodes in the atomic orbital, n + ℓ, the higher is its energy

If n + ℓ is the same, then lower n

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Atomic Term Symbols

Electronic state of an atom/ion depends on its incompletely filled sub shells = valence shell

Electrons in the inner closed shells – rare gas core – distribute themselves in a symmetric manner canceling out each other's momenta

Russell-Saunders / L-S Term Symbol
Up to first transition row (s-s > o-o > s-o)

$$^{2S+1}L_J$$

Orbit-Orbit coupling - The Total Orbital Angular Momentum Quantum Number L
Vector sum of the l_i values of the individual electrons
$L = \Sigma \, l_i$ $\qquad L = |l_1 + l_2|, \, |l_1 + l_2 - 1|,...,|l_1 - l_2|$
$|L| = 0, 1, 2, 3, 4... = $ S, P, D, F, G, ...

Spin-Spin coupling - The Total Spin Quantum Number S
$S = |s_1 + s_2|, \, |s_1 + s_2 - 1|,...,|s_1 - s_2|$
Multiplicity M = 2S + 1

Spin-Orbit coupling - The Total Angular Momentum Quantum Number J
$J = L + S$ $\qquad J = |L + S|, \, |L + S - 1|,...,|L - S|$

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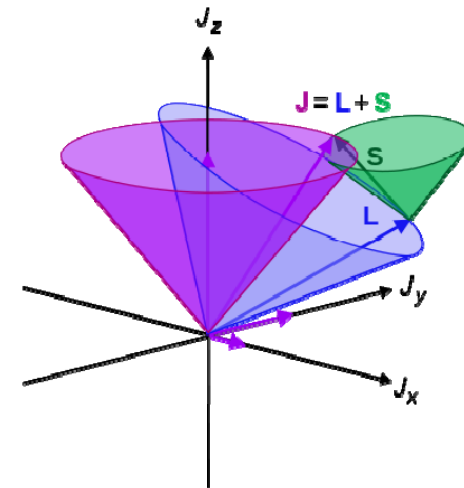
Hund's Rules

The ground state energy of a many-electron system depends on the total orbital angular momentum and total spin angular momentum of the state

Hund's First Rule (Maximize Spin Multiplicity)

State with **the largest value of S is most stable** and stability decreases with decreasing S = electrons always enter an empty orbital before they pair up (Energy ^{1}P > ^{3}P)

The e in singly occupied orbitals are less effectively screened or shielded from the nucleus = more tightly bound

A Coulomb repulsion between two e in the same orbital = a spin pairing energy

Hund's Second Rule (Maximize Orbital Angular Multiplicity)

For states with same values of S, the state with **the largest value of L is the most stable** (Energy ^{1}D < ^{1}S)

The total (scalar) angular momentum, the *relative* momentum vectors of the various e

Hund's Third Rule (Minimize less than ½ filled or maximize greater than ½ filled shells)

If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is the most stable

Hund's Rules and Exchange Energy
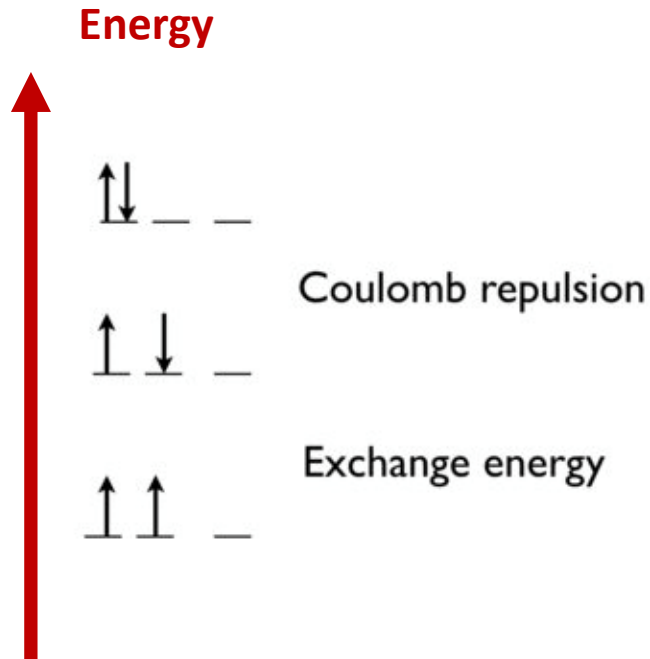
Energy

Hund's first rule: a set of degenerate orbitals are singly occupied first – a Coulomb repulsion

Hund's second rule: the lowest energy state has parallel spins to maximize the exchange energy - a quantum mechanical effect

The exchange energy (favorable) increases with the number of possible exchanges between electrons with the same spin and energy

Pairing energy = Coulomb (destabilizing) + Exchange (stabilizing)

Exchange Energy

Exchange energy (**K**) = the energy released when two or more e with **the same spin** exchange their positions in **the degenerate orbitals** of a subshell

The result of spin correlation = e do not move independently

A pair of e with parallel spins ↑↑ has less repulsion than a pair with anti-parallel spins ↑↓

↑↓ may occupy smaller volume than ↑↑ $\Rightarrow$ ↑↓ experience more repulsion than ↑↑

Exchange energy **decreases** orbital energy - lower orbital energy = the orbital is closer to nucleus - electrons are more tightly bound which gives extra stability of electrons of valence shell

Relative exchange energy = number of pairs with parallel spins × K

3 K

1 K

Exchange Energy

Calculate exchange energies for configurations p^1 to p^6

Calculate exchange energies for configurations
d^1 to d^{10}
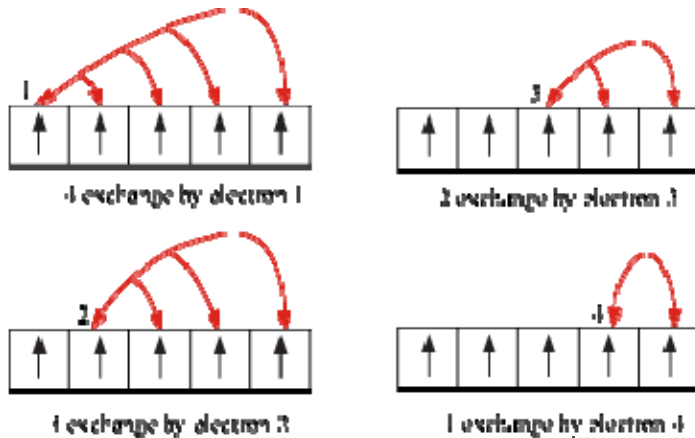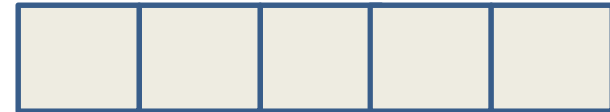
exchange energy for d^5 = 10 K

For every pair of electrons with parallel spins, there is a corresponding exchange
energy K that reduces the value of the orbital energy

Which configuration is the most stable Cr (Ar) $3d^4 4s^2$ or $3d^5 4s^1$

Orbital Energies
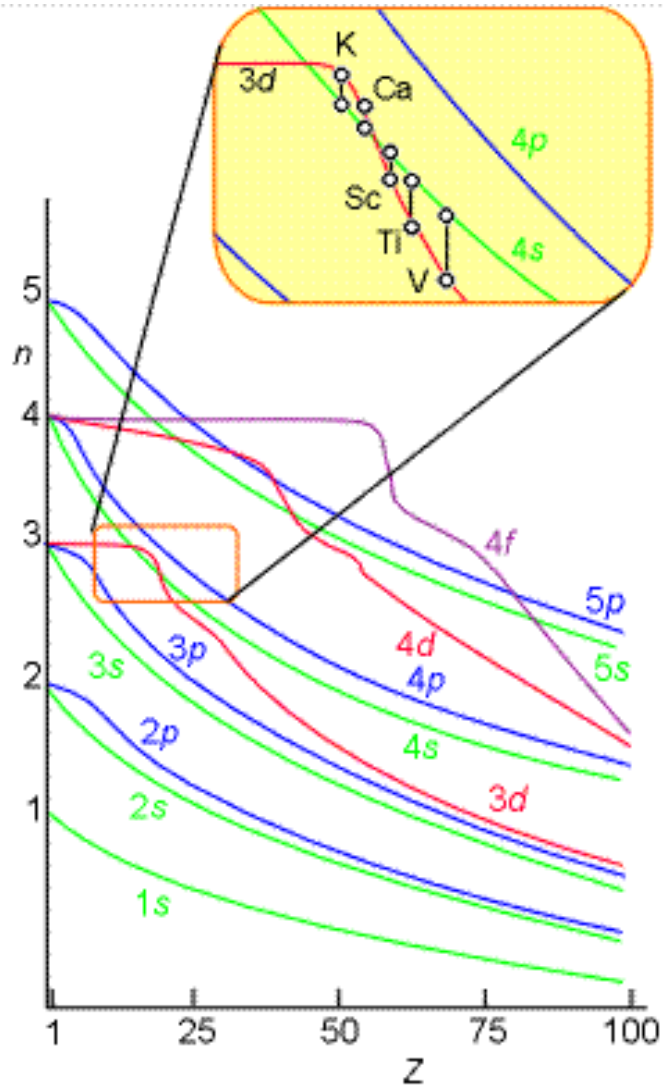
Cu Ag, Au
Cr, Mo, W
Ru, Rh, Pd
Nb
La, Ce, Pr, Gd
Cm, Th, Pa, Np

Ni [Ar] $3d^9 4s^1$ ($4p^0$)   free atom in vacuum

Ni [Ar] $3d^8 4s^2$ ($4p^0$) very close in energy

Ni [Ar] $3d^{10}$ ($4s^0 4p^0$) in molecules, $Ni(CO)_4$

Lanthanides

Xe	[Kr] $4d^{10}$ $5s^2$ $5p^6$	Xenon core
Cs	[Xe] $6s^1$ $4f^0$ $5d^0$	$E(4f) > E(6s)$
Ba	[Xe] $6s^2$ $4f^0$ $5d^0$	
La	[Xe] $4f^0$ $5d^1$ $6s^2$	transition metal
Ce	[Xe] $4f^1$ $5d^1$ $6s^2$	$E(4f) < E(6s), E(5d)$
Pr	[Xe] $4f^3$ $5d^0$ $6s^2$	
Eu	[Xe] $4f^7$ $5d^0$ $6s^2$	4f half-filled
Gd	[Xe] $4f^8$ $5s^2$ $5p^6$ $5d^0$ $6s^2$	
Gd	[Xe] $4f^7$ $5s^2$ $5p^6$ $5d^1$ $6s^2$	4f half-filled
Tm	[Xe] $4f^{13}$ $5d^0$ $6s^2$	
Yb	[Xe] $4f^{14}$ $5d^0$ $6s^2$	
Lu	[Xe] $4f^{14}$ $5d^1$ $6s^2$	4f full

Lanthanides

Pr   [Xe] 4f^3 5s^2 5p^6 5d^0 6s^2
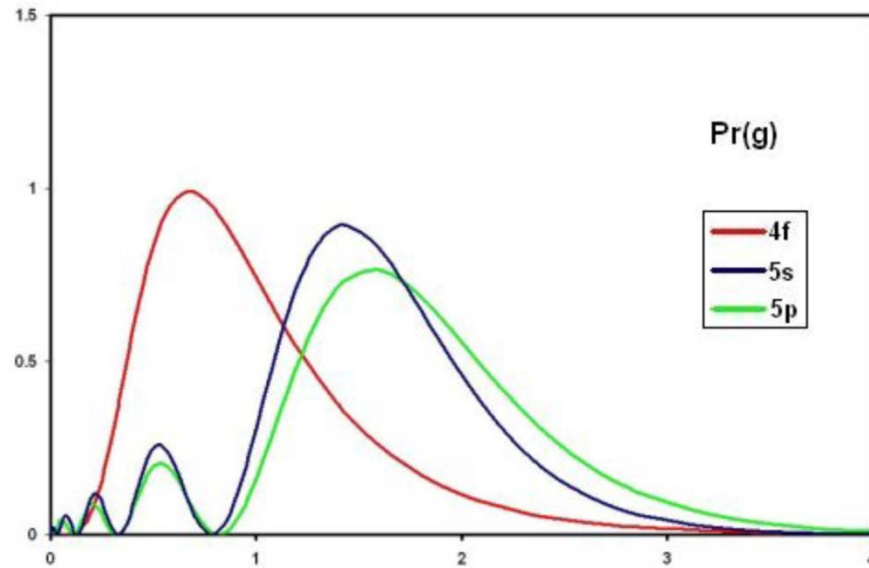
- The 4f electron is most likely to be found at a distance that lies inside the highest peaks in the 5s and 5p distributions = inside the xenon core
- The 4f electron spends most of its time closer to the nucleus than either a 5s or 5p electron
- The 4f electrons are inner electrons and lie inside the noble gas core

Lanthanides

Pr $\qquad$ [Xe] $4f^3$ $5s^2$ $5p^6$ $5d^0$ $6s^2$

Why Pr^{3+} ? $\qquad$ [Xe] $4f^2$ $5s^2$ $5p^6$ $5d^0$ $6s^0$

- The inner 4f electron is easier to remove than the outer 5s and 5p electrons of the xenon core
- The 4f distribution contains one maximum, the 5s four and 5p three smaller maxima
- The 5s and 5p electrons penetrate deeply into the core and spend more time very close to the nucleus - experience very large values of Z at very small distances r
- The energies of the 5s and 5p electrons are more negative than 4f

Pr $\qquad$ [Xe] $5s^2$ $5p^6$ $4f^3$ $5d^0$ $6s^2$
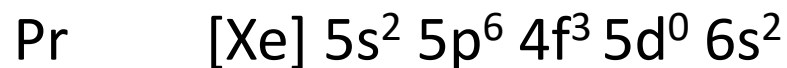
Ionization Energies
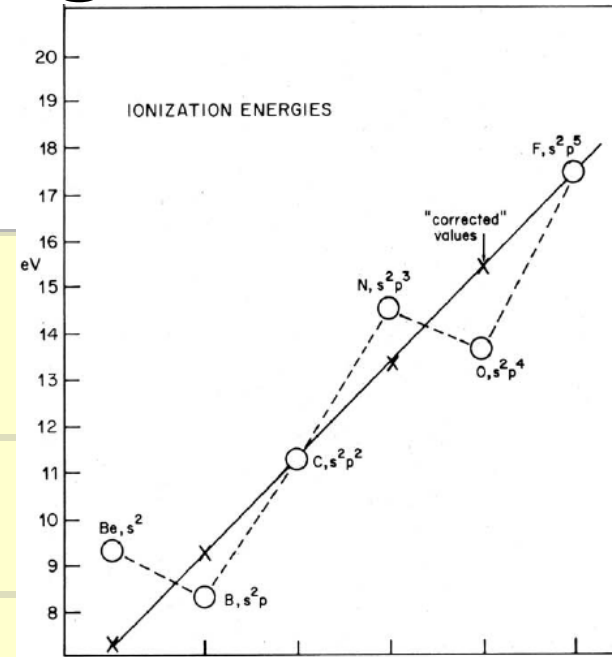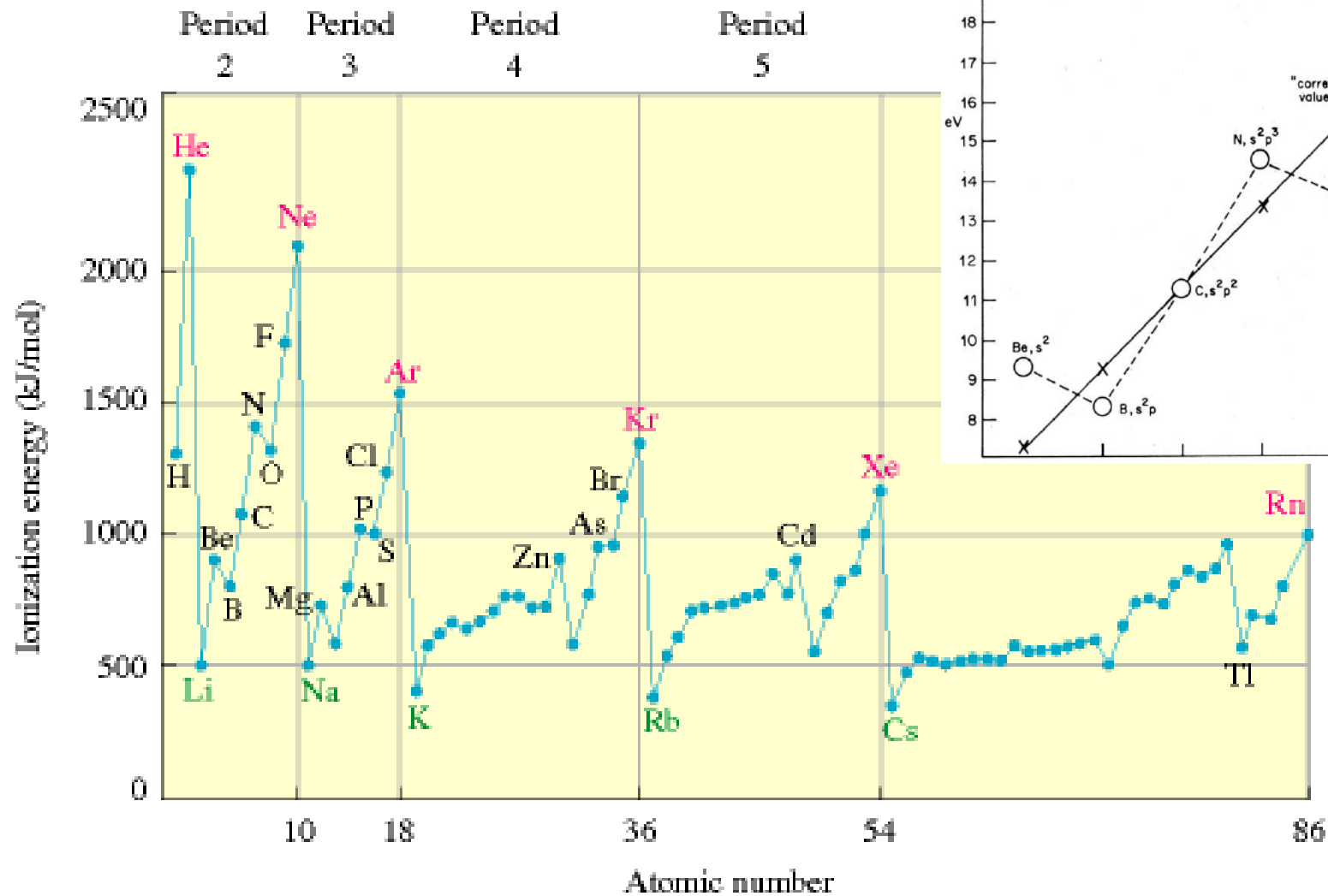
Electron Affinities

Atomic Volumes

1869

Julius Lothar Meyer
1830 - 1895

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Atomic Radii

Atomic Radii

Atomic Radii:

Note: no significant increase from 2nd to 3rd row of d-block

Lanthanide Contraction- a result of poor shielding properties of electrons in f-orbitals and subsequent failure to compensate for increasing nuclear charge.

Metallic Radii CN = 12

r, pm

Sc 162
Ti 147
V 134
Cr 128
Mn 127
Fe 126
Co 125
Ni 124
Cu 128
Zn 134
Ga

K C Y 180
Zr 160
Nb 146
Mo 139
Tc 136
Ru 134
Rh 134
Pd 137
Ag 144
Cd 151
In

Rb S La 187
Hf 159
Ta 146
W 139
Re 137
Os 135
Ir 136
Pt 138
Au 144
Hg 151
Tl

Cs Ba

Metallic radii for 12

Atomic radius, pm / Increasing atomic number →
La, Y, Sc, Zr, Hf, Ti, Nb, Ta, V, Cr, Mn, Fe, Co, Ni, Mo, Tc, W, Re, Os, Ru, Rh, Ir, Pt, Pd, Au, Ag, Hg, Cd, Cu, Zn

Radius vs. CN:
CN = 12   Rel. R = 1.00
CN = 8   Rel. R = 0.97
CN = 6   Rel. R = 0.96
CN = 4   Rel. R = 0.88

Solid solutions: a linear relationship = Vegard law

Li	Be												
1.57	1.12												
Na	Mg	Al											
1.91	1.60	1.43											
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
2.35	1.97	1.64	1.47	1.35	1.29	1.37	1.26	1.25	1.25	1.28	1.37	1.53	1.39
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
2.50	2.15	1.82	1.60	1.47	1.40	1.35	1.34	1.34	1.37	1.44	1.52	1.67	1.58	1.61
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
2.72	2.24	1.88	1.59	1.47	1.41	1.37	1.35	1.36	1.39	1.44	1.55	1.71	1.75	1.82

4f elements: Ce (1·82)–Lu (1·72) but Eu, 2·06, Yb, 1·94

5f elements: Th   Pa   U   Np   Pu   Am   Cm
                 1.80 1.63 1.56 1.56 1.64 See Table 29.4

Ionic Radii

r, Å

Li⁺ Li	Be²⁺ Be	B³⁺ B	O O²⁻	F F⁻
0.68 1.52	0.31 1.13	0.23 0.88	0.73 1.40	0.71 1.33
Na⁺ Na	Mg²⁺ Mg	Al³⁺ Al	S S²⁻	Cl Cl⁻
0.97 1.86	0.66 1.60	0.51 1.43	1.04 1.84	0.99 1.81
K⁺ K	Ca²⁺ Ca	Ga³⁺ Ga	Se Se²⁻	Br Br⁻
1.33 2.27	0.99 1.97	0.62 1.22	1.17 1.98	1.14 1.96
Rb⁺ Rb	Sr²⁺ Sr	In³⁺ In	Te Te²⁻	I I⁻
1.47 2.47	1.13 2.15	0.81 1.63	1.43 2.21	1.33 2.20
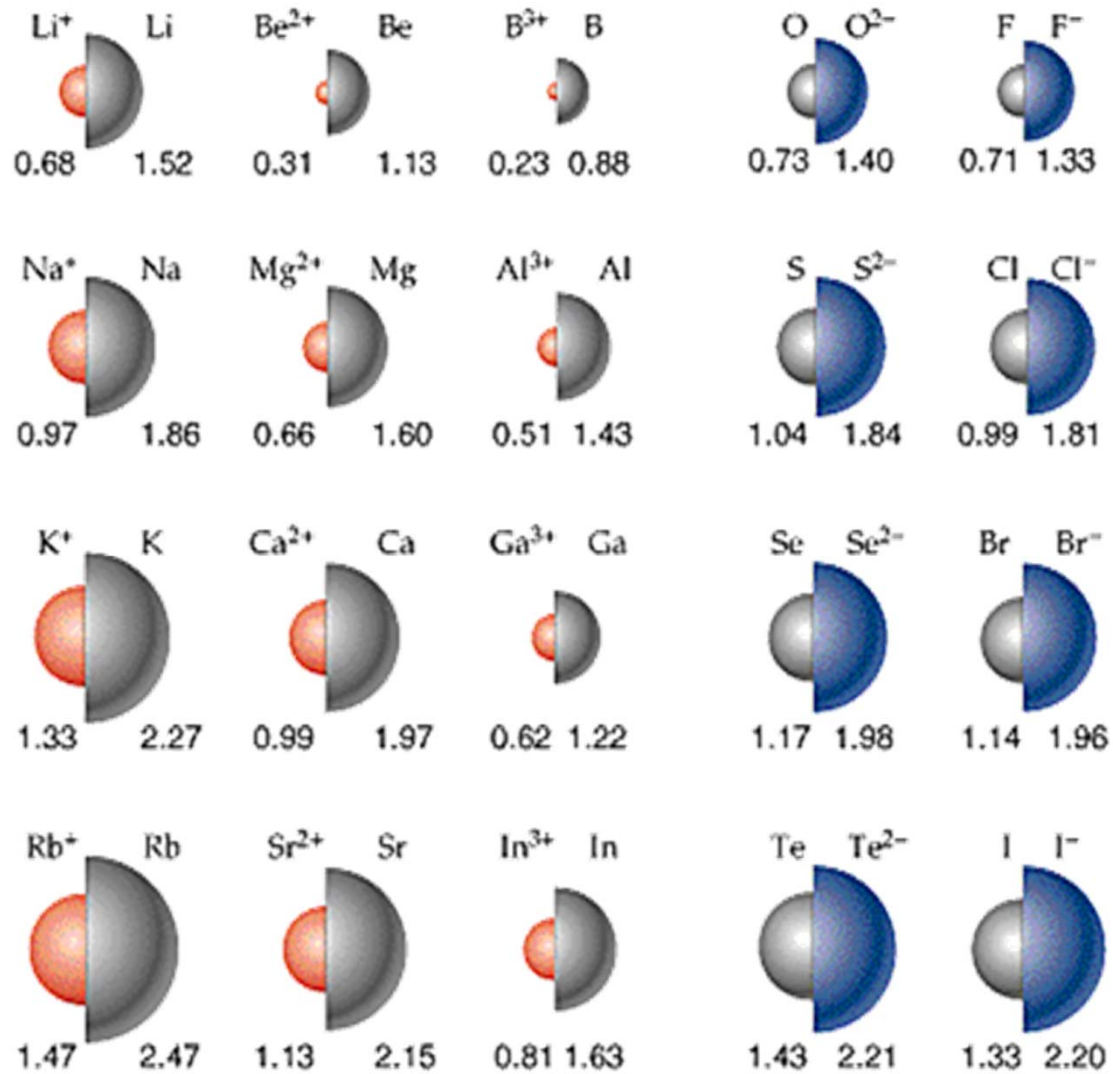
Oxidation State

1835 Wöhler Unorganische Chemie – oxydationsstufe

IUPAC "Gold Book" **Compendium of Chemical Terminology**

The oxidation state is the atom's charge after ionic approximation of its bonds

1. Atoms in an **element** have oxidation state **0**
2. **The sum** of the oxidation states for atoms in a compound is 0, in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion
3. Fluorine in compounds has the oxidation state -1
4. Alkaline metals in compounds have the oxidation state +1, alkaline-earth metals +2 (except alkalides M^{1-}, molecules with $Mg-Mg$ bonds, inverse sandwich Ca^{1+} complex)
5. Hydrogen in compounds has the oxidation state +1 (except hydrides -1)
6. Oxygen in compounds has the oxidation state -2 (except peroxides -1)

Oxidation State

Ionic approximation - the oxidation state of an atom in a compound is given by the hypothetical charge of the corresponding atomic ion that is obtained by **heterolytically** cleaving its bonds such that **the atom with the higher electronegativity** in a bond is allocated all electrons in this bond

Bonds between like atoms (having the same formal charge) are cleaved **homolytically**

Criteria for **the ionic approximation**:

1) Extrapolation of the bond's polarity
      a) from the electronegativity difference
      b) from the dipole moment (caveat: C←O)
      c) from quantum-chemical calculations of charges

2) Assignment of electrons according to the atom's contribution to the molecular orbital (MO)

$$\Psi_- = c_A \Psi_A - c_B \Psi_B \qquad c_B < c_A$$

$$\Psi_+ = c_A \Psi_A + c_B \Psi_B \qquad c_B > c_A$$

ionicity sign

covalency
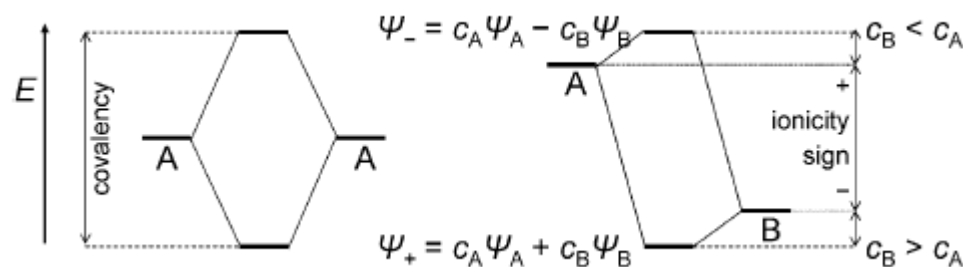
Oxidation State

The oxidation state of a bonded atom equals its charge after ionic approximation
Only heteronuclear bonds are extrapolated to be ionic

The atom to become negative is the one that **contributes more to the** **bonding MO**

NO

N$_2$O

Oxidation State

N$_2$O

112.6 pm   118.6 pm
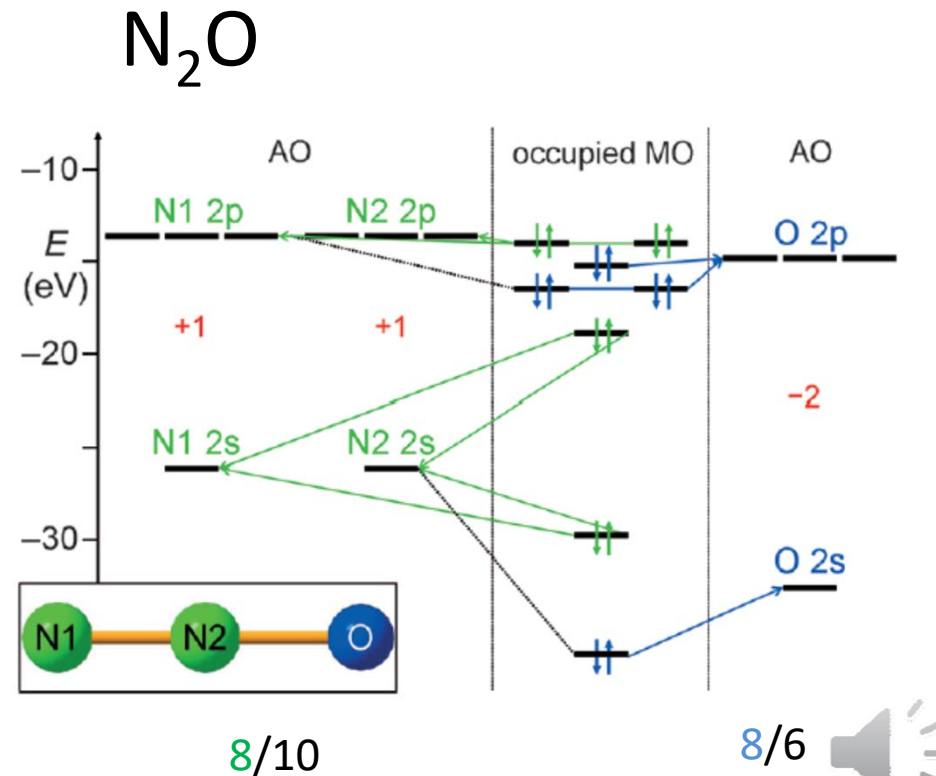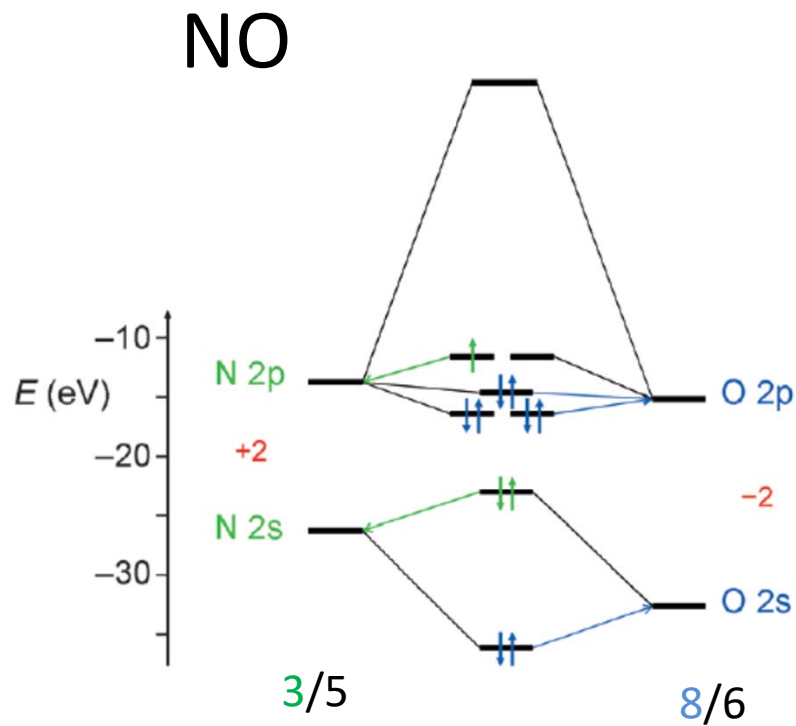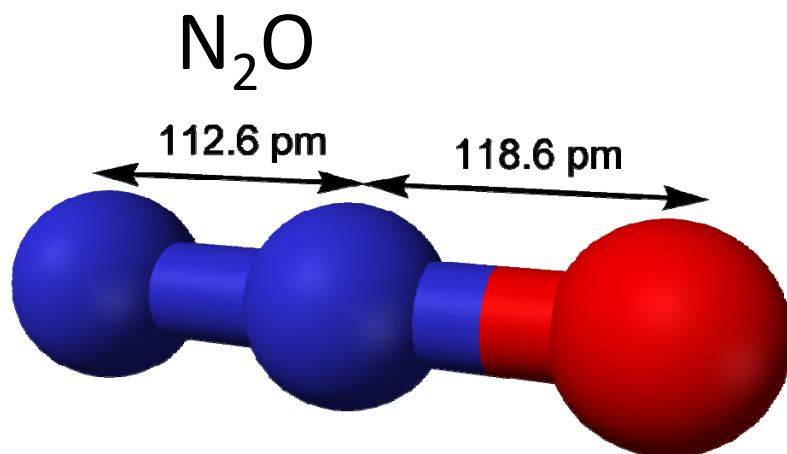
triple 1.097 Å in N$_2$
double 1.247 Å in N$_2$H$_2$

Lewis electronic structures

- Conform to octet rule
- Minimum formal charge separation
- Negative charge on the most electronegative atom

NBO/DF-BP86/def2-SVP   Lewis Character

1   :N——N̈=Ö: 90.6 %

2   :N≡N=Ö: 88.9 %*

3   :N≡N⊕—Ö⊖:   96.4 %

4   :N⊖=N⊕=Ö: 94.0 %

5   ⊖⊖:N——N⊕≡O⊕:   91.7 %

* if treated as excited state.

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Oxidation State +IX

The highest known oxidation state of any chemical element is +VIII
The maximum oxidation state coincides with the number of valence electrons

XeO_4, XeO_3F_2 and other xenon compounds
RuO_4 and OsO_4
IrO_4 - prepared under cryogenic conditions by matrix-isolation
d^1 = one unpaired valence electron

$[IrO_4]^+$

Isoelectronic d^0 series: $[Re^{VII}O_4]^-$ $Os^{VII}O_4$ $[Ir^{IX}O_4]^+$

OXIDATION STATE	EXAMPLE
−3	$[Ir(CO)_3]^{3-}$
−2	Unknown
−1	$[Ir(CO)_3(P[C_6H_5]_3)]^-$
0	$Ir_4(CO)_{12}$
+1	$Ir(CO)Cl(P[C_6H_5]_3)_2$
+2	$IrCl_2$
+3	$Ir(CO)Cl(H)_2(P[C_6H_5]_3)_2$
+4	$IrTe_2$
+5	$Ir(mesityl)_3O$
+6	IrF_6
+7	$[(\eta^2\text{-}O_2)IrO_2]^+$
+8	IrO_4
+9	IrO_4^+

Calculated as a minimum on the potential energy surface, T_d symmetry, an electron configuration $^1A_1$
Stable with respect to unimolecular elimination of O_2 (+256.9 kJ mol^{-1})
May be stabilized as a salt with a large counter anion $[IrO_4]^+$ $[Al(OC(CF_3)_3)_4]^-$

2014 - made by pulsed-laser vaporisation of Ir in the gas phase, identification by IR photodissociation spectroscopy

Electronegativity - the 3rd Dimension of the Periodic Table

Electronegativity - a quantified chemical concept, **correlates** the ability of chemical species (atoms, molecules, ions, radicals) to attract electrons during their contact with other species **with measurable quantities**, such as dissociation energies, dipole moments, ionic radii, ionization potentials, electron affinities and spectroscopic data

There is not one uniform definition of electronegativity up to the present day

The electronegativity, χ of an element is the power of its atoms to draw electrons to itself when it is part of a molecule, the polarity of a bond depends on the relative electronegativities of the elements

Electronegativity **cannot be directly measured**, must be determined by indirect quantification approaches: - thermochemical
                                          - spectroscopic
                                          - electrostatic

Pauling 1932
electronegativity χ_P based on excess energies of polar bonds, ability of an atom in a molecule to attract electrons for itself

Electronegativity - the 3rd Dimension of the Periodic Table

Mulliken 1934

electronegativity χ_M is an average of ionization energy (IE) and electron affinity (EA), orbital, "absolute electronegativity"

Gordy 1946 and Allred + Rochow 1958

χ_A electronegativity is "a force" needed to remove an electron from the atom's ground state (similarity to Coulomb's Law)

Allen 1989

χ_{spec} is an average valence-electron energy of the free atom

Sanderson 1951

S is a ratio of average electron density to that of corresponding rare gas atom, tendency of an atomic orbital to attract electrons from another atomic orbital with which it has combined to form a bond, chemical potential

Mulliken-Jaffe

the slope of the energy-vs-charge curve as it passes through the origin

Pauling Electronegativity

Pauling 1932 - the thermochemical approach

The empirically measured bonding energies
Excess energies of polar bonds

$$\Delta = E_{AB} - \sqrt{E_{AA} \times E_{BB}}$$

$$\Delta = k(\chi_A - \chi_B)^2$$

Postulated one element as the reference
$\chi(H) = 2.1$
$\chi(F) = 4.0$

A major difficulty - lack of
measured values for many
single bonds, especially for
metallic bonds
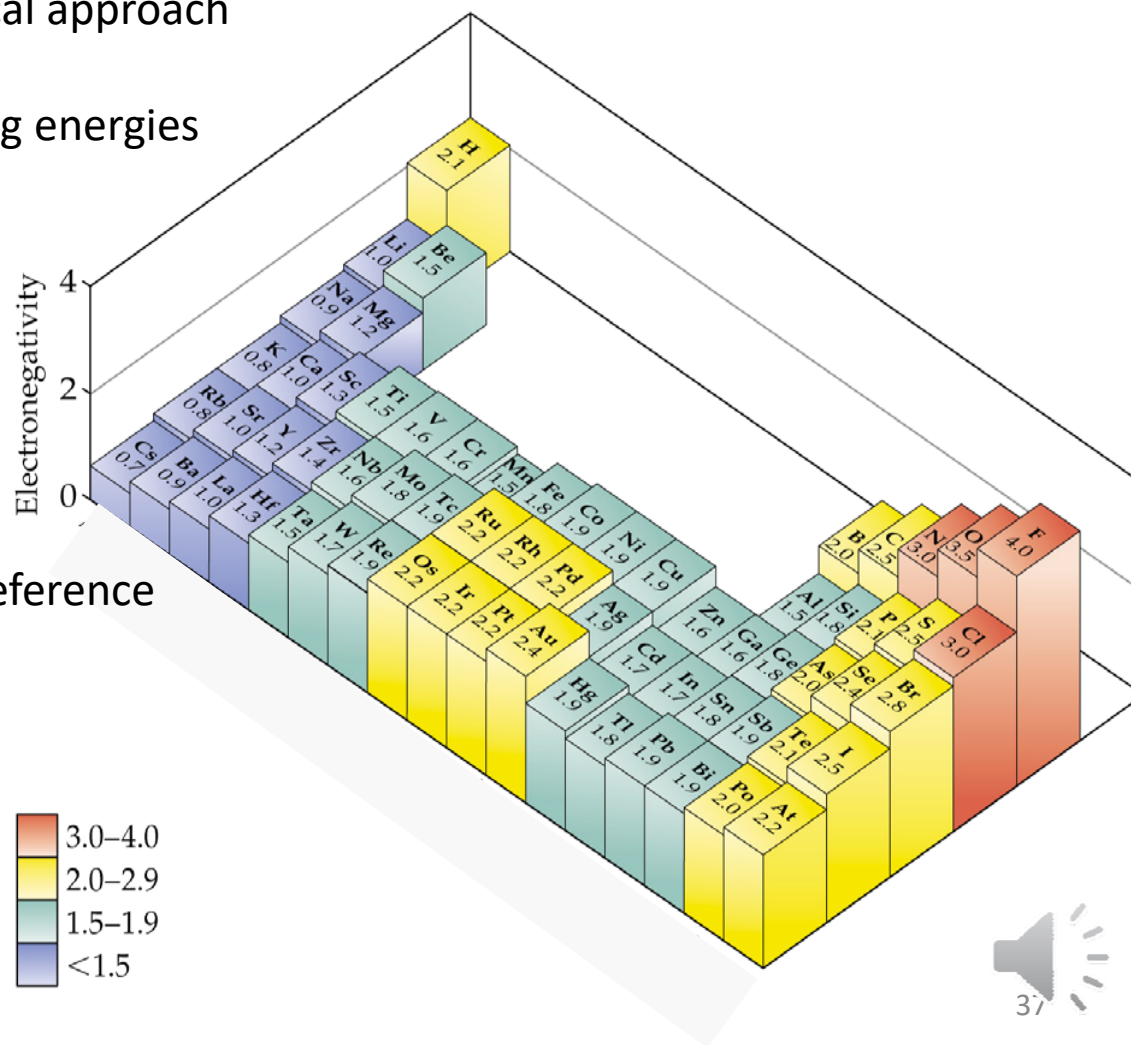
Allred + Rochow Electronegativity

Spectroscopic approach

$$\chi = \frac{aZ_{eff}}{r^2} + b$$

r - the atomic radius
Z_{eff} - the effective nuclear charge
a, b - the coefficients that relate this χ values with those of thermo-chemical measurements

Allred and Rochow 1958
the force of attraction between the screened nucleus and an electron at the covalent radius

Z_{eff} obtained empirically from X-ray spectroscopy or by using Slater's rules

Allred, A.L., Rochow, E.G.: J. Inorg. Nucl. Chem. 1958, 5, 264–268

χ is different for each orbital of an atom and depends on electron filling (i.e., charge)

Gordy Electronegativity

Spectroscopic approach

$$\chi = \frac{aZ_{eff}}{r} + b$$

r - the atomic radius
Z_{eff} - the effective nuclear charge
a, b - the coefficients that relate this χ values with those of thermo-chemical measurements

Gordy 1946
electrostatic potential (energy/electron)

$Z_{eff} = V - s(V - 1)$
the difference between the valence electrons (V) and the shielding constant of the valence shell (s = 0.5)

χ from the bond-stretching force constant k measured in radio frequency spectroscopy, the bond length d and the bond order N

$$k = aN\left(\frac{\chi_A\chi_B}{d^2}\right)^{\frac{3}{4}} + b$$

Sanderson Electronegativity

Sanderson 1951

the ability of an atom or ion to attract electrons to itself is dependent upon the **effective nuclear charge** felt by the outermost valence electrons

As the effective nuclear charge increases the size of the atom decreases
The average electron density of the atoms - compactness of the electronic sphere around the atomic nucleus - the more compact, the greater the holding power

Electronegativity **S** (stability ratio) is proportional to the compactness of an atom, i.e., how tightly the electrons are held:

$$S \approx \frac{D}{D_0} \qquad\qquad D = \frac{Z}{\frac{4}{3}\pi r^3}$$

D is the electron density of an atom (its atomic number divided by its atomic volume (covalent radius cubed)) and D_0 is the expected electron density of an atom, calculated from extrapolation between the noble gas elements

$$\sqrt{\chi_P} = a \times S + b$$

Sanderson Electronegativity

$$\sqrt{\chi_P} = a \times S + b$$
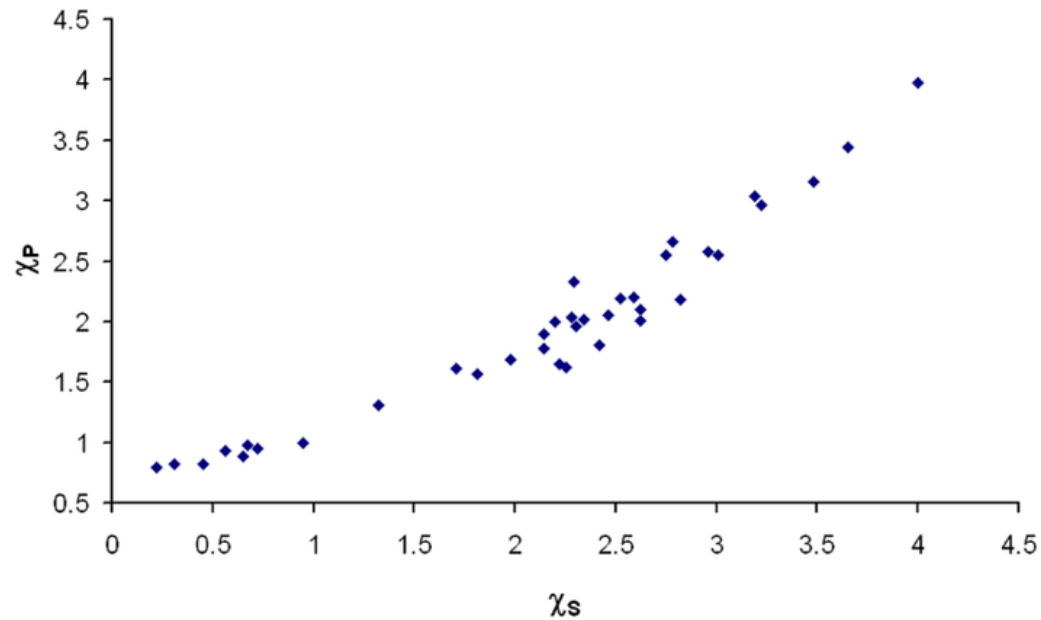
Mulliken Electronegativity

Mulliken 1934

The average of the electron affinity (EA – taken positive) and the ionization potential (IE)

$$\chi_M = \frac{1}{2}(IE + EA) = -\mu$$

Chemical potential of the electrons

$$\chi_M = 0.178(IE + EA) + 0.17$$

Pauling scale, IE and EA in eV

$$\chi_M = 1.97 \times 10^{-3}(IE + EA) + 0.19$$

Pauling scale, IE and EA in kJ mol^{-1}
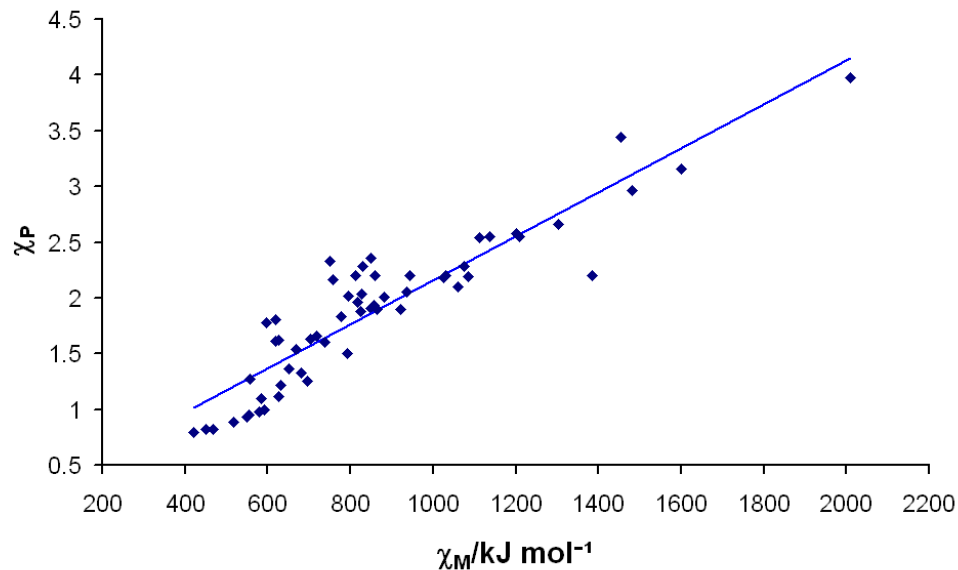
$$\chi_P = 0.168(\chi_M - 1.23)$$

Mulliken Electronegativity

The ionization potential can be inferred for **different valence states**

Hinze and Jaffe 1962 - orbital electronegativity - the electronegativity of the orbital which the atom will use in its bond

The electronegativity of an atom is (in part) a function of its environment

H
s 7.2

Li		Be		B		C		N		O		F	
s 3.1		di^2 4.8		tr^3 6.4		$di^2\pi^2$ 10.4, 5.7		$di^3\pi^2$ 15.7, 7.9		$tr^5\pi$ 17.1, 20.2		s 31.3	
p 1.8		te^2 3.9		te^3 6.0		$tr^3\pi$ 8.8, 5.6		$tr^4\pi$ 12.9, 8.0		$di^2\pi^4$ 19.1		p 12.2	
						te^4 8.0		te^5 11.6		te^6 15.3			

in eV

Na		Mg		Al		Si		P		S		Cl	
s 2.9		di^2 4.1		tr^3 5.5		$di^2\pi^2$ 9.0, 5.7		$di^3\pi^2$ 11.3, 6.7		$tr^4\pi^2$ 10.9		s 19.3	
p 1.6		te^2 3.3		te^3 5.4		$tr^3\pi$ 7.9, 5.6		$tr^4\pi$ 9.7, 6.7		te^6 10.2		p 9.4	
						te^4 7.3		te^5 8.9					

K		Ca		Ga		Ge		As		Se		Br	
s 2.9		di^2 3.4		tr^3 6.0		$di^2\pi^2$ 9.8, 6.5		$di^3\pi^2$ 9.0, 6.5		$tr^4\pi^2$ 10.6		s 18.3	
p 1.8		te^2 2.5		te^3 6.6		$tr^3\pi$ 8.7, 6.4		$tr^4\pi$ 8.6, 7.0		te^6 9.8		p 8.4	
						te^4 8.0		te^5 8.3					

Rb		Sr		In		Sn		Sb		Te		I	
s 2.1		di^2 3.2		tr^3 5.3		$di^2\pi^2$ 9.4, 6.5		$di^3\pi^2$ 9.8, 6.3		$tr^4\pi^2$ 10.5		s 15.7	
p 2.2		te^2 2.2		te^3 5.1		$tr^3\pi$ 8.4, 6.5		$tr^4\pi$ 9.0, 6.7		te^6 9.7		p 8.1	
								te^5 8.5					

Values can be computed only for orbitals holding 1 electron. For the carbon and nitrogen families it is possible to have both hybrid and π atomic orbitals half-filled. *digonal* $\equiv$ *sp* hybrid, *trigonal* $\equiv$ *sp²* hybrid, *tetrahedral* $\equiv$ *sp³* hybrid.

The lack of empirical measurements for IE and EA for some elements (transition metals)

Hybridization and Electronegativity

Hybridization has a profound effect on electronegativity

The s orbitals have lower energy than p and d, hence greater electron attracting power

The greater the s character - the greater the electronegativity

The factor affecting the acidity of hydrogen is the difference in electronegativity between hydrogen and the atom to which it is bonded

- Acetylene has highly acidic hydrogen as the C atom is sp hybridized (50% s character) and has almost the same electronegativity as Cl atom
- Methane in which the C atom is sp^3 hybridized (25% s character) and is not reactive

As the s-character in hybridization of nitrogen increases its basicity will decrease, the more electronegative the N atom, the less is the tendency to share the lone pair of electron, the basicity therefore decreases

- The N atom in ethane nitrile is sp hybridized and hence very electronegative and not basic
- Amine N has a low s character and thus it is very basic

Hybridization and Electronegativity

acidity increases
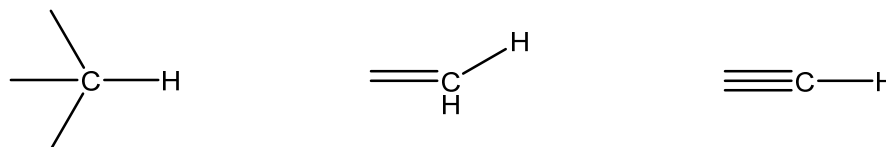
Hybridization	sp^3	sp^2	sp
C	2.48	2.75	3.29
N	3.68	3.94	4.67
s%	25	33	50
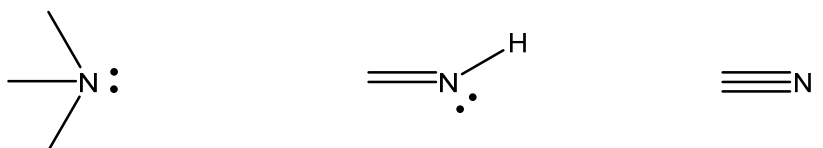
basicity increases

Allen Electronegativity

Allen 1989

The *average* one-electron energy of the valence-shell electrons in ground-state free atoms - the average ionization energy of valence electrons

The average force with which an atom holds its valence electrons

L.C. Allen, J. Am. Chem. Soc., 1989, **111**, 9003-9014

Only the Allen electronegativity is truly independent of the oxidation state, as it relates to the average valence-electron energy of the free atom

Spectroscopic electronegativity:

Configuration energy

m, n = number of p and s electrons, respectively

ε_s, ε_p = multiplet-averaged ionization potentials of s and p electrons (experimental data), the difference between the ground state and the first ionized state

$$\chi_{spec} = \frac{m\varepsilon_p + n\varepsilon_s}{m+n}$$

Allen Electronegativity

C [He] $2s^2 2p^2$ valence shell is n = 2

Energy of **the ground state** is given by the average of the energy of each **microstate**

There are 15 possible ways of filling 2 electrons into the three *p* orbitals

15 microstates - some of these microstates have the same energy, some have different

$$E_{GS} = \frac{1}{15}\left[E(^1S) + 5E(^1D) + 9E(^3P)\right]$$

Allen Electronegativity
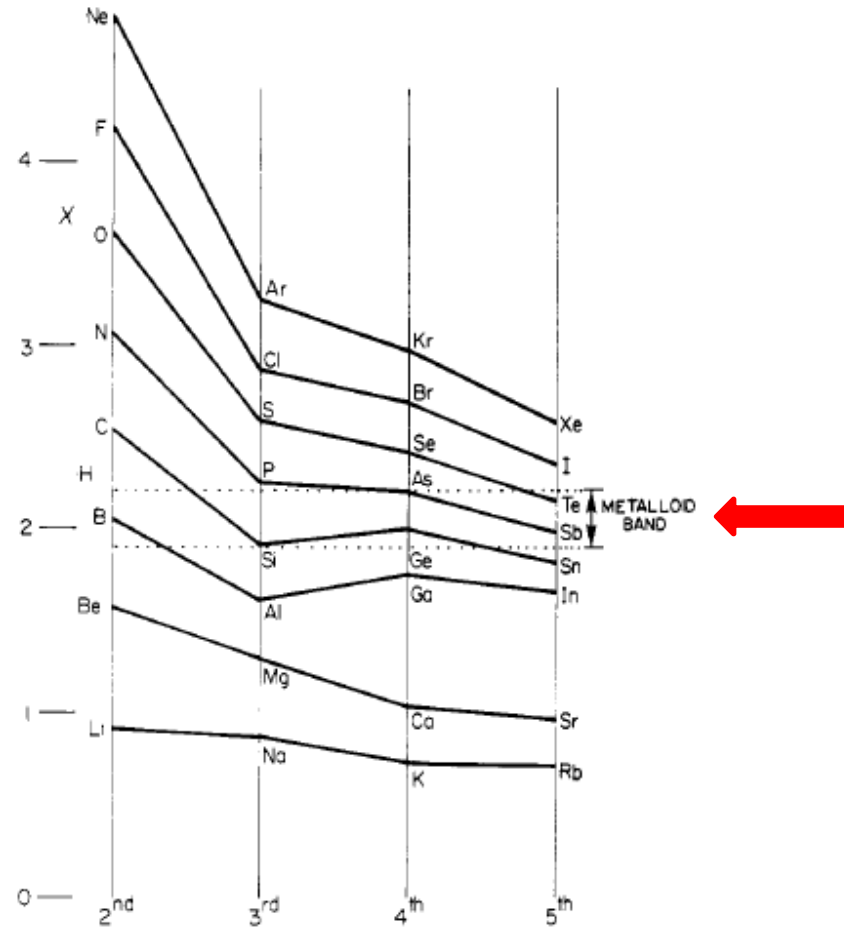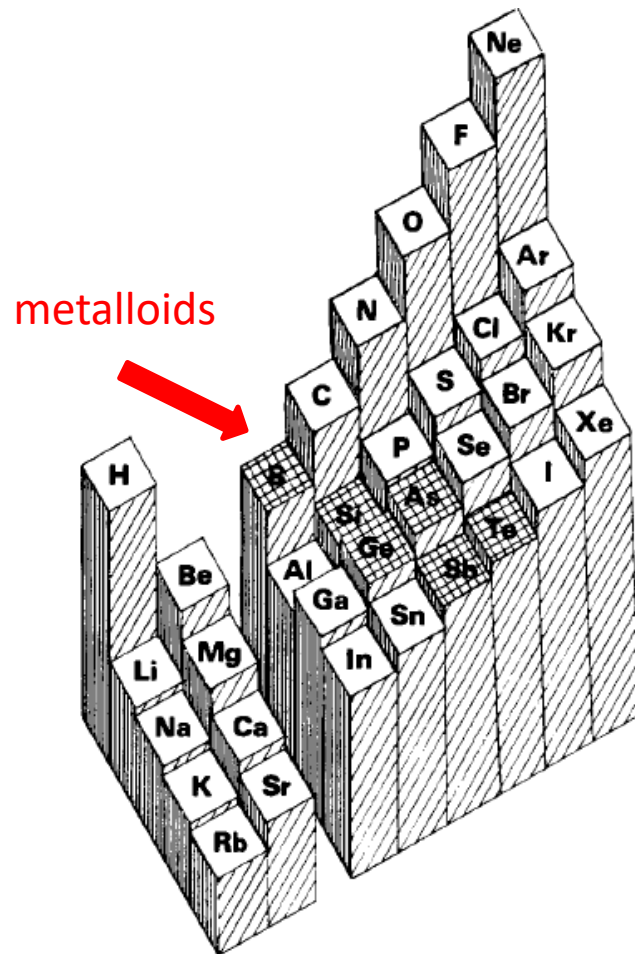
The "metalloids" are the elements roughly along the diagonal from B to Po
Some metalloids have both metallic and non-metallic allotropes

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The Alternation Effect

B > Al < Ga
C > Si < Ge

Table 1: Allen electronegativities[18–20] (in Pauling units).

H 2.300							He 4.16
Li 0.912	Be 1.576	B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.787
Na 0.912	Mg 1.293	Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
K 0.734	Ca 1.034	Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685	Kr 2.966
Rb 0.706	Sr 0.963	In 1.656	Sn 1.834	Sb 1.984	Te 2.158	I 2.359	Xe 2.582
Cs 0.659	Ba 0.881	Tl 1.789	Pb 1.854	Bi 2.01	Po 2.19	At 2.39	Rn 2.60

Sc 1.19	Ti 1.38	V 1.53	Cr 1.65	Mn 1.75	Fe 1.80	Co 1.84	Ni 1.88	Cu 1.85	Zn 1.59
Y 1.12	Zr 1.32	Nb 1.41	Mo 1.47	Tc 1.51	Ru 1.54	Rh 1.56	Pd 1.58	Ag 1.87	Cd 1.52
Lu[a] 1.09	Hf 1.16	Ta 1.34	W 1.47	Re 1.60	Os 1.65	Ir 1.68	Pt 1.72	Au 1.92	Hg 1.76

[a] The variation across the lanthanoid series has not been evaluated.

Increased nuclear charge accompanies filling of the **3d orbitals**, the 3d electrons shield the 4p electrons poorly, making Ga and Ge more electronegative

Electronegativity Equalization

Sanderson 1951

When two or more atoms initially different in electronegativity combine chemically, they adjust to have the same **intermediate (equalized) electronegativity** within the molecule

This intermediate electronegativity is given by **the geometric mean** of the individual electronegativities of the component atoms

The electron density will **flow from the more electropositive atom to the more electronegative atom**, creating a partial positive charge on the former and a partial negative charge on the latter

$$\uparrow \delta+ \qquad\qquad \uparrow \delta-$$

$$A \xrightarrow{\quad e \quad} B$$

$$\chi_A \uparrow \qquad\qquad \chi_B \downarrow$$
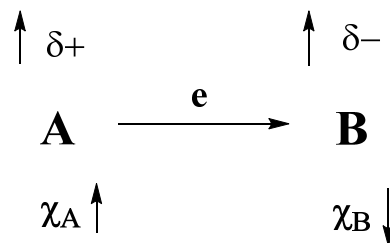
As the positive charge on the electropositive atom increases, its effective nuclear charge increases, hence its electronegativity increases

The same trend happens in the opposite direction for the more electronegative atom, until the two have the same electronegativity – **electronegativities are equalized** and charge transfer stops

Electronegativity Equalization

The intermediate electronegativity is given by **the geometric mean** of the individual electronegativities of the component atoms

$S(SnO_2) = (S_{Sn} \times S_O^2)^{1/3} = (4.28 \times 4.90^2)^{1/3} = 4.68$

$S(SrTiO_3) = (S_{Sr} \times S_{Ti} \times S_O^3)^{1/5} = (1.28 \times 2.09 \times 4.90^3)^{1/5} = 3.16$

The partial **ionic charge** and **ionic radius** of an ion are not constants, but vary depending upon the **electronegativity of the surrounding atoms**

The partial charge on an atom never exceeds +1 or −1
The oxidation states do not reflect the true charge of an ion

Electronegativity Equalization

Electronegativity of an atom in an A−B bond depends on its partial charge, δ

$$\chi_A = a_A + b_A \delta_A \qquad\qquad \chi_B = a_B + b_B \delta_B$$

$\uparrow \delta+$ $\qquad\qquad$ $\uparrow \delta-$

$$A \xrightarrow{\ e\ } B$$

$\chi_A \uparrow$ $\qquad\qquad$ $\chi_B \downarrow$
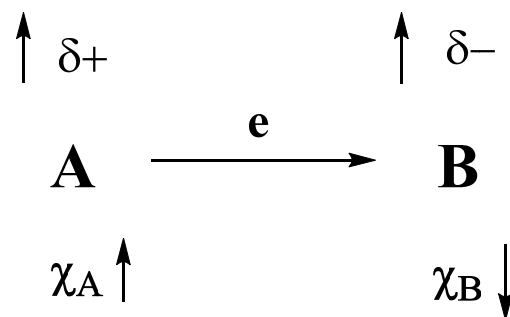
Charge transfer causes that electronegativities are equalized

$$\chi_A = \chi_B$$

$$\delta_A = -\delta_B$$

$$\delta_A = \frac{a_B - a_A}{b_A + b_B}$$

Mulliken-Jaffe Electronegativity

Iczkowski and Margrave

When **the total energy** (the ionization energies and electron affinities) of atoms are plotted against the oxidation state a smooth curve results and can be described by a quadratic formula

$$E = \alpha q + \beta q^2$$

Jaffe said that the Mullikan definition of electronegativity is the slope of this curve as it passes through the origin
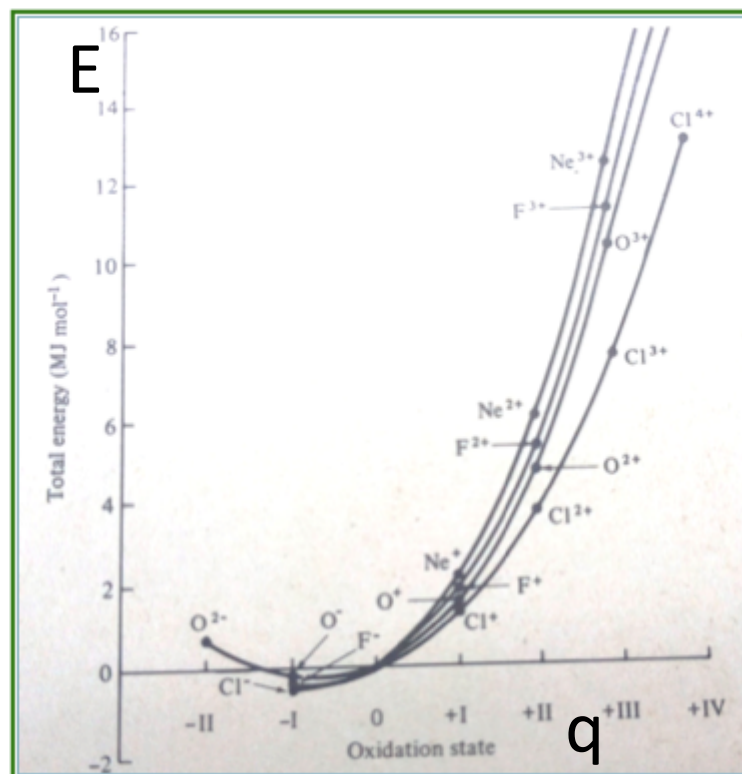
E = total energy of an atom

q = oxidation state, ionic charge

Mullikan electronegativity

A derivative of energy with respect to charge at q = 0

$$\chi_M = \left(\frac{\partial E}{\partial q} \right) = \alpha + 2\beta q$$

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Mulliken-Jaffe Electronegativity

$$E = \alpha q + \beta q^2$$

For q = 0   Neutral atom, **E = 0**

For q = +1   The energy of the system corresponds to **the first ionization energy, IE$_V$** (in a particular valence state)

For q = −1   The energy of the system corresponds to the **negative** of **electron affinity, −EA$_V$**

IE_V = α + β   (2)   and $−EA_V$ = −α +β   (3)

Therefore on adding equation (2) and (−3): IE_V + EA_V = 2α

where **α** stands for **Mulliken electronegativity** χ$_M$

$$\chi_M = \frac{1}{2}(IE_V + EA_V)$$

Mulliken-Jaffe Electronegativity

χ_M involves valence state ionization energy and electron affinities (calculated for atoms in the valence state as they exist in a molecule), takes into account the electronegativity of partially charged atoms emphasizing the effect **the partial charge** can have on the electronegativity of the atom

$$E = \alpha q + \beta q^2 \qquad \chi_M = \left(\frac{\partial E}{\partial q} \right) = \alpha + 2\beta q = a + b\delta$$

δ = the partial ionic charge

a = inherent or neutral atom electronegativity

b = charge coefficient (rate of change of electronegativity with charge)

Large soft atoms – low b
Small hard nonpolarizable atoms – high b
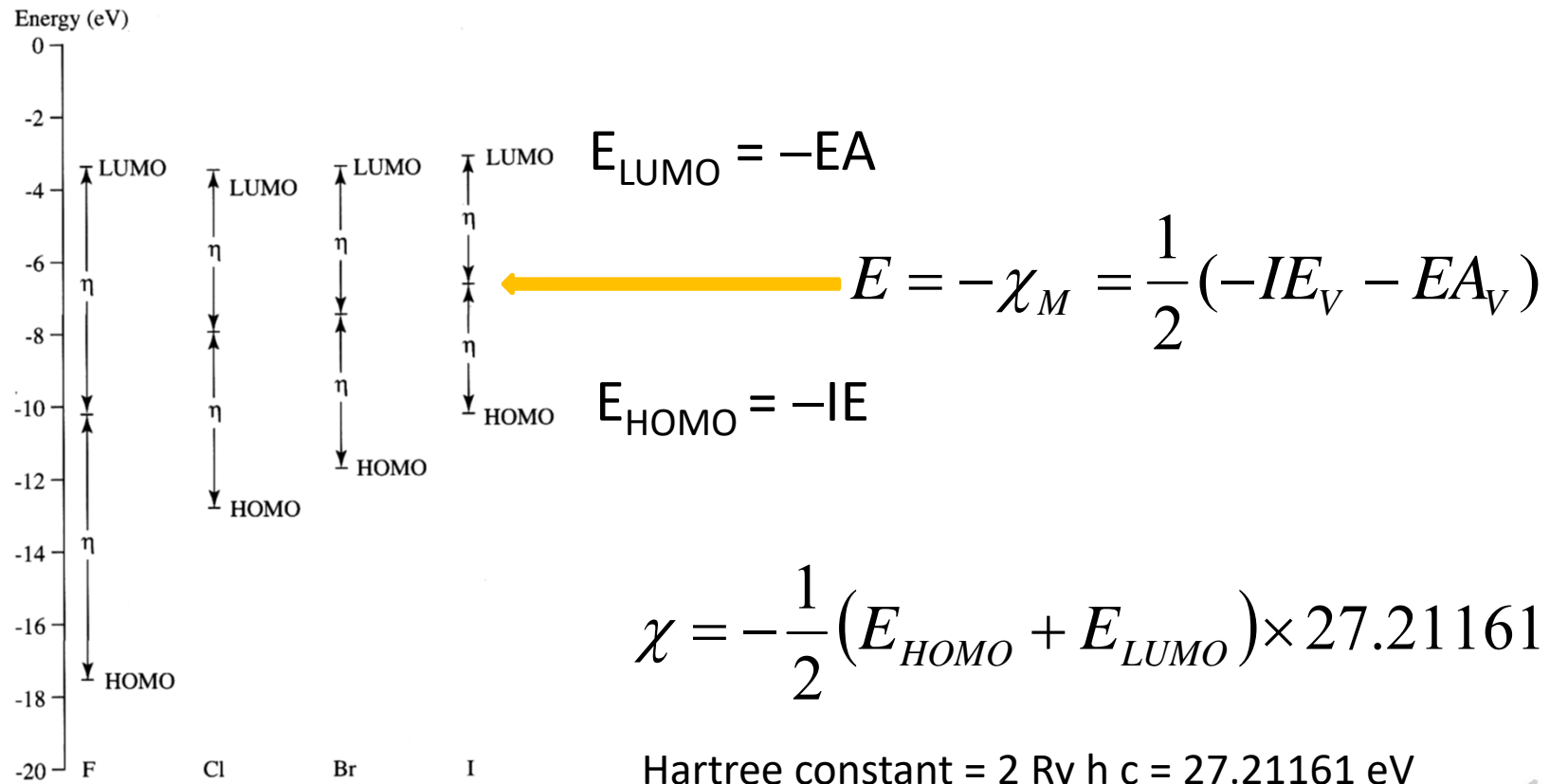
1/b = charge capacity, ability to donate/absorb electrons

Absolute Electronegativity

Koopman's theorem

$E_{HOMO} = -IE$
$E_{LUMO} = -EA$

IE ≥ EA for a neutral species

$E_{LUMO} = -EA$

$$E = -\chi_M = \frac{1}{2}(-IE_V - EA_V)$$

$E_{HOMO} = -IE$

$$\chi = -\frac{1}{2}\left(E_{HOMO} + E_{LUMO}\right) \times 27.21161$$

Hartree constant = 2 Ry h c = 27.21161 eV
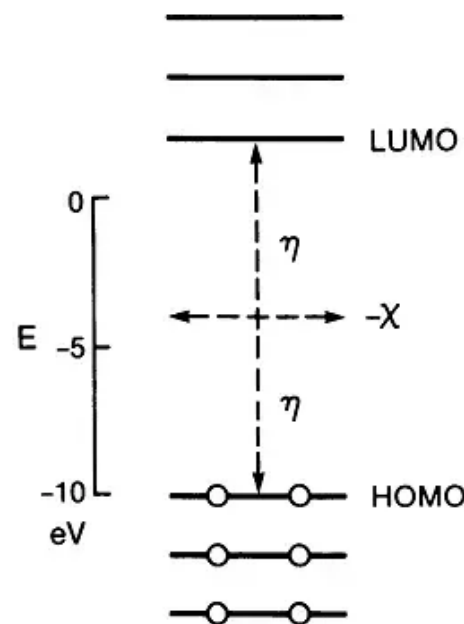
56

Absolute Hardness

Pearson and Parr - R.G. Parr, R.G. Pearson, JACS 1983, 105, 7512-7516

Absolute Hardness, η - the **resistance** of the chemical potential **to change the number of electrons**

The **harder** a chemical species, the more **difficult** it will be **to change its oxidation state**

The larger the energy gap $\Delta E = E_{LUMO} - E_{HOMO}$, the harder the chemical species

$$\eta = \frac{1}{2}\left(IE - EA\right)$$

$$-\chi_M = \frac{1}{2}\left(-IE_v - EA_v\right)$$

LUMO

η

$-\chi$

η

0

E -5

-10

eV

HOMO

Absolute Hardness

Absolute Hardness, η - the **resistance** of the chemical potential **to change the number of electrons**

The larger the energy gap $\Delta E = E_{LUMO} - E_{HOMO}$, the harder the chemical species

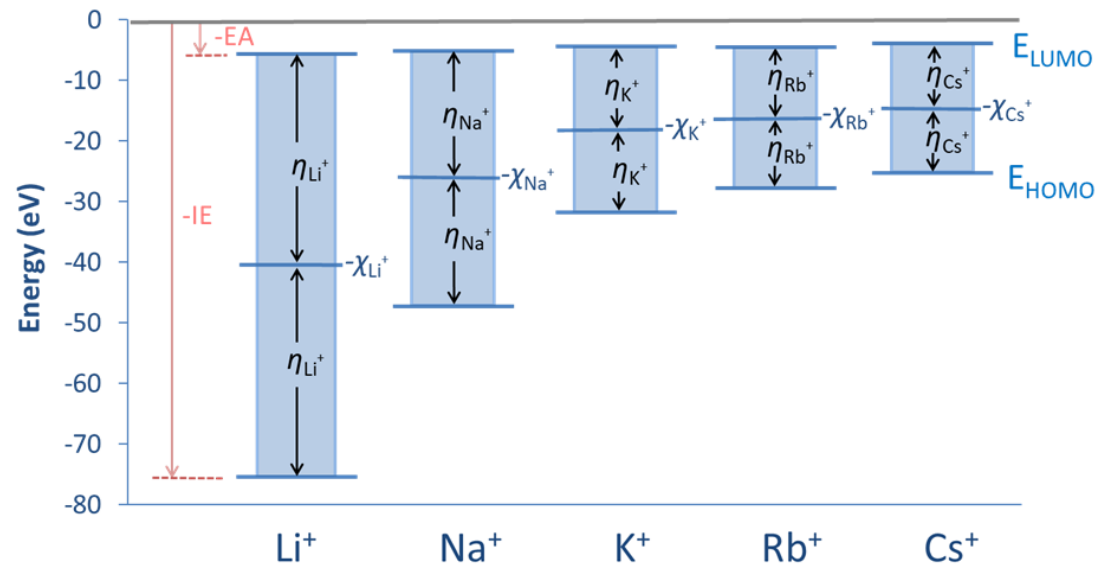$$\eta = \frac{1}{2}(IE - EA)$$

$$\chi_M = \frac{1}{2}(IE_V + EA_V)$$

Polarizability

Polarizability, α - an atom's ability to be **distorted by an electric field**

(of a neighboring ion)

Atoms (and ions) are highly polarizable if their electron distribution can be distorted readily - unfilled atomic orbitals lie close in energy to the highest occupied atomic orbital(s), i.e., a small energy difference between HOMO and LUMO orbitals

Closely separated frontier orbitals - large, heavy atoms and ions
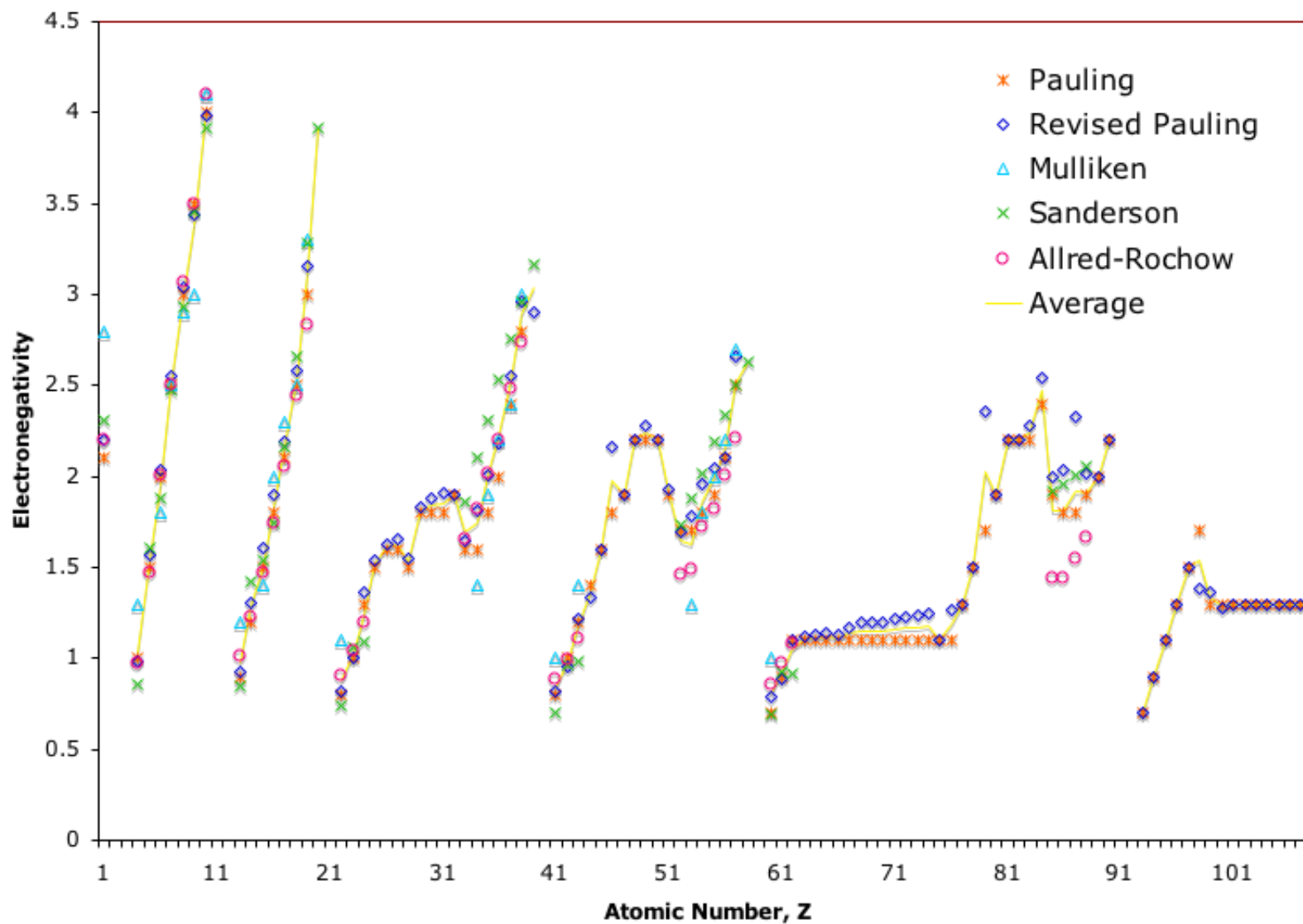
Widely spaced energy levels - small, light atoms

Fajan's rules
1. Small, highly charged cations are able to polarize other atoms (high polarizing ability)
2. Large, highly charged anions are easily polarized
3. Cations that do not have a noble-gas electron configuration are easily polarized (transition metals)

Electronegativity from Different Scales

Electronegativity from Different Scales

Element	Pauling	Mulliken and Jaffe	Allred and Rochow	Gordy	Sanderson	Allen
H	2.2	2.1 (s)	2.20	2.17	2.31	2.3
Li	0.98	0.84 (s)	0.97	0.96	0.86	0.912
Be	1.57	1.40 (sp)	1.47	1.38	1.61	1.576
B	2.04	1.93 (sp^2)	2.01	1.91	1.88	2.051
C	2.55	2.48 (sp^3)	2.50	2.52	2.47	2.544
N	3.04	2.28 (p)	3.07	3.01	2.93	3.066
O	3.44	3.04 (p)	3.50	3.47	3.46	3.610
F	3.98	3.90 (p)	4.10	3.94	3.92	4.193

Pauling - (Energy)$^{1/2}$
Mulliken - Energy
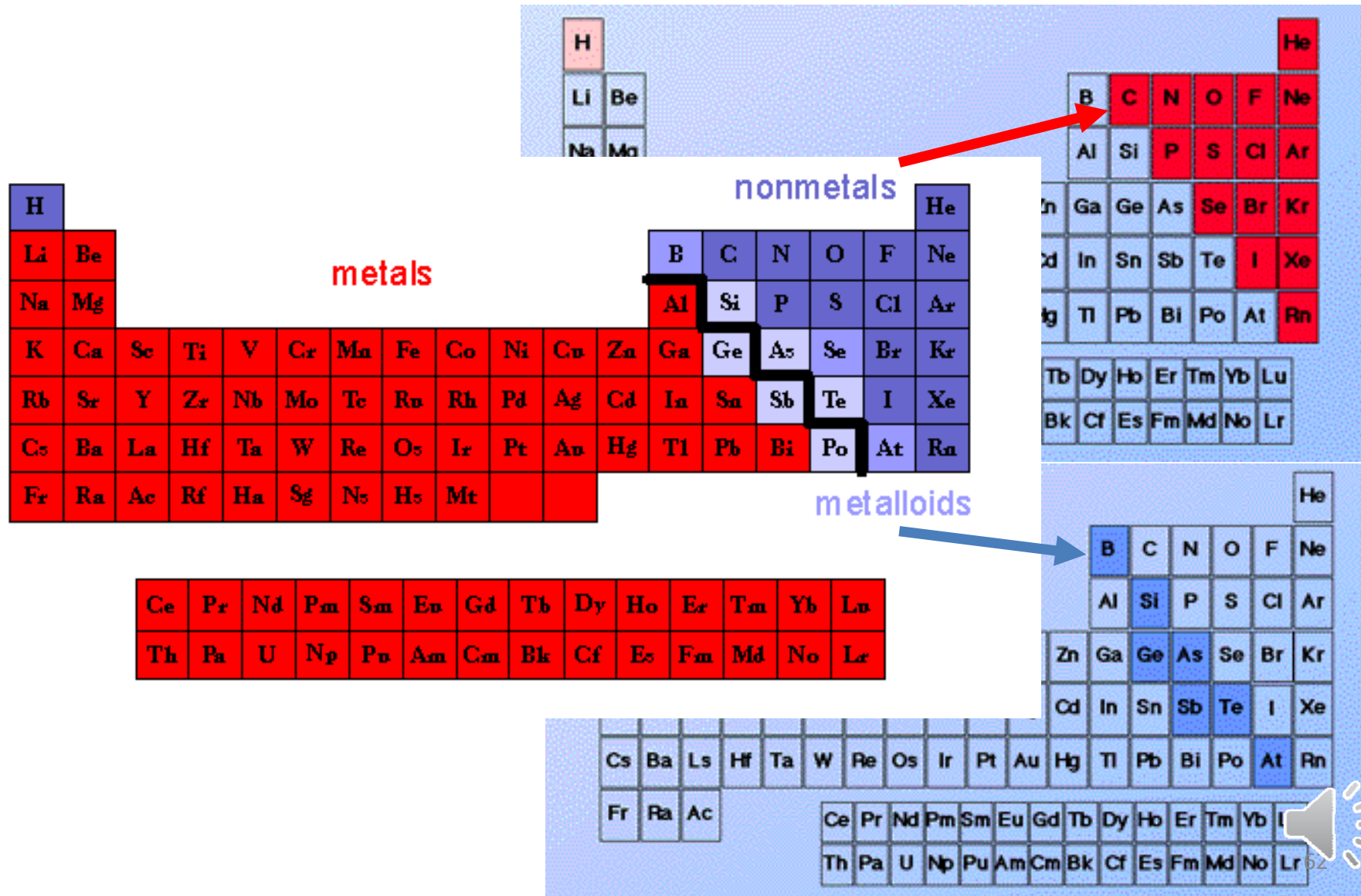Allred-Rochow - Force
Gordy - Energy/electron
Sanderson - Dimensionless

Conclusion
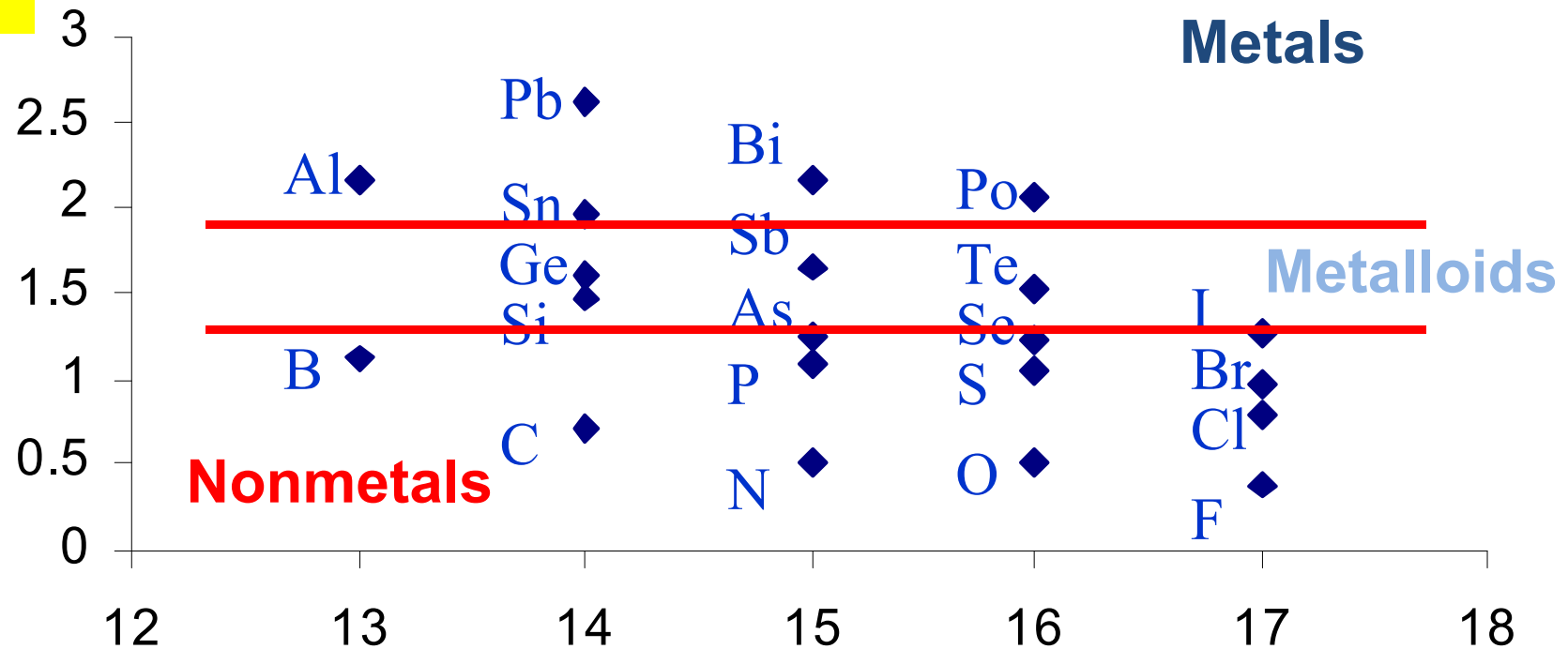**There is no agreement as to the specific physical meaning of electronegativity**

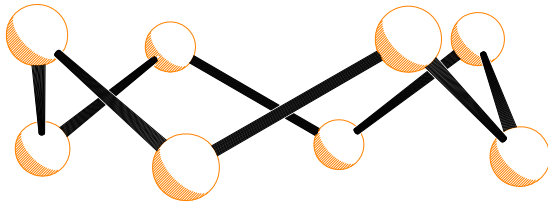61

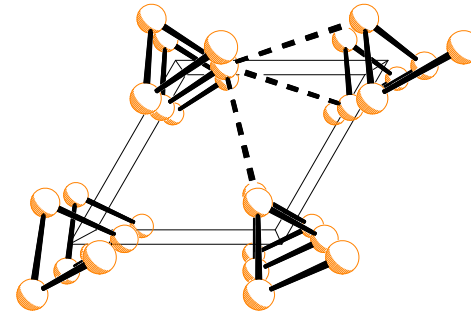# Electronegativity and Chemical Properties

Chemical Properties
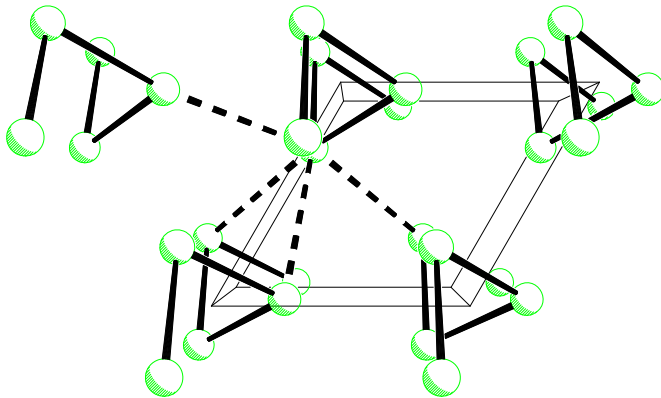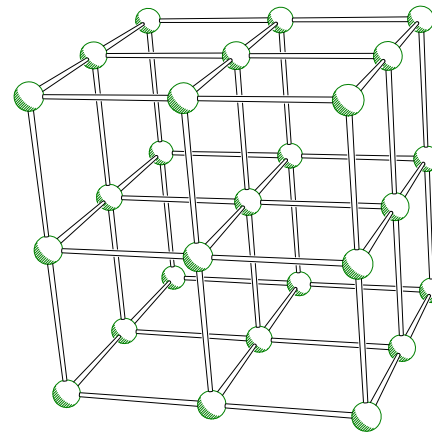
Chemical Properties

S, red Se - nonmetals

Gray Se - metalloid

Te - metalloid

Po - metal

Metals and Non-metals

The Goldhammer–Herzfeld Criterion

An element becomes a metallic conductor when **the molar volume** (V) becomes less than, or equal to, that of its gas-phase atomic **molar refractivity** (R)
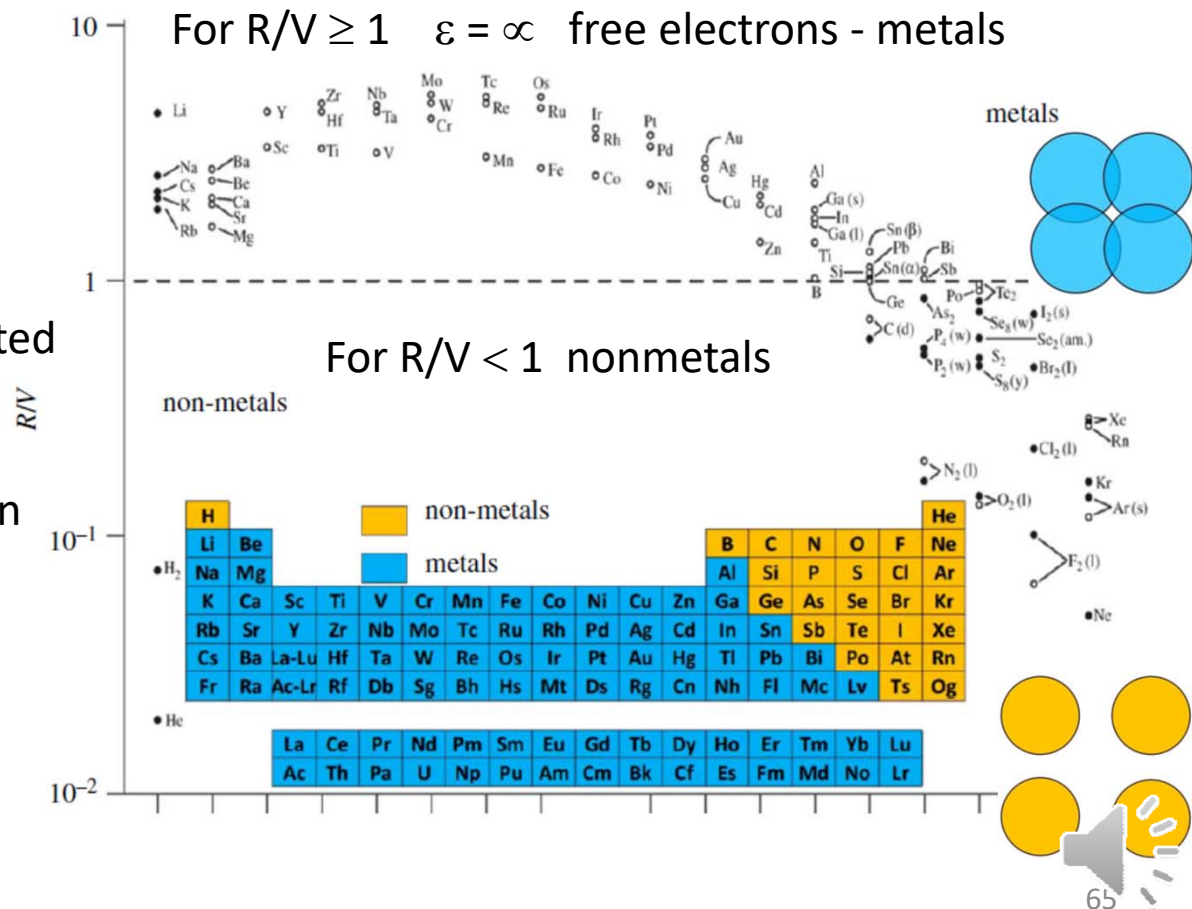
$$R = \frac{4\pi\alpha}{3} N_A$$

Polarizability $\alpha = r^3$
r = atomic radius

R/N_A = the **volume** of an isolated atom in the gas phase

The Clausius–Mossotti relation (non-metallics)
n = the index of refraction
ε = the dielectric constant

$$\frac{n^2-1}{n^2+2} = \frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi\alpha}{3V} N_A = \frac{R}{V}$$

For R/V ≥ 1 $\varepsilon = \infty$ free electrons - metals

metals

For R/V < 1 nonmetals

non-metals

non-metals

metals

Dictionary of Used Terms

Screening – stínění

Node – nodální plocha, plocha s nulovou elektronovou hustotou

Exchange energy – výměnná energie

Angular momentum – úhlový moment hybnosti

Ground state – základní stav, stav s nejnižší energií

Geometric mean – geometrický průměr

Total energy – celková energie

Core electrons – elektrony ve zcela zaplněných vnitřních slupkách (vzácné plyny)