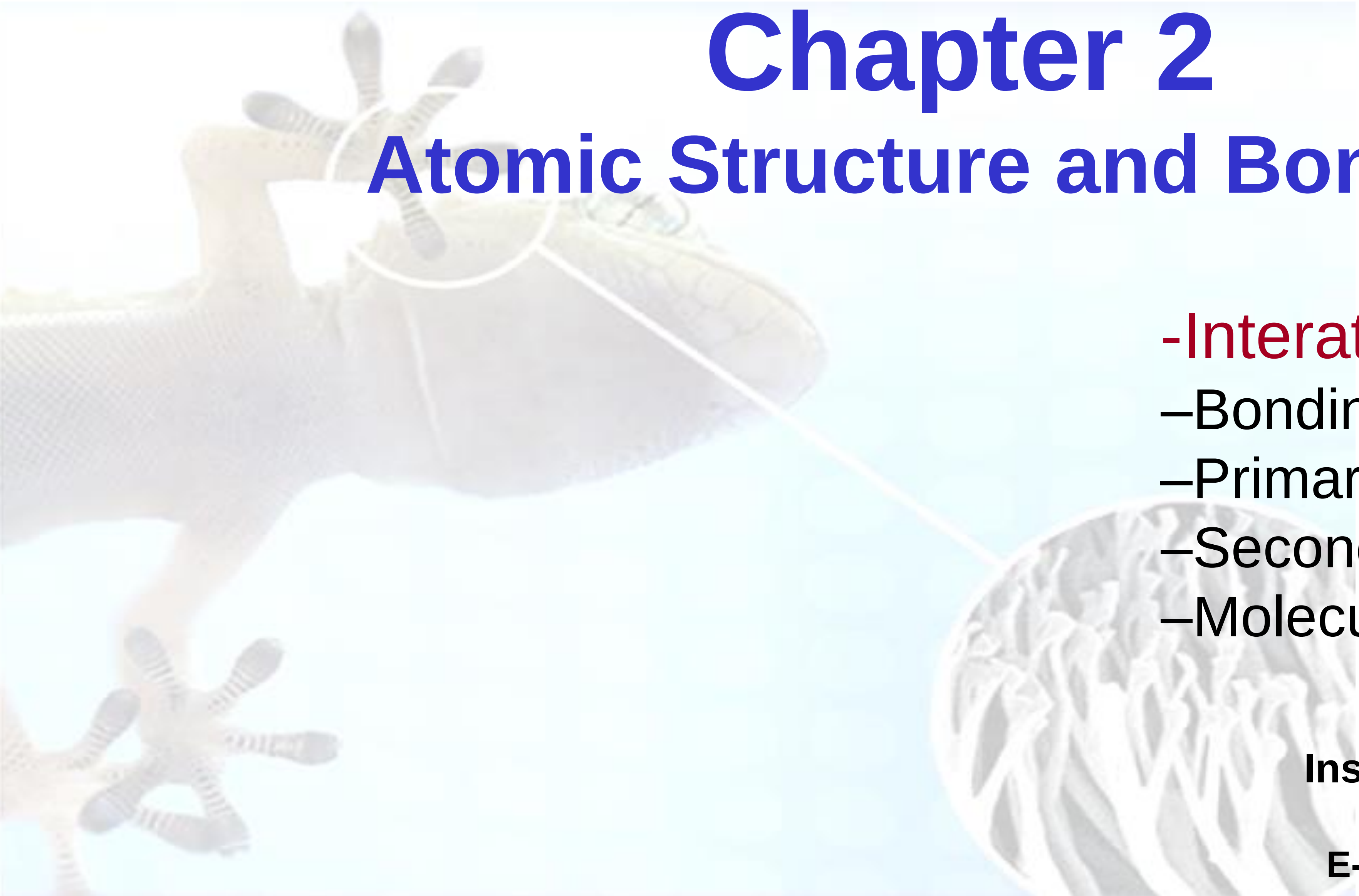
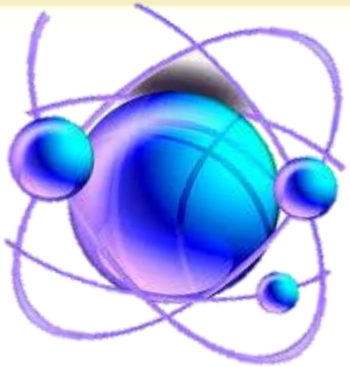


Chapter 2

Atomic Structure and Bonding



-Interatomic Bonding

–Bonding forces and energies

–Primary interatomic bonds

–Secondary bonding

–Molecules

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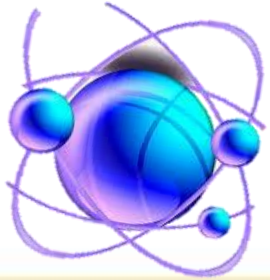
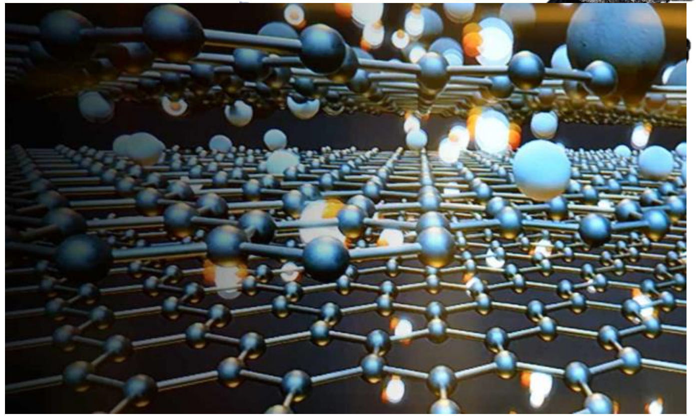
Learning Objectives

- Define four **quantum numbers** for electrons and explain the significance of each.
- Explain the arrangement of the elements in the **periodic table**.
- State the **electronic structure** of the elements.
- Explain the role of **electronegativity in bonding**.
- Define four different **mechanisms of bonding** in materials.
- Understand how **interactions between atoms or between ions** influence materials properties.
- Recognize that even though **allotropes** are composed of the same element, they can display dramatically different materials properties based on their structure (e.g., the allotropes of carbon).



Nature of Interatomic Bonding

Why the individual atoms coalesce into larger structures and take on the characteristics and properties of many different materials?

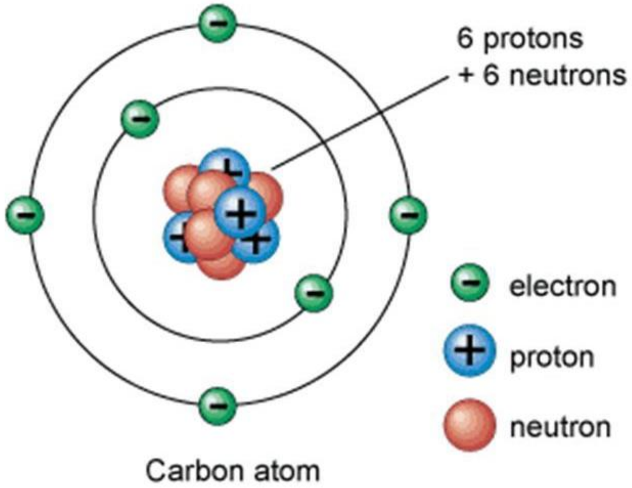


The bonding mechanisms between atoms are closely related to the structure of the atoms themselves.

Atoms = **nucleus** (protons and neutrons) + **electrons**

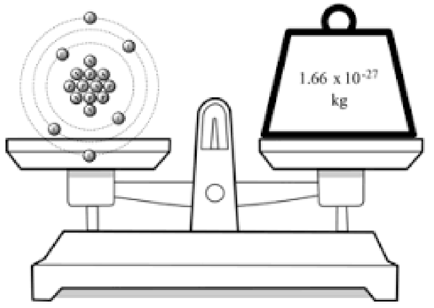
Charges: **Electrons** and **protons** have negative and positive charges of the same magnitude, 1.6×10^{-19} Coulombs.

Neutrons are electrically neutral.



Masses: **Protons and Neutrons** have the same mass, 1.67×10^{-27} kg.
Mass of an electron is much smaller, 9.11×10^{-31} kg and can be neglected in calculation of atomic mass.

The atomic mass (A) = **mass of Protons** + **mass of Neutrons**



protons gives chemical identification of the element

 # protons = atomic number (Z)

neutrons defines isotope number

Atomic mass units. Atomic weight

The atomic mass unit (amu) is often used to express **atomic weight**.
1 amu is defined as 1/12 of the atomic mass of the most common isotope of carbon atom that has 6 protons (Z=6) and six neutrons (N=6).

$M_{proton} \approx M_{neutron} = 1.66 \times 10^{-24}$ g = 1 amu.

The atomic mass of the ^{12}C atom is 12 amu.

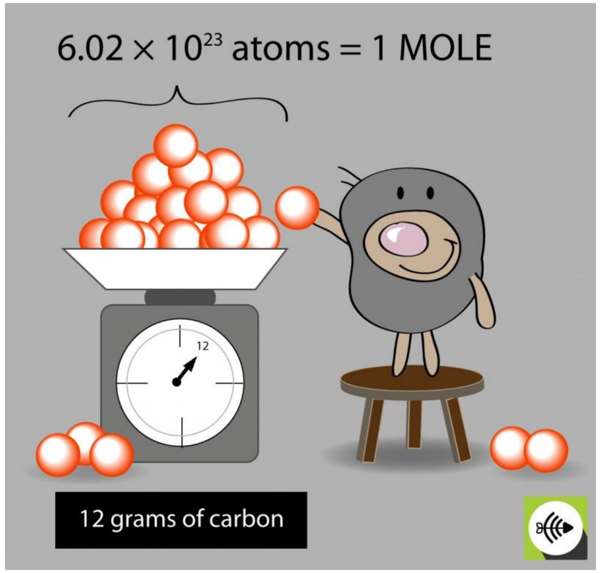
The atomic weight of an element = weighted average of the atomic masses of the atoms naturally occurring isotopes. Atomic weight of carbon is 12.011 amu. The atomic weight is often specified in mass per mole.

A mole is the amount of matter that has a mass in grams equal to the atomic mass in ***amu*** of the atoms (A mole of carbon has a mass of 12 grams).

The number of atoms in a mole =
Avogadro number, $N_{av} = 6.023 \times 10^{23}$

1 amu/atom = 1 gram/mol

Example: Atomic weight of iron (Fe) = 55.85 amu/atom = 55.85 g/mol



Some simple calculations

The number of atoms per cm^3, n, for material of density d(g/cm^3) and atomic mass M (g/mol):

$$n = N_{av} \times d / M$$

Graphite (carbon): d = 2.3 g/cm^3, M = 12 g/mol,
n = 6×10^{23} atoms/mol × 2.3 g/cm^3 / 12 g/mol = 11.5 × 10^{22} atoms/cm^3

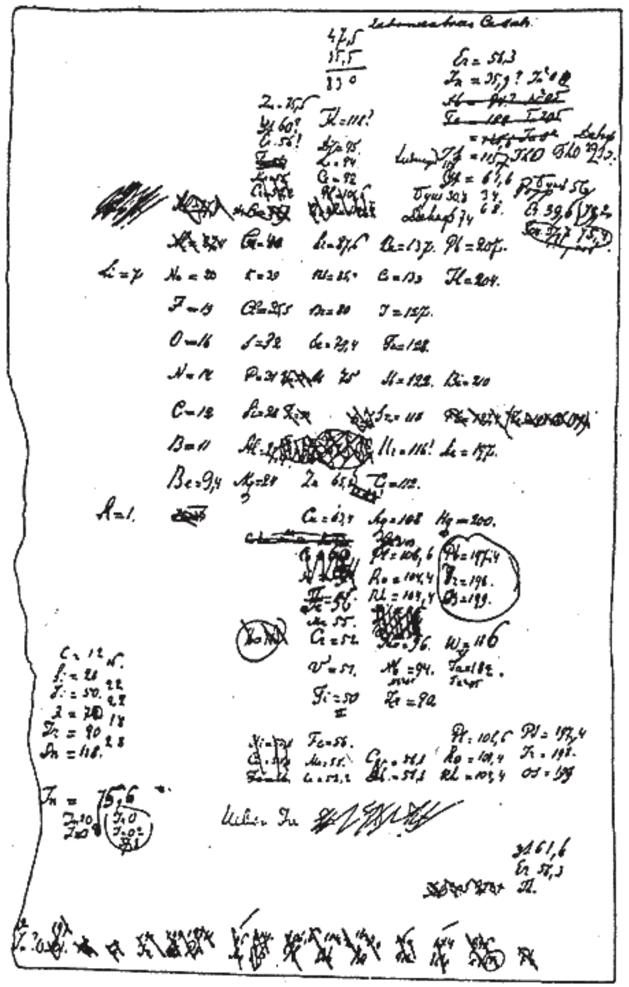
Diamond (carbon): d = 3.5 g/cm^3, M = 12 g/mol
n = 6×10^{23} atoms/mol × 3.5 g/cm^3 / 12 g/mol = 17.5 × 10^{22} atoms/cm^3

For material with n = 6 × 10^{22} atoms/cm^3 we can calculate mean distance between atoms L = $(1/n)^{1/3}$ = 0.25 nm.

Water (H_2O) d = 1 g/cm^3, M = 18 g/mol
n = 6×10^{23} molecules/mol × 1 g/cm^3 / 18 g/mol
= 3.3 × 10^{22} molecules/cm^3

Periodic Table

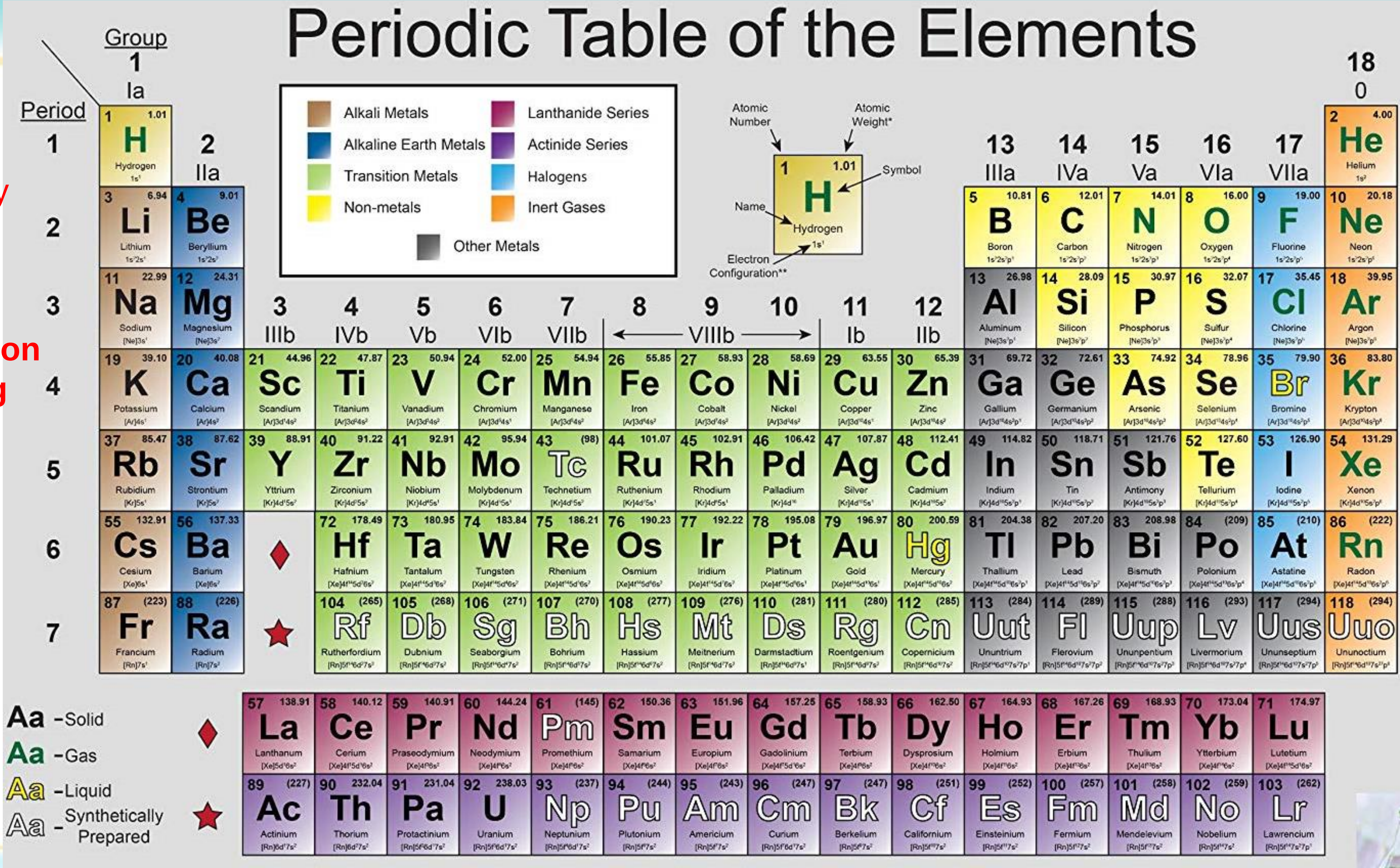
The first accepted periodic table of elements was published in **1869 by Mendeleev**. In the same year, a German chemist Lothar Meyer independently published a very similar table, but his contribution is generally ignored.



All elements in the periodic table have been classified **according to the electron configuration**.

Draft of the periodic table, Mendeleev, 1869

Arranged by **atomic number, electron configuration & recurring chemical properties**



Electrons in Atoms

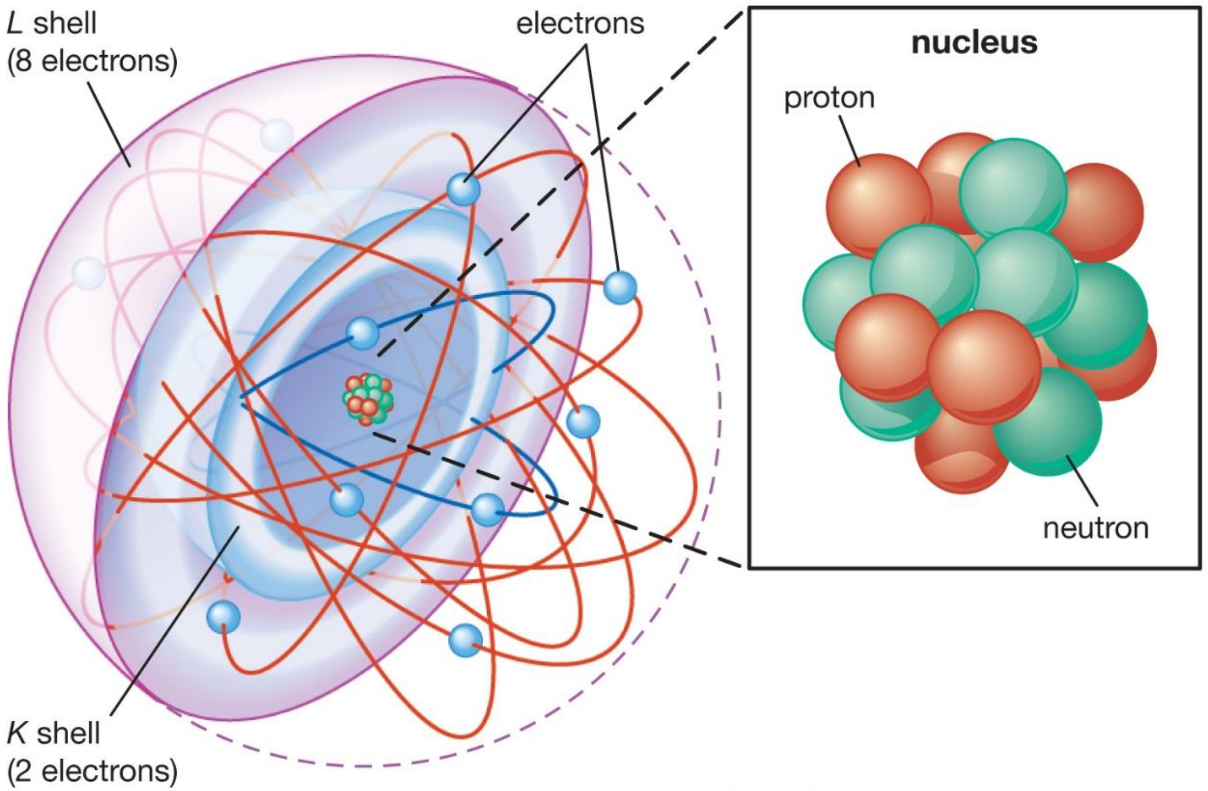
The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.

Only certain “orbits” or shells of electron probability densities are allowed

The shells are identified by a **principal quantum number n**, which can be related to the size of the shell, n = 1 is the smallest;
n = 2, 3 .. are larger.

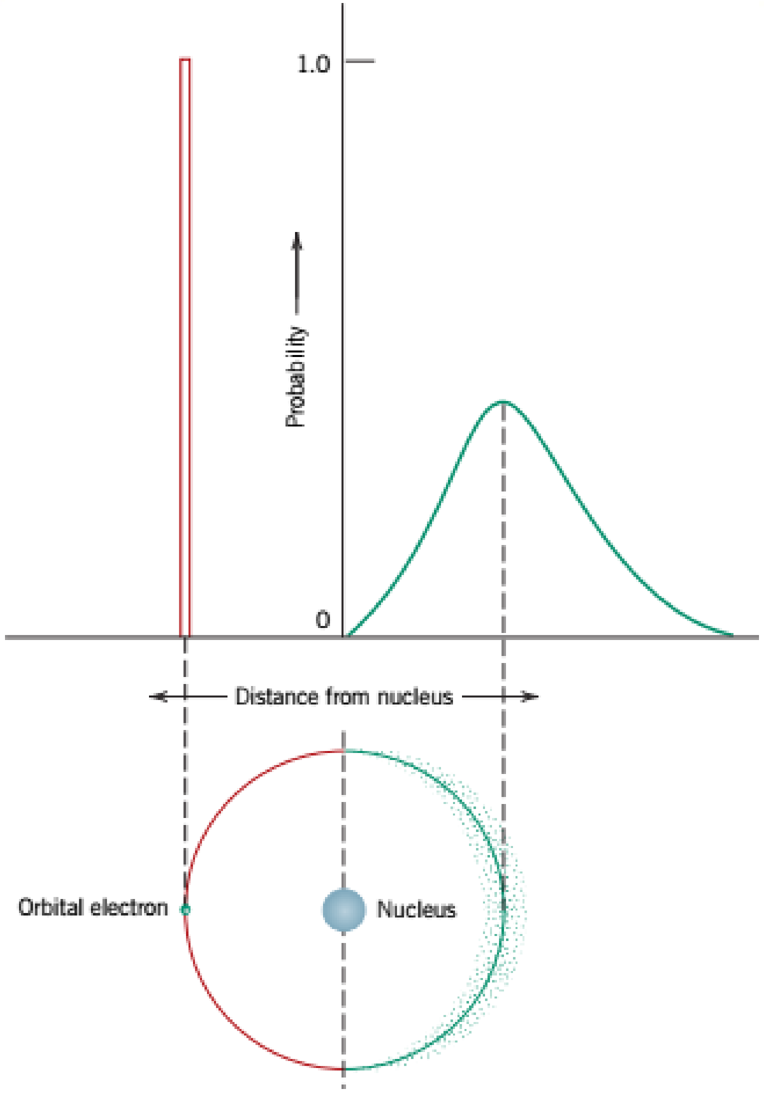
The second quantum number l, defines subshells within each shell.

Two more quantum numbers characterize states within the subshells.



Pauli Exclusion Principle: only one electron can have a given set of the four Quantum numbers.

Quantum Numbers



Comparison of the (*a*) Bohr and (*b*) wave mechanical atom models in terms of electron distribution

The quantum numbers arise from solution of Schrodinger's equation

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\mathrm{r}) + V(r)\Psi(\mathrm{r}) = E\Psi(\mathrm{r})$$

$$\text{Kinetic Energy} + \text{Potential Energy} = \text{Total Energy}$$

Eigenvalues are discrete energy levels for electron

Square of eigenfunction gives probability density (where electron can be found)

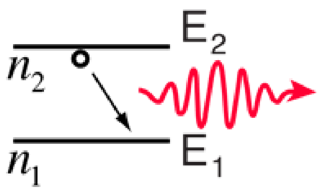
$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0{}^2\hbar^2}\left(\frac{1}{n^2}\right)$$

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}\,a_0^{3/2}}\, e^{-r/a_0}$$

α_0= Bohr radius

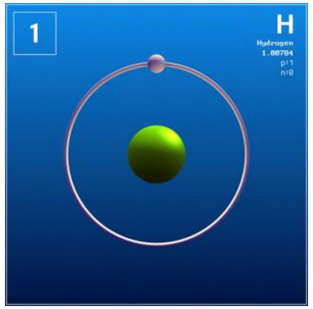
Electrons in Hydrogen Atoms

The Bohr model for an electron transition in H between quantized energy levels with different quantum numbers ***n*** yields a photon by emission with quantum energy:



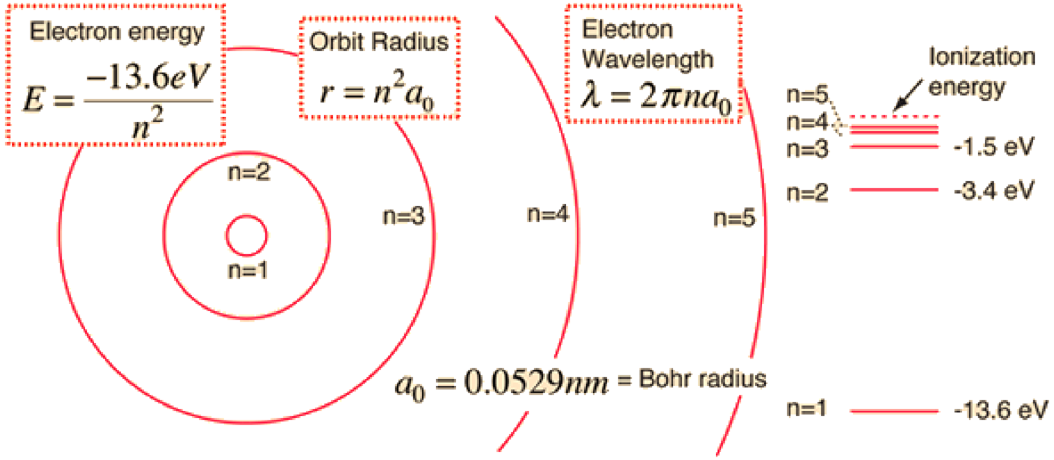
A downward transition involves emission of a photon of energy:

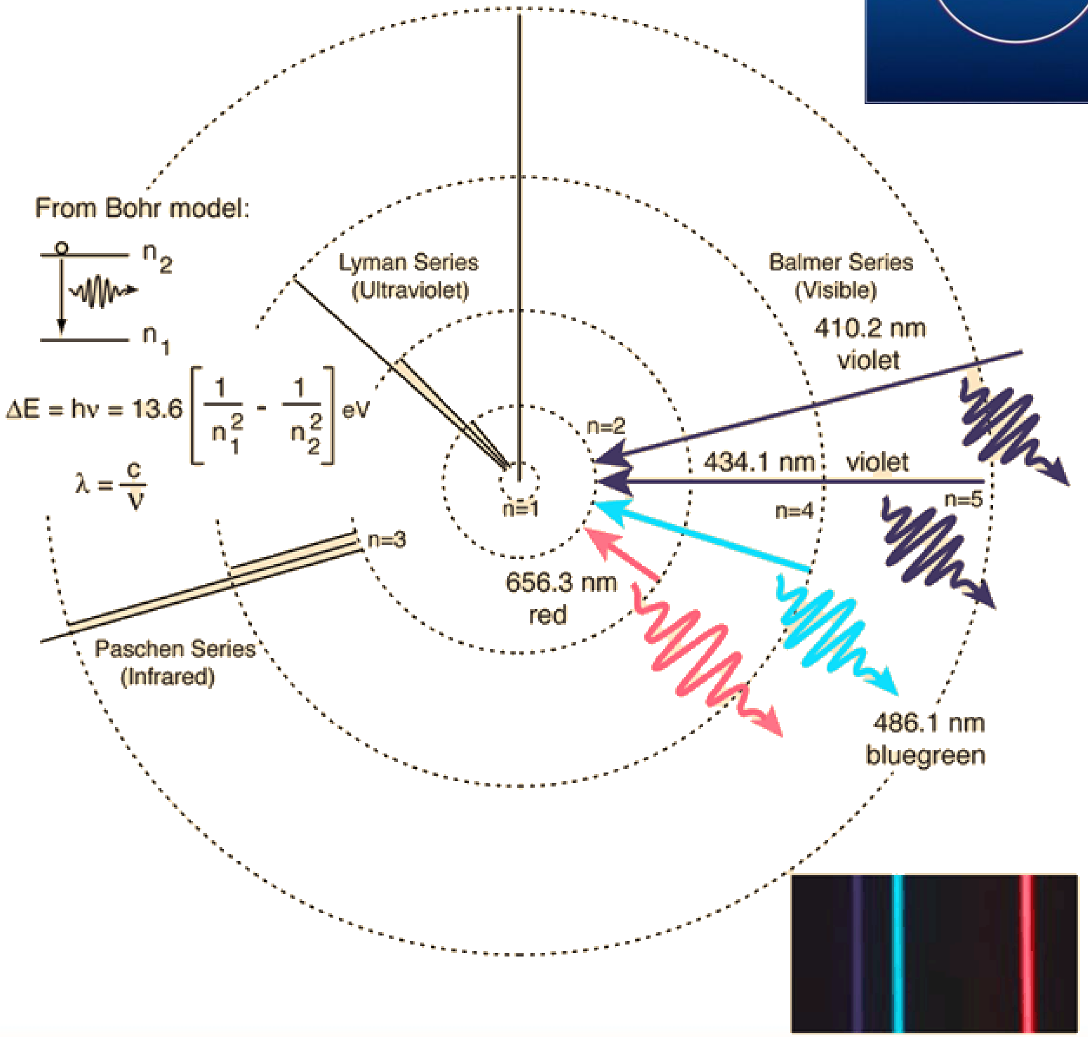
$$E_{photon} = h\upsilon = E_2 - E_1$$



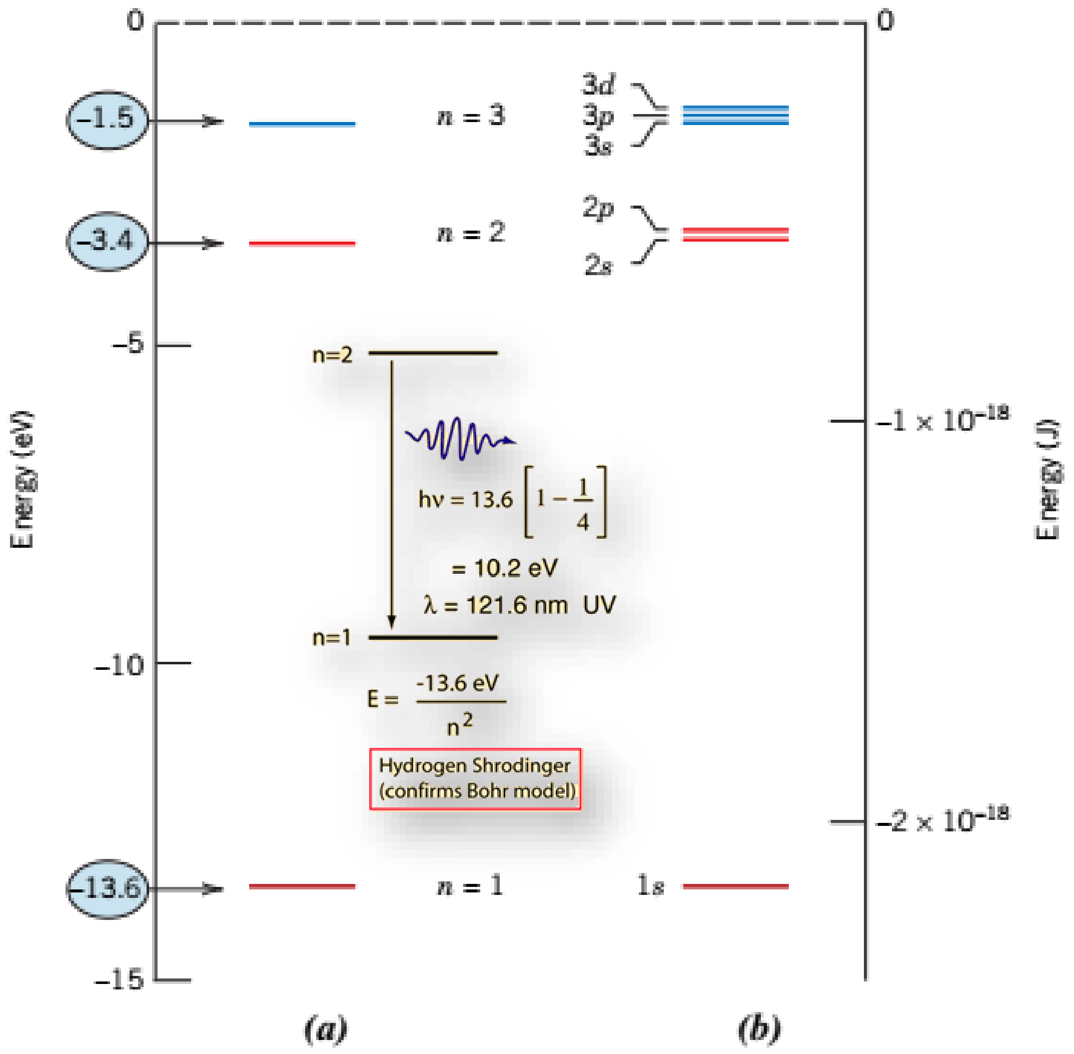
Given the expression for the energies of the hydrogenic electron states for atoms of atomic number Z:

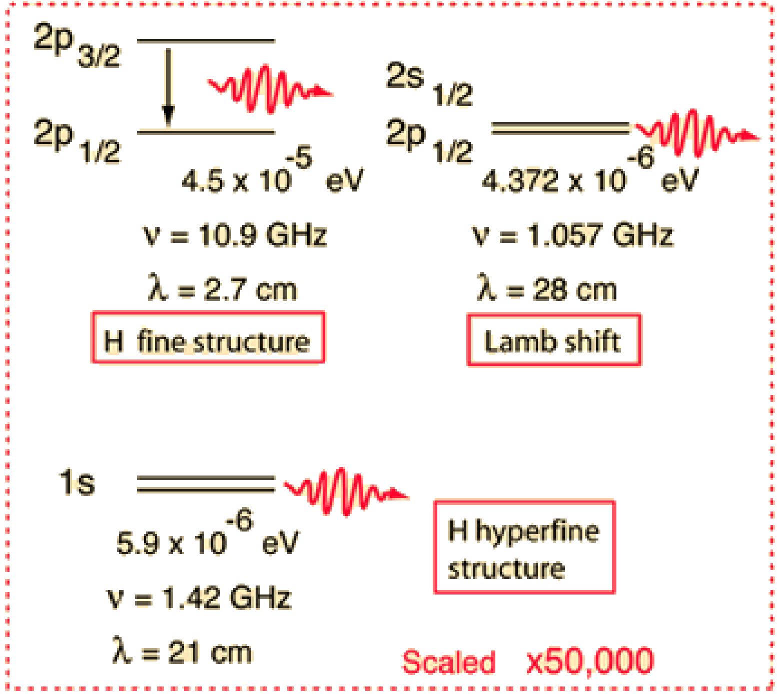
$$h\upsilon = \frac{Z^2 m e^4}{8h^2\varepsilon_0^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = -13.6Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] eV$$

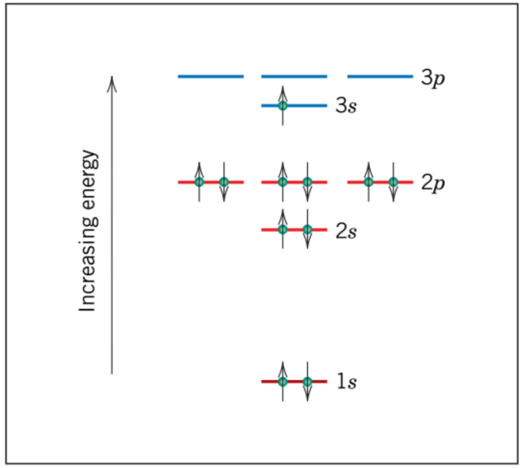




Electrons in Hydrogen Atoms







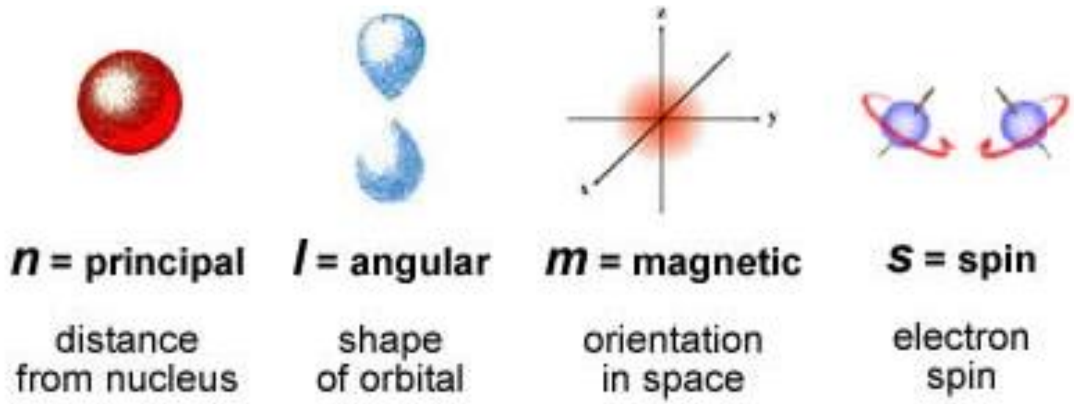
(a) The first three electron energy states for the Bohr hydrogen atom.
(b) Electron energy states for the first three shells of the wave-mechanical hydrogen atom

Quantum Numbers

In wave mechanics, every electron in an atom is characterized by four parameters called **quantum numbers.**

The size, shape, and spatial orientation of an electron's probability density (or orbital) are specified by 4 quantum numbers, n, l, m_l, m_s

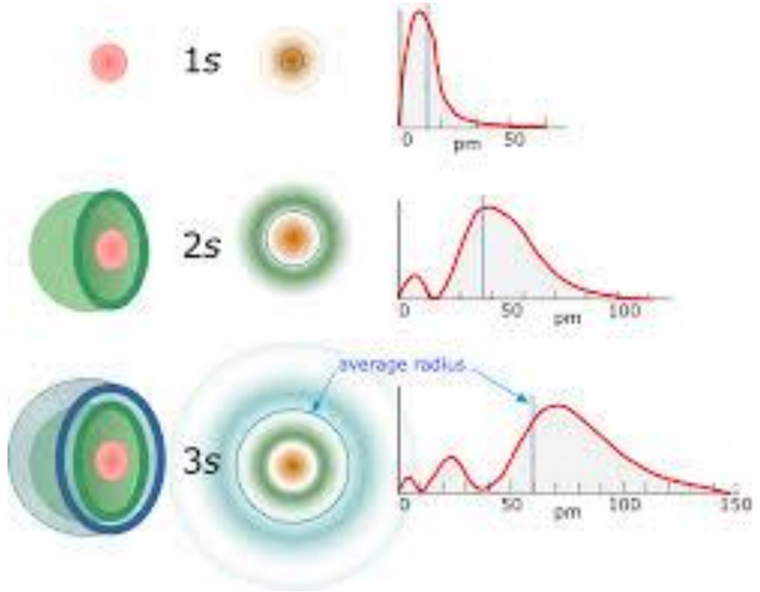
- Principal quantum number (n) = 1, 2, 3, …. ;
- Azimuthal or subsidiary quantum number (l) = 0, 1, 2, n-1
- Magnetic quantum number (m_l) = 0, 1, 2, ±l ;
- Electron Spin Quantum Number (m_s) = ± ½ called "spin up" or "spin down"



Quantum number	Name	What it labels	Possible values	Notes
n	principal	electron energy level or shell number	1, 2, 3, …	Except for d-orbitals, the shell number matches the row of the periodic table.
ℓ	azimuthal	orbital type: s, p, d, f	0, 1, 2, …, n-1	0 = s orbital 1 = p orbital 2 = d orbital 3 = f orbital Sub-energy levels-subshells
m_ℓ	magnetic	orbital sub-type	integers between and including $-\ell$ and $+\ell$: $-\ell, -\ell+1, \ldots \ell-1, \ell$	ℓ = 0 (s): 2 e^- in one orbital ℓ = 1 (p): 2 e^- in each of three sub orbitals (p_x, p_y, p_z) ℓ = 2 (d): 2 e^- in each of 5 sub orbitals (d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2})
m_s	spin	electron spin	$\pm\frac{1}{2}$	Spins in any single sub-orbital must be paired.

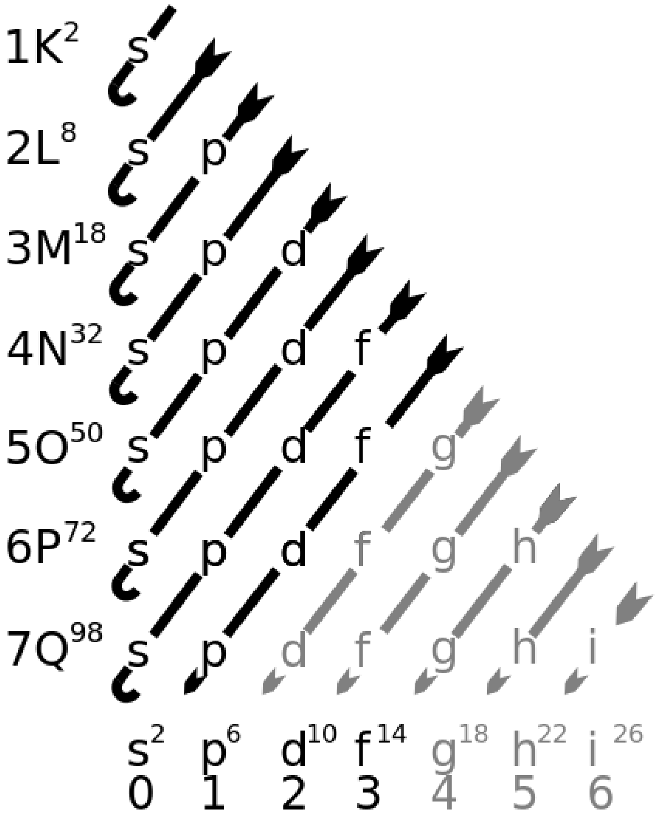
Very minor effect on the energy of an e-

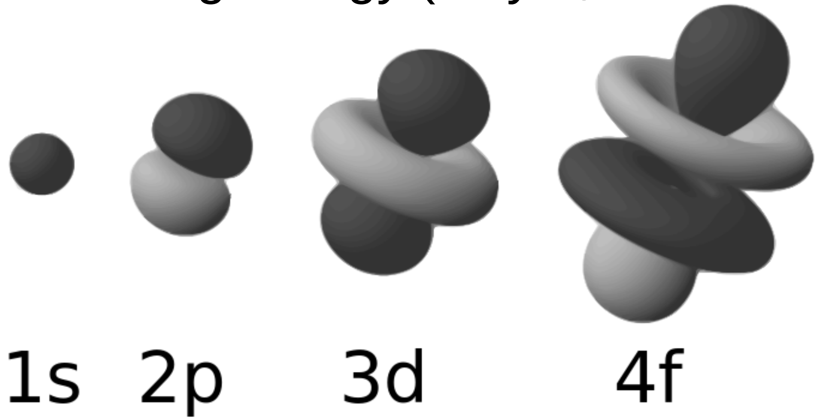
Specifies the spatial orientation of the atomic orbitals and has little effect on the energy of e^-

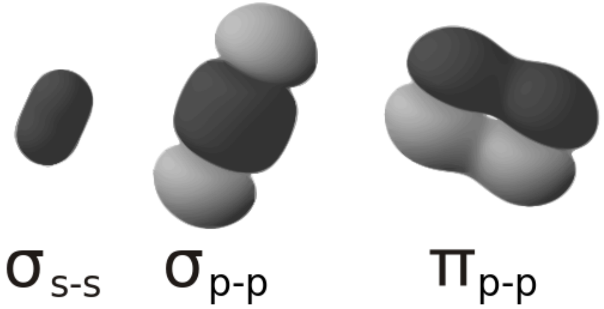


Quantum Numbers: Filling of Orbitals

Electrons that occupy the outermost filled shell – **the valence electrons** – they are responsible for bonding. Electrons fill quantum levels in order of increasing energy (only n, *l* make a significant difference).







$1s^2_2\,2s^2_4\,2p^6_{10}\,3s^2_{12}\,3p^6_{18}\,4s^2_{20}\,3d^{10}_{30}\,4p^6_{36}\,5s^2_{38}\,4d^{10}_{48}\,5p^6_{54}\,6s^2_{56}\,4f^{14}_{70}\,5d^{10}_{80}\,6p^6_{86}\,7s^2_{88}\,5f^{14}_{102}\,6d^{10}_{112}\,7p^6_{118}$

Examples:	Argon, Z = 18: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ Iron, Z = 26: $1s^2\,2s^2\,2p^6 3s^2\,3p^6\,3d^6\,4s^2$

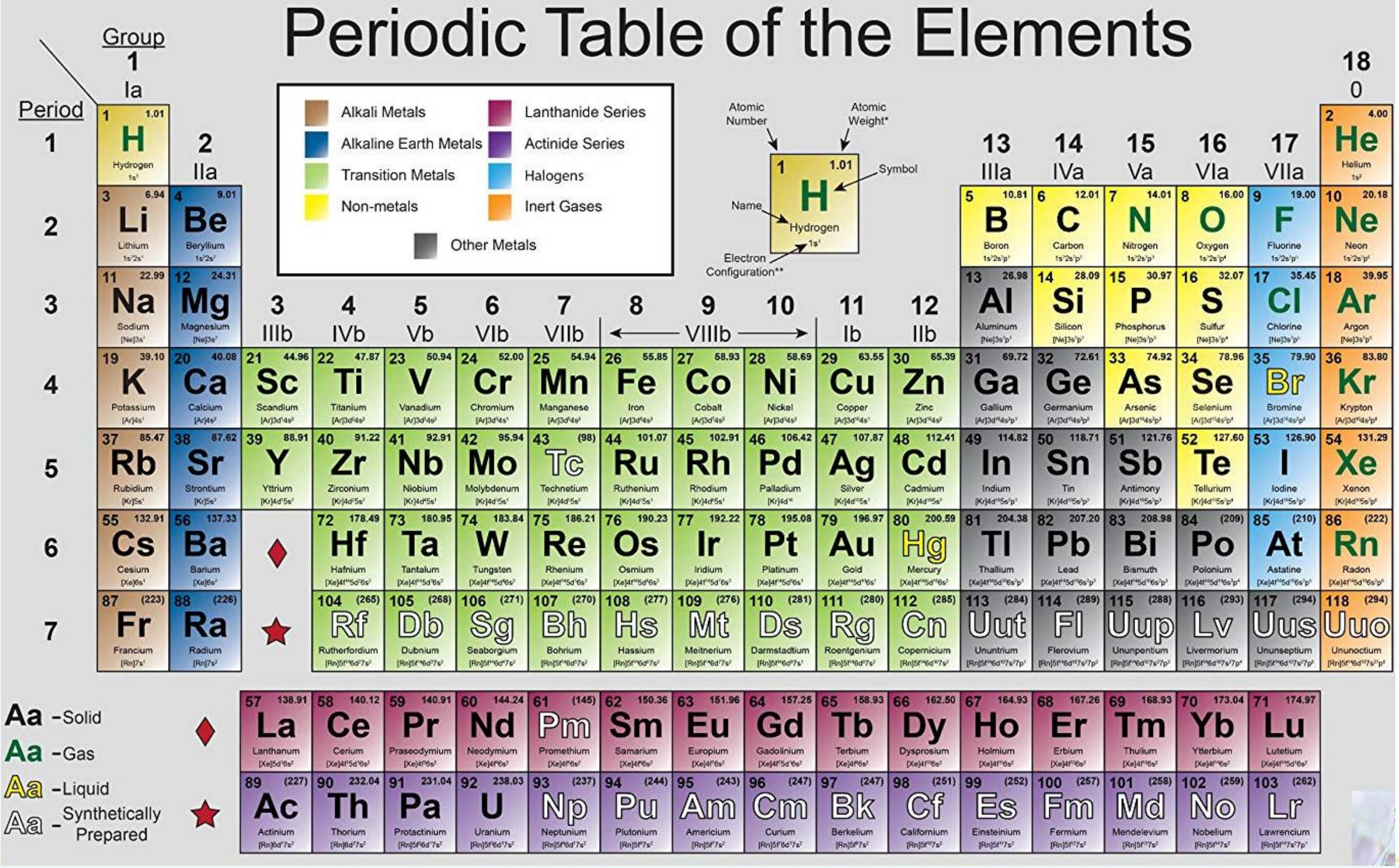
Electrons in Atom: Filling of Orbitals

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Electron configurations where all states within valence electron shell are filled are stable → unreactive inert or noble gas.

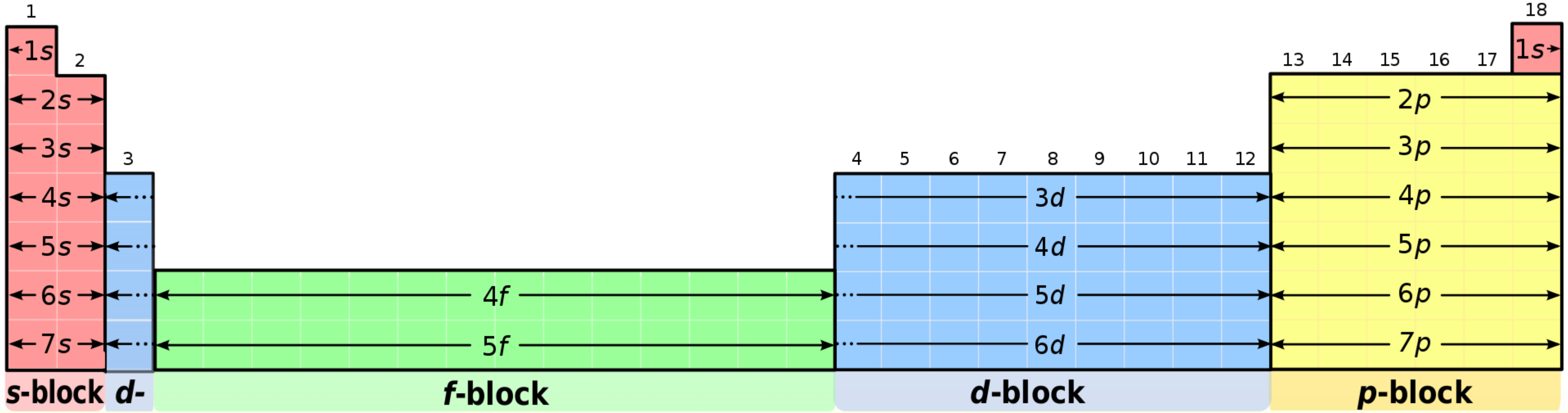
Periodic Table

Arranged by **atomic number, electron configuration & recurring chemical properties**



Electrons in Atom: Filling of Orbitals

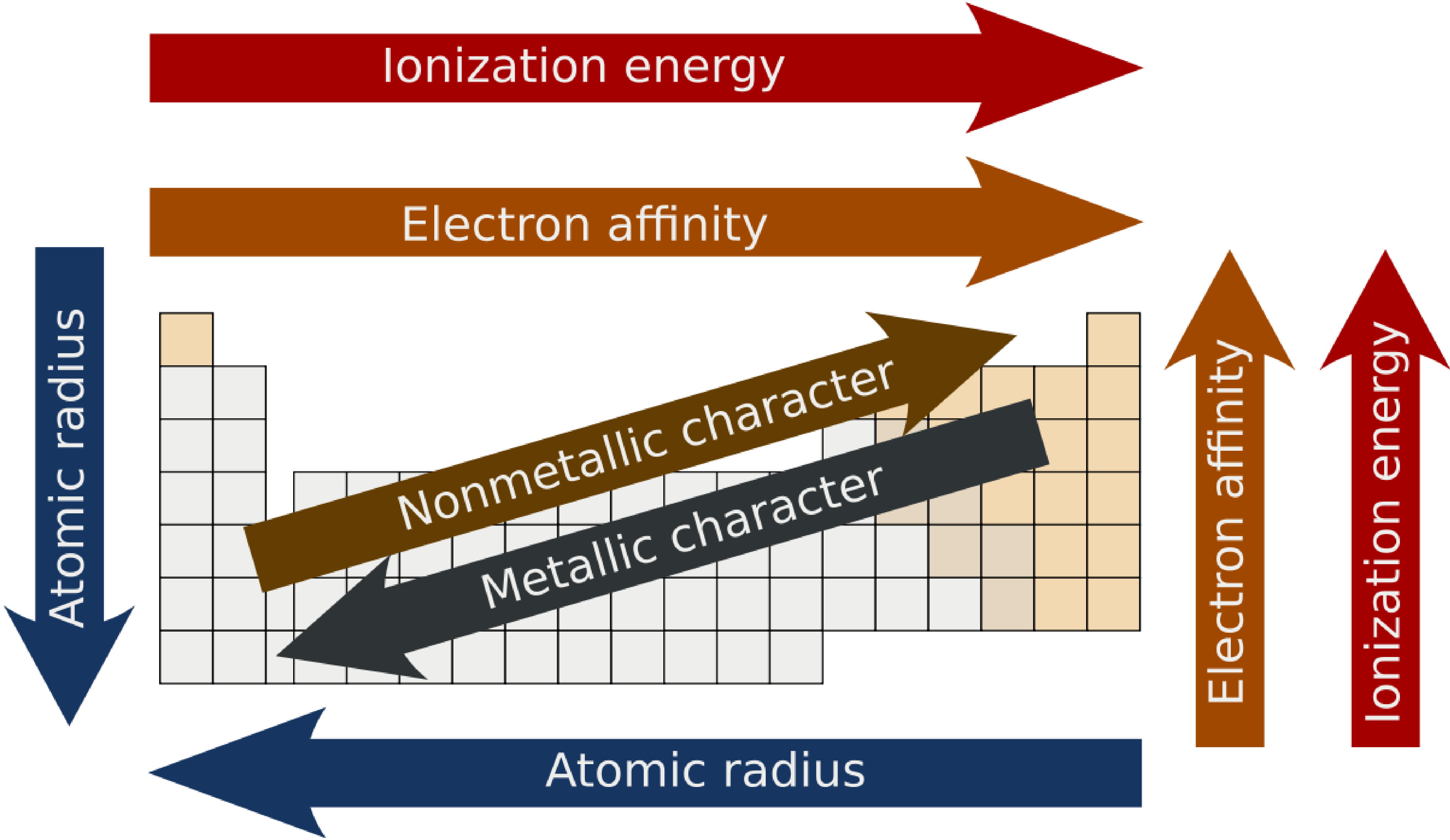
Group → / Period ↓	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og



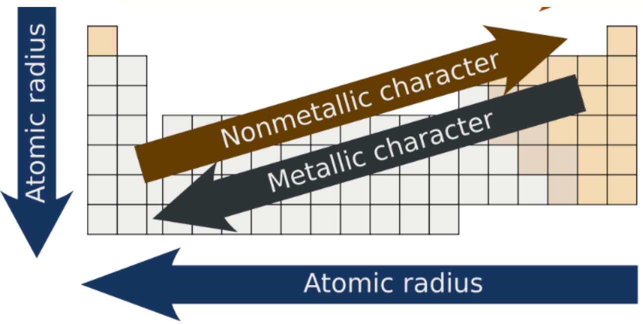
Electrons in Atom: Physical and Chemical properties

- **Ionization energy** is the minimum amount of energy required to remove the valence electron, of an isolated neutral gaseous atom or molecule

- **Electron affinity** is defined as the amount of energy released when an electron is attached to a neutral atom or molecule

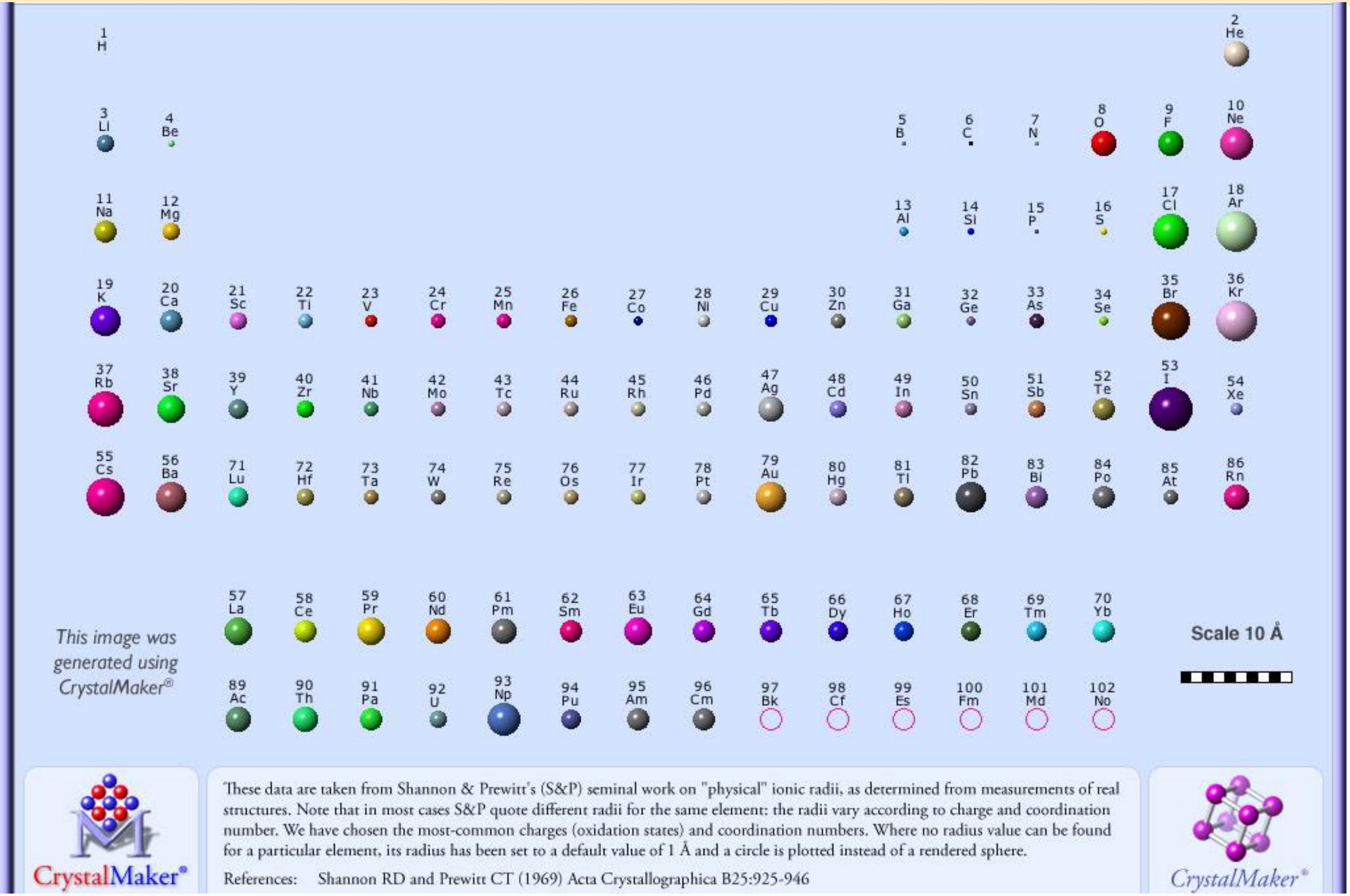


Periodic Table –Atomic Radius



- Atomic radius increases with increasing period

- Atomic radius decreases with increasing group



Electronegativity, χ

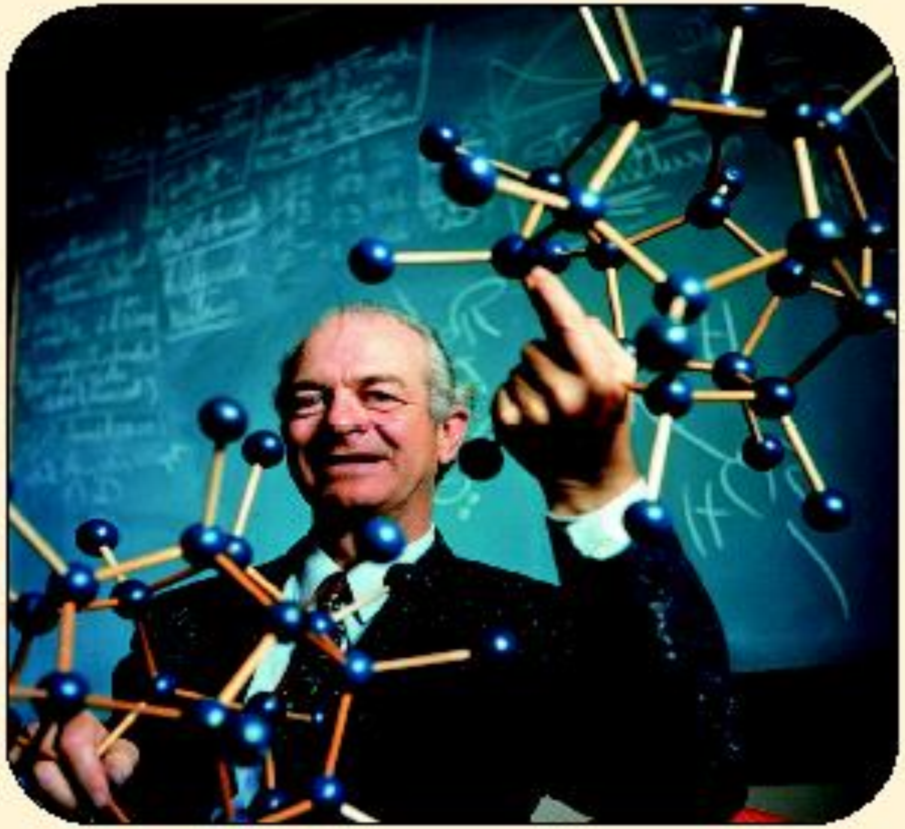
χ is a measure of the ability of an atom in a molecule to attract electrons to itself.

Concept proposed by Linus Pauling 1901-1994

The only person to receive two unshared Nobel prizes

(for Peace and Chemistry).

Chemistry areas: bonding, electronegativity, protein structure



▲ Linus Pauling 1901–1994 *(Thomas Hollyman/ Photo Researchers, Inc.)*

Periodic Table

give up 1e-

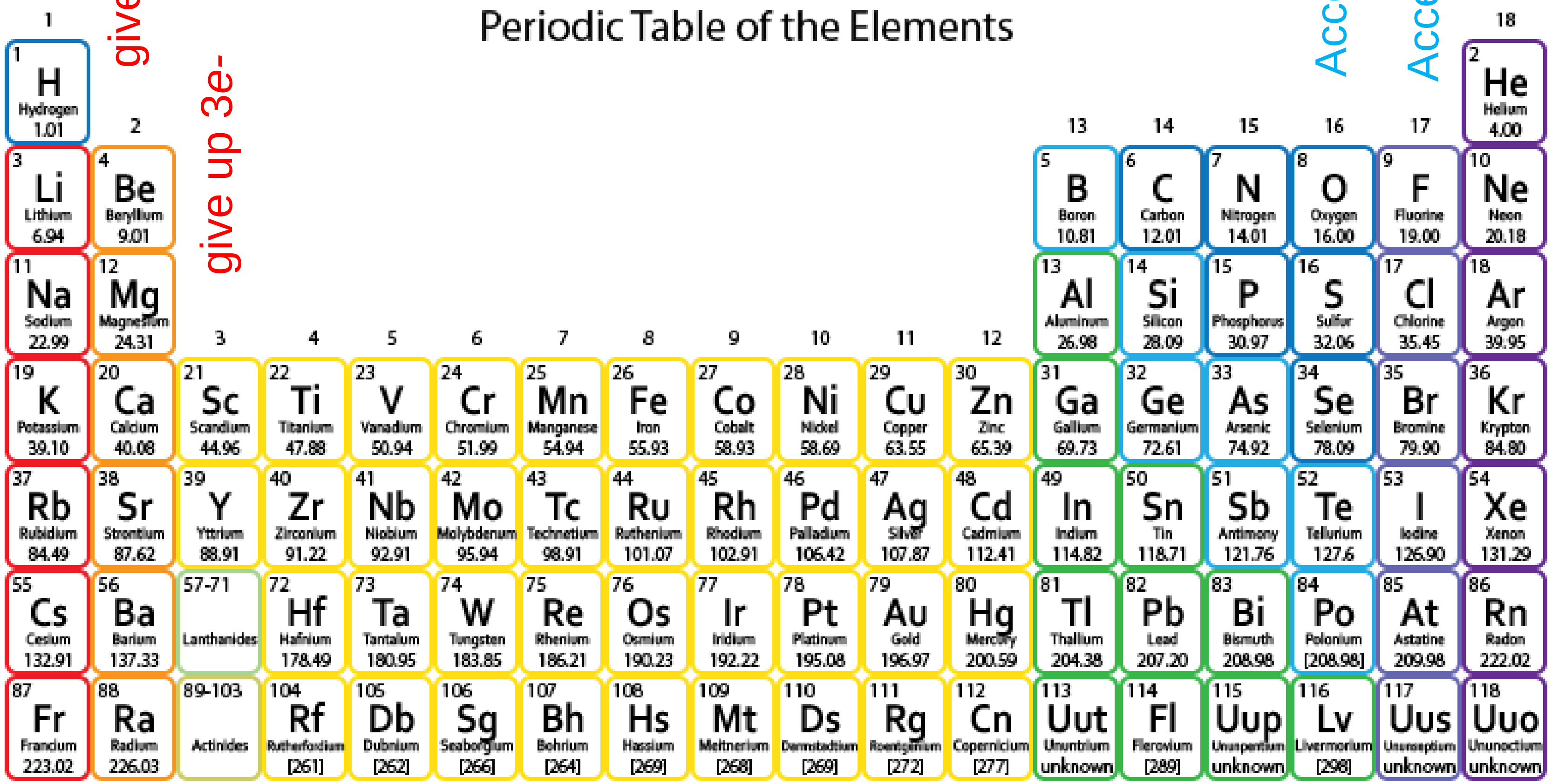
give up 2e-

give up 3e-

Accept 2e-

Accept 1e-

Inert gases



Electropositive elements:
Readily give up electrons to become + ions.

Electronegative elements:
Readily acquire electrons to become - ions.

Periodic Table - Electronegativity

1.5 - 1.9

2.0 - 2.4

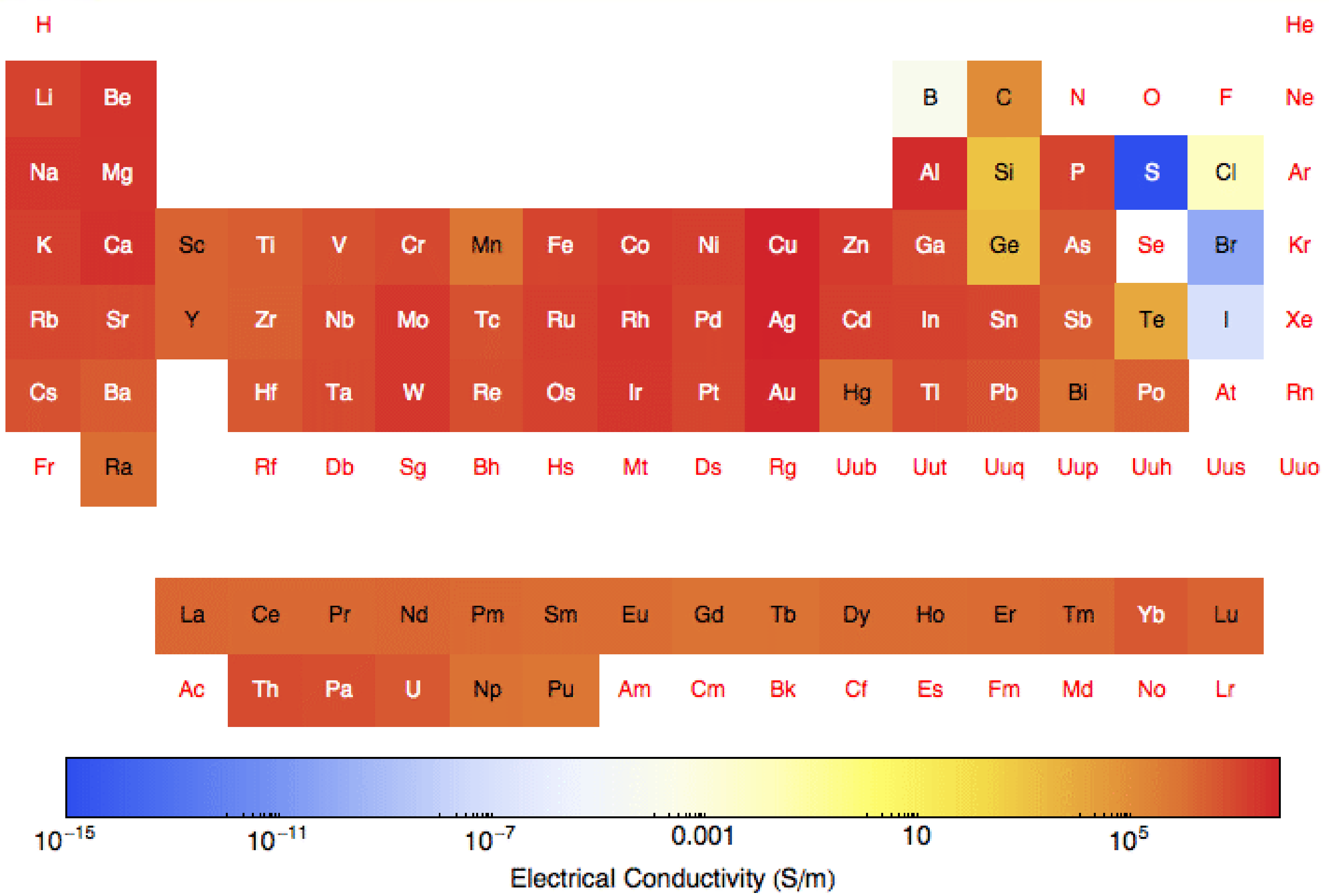
3.6 - 3.9

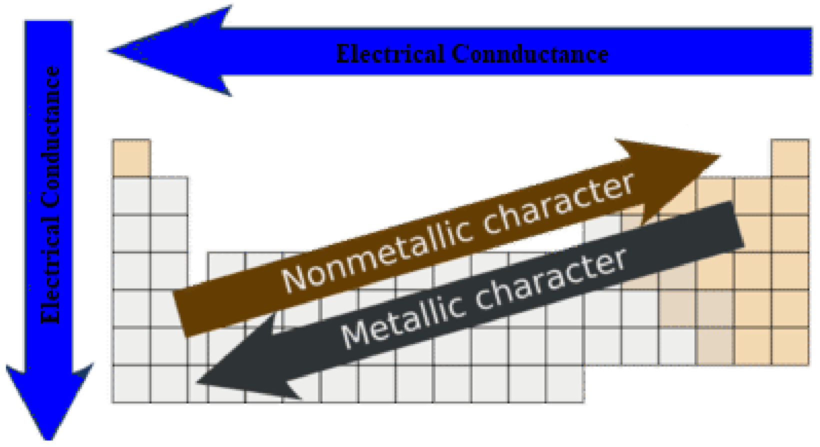
4.0 +

H 2.1																	He --
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne --
Na 0.9	Mg 1.3	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	Al 1.6	Si 1.9	P 2.2	S 2.5	Cl 3.0	Ar --
K 0.8	Ca 1.3	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 2.8	Kr --
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 2.1	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe 2.6
Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At 2.2	Rn --
Fr 0.7	Ra 0.9	Ac 1.1	Rf --	Db --	Sg --	Bh --	Hs --	Mt --	Uun --	Uuu --	Uub --		Uuq				

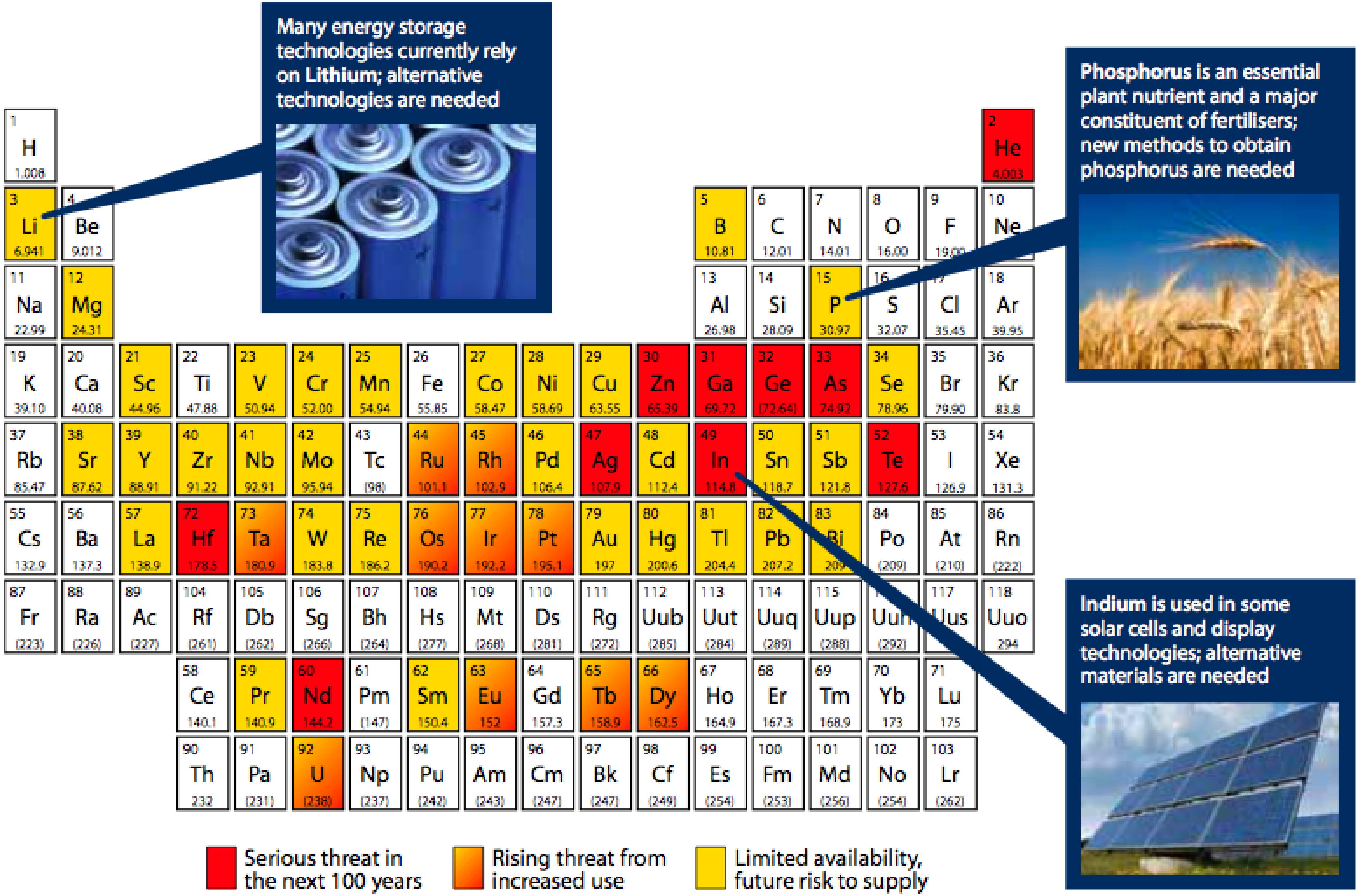
- **Electronegativity** - a measure of how willing atoms are to accept electrons
- **Subshells with one electron** → low electronegativity
- **Subshells with one missing electron** → high electronegativity
- **Electronegativity increases from left to right**
- **Metals are electropositive** – they can give up their few valence electrons to become positively charged ions

Periodic Table – Electrical Conductivity

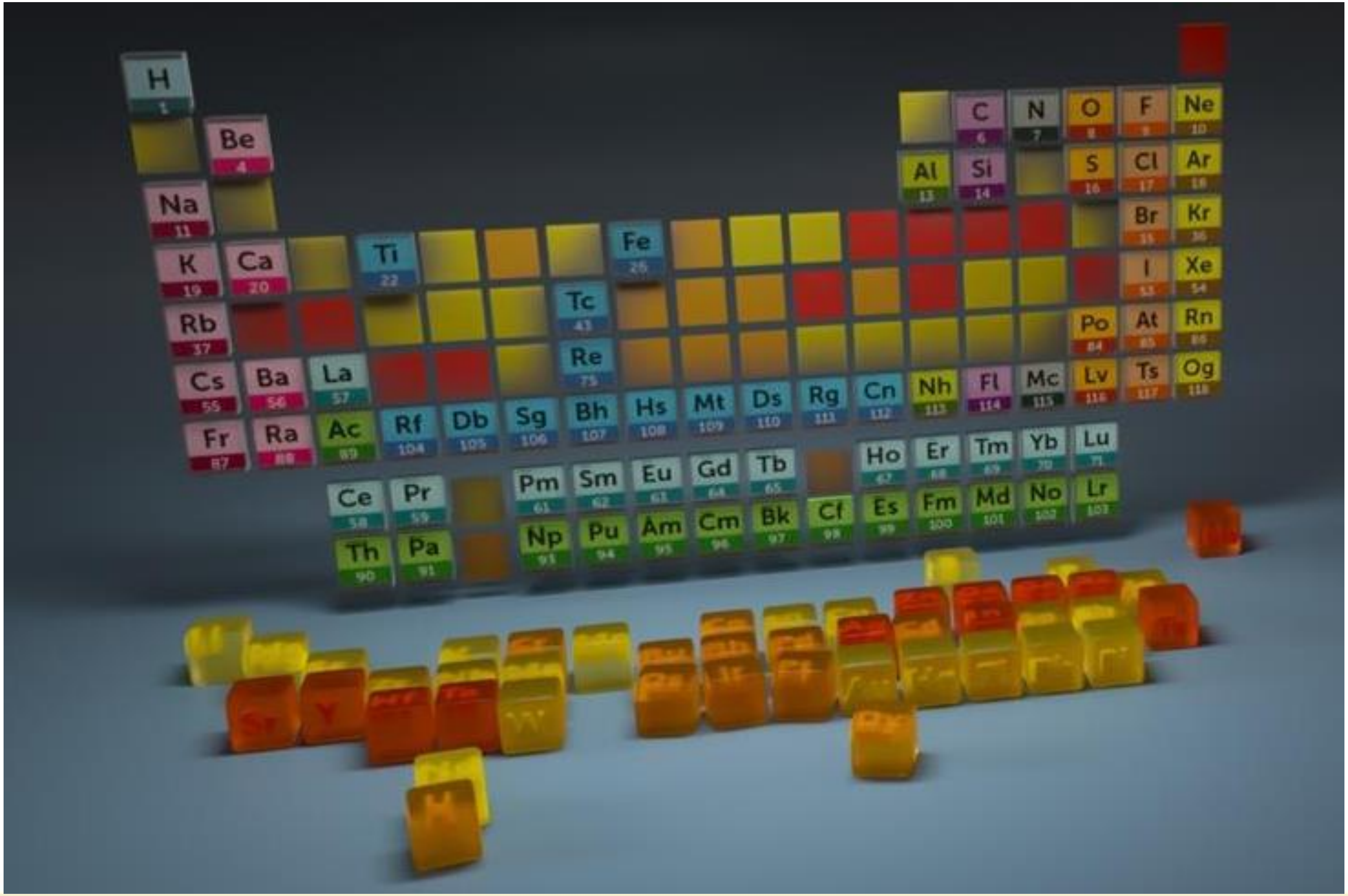




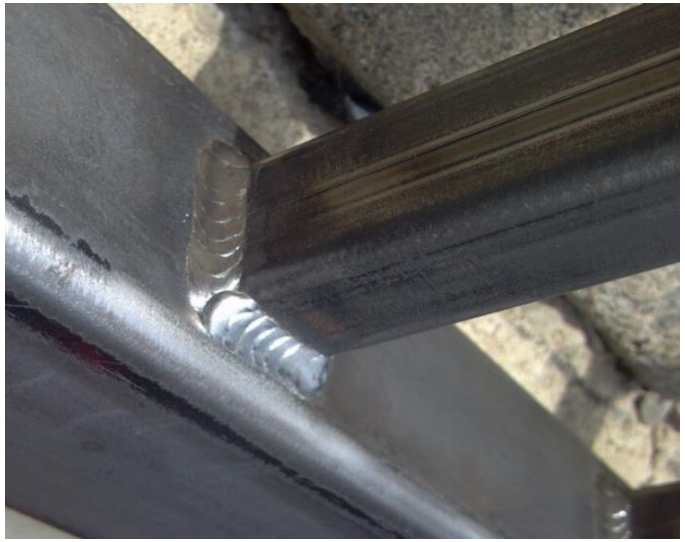
Endangered Elements and their Conservation

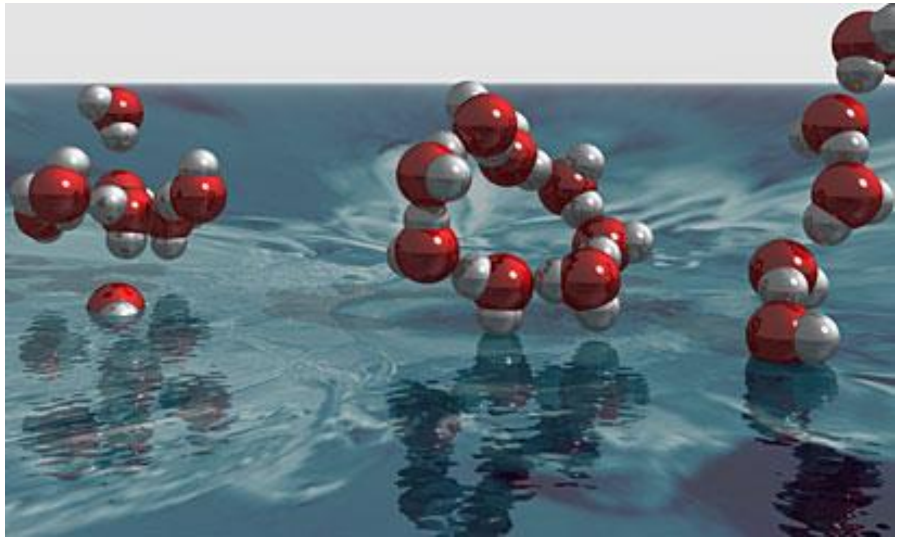


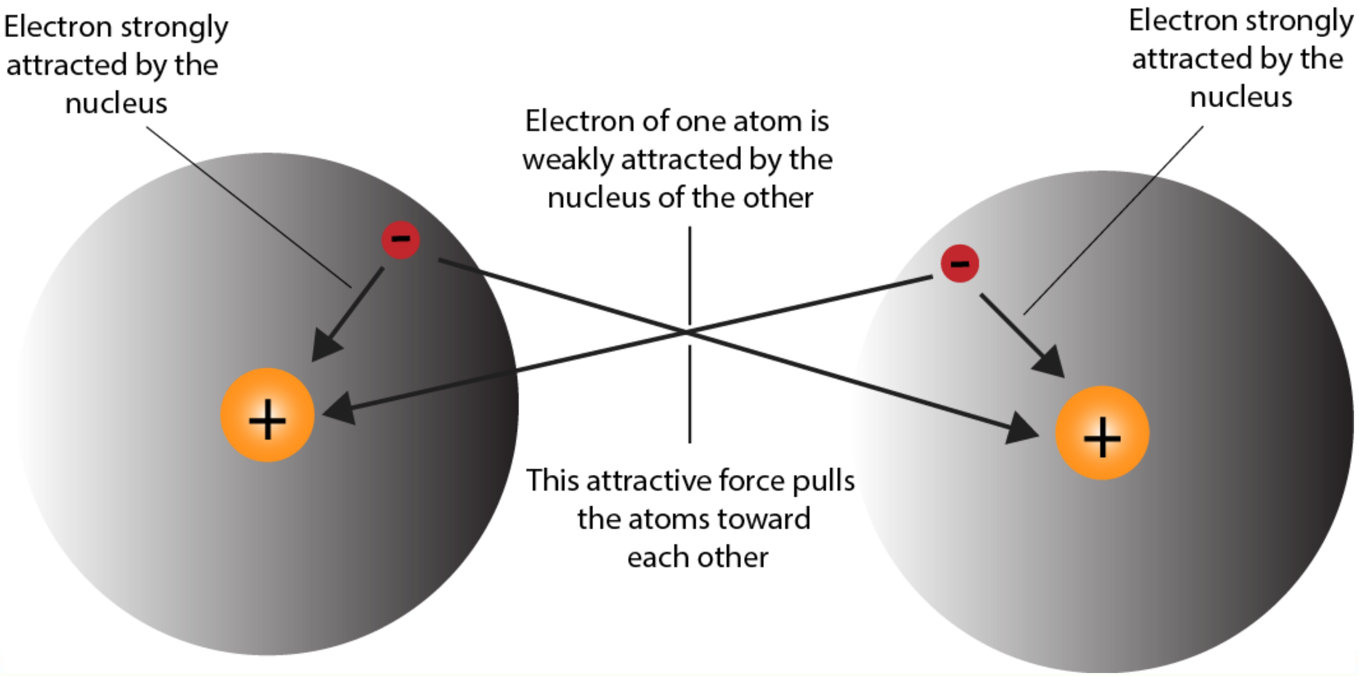
How will we save our endangered elements?



Bonding Forces and Energies

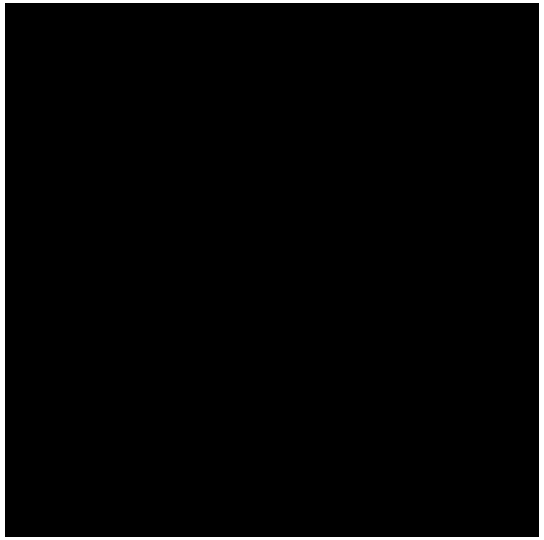






Considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.

Will the atoms collapse on themselves?



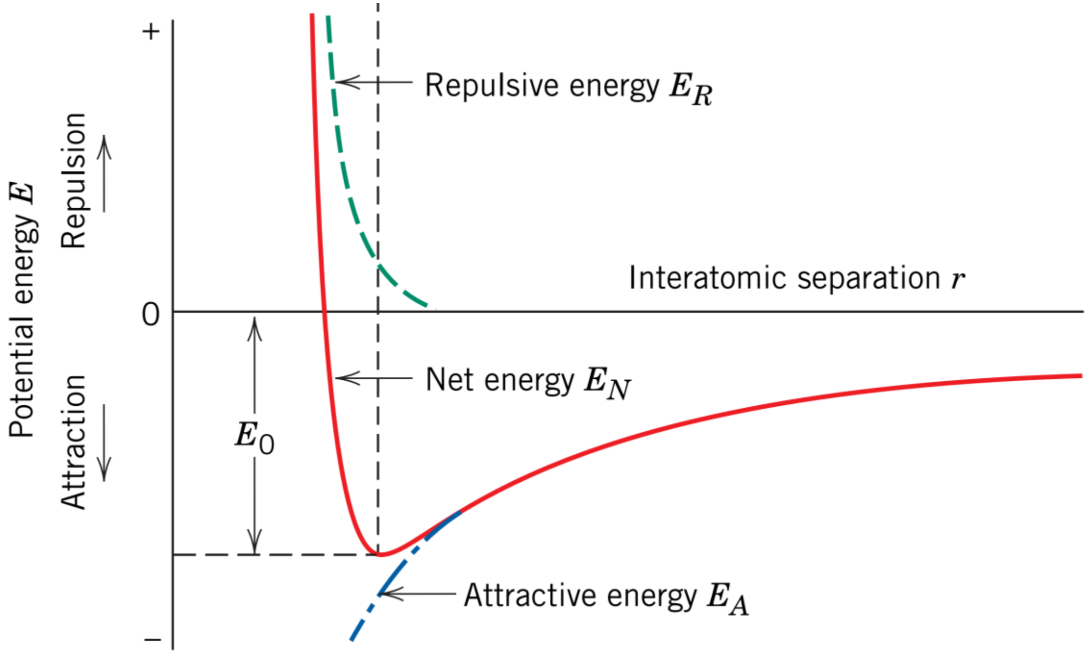
The net force F_N between the two atoms is just the sum of both attractive and repulsive components;

$$\boldsymbol{F_{Net} = F_{Attractive} + F_{Repulsive}}$$

At the state of Equilibrium: F_A and F_R are equal in magnitude but opposite in sign, there is no net force— $F_A + F_R = 0$

It is more convenient to work with the potential energies between two atoms instead of forces. Mathematically, energy (E) and force (F) are related as

$$E = \int F\,dr$$



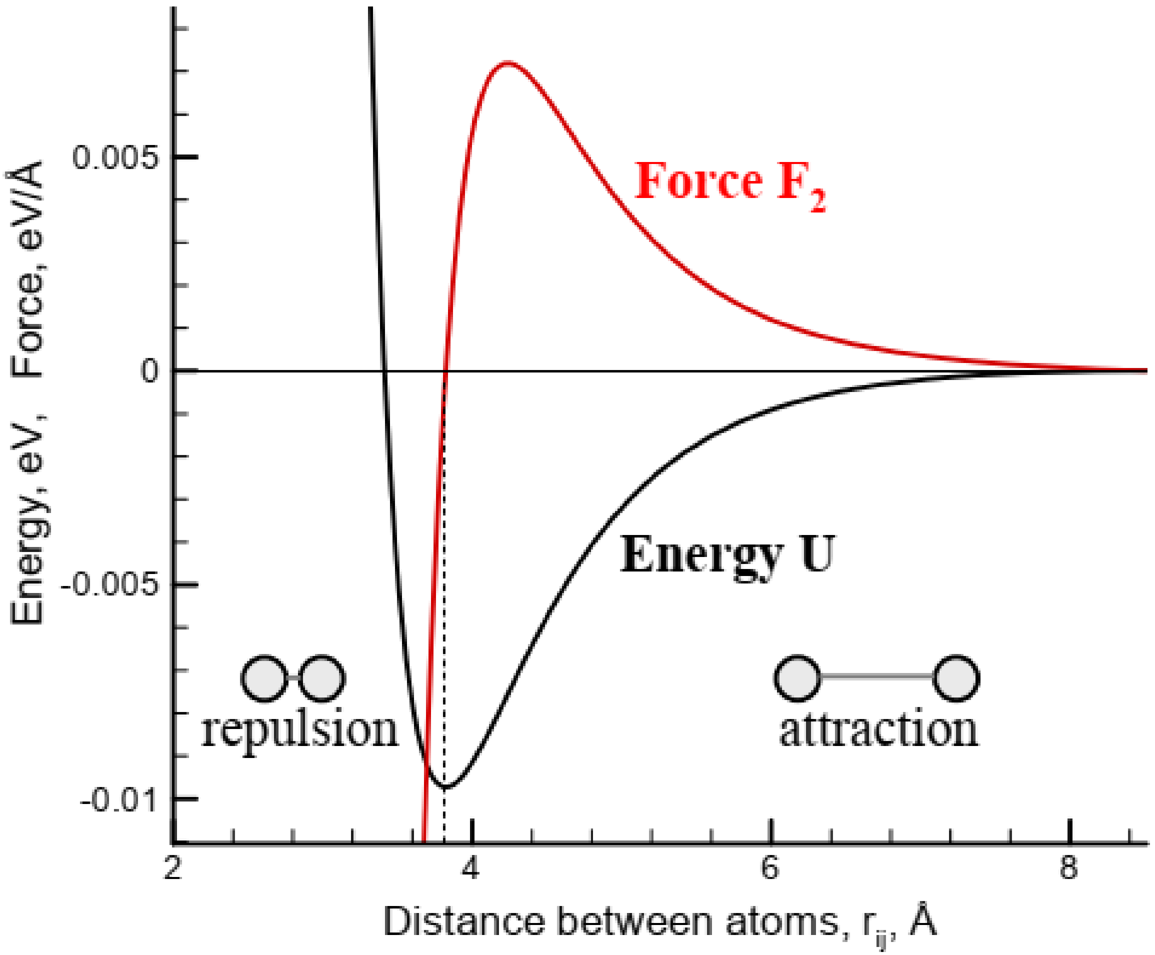
For atomic systems

$$E_N = \int_r^\infty F_N\,dr \quad = \int_r^\infty F_A\,dr + \int_r^\infty F_R\,dr \quad = E_A + E_R$$

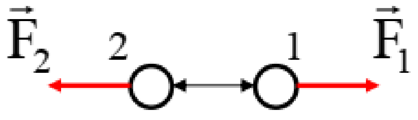
E_N, E_A, and E_R are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms.

Bonding energy for these two atoms, E_0, corresponds to the energy at this minimum point

Bonding Energies and Forces



$$\vec{F}_1 = -\vec{F}_2 = -\frac{dU(r_{12})}{dr_{12}}$$



$$r_{12} = \left|\vec{r}_1 - \vec{r}_2\right|$$

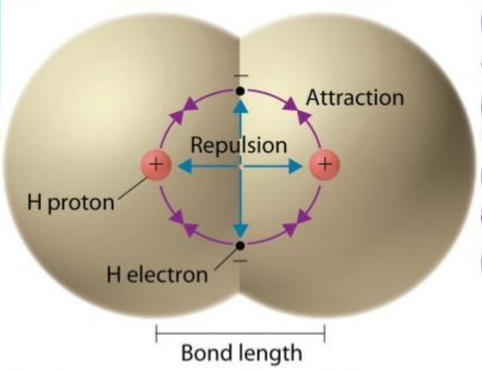
Forces can be calculated from the potential energy of interatomic interaction.

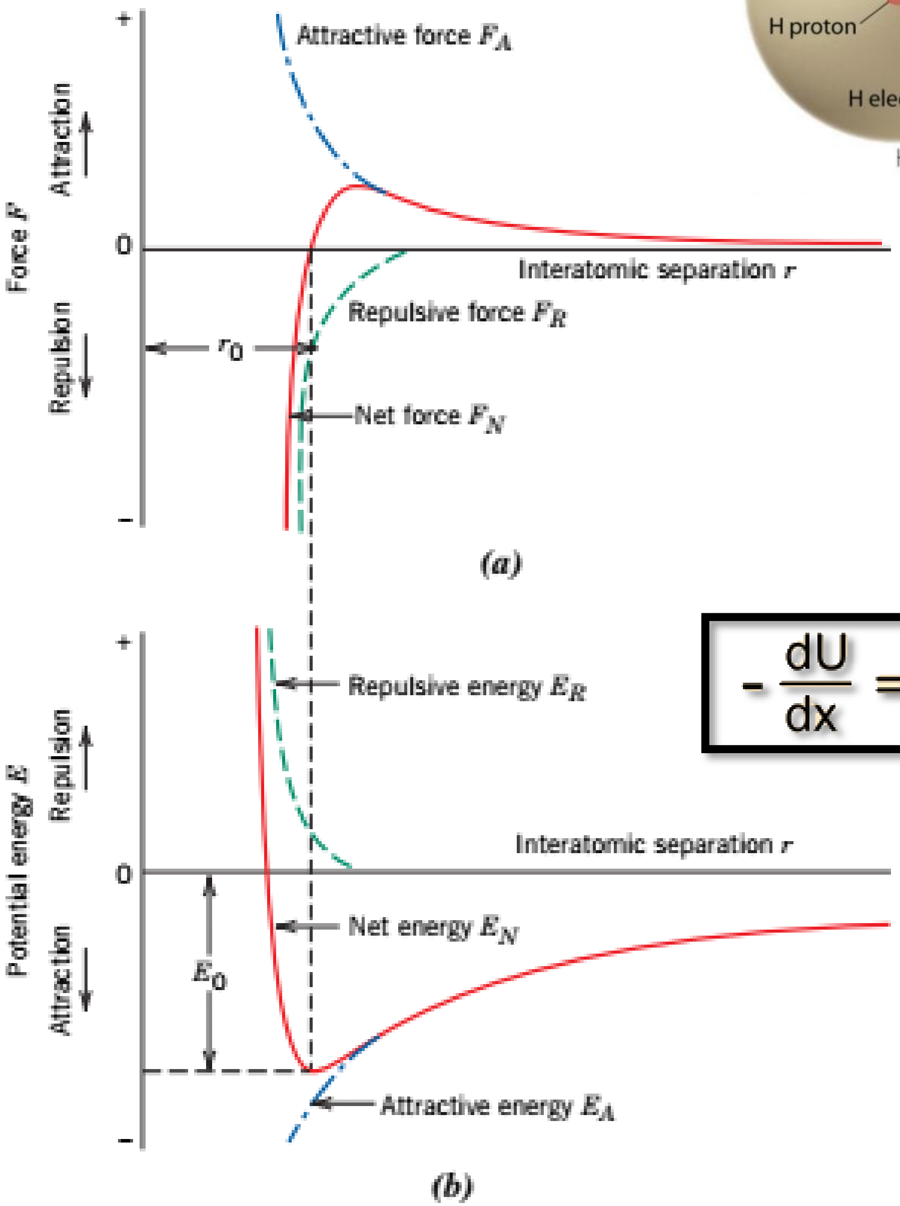
For example, for a system of two atoms (e.g. a diatomic molecule), the potential energy depends only on the distance between the two atoms $U(r_{12})$

Bonding Forces and Energies

- Considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.
- At larger distances, the interactions are negligible.
- As the atoms approach, each exerts forces on the other.
  – **Attractive**
  – **Repulsive**

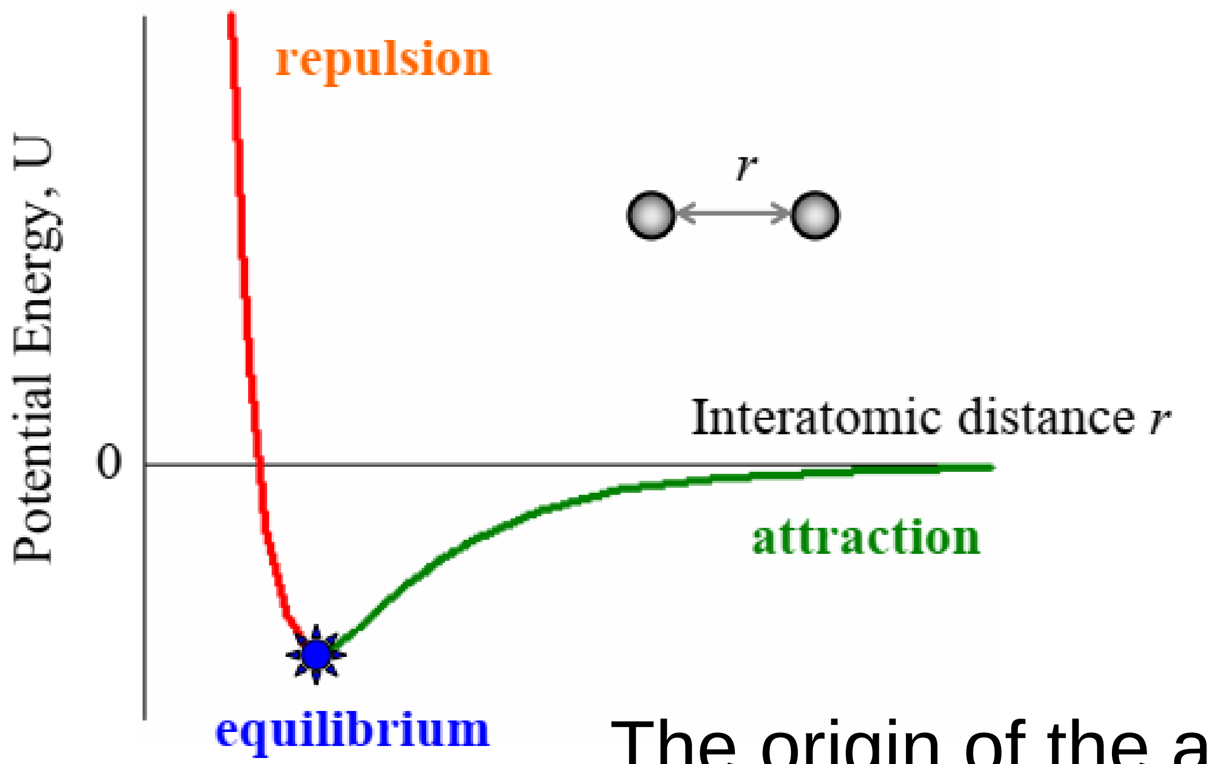
Ultimately, the outer electron shells of the two atoms begin to overlap, and a strong repulsive force comes into play





$$-\frac{dU}{dx} = F(x)$$

Bonding Models



The repulsion between atoms, when they are brought close to each other, is related to the **Pauli principle**: when the electronic clouds surrounding the atoms starts to overlap,
the energy of the system increases abruptly.

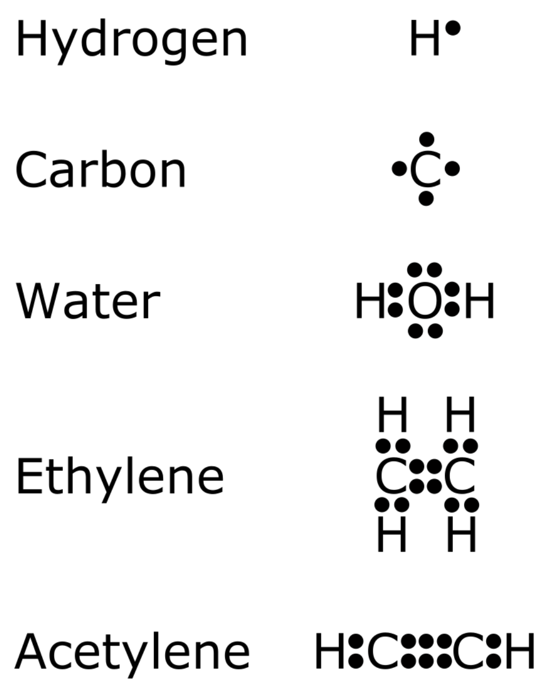
The origin of the attractive part, dominating at large distances, depends on the particular type of bonding.

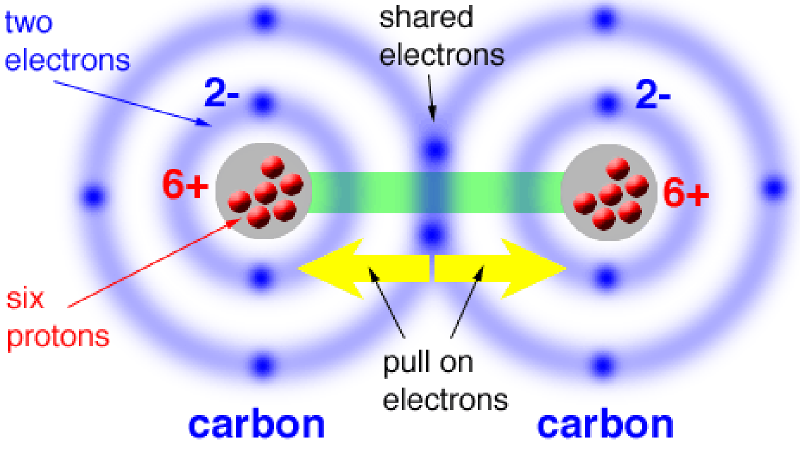
https://phet.colorado.edu/sims/html/atomic-interactions/latest/atomic-interactions_en.html

<iframe src="https://phet.colorado.edu/sims/html/atomic-interactions/latest/atomic-interactions_en.html" width="800" height="600" scrolling="no" allowfullscreen></iframe>

Types of Bonding

- The electronic structure of atoms defines the character of their interaction among each other.
- Filled outer shells result in a stable configuration as in noble inert gases.
- Atoms with incomplete outer shells strive to reach this noble gas configuration by sharing or transferring electrons among each other for maximal stability.
- Strong "primary" bonding results from the electron sharing or transfer.





The electron volt (eV)

– energy unit convenient for description of atomic bonding

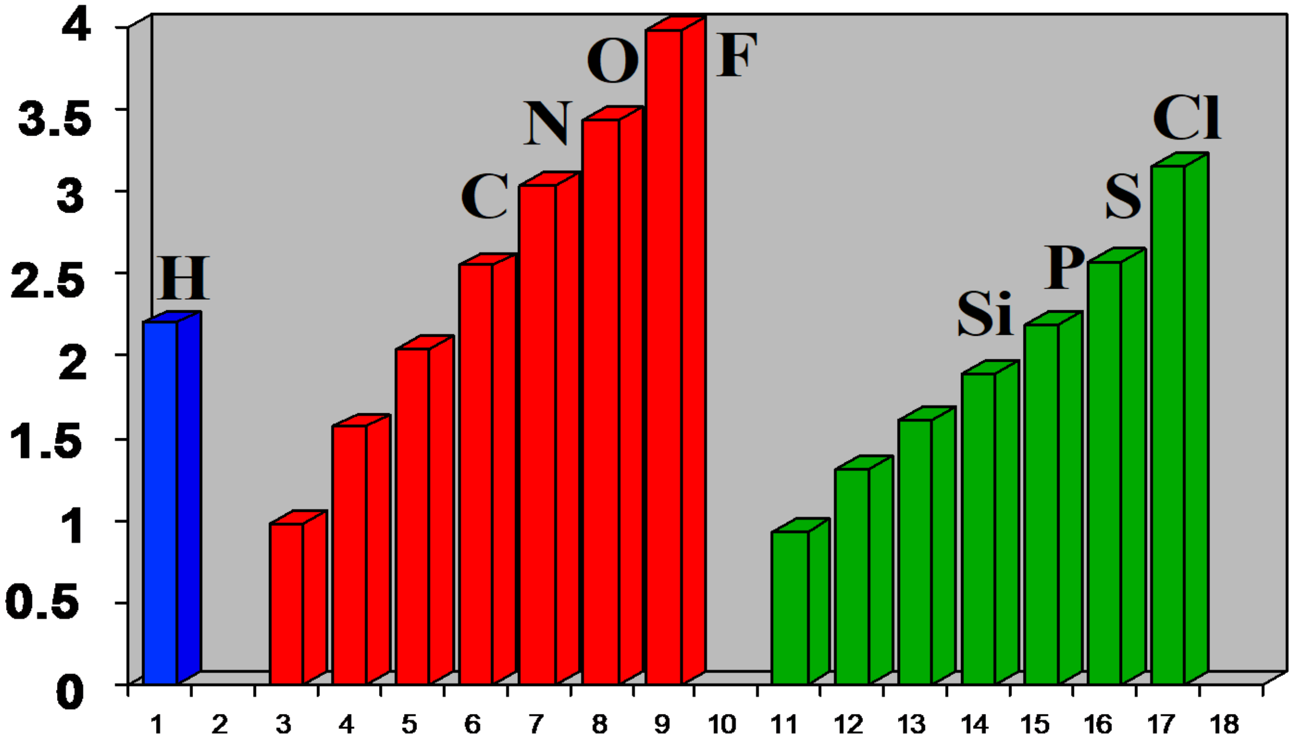
Electron volt - the energy lost / gained by an electron when it is taken through a potential difference of one volt.

$$\mathbf{E = q \times V}$$

for $q = 1.6 \times 10^{-19}$ Coulombs and $V = 1$ volt

$$\mathbf{1\ eV = 1.6 \times 10^{-19}\ J}$$

Electronegativity, χ



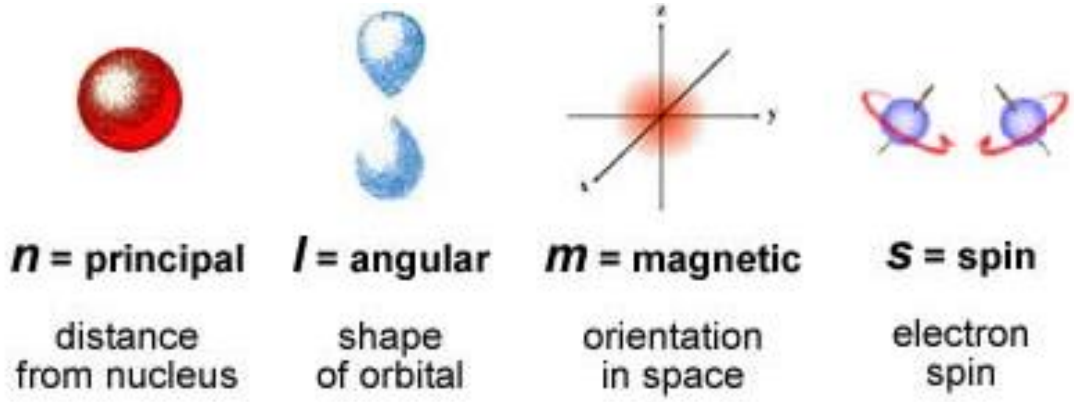
- F has maximum χ.
- Atom with lowest χ is the center atom in most molecules.
- Relative values of χ determine BOND POLARITY (and point of attack on a molecule).

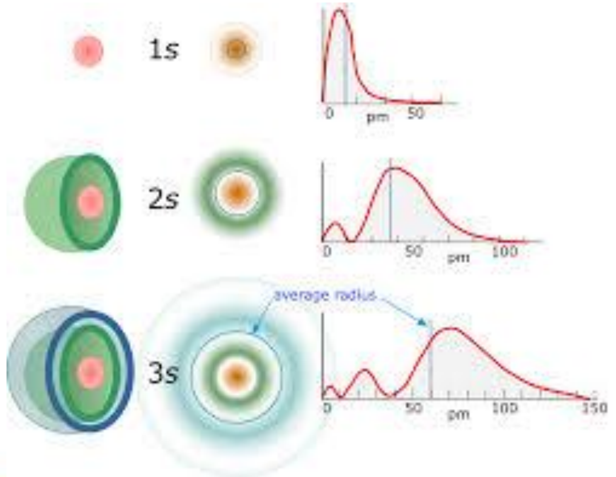
Quantum Numbers

Table 2.1 Summary of the Relationships among the Quantum Numbers n, l, m_l and Numbers of Orbitals and Electrons

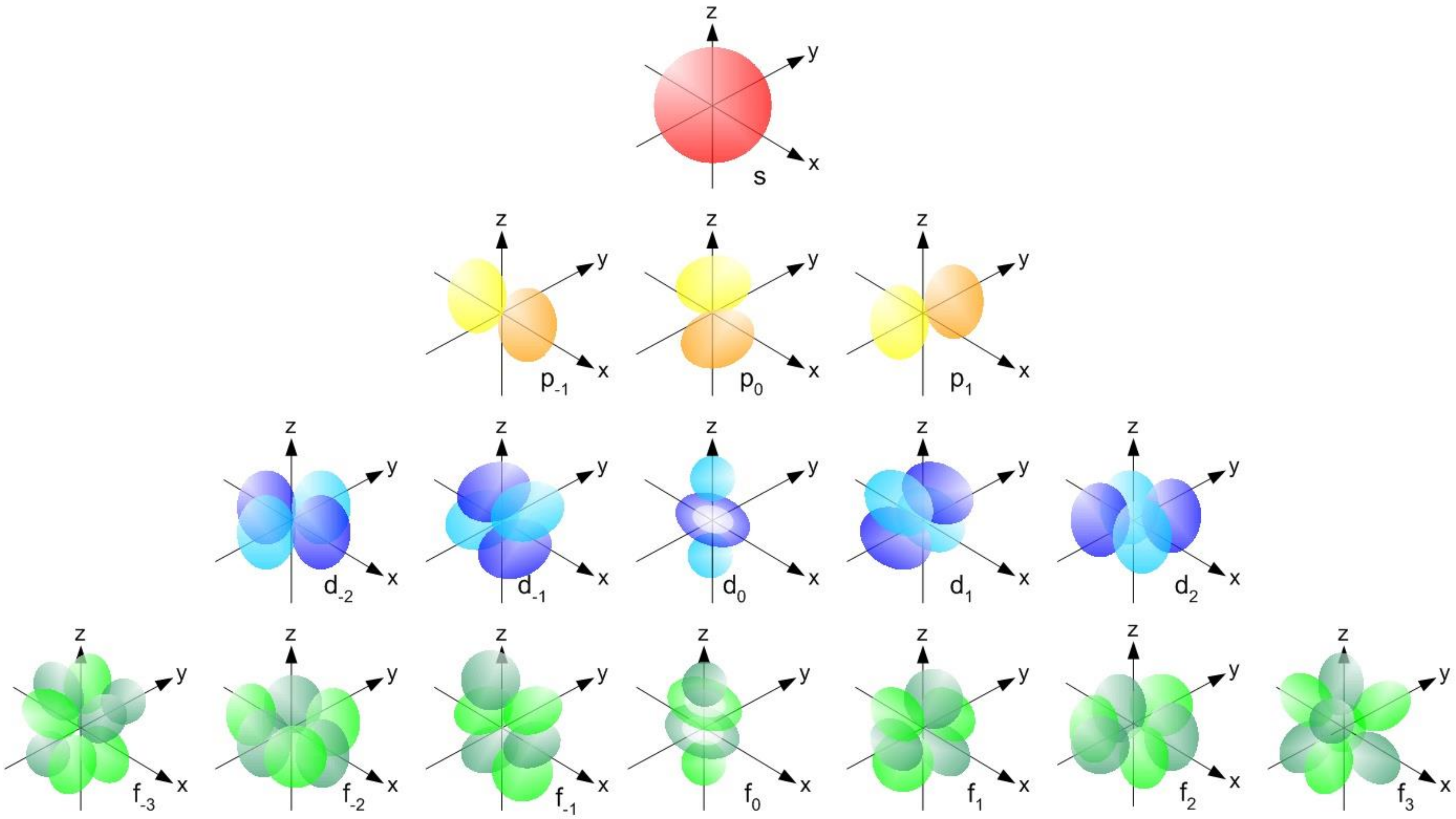
Value of n	*Value of l*	*Values of m_l*	*Subshell*	*Number of Orbitals*	*Number of Electrons*
1	0	0	1*s*	1	2
2	0	0	2*s*	1	2
	1	−1, 0, +1	2*p*	3	6
3	0	0	3*s*	1	2
	1	−1, 0, +1	3*p*	3	6
	2	−2, −1, 0, +1, +2	3*d*	5	10
4	0	0	4*s*	1	2
	1	−1, 0, +1	4*p*	3	6
	2	−2, −1, 0, +1, +2	4*d*	5	10
	3	−3, −2, −1, 0, +1, +2, +3	4*f*	7	14

Source: From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.





Quantum Numbers



Orientations and shapes of electron orbitals