

Topic 1

Atomic Structure and Periodic Properties

Atomic Structure

- History
- Rutherford's experiments
- Bohr model → Interpretation of hydrogen atom spectra
- Wave - particle duality
- Wave mechanics
 - Heisenberg's uncertainty principle
 - Electron density and orbitals
 - The Schrödinger equation and its solutions
 - Electron spin, the Pauli principle, Hund's rule
 - Aufbau principle
 - Effective nuclear charge, shielding and penetration
 - Structure of the periodic table

History

- Democritus (470 - 380 BC): *atoms*
- Lucretius: (94-55 BC): *atoms assembled*
- Aristoteles (384-322) BC: *matter and essence*
- Robert Boyle: (1627-91) revived Democritus ideas
- John Dalton's experiments (1808):
showed that matter consists of elementary particles (=atoms), which, combined in fixed relative portions, form molecules

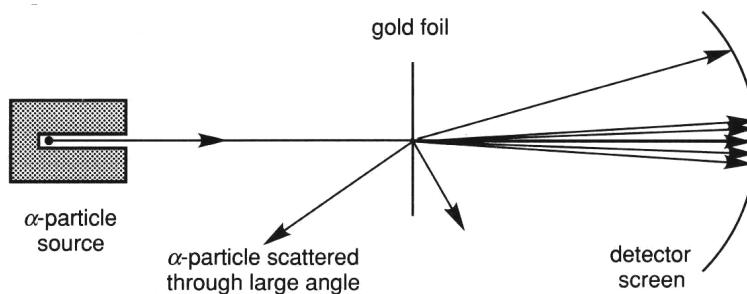
John Dalton



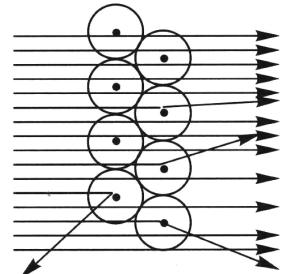
"We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen."

John Dalton (A New System of Chemical Philosophy, 1808)

Rutherford's experiment (1906)



Atoms must consist of a small, but very massive, positively charged nucleus in order to explain the observed scattering of α -particles on gold atoms.

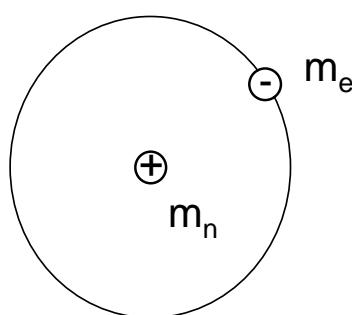


The results of the Rutherford α -particle scattering experiment.

The Bohr Model (1913)

- First model that could account for the spectra of atomic hydrogen

centrifugal force = coulombic attraction



Energy = kinetic energy + potential energy

Bohr introduced quantization

- Atomic spectra of hydrogen is not continuous but consists of discrete lines
→ Bohr suggested that the electron can adopt only certain distances r (orbits)

where k is a constant (Bohr radius = 52.9 pm, also a_0), and n is any integer = **QUANTUM NUMBER** of the orbit

- Each allowed orbit corresponds to a different energy level:

$$E_n = -\frac{me^4Z^2}{8\epsilon_0^2 h^2 n^2} = -\frac{k'}{n^2}$$

More mathematical background...

from centrifugal force = coulombic attraction

$$4\pi\epsilon_0 r m v^2 = Z e^2$$

quantizing of the angular momentum:

$$mvr = \frac{nh}{2\pi}$$

Energy = kinetic energy + potential energy

$$E = \frac{1}{2}mv^2 - \frac{1}{4\pi\epsilon_0} \cdot \frac{Ze^2}{r}$$

With these three equations, the radius, the energy and the velocity of the electron of the H atom with quantum number n (and nuclear charge Z) can be calculated:

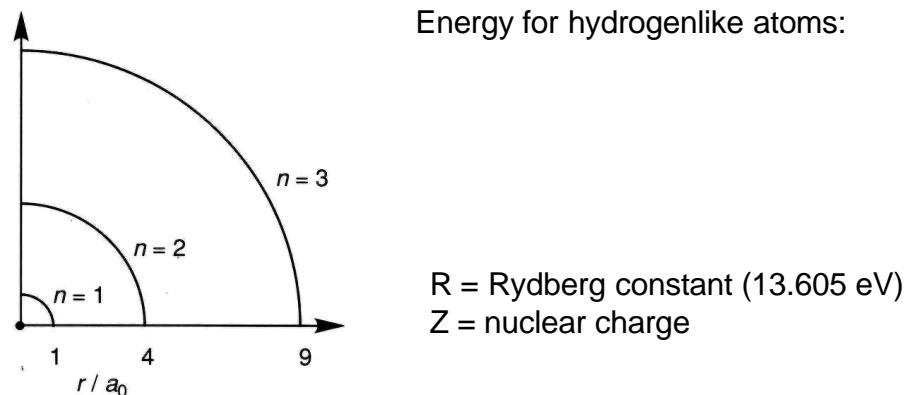
$$\begin{aligned} m &= 9.10939 \times 10^{-31} \text{ kg} \\ e &= 1.60218 \times 10^{-19} \text{ C} \end{aligned}$$

$$\begin{aligned} h &= 6.62608 \times 10^{-34} \text{ Js} \\ \epsilon_0 &= 8.85419 \times 10^{-12} \text{ F m}^{-1} \end{aligned}$$

$$\begin{aligned} 1 \text{ eV} &= 1.602 \times 10^{-19} \text{ J} \\ 1 \text{ J} &= 5.034 \times 10^{22} \text{ cm}^{-1} \end{aligned}$$

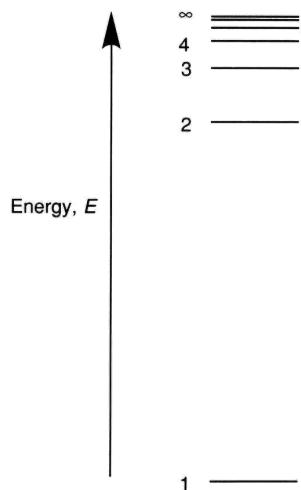
Radii and energies of the first four Bohr radii

n	n^2	r/pm	E_n/J	E_n/cm^{-1}
1	1	52.918	-21.799×10^{-19}	-109679
2	4	211.671	-5.450×10^{-19}	-27420
3	9	476.259	-2.422×10^{-19}	-12186
4	16	846.683	-1.362×10^{-19}	-6855



Energy levels

- Each orbit corresponds to a specific energy level
- The allowed energies are often displayed in a energy level diagram:

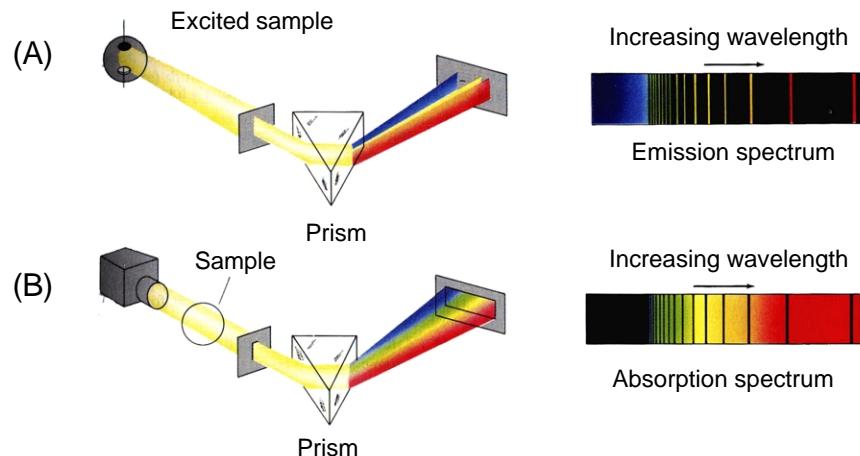


Note: The energy levels are *negative* numbers and indicate the energy of an electron in the corresponding orbit:
 This is the energy required to remove this electron from the orbit
 (=ionization energy).

The principle quantum number n determines this energy value.

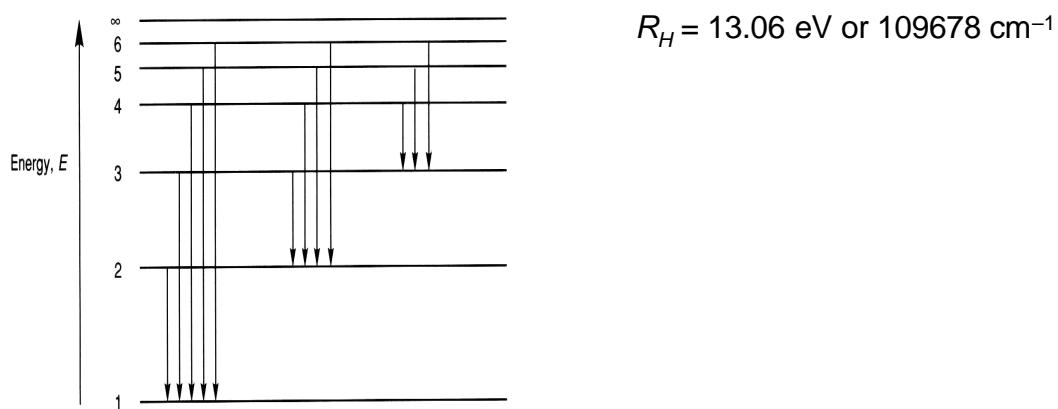
Emission and Absorption Spectra

- Atoms are excited either via electrical discharge (A) or with a white light source
- After passing through a prism the absorbed energy appears as discrete lines



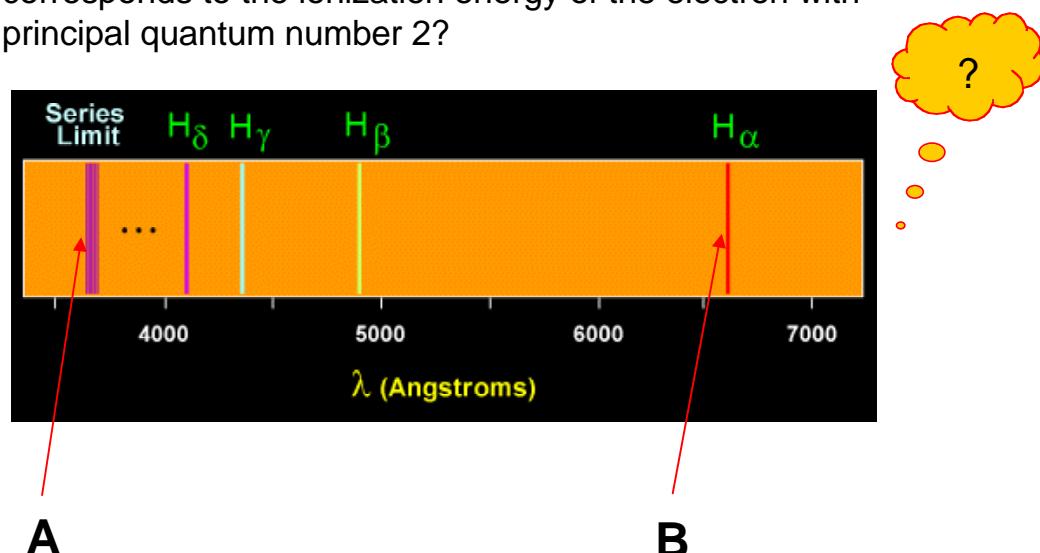
Emission Spectrum of Hydrogen

Transition between energy levels



Quiz: Ionization Energy

- What line in the hydrogen spectrum (Balmer series) corresponds to the ionization energy of the electron with principal quantum number 2?



Conclusions

- Ionization energy is proportional to Z^2 (nuclear charge)
- Radius of hydrogen atom in ground state ($n=1$) is 52.9 pm (= Bohr radius)
The radius is inversely proportional to Z
- The excited state radius is proportional to n^2
- In the ground state the electron has a velocity of
 $v = 2.187 \cdot 10^8 \text{ cms}^{-1}$
- Bohr's model allows accurate prediction of the hydrogen atom spectrum
BUT fails to describe atoms or ions with more than ONE electron
- \Rightarrow New theory required, which is not based on classical mechanics

Electron: Particle or Wave?

- Depending on the experimental conditions, electrons appear either as *particles*, or show properties usually associated with *waves*
 - Electrons are diffracted by crystalline materials, just as observed with X-rays
 - De Broglie relationship:

h : Planck's constant

$m_e v$: momentum of electron

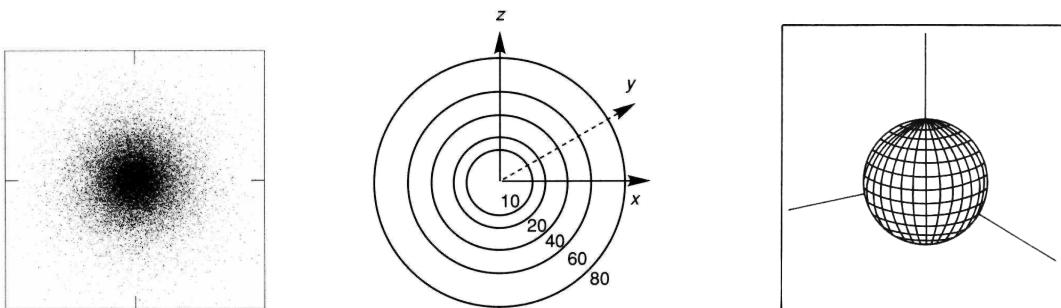
- The photoelectric effect revealed a linear relationship between the kinetic energy of the photon and frequency:

$$E = \frac{1}{2} m_e v^2 = h(v - v_0) \quad \Delta E = h\nu$$

From Orbits to Orbitals: The Uncertainty Principle

- Werner Heisenberg (1927):
It is not possible to determine simultaneously the position **and** momentum of an electron with good precision:
- But: the probability of finding an electron at a particular point can be calculated
- this probability distribution is called an ORBITAL rather than an orbit.

Representation of Orbitals



The Schrödinger Equation

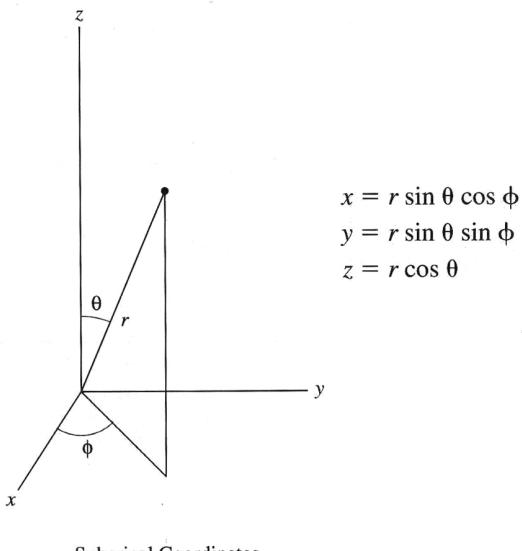
- The probability distribution and energy levels for electrons in atoms and molecules can be calculated using the Schrödinger equation:

$$H\Psi = E\Psi$$

H: Hamilton Operator (Energy)
E: Energy of solution Ψ
 Ψ : wavefunction

- Each solution Ψ of the equation corresponds to a different electron probability distribution with a distinct energy E
- The probability of finding an electron at some point is proportional to $\Psi\Psi^*$ (Ψ^* is the complex conjugate of Ψ)

The Wavefunction



Atomic wavefunctions are expressed in *polar coordinates*:

→ value of Ψ at any given point in space is specified by r , θ and ϕ

The wave function Ψ can be written as:

$$\Psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$$

Quantum Numbers

- Each of the solutions of the Schrödinger equation is labeled by a set of quantum numbers n , l , and m_l
 - n = principle quantum number
 - l = angular momentum quantum number
 - m_l = magnetic quantum number
- Hydrogen atom:
 - n determines the *energy and size* of the orbital
→ can be any integer
 - l determines the *shape* of the orbital
→ any integer between $(n-1)$ and 0
 - m_l determines the *orientation* of the orbital
→ any integer between $+l$ and $-l$

Relationship of quantum numbers to orbital names

<i>n</i>	1	2	2	2	2	3	3	3	3	3	3	3	3
<i>l</i>	0	0	1	1	1	0	1	1	1	2	2	2	2
<i>m_l</i>	0	0	-1	0	1	0	-1	0	1	-2	-1	0	1
name	1s	2s	2p	2p	2p	3s	3p	3p	3p	3d	3d	3d	3d

The names s, p, d, and f is historical and connected with the appearance of the atomic spectroscopy lines:

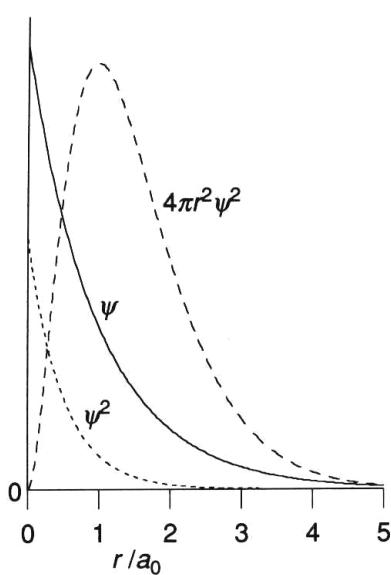
Dependence of orbital name on *l*

<i>l</i>	name	origin of name
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental

The Radial Distribution Function

- The radial part $R(r)$ of a wavefunction $\psi(r)$ is related to the probability [$\psi(r)\psi(r)^*$ or ψ^2] of finding an electron at a specific point with distance r from the nucleus
- The probability of finding an electron at a given distance r from the nucleus is described by the radial probability density function:

Radial Distribution Function



$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-r/a_0}$$

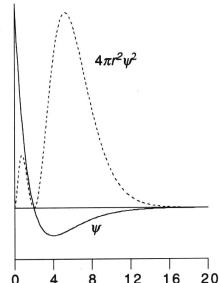
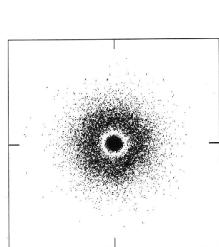
or using a_0 as unit of length ($a_0=1$):

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$$

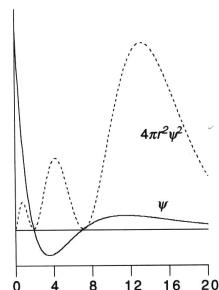
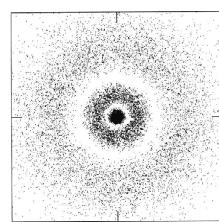
Note: the *maximum probability* is found at $r = a_0$

2s and 3s Orbitals

The s orbitals with $n > 1$ have radial nodes (change of function sign):



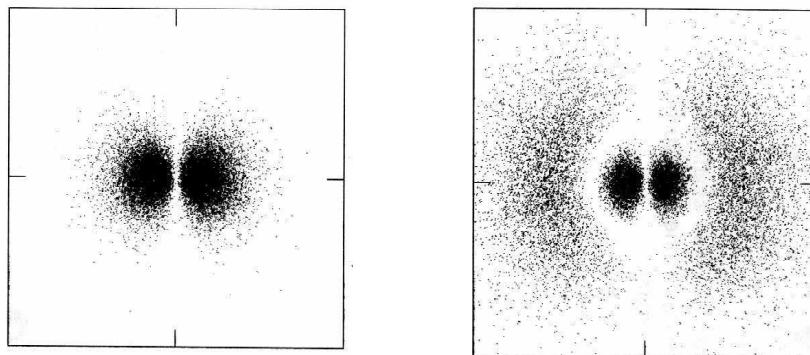
$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} (2-r)e^{-r/2}$$



$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} (27 - 18r + 2r^2) e^{-r/3}$$

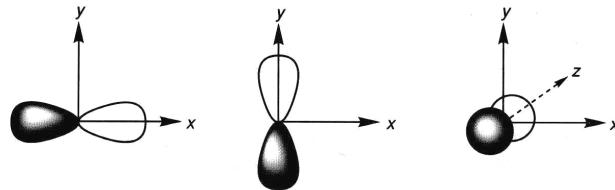
Hydrogen p Orbitals

- Unlike s orbitals, p orbitals are not spherically symmetric
- → they are *directional* and have an angular node:



p_x , p_z and p_y Orbitals

- According to their orientation in space, the three p orbitals are denoted p_x , p_y and p_z



However, the solutions for $m_l = +1$ and -1 with exponential imaginary functions.

→ these can be converted to real functions using their linear combinations:

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{2p_1} + \psi_{2p_{-1}})$$

$$\psi_{2p_y} = \frac{1}{\sqrt{2}}(\psi_{2p_1} - \psi_{2p_{-1}})$$

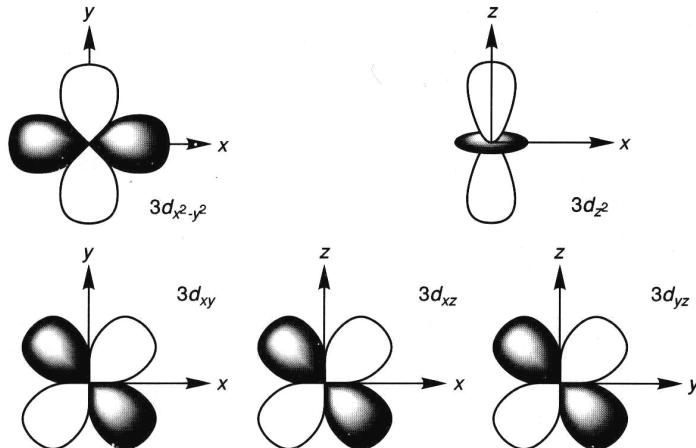
Orbital Shading and Wavefunction Sign

- Wavefunctions are signed quantities
- The sign is important when we consider bonding in molecules
- The wavefunctions sign is often indicated graphically by shading:

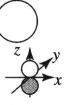
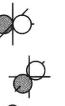
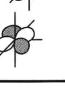
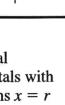
Note: The orbital represents a probability function [$\psi(r)\psi(r)^*$ or ψ^2], which sign is always positive. Only $\psi(r)$ or is a signed quantity!

The Five d Orbitals

- As for the p orbitals, only one d orbital ($3d_{z^2}$) corresponds directly to the value of m_l ($= 0$).
- The wavefunction solutions with $m_l = \pm 1$ and ± 2 are exponential imaginary functions. A real wavefunction is again obtained by linear combinations of these solutions.



Hydrogen Atom Wavefunctions: Angular Factors

Angular factors				Real wave functions		
		Related to angular momentum	Functions of θ	In Polar coordinates	In Cartesian coordinates	Shapes
l	m_l	Φ	Θ			
0(s)	0	$\frac{1}{\sqrt{2}\pi}$	$\frac{1}{\sqrt{2}}$		$\Theta \Phi(\theta, \phi)$	$\Theta \Phi(x, y, z)$
1(p)	0	$\frac{1}{\sqrt{2}\pi}$	$\frac{\sqrt{6}}{2} \cos \theta$		$\frac{1}{2\sqrt{\pi}} \frac{\sqrt{3}}{\pi} \cos \theta$	
	+1	$\frac{1}{\sqrt{2}\pi} e^{i\phi}$	$\frac{\sqrt{6}}{2} \sin \theta$		$\frac{1}{2\sqrt{\pi}} \frac{\sqrt{3}}{\pi} \sin \theta \cos \phi$	
	-1	$\frac{1}{\sqrt{2}\pi} e^{-i\phi}$	$\frac{\sqrt{6}}{2} \sin \theta$		$\frac{1}{2\sqrt{\pi}} \frac{\sqrt{3}}{\pi} \sin \theta \sin \phi$	
2(d)	0	$\frac{1}{\sqrt{2}\pi}$	$\frac{1}{2\sqrt{2}} (3 \cos^2 \theta - 1)$		$\frac{1}{4\sqrt{\pi}} \frac{\sqrt{5}}{\pi} (3 \cos^2 \theta - 1)$	
	+1	$\frac{1}{\sqrt{2}\pi} e^{i\phi}$	$\frac{\sqrt{15}}{2} \cos \theta \sin \theta$		$\frac{1}{2\sqrt{\pi}} \frac{\sqrt{15}}{\pi} \cos \theta \sin \theta \cos \phi$	
	-1	$\frac{1}{\sqrt{2}\pi} e^{-i\phi}$	$\frac{\sqrt{15}}{2} \cos \theta \sin \theta$		$\frac{1}{2\sqrt{\pi}} \frac{\sqrt{15}}{\pi} \cos \theta \sin \theta \sin \phi$	
	+2	$\frac{1}{\sqrt{2}\pi} e^{2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$		$\frac{1}{4\sqrt{\pi}} \frac{\sqrt{15}}{\pi} \sin^2 \theta \cos 2\phi$	
	-2	$\frac{1}{\sqrt{2}\pi} e^{-2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$		$\frac{1}{4\sqrt{\pi}} \frac{\sqrt{15}}{\pi} \sin^2 \theta \cos 2\phi$	

SOURCE: Adapted from G. M. Barrow, *Physical Chemistry*, 5th ed., McGraw-Hill, New York, 1988, with permission.

NOTE: The relations $(e^{i\phi} - e^{-i\phi})/(2i) = \sin \phi$ and $(e^{i\phi} + e^{-i\phi})/2 = \cos \phi$ can be used to convert the exponential imaginary functions to real trigonometric functions, combining the two orbitals with $m_l = \pm 1$ to give two orbitals with $\sin \phi$ and $\cos \phi$. In a similar fashion, the orbitals with $m_l = \pm 2$ result in real functions with $\cos^2 \phi$ and $\sin^2 \phi$. These functions have then been converted to Cartesian form by using the functions $x = r \sin \phi$, $y = r \cos \phi$, and $z = r \cos \theta$.

Hydrogen Atom Wavefunctions: Radial Factors

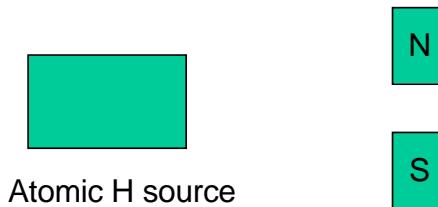
Radial factors $R(r)$, with $\sigma = Zr/a_0$				
Orbital	n	l	$R(r)$	
1s	1	0	$R_{1s} = 2 \left[\frac{Z}{a_0} \right]^{3/2} e^{-\sigma}$	
2s	2	0	$R_{2s} = \left[\frac{Z}{2a_0} \right]^{3/2} (2 - \sigma) e^{-\sigma/2}$	
2p		1	$R_{2p} = \frac{1}{\sqrt{3}} \left[\frac{Z}{2a_0} \right]^{3/2} \sigma e^{-\sigma/2}$	
3s	3	0	$R_{3s} = \frac{2}{27} \left[\frac{Z}{3a_0} \right]^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$	
3p		1	$R_{3p} = \frac{1}{81\sqrt{3}} \left[\frac{2Z}{a_0} \right]^{3/2} (6 - \sigma) \sigma e^{-\sigma/3}$	
3d		2	$R_{3d} = \frac{1}{81\sqrt{15}} \left[\frac{2Z}{a_0} \right]^{3/2} \sigma^2 e^{-\sigma/3}$	

Multielectron Atoms

- The Schrödinger equation can be solved accurately only for H, He⁺, Li²⁺ etc.
→ He corresponds to the classic “three body problem” in physics and can be solved only through approximation (Hartree-Fock method or self consistent field (SCF) method)
 - Results from these calculations:
 - Compared to the H atom, the orbitals are somewhat contracted due to the increased nuclear charge
 - Within a given major energy level (quantum number n), the energy increases with s < p < d < f
- But: At higher energy levels staggering may occur:

Electron Spin

- Beam of hydrogen atoms (ground state, $n = 1, l = 0, m_l = 0$) is split when sent through a magnetic field



→ introduction of a fourth quantum number, m_s explains experiment

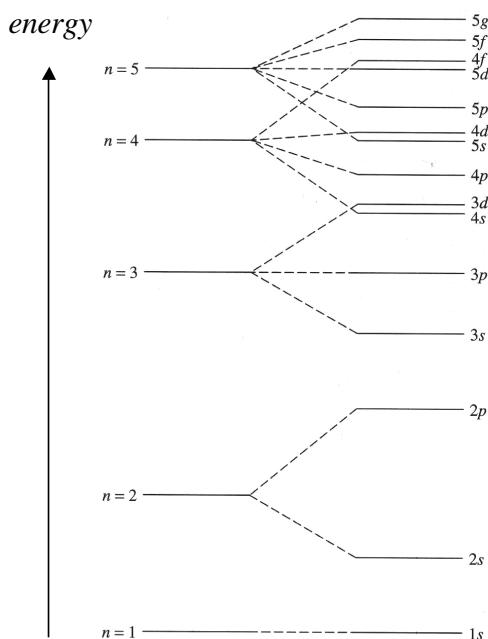
Note: the spin quantum number comes from relativistic effects (not included in the Schrödinger equation)

The Pauli Principle

- “In a given atom, no two electrons may have all four quantum numbers n , l , m_l , and m_s identical”
→ each orbital can contain maximal two electrons with

Diamagnetic Atom: total spin $S = 0$ (all electrons are paired)
 Paramagnetic Atom: total spin $S \neq 0$ (one or more unpaired electrons)

The Aufbau Principle (Filling Principle)

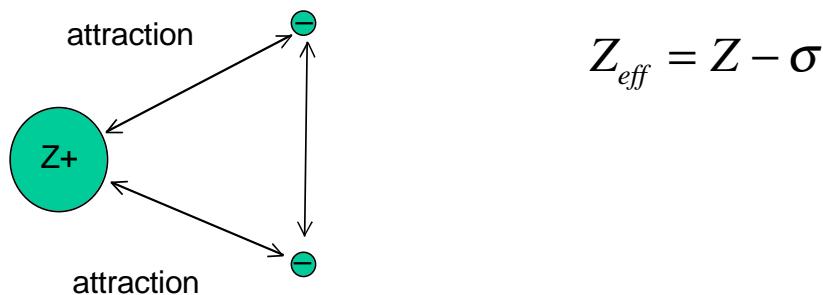


Based on the Pauli principle, the distribution of electrons among the atom orbitals can be determined (= *electron configuration*)

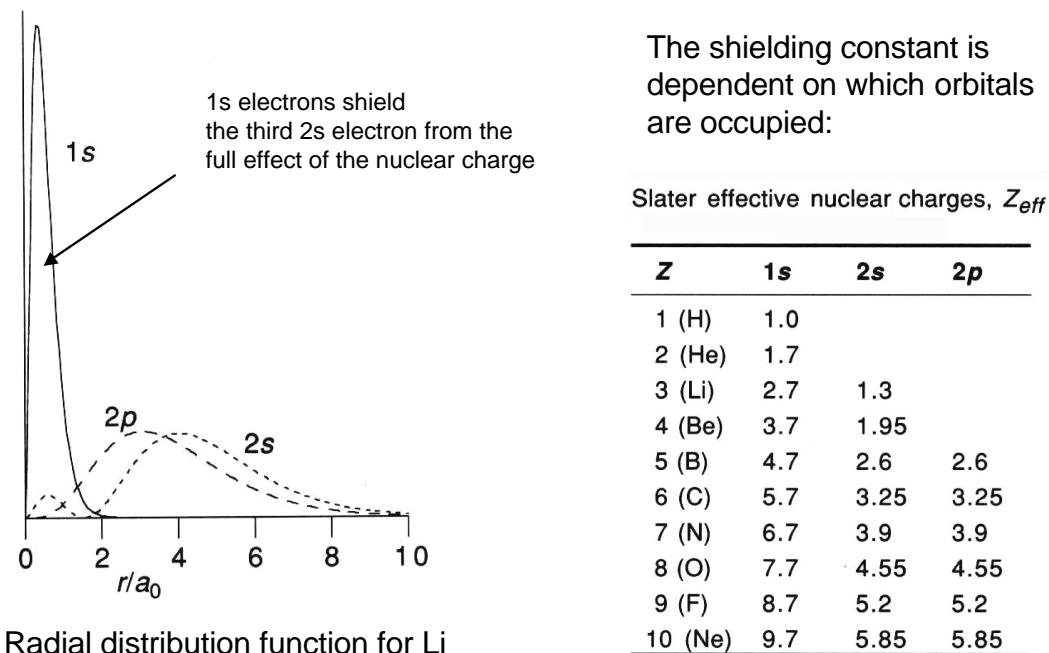
The electrons fill up the available energy levels (orbitals), starting with the lowest available level

Orbital Energies

- The energy of orbitals in a multielectron atom is not identical with the corresponding orbitals of the hydrogen atom
→ the electrons experience an effective nuclear charge (Z_{eff}) that is different from 1.0.
- Each electron is attracted by the nucleus and repelled by all the other electrons

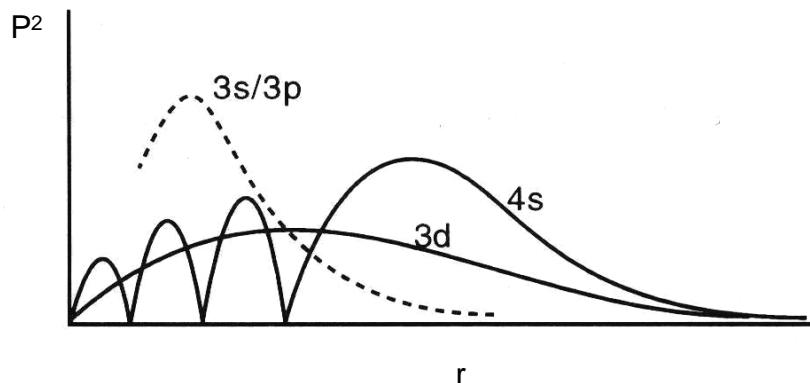


Shielding

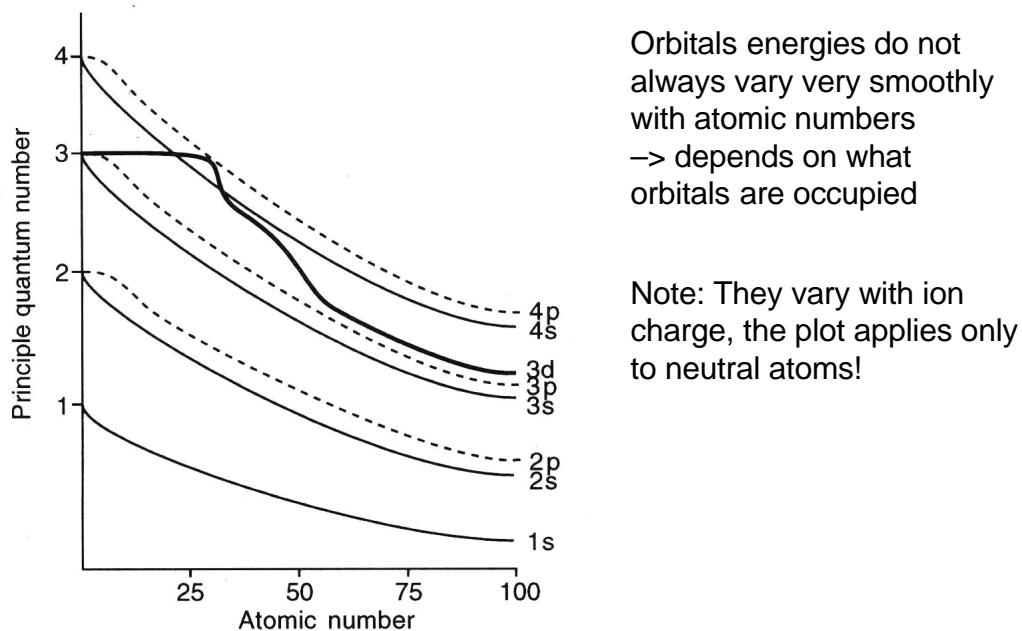


Orbital Penetration

- The 4s orbital shows a considerable electron probability with maxima close to the nucleus
- it is therefore more penetrating than the 3d orbital, even though the principle quantum number is larger



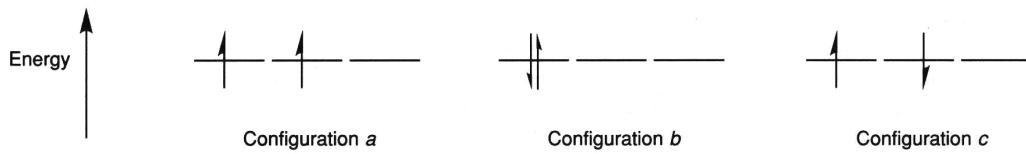
Variation of Orbital Energy with Z



Hund's Rule

- There is often more than one way of arranging electrons within a set of degenerate (=energetically equivalent) orbitals
- → they correspond often to different energies
- Hund's rule of maximum multiplicity:

"The ground state of an atom will be the one having the greatest multiplicity"



Three possible configurations for two electrons occupying a set of three degenerate $2p$ orbitals.

Electron configuration for atoms

- Some atoms do not have the electron configuration you would expect based on the Aufbau principle:
- Half filled and filled subshells (here the five $3d$ orbitals) provide additional stabilization

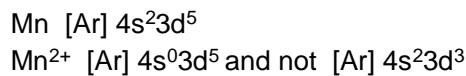
$[Ar] 4s^1 3d^{10}$ is the lower energy configuration compared to $4s^2 3d^9$

Table 1.8. Electronic structures of elements 1–36 (gas phase)

Z	Symbol	Electronic configuration	Shorthand form
1	H	$1s^1$	$1s^1$
2	He	$1s^2$	$1s^2$
3	Li	$1s^2 2s^1$	$[He]2s^1$
4	Be	$1s^2 2s^2$	$[He]2s^2$
5	B	$1s^2 2s^2 2p^1$	$[He]2s^2 2p^1$
6	C	$1s^2 2s^2 2p^2$	$[He]2s^2 2p^2$
7	N	$1s^2 2s^2 2p^3$	$[He]2s^2 2p^3$
8	O	$1s^2 2s^2 2p^4$	$[He]2s^2 2p^4$
9	F	$1s^2 2s^2 2p^5$	$[He]2s^2 2p^5$
10	Ne	$1s^2 2s^2 2p^6$	$[He]2s^2 2p^6$
11	Na	$1s^2 2s^2 2p^6 3s^1$	$[Ne]3s^1$
12	Mg	$1s^2 2s^2 2p^6 3s^2$	$[Ne]3s^2$
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	$[Ne]3s^2 3p^1$
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	$[Ne]3s^2 3p^2$
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	$[Ne]3s^2 3p^3$
16	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	$[Ne]3s^2 3p^4$
17	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	$[Ne]3s^2 3p^5$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	$[Ne]3s^2 3p^6$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$[Ar]4s^1$
20	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$[Ar]4s^2$
21	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	$[Ar]4s^2 3d^1$
22	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	$[Ar]4s^2 3d^2$
23	V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	$[Ar]4s^2 3d^3$
24	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4 3p^1$	$[Ar]4s^1 3d^4$
25	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	$[Ar]4s^2 3d^5$
26	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	$[Ar]4s^2 3d^6$
27	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	$[Ar]4s^2 3d^7$
28	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	$[Ar]4s^2 3d^8$
29	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	$[Ar]4s^1 3d^{10}$
30	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	$[Ar]4s^2 3d^{10}$
31	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$	$[Ar]4s^2 3d^{10} 4p^1$
32	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$	$[Ar]4s^2 3d^{10} 4p^2$
33	As	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$	$[Ar]4s^2 3d^{10} 4p^3$
34	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$	$[Ar]4s^2 3d^{10} 4p^4$
35	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	$[Ar]4s^2 3d^{10} 4p^5$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$	$[Ar]4s^2 3d^{10} 4p^6$

Electron Configuration for Ions

- Ease of removal of an electron (=ionization energy) often does not mirror the filling order embodied in the Aufbau principle



Different electron configurations correspond to different species, and have different properties (color, magnetic behavior, etc.)

Note: All transition metal atoms lose their ns electrons before their (n-1)d electrons!

Periodic Trends in Atomic Properties

- Effective nuclear charge
- Ionization energies
- Electron affinities
- Covalent and ionic radii
- Bond strength
- Electronegativity
- Orbital energies
- Promotion energies
- Common oxidation states
- Relativistic effects

Effective Nuclear Charge

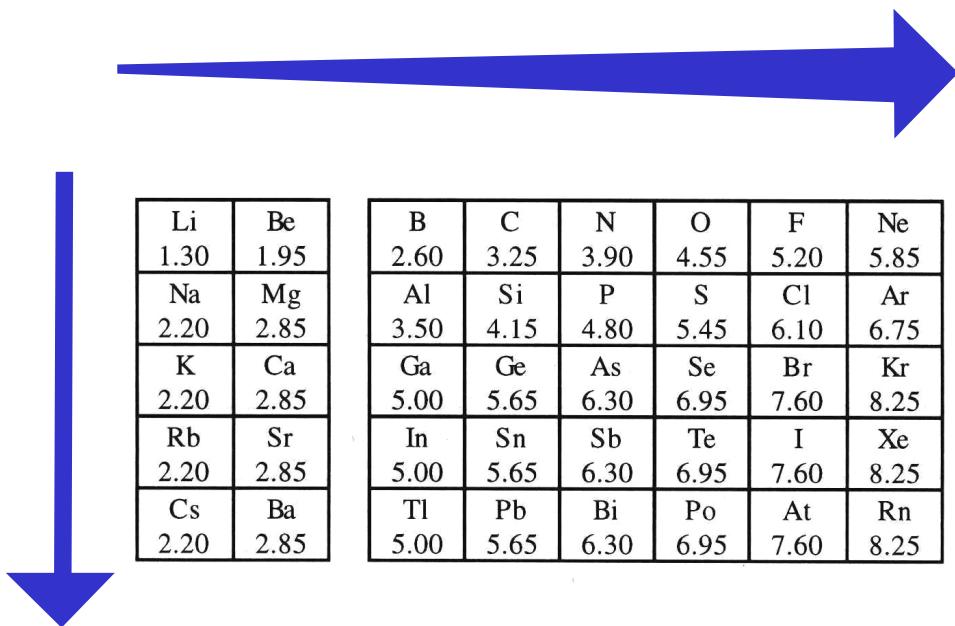
- The valence shell electrons feel a nuclear charge much less due to shielding effects of the core electrons
 - Many atomic properties can be rationalized by understanding how the effective nuclear charge varies throughout the periodic table
- Slater's rules allow estimation of Z_{eff} by simple empirical rules

Slater's Rules

[1s] [2s2p] [3s3p] [3d] [4s4p] [4d] [4f] [5s5p] [5d] [5f]

- All electrons to the right contribute 0 to shielding
- All electrons in the same group (n) contribute 0.35
- For s and p electrons: all electrons in the $(n-1)$ shell contribute 0.85 each
- All other electrons to the left contribute 1.0
- For [nd] or [nf] electrons: all electrons to the left contribute 1.0

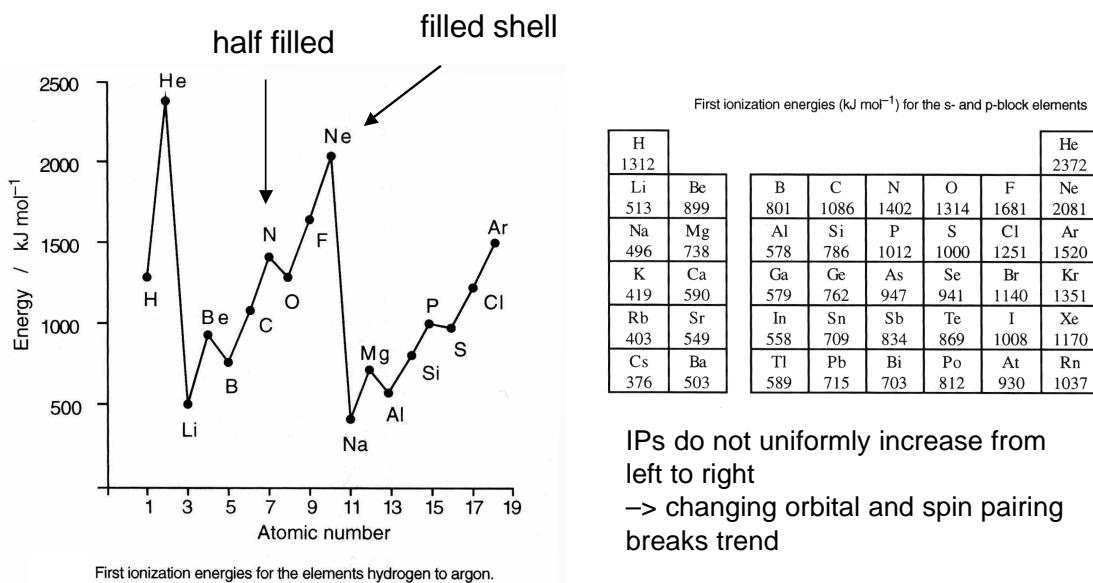
Periodic Variation of Z_{eff}



Ionization Energies

- Energy required to remove an electron from an atom or ion
 - 1st ionization energy or potential (IE or IP)
 - 2nd ionization energy or potential
- Depends on the effective nuclear charge experienced by the electron and the average distance from the nucleus
- → with increasing Z_{eff} increases IP
- → with increasing distance decreases IP
- Note: Distance increases as principle quantum number increases (n)

Periodic Trends in Ionization Energies



IPs do not uniformly increase from left to right
→ changing orbital and spin pairing breaks trend

IPs do not always decrease going down a group
→ transition series and actinides upset this trend

Electron Affinity

- Energy change associated with addition of an electron to an atom or ion

1st electron affinity (EA)

- Favorable process for most elements
- Influenced by Z_{eff} and atom size (principle quantum number)
- Note: Positive sign per definition:

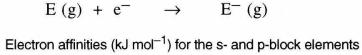
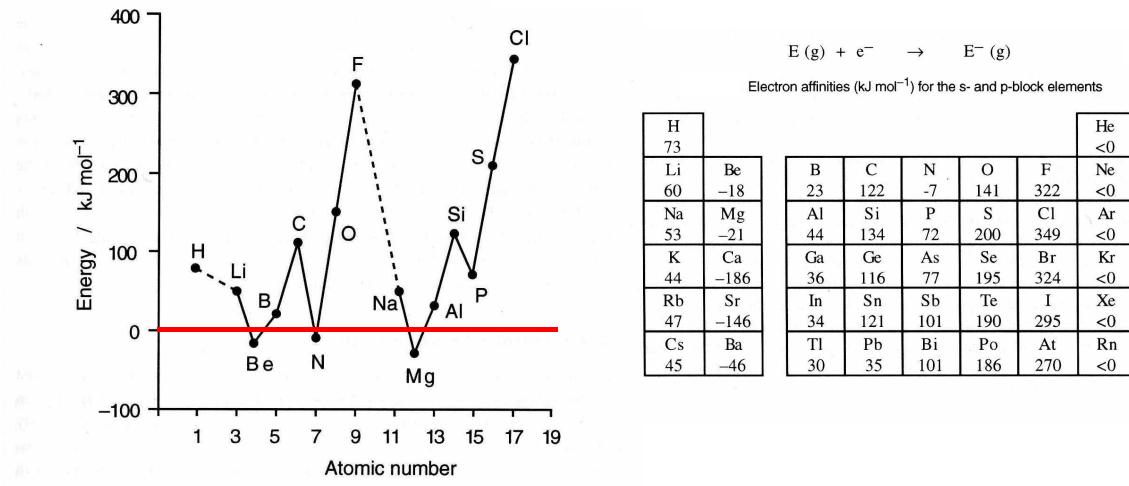


- Trends in EAs parallel those of IPs, but for one lower Z value
- Exceptions:

- EA of F is lower than of Cl
- EA of N is lower than of P
- EA of O is lower than of S

→ smaller size of F (and N or O) causes greater electron-electron repulsion!

Trends in Electron Affinities



H		He <0					
Li	60	B	23	C	122	N	-7
Na	53	Al	44	Mg	-21	O	141
K	44	Ga	36	Si	134	F	322
Rb	47	In	34	P	72	Cl	349
Cs	45	Sn	121	S	200	Ar	<0
		Bi	101	Se	195	Br	324
		Po	101	Te	190	I	295
		At	186	Xe	—	Rn	<0
		Tl	30				
		Pb	35				

Covalent Radii

- Covalent radius of an atom A = half the distance between a diatomic molecule A–A
- They are approximately *additive*: For a non-polar molecule A–B the sum of the radii of A and B should be equal to the A–B bond length
- Note: For polar molecules this approximation does not work as well!

→

Covalent radii (Å) for the s- and p-block elements

H		He					
0.30		B	0.88	C	0.77	N	0.70
Li	1.23	Al	1.25	Si	1.17	P	0.66
Na	1.54	Ga	1.25	As	1.21	S	0.64
K	2.03	In	1.50	Se	1.17	Cl	—
Rb	—	Tl	1.55	Br	1.14	Ar	—
Cs	2.35	Pb	1.54	I	1.33	Kr	—
		Bi	1.52	Xe	1.30		—
		Po	1.53			Rn	—



Ionic Radii

- The sizes of ions follow similar trends
BUT: Changes in charge have a very big impact on size

	Radius (\AA)		
	Covalent	+2 ionic	+4 ionic
Ge	1.22	0.87	0.67
Sn	1.40	1.12	0.83

Bond Strength

- The bond energy is the energy needed to break a chemical bond
- Strong bond: $> 800 \text{ kJmol}^{-1}$
- Average bond: 500 kJmol^{-1}
- Weak bond: $< 200 \text{ kJmol}^{-1}$
- Bond strength often depend upon the size of the elements that are bonded together
→ bond strength often decreases on going down a group
Example:
HF 568 kJmol^{-1} , HCl 432 kJmol^{-1} , HBr 366 kJmol^{-1} , HI 298 kJmol^{-1}

Electronegativity (EN)

- Pauling (1930):

Electronegativity = “*the ability of an atom to attract electron density towards itself in a molecule*”

 - Not amenable to direct experimental measurement
 - But: very useful concept which allows to predict, whether a given combination of elements is likely to result a molecule with polar bonds
- Various quantifications of EN:
 - Pauling: based on bond-strength
 - Alfred-Rochow: based on size and effective nuclear charge
 - Mulliken: based on IPs and EAs
 - Allen’s spectroscopic values: based on orbital energies

Pauling Scale of ENs

- Based on differences in bond strength:

→ For a polar molecule A–B the strength of the A–B bond is greater than the average of the strength of A–A and B–B
(due to an ionic contribution to the bonding)

→ This difference in bond strength, Δ , was related to the difference in electronegativity using the expression:

$$\Delta = 96.49(\chi_A - \chi_B)^2 \quad (\Delta \text{ in } \text{kJmol}^{-1})$$

χ_E is the electronegativity of element E

Mulliken Electronegativity

- Defined as the average of the ionization energy and electron affinity:

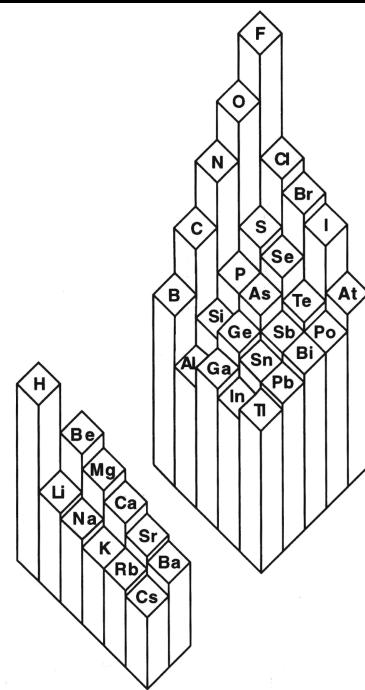
$$\chi = \frac{IE + EA}{2}$$

-> Can easily calculated from tabulated values

Periodic Trends in Electronegativity

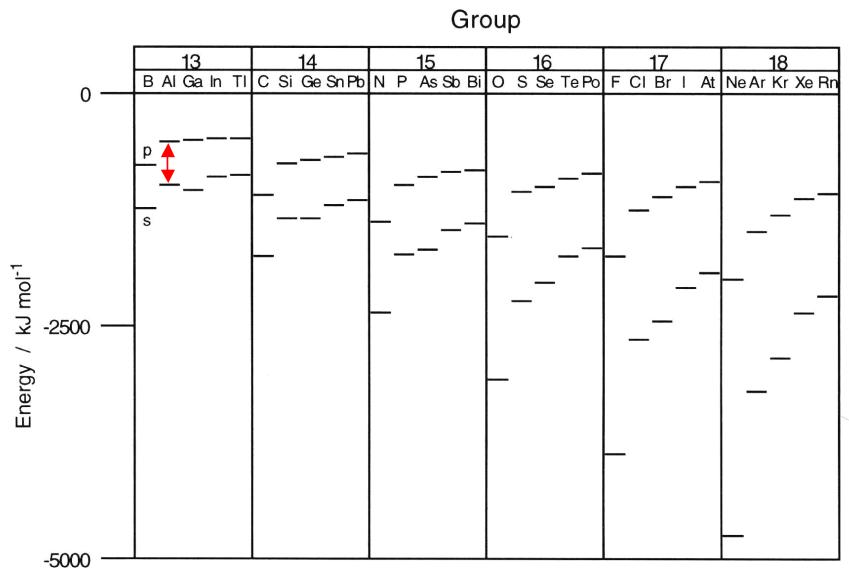
H 2.20						Hc —
Li 0.98	Be 1.57					
Na 0.93	Mg 1.31					
K 0.82	Ca 1.00					
Rb 0.82	Sr 0.95					
Cs 0.79	Ba 0.89					

B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne —
Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar —
Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr —
In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe —
Tl 2.04	Pb 2.33	Bi 2.02	Po (2.0)	At (2.2)	Rn —



A view of the periodic table for the s- and p-block elements showing electronegativity as a third dimension

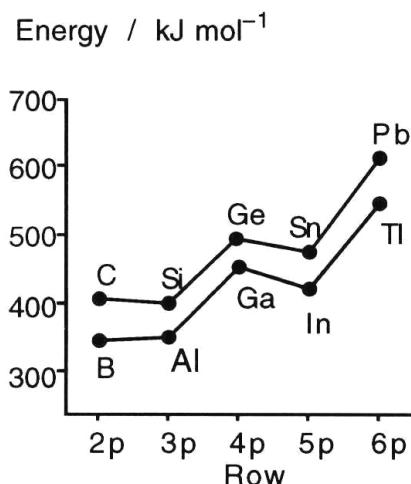
Orbital Energies



Note: Separation between s and p orbitals increases when going from left to right

Promotion Energy

- Many atoms form more bonds than they are expected based on the number of unpaired electrons in their ground states



Carbon Atom:

$1s^2 2s^2 2p^2 \rightarrow$ has only 2 unpaired electrons, but forms 4 covalent bonds

Prior to bonding interaction, one of the 2s electrons is promoted to the empty 2p orbital (=promotion energy):
 $1s^2 2s^1 2p^3 \rightarrow$ 4 unpaired electrons can form 4 bonds

Note: Promotion energies increase when going down the B or C group

Relativistic Effects

- Important for heavy metal elements:
 - Einstein's special relativity theory: Objects moving close to the speed of light increase in mass
 - Due to the high nuclear charge of heavy elements electrons close to the nucleus (s orbitals!) have a big velocity
 - mass of electron increases
 - effective size of orbital decreases (relativistic orbital contraction)
 - energy of electron is lowered
 - The contraction of the s orbitals (and somewhat also the p orbitals) leads to an expansion of the d and f orbitals due to increased shielding of the nuclear charge