화학 General Chemistry
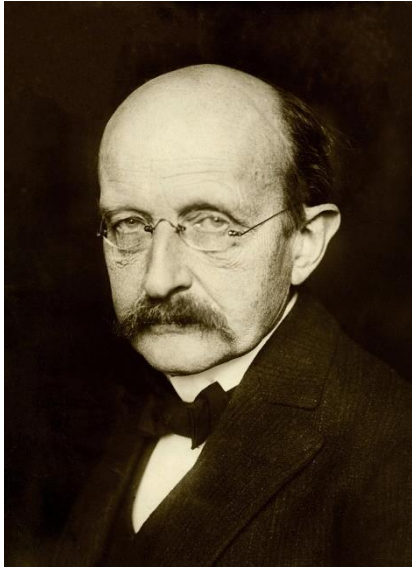## 034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302
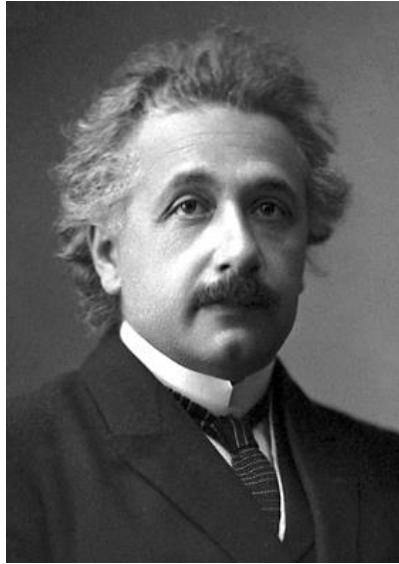
송윤주 woonjusong@snu.ac.kr

Max Planck	Albert Einstein	Niels Bohr	Erwin Schrödinger
(1858 –1947)	(1879 -1955)	(1885 –1962)	(1887–1961)
Nobel Prize in Physics in 1918	Nobel Prize in Physics in 1921	Nobel Prize in Physics in 1922	Nobel Prize in Physics in 1933
Quantum theory	Photoelectric effect		

1.7. Wave functions and Energy Levels

A particle has wave-like property; wavefunction

Wave function (ψ)

Probability density Function ($ψ^2$)

Max Born
(1882-1970)
Nobel Prize in Physics (1954)

Schrödinger equation

$$H \, \psi = E \, \psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

(Matter) Wave function: $\Psi_n(x)$
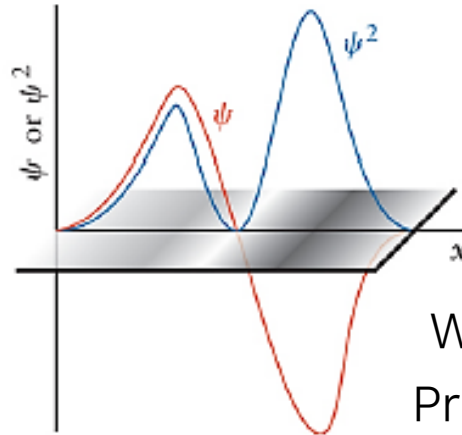
Born interpretation
: statistical interpretation of the wave function, probability density function

m : mass of the particle

Quantized energy levels: E
Hamiltonian: H

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x)+V(x)\Psi(x)=E\Psi(x)$$

$$\Psi_n(x,y,z)$$

Matter wave associated with the particle.

$$P(x,y,z)=\left|\Psi_n(x,y,z)\right|^2=\Psi_n^*(x,y,z)\times\Psi_n(x,y,z)$$
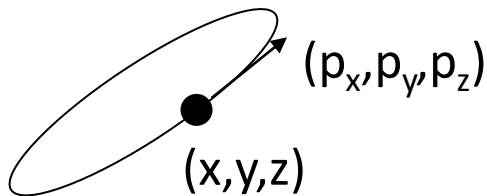
$|\Psi|^2$ dxdydz
= Probability to find a particle at (x,y,z)

Wave function (ψ)

Probability density (ψ²)

Classical Mechanics

Position and momentum
of a particle can be determined

(p_x, p_y, p_z)

(x,y,z)

Energy is continuous

Quantum Mechanics

Position and momentum
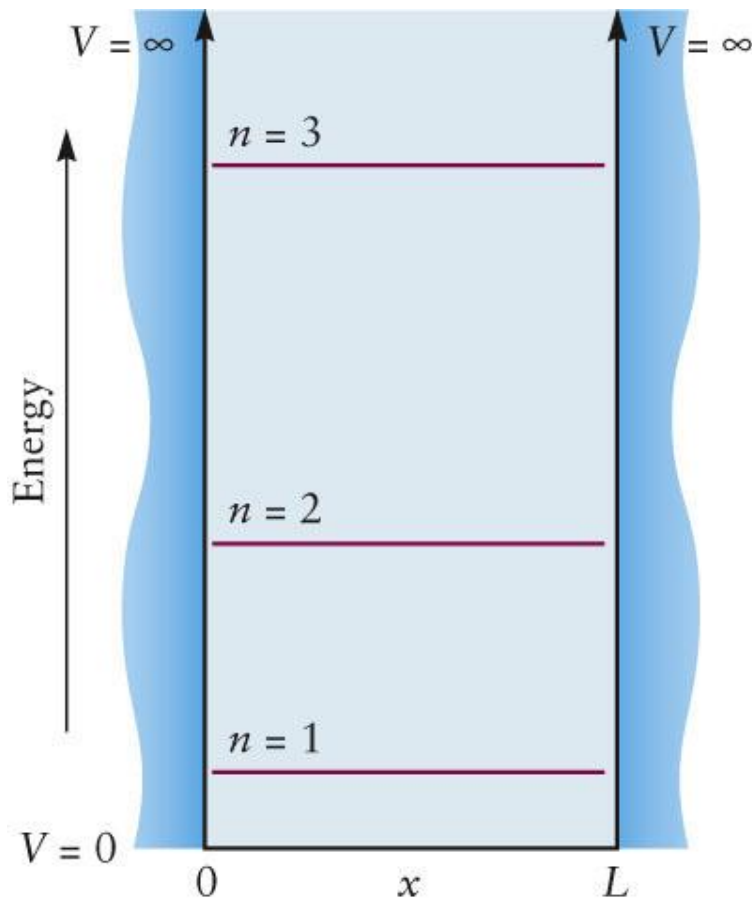of a particle cannot be determined
simultaneously

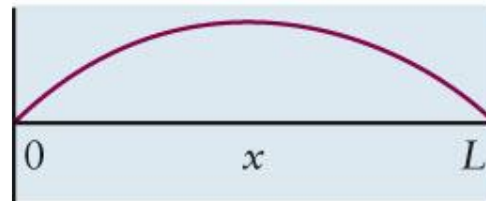Ψ

Energy is discrete (quantized)

One-dimensional boxes:
Zero potential energy inside the box
And infinite potential energy outside

$|\Psi|^2$

$V = \infty$ $V = \infty$

$n = 3$

$n = 2$

$n = 1$

$V = 0$

0   x L

(a)   Energy levels

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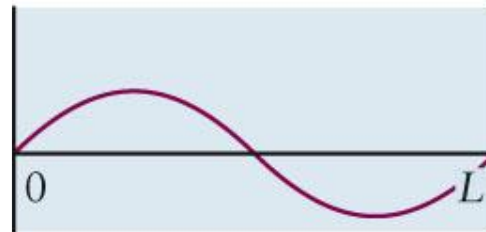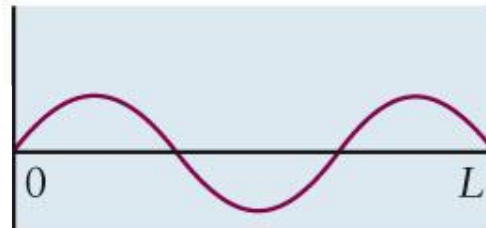
Wave functions   (c)   Probabilities

ψ_3^2

ψ_2^2

ψ_1^2
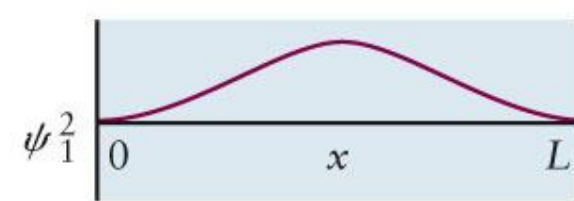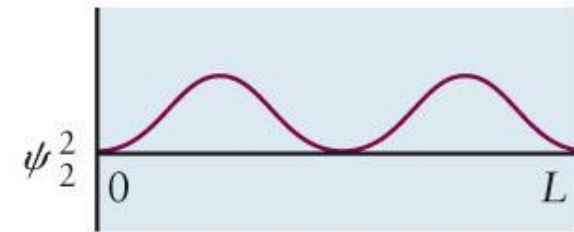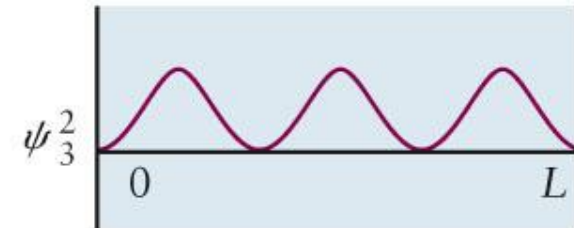
Energy is quantized
(determined by n)!

$$E_n = \frac{h^2 n^2}{8mL^2}, \Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

$$E_n = \frac{h^2 n^2}{8mL^2}, \Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$$

$$E_{n+1} - E_n = \frac{h^2(n+1)^2}{8mL^2} - \frac{h^2 n^2}{8mL^2} = (2n+1)\frac{h^2}{8mL^2}$$

(a)   Energy levels
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1. Energy level is quantized.
2. As the L or m increases, the separation between neighboring energy levels decreases: The quantized energy level is obvious in an electron in a hydrogen atom.
3. It is impossible to have no energy (E≠0). The lowest energy state is when n=1: E_1 = zero-point energy.
4. There is always some degrees of kinetic energy = always moving (linear momentum)= uncertainty in the position.
5. With large quantum number, the quantum mechanics should converge to classical mechanics: Correspondence Principle
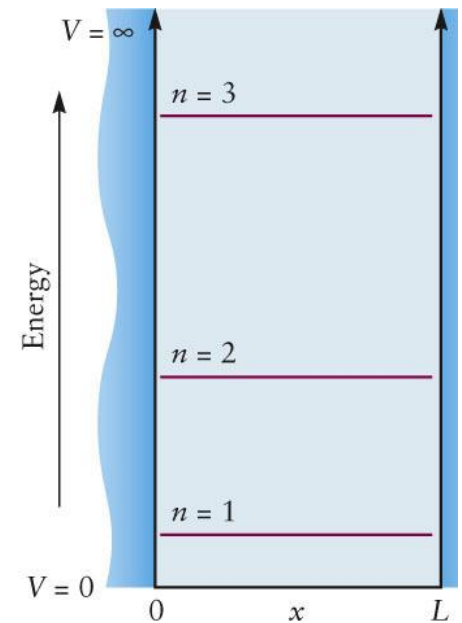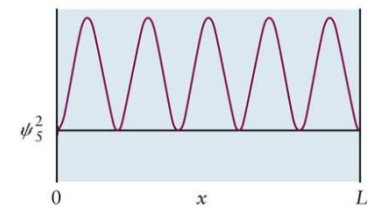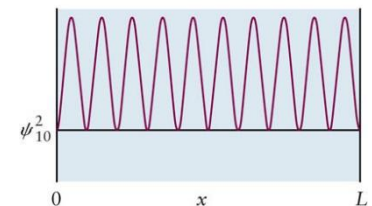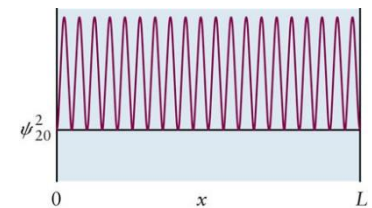
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Energy: Principle Quantum Number (n)

Wave function:

4 Quantum Numbers:

$n = 3$

$n = 2$

$n = 1$

$+Ze$

$\Delta E = hf$
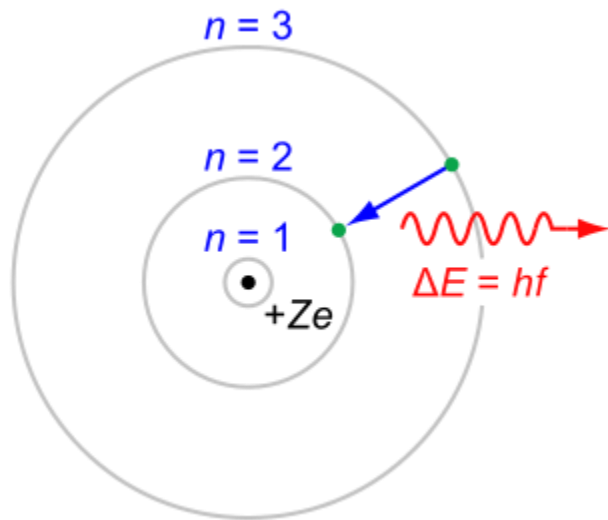
The Rutherford–Bohr model of the hydrogen atom

1.8. The Principal Quantum Number

Similarly to a particle in a box, an electron in an atom

For Hydrogen Atom, V(r) = Coulomb potential energy

$$V(r) = \frac{(-e)(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

where, ε_0 = vacuum permittivity

Solutions of the Schrödinger equation, $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$

$$E_n = -\frac{hR}{n^2} \qquad R = \frac{m_e e^4}{8h^3\varepsilon_0^2} \qquad n = 1, 2, \ldots$$

where, R = 3.29 x 10^{15} Hz ⟶ Rydberg constant!

For other one-electron ions, such as He^+, Li^{2+} and even C^{5+}

$$E_n = -\frac{Z^2 hR}{n^2} \qquad n = 1, 2, \ldots$$

Proportional to Z^2
= charge effect+ distance effect

Z = atomic number; n = principal quantum number
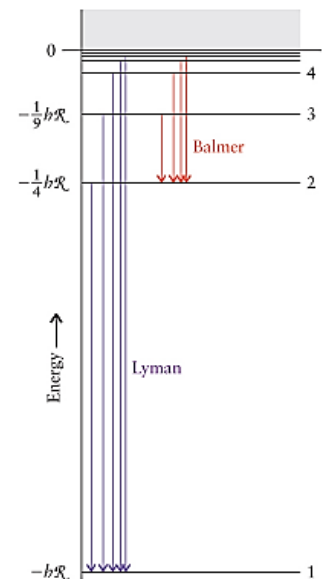
1.9. Atomic Orbitals

◈ Atomic Orbitals: the wave functions of electrons in atoms

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\psi = E\psi$$

Kinetic energy — Potential energy — Total energy

$$\psi(r, \theta, \phi) = R(r)\,Y(\theta, \phi)$$

Radial wavefunction — Angular wavefunction

$$V = \infty$$

$$n = 3$$

$$n = 2$$

$$n = 1$$

$$V = 0$$

(a) Energy levels
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$$E_n = \frac{h^2 n^2}{8mL^2}, \Psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

x = r cosθ sinφ
y = r sinθ sinφ
z = r cosθ
x²+y²+z² = r²
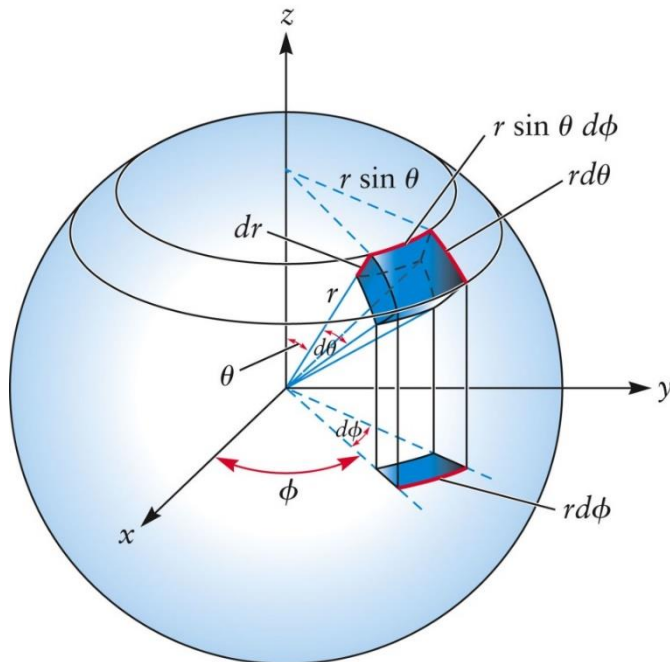
Spherical Coordinate:
(x, y, z) → (r, θ, φ)

→ n, l, m$_l$

TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions, $R_{nl}(r)$

n	l	$R_{nl}(r)$
1	0	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$
	1	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$\dfrac{1}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(3 - \dfrac{2Zr}{a_0} + \dfrac{2Z^2r^2}{9a_0{}^2}\right)e^{-Zr/3a_0}$
	1	$\dfrac{2}{27\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{3a_0}\right)e^{-Zr/3a_0}$
	2	$\dfrac{4}{81\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

n = principal quantum number 1, 2, $\cdots$
l = orbital angular momentum quantum number
    0, 1, 2, …n-1
m_l = magnetic quantum number l, l-1, $\cdots$-l

(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$

l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
1	x	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	y	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
	z	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
2	xy	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$
	yz	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$
	zx	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$
	$x^2 - y^2$	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$
	z^2	$\left(\dfrac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$

Note: In each case, $a_0 = 4\pi\varepsilon_0{}^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.
*In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

n: principal quantum number
→ related to the **size** and **energy** of the orbital; 1, 2, ⋯
→ radius of orbit

l: orbital angular momentum quantum number (l = 0, 1, 2, …, n–1)
→ related to the orbital **angular momentum** of the electron;
→ s, p, d, f orbital

m_l: magnetic quantum number (m_l = l, l–1, l–2, ⋯, –l)
→ related to the **orientation** of the orbital motion of the electron

Energy is dependent only on n; Total number of orbital = n^2

Representation of energy levels
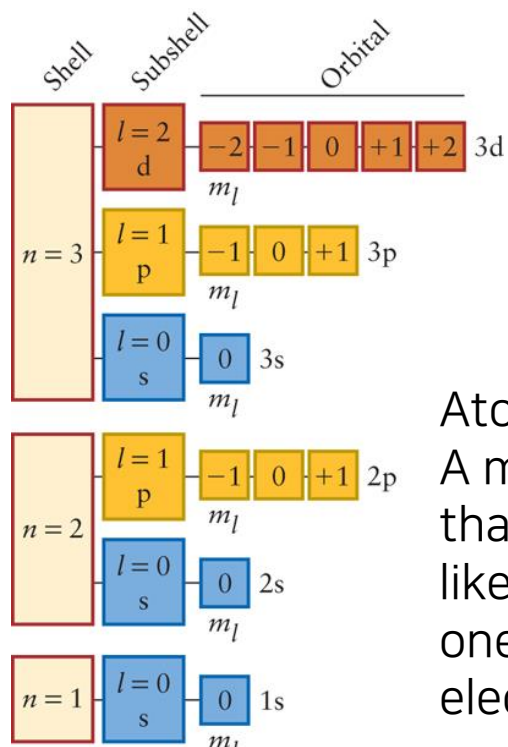
Atomic Orbital =
A mathematical function that describes the wave-like behavior of either one electron or a pair of electrons in an atom.

TABLE 7.2 Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

n	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
	1	2p	−1, 0, +1	3
3	0	3s	0	1
	1	3p	−1, 0, 1	3
	2	3d	−2, −1, 0, 1, 2	5
4	0	4s	0	1
	1	4p	−1, 0, 1	3
	2	4d	−2, −1, 0, 1, 2	5
	3	4f	−3, −2, −1, 0, 1, 2, 3	7
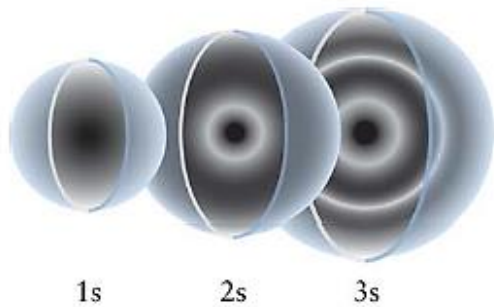
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Shape of orbitals

1s   2s   3s

Spherically symmetric.
Number of nodes increase with n

d_{z^2} $d_{x^2-y^2}$ d_{xy} d_{zx} d_{yz}

P_x P_y

Nodal plane

P_z

$5z^3 - 3zr^2$ $5xz^2 - xr^2$ $zx^2 - zy^2$ xyz

$y^3 - 3yx^2$ $5yz^2 - yr^2$ $x^3 - 3xy^2$

p_x, p_y and p_z have the same energy:
(degenerate states)
p-orbitals have nodal plane along
xy, yz, and zx planes

Size and Shape of orbitals

l = 0: s-orbitals:

Spherically symmetric.

Number of nodes increase with n

(a) Radial wavefunctions, $R_{nl}(r)$

n	l	$R_{nl}(r)$
1	0	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$
	1	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$\dfrac{1}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(3 - \dfrac{2Zr}{a_0} + \dfrac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$

(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$

l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
1	x	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	y	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
	z	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
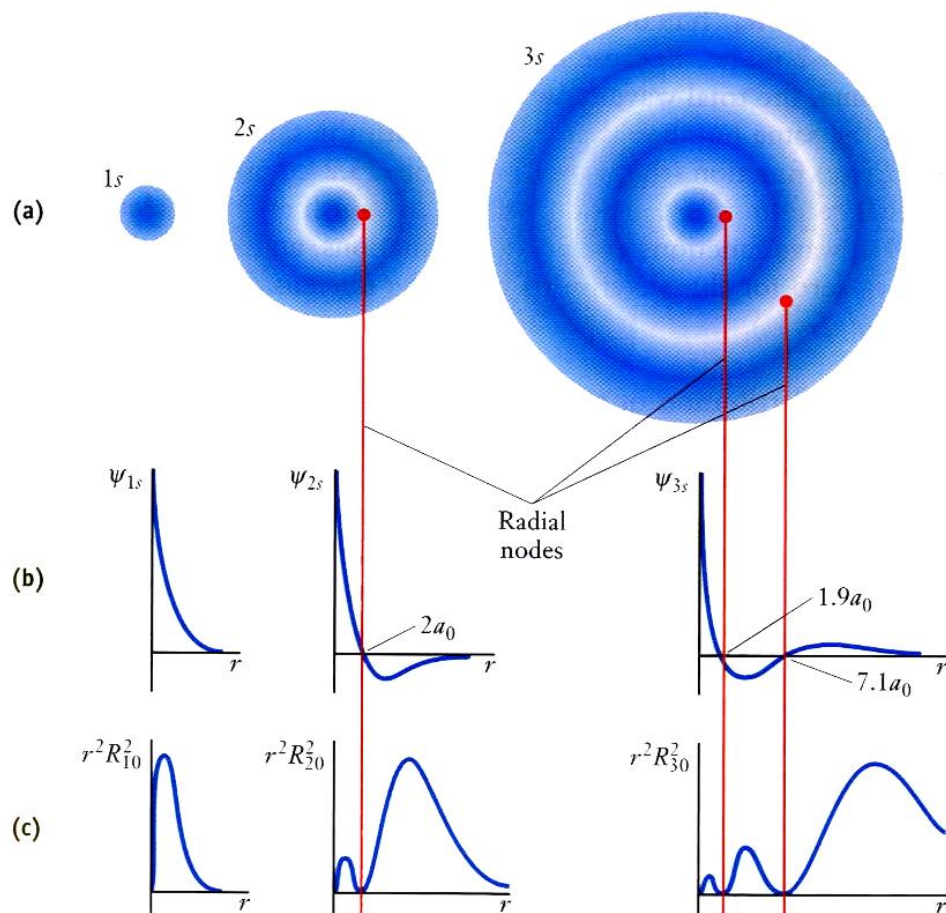
$a_0 = 4\pi\varepsilon_0^2/m_e e^2$, or close to 52.9 pm; Bohr radius

Hydrogen Wavefunctions

2p-orbital: p$_x$, p$_y$ and p$_z$

- p$_x$, p$_y$ and p$_z$ have the same energy = degenerate states
- p-orbitals have nodal plane along xy, yz, and zx planes

$2p_z$ $3p_z$ $4p_z$

2p$_x$

2p$_y$

2p$_z$

TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

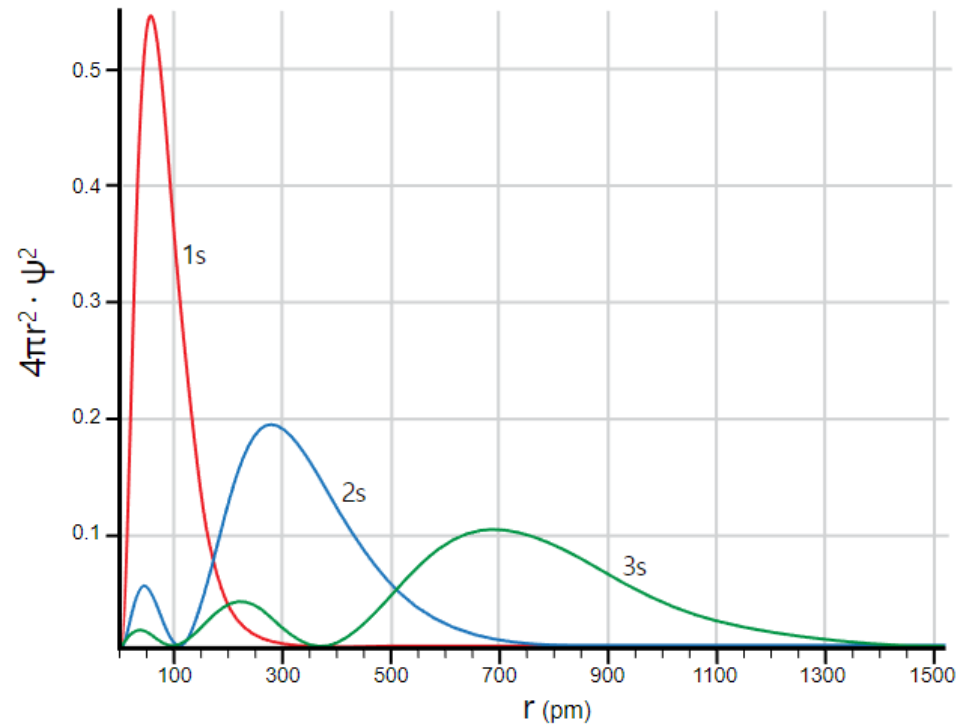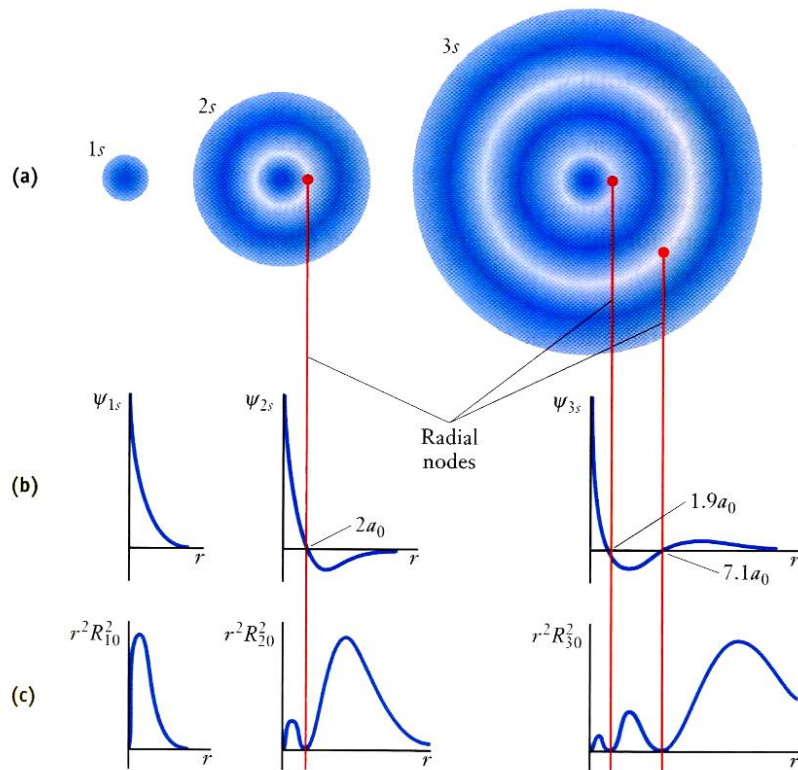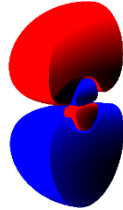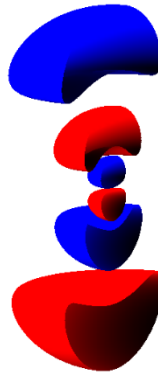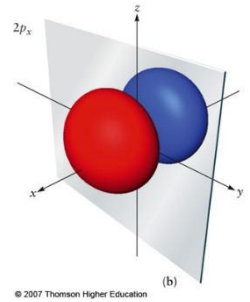| (a) Radial wavefunctions, $R_{nl}(r)$			(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$		
n	l	$R_{nl}(r)$	l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
1	0	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
2	0	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	1	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$		y	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3	0	$\dfrac{1}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(3 - \dfrac{2Zr}{a_0} + \dfrac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$		z	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
	1	$\dfrac{2}{27\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos2\phi$
	2	$\dfrac{4}{81\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$

Node: yz plane: Φ = 90

Node: xz plane: Φ = 0

Node: xy plane: θ = 90

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$
$x^2 + y^2 + z^2 = r^2$

3*d*-orbital

TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

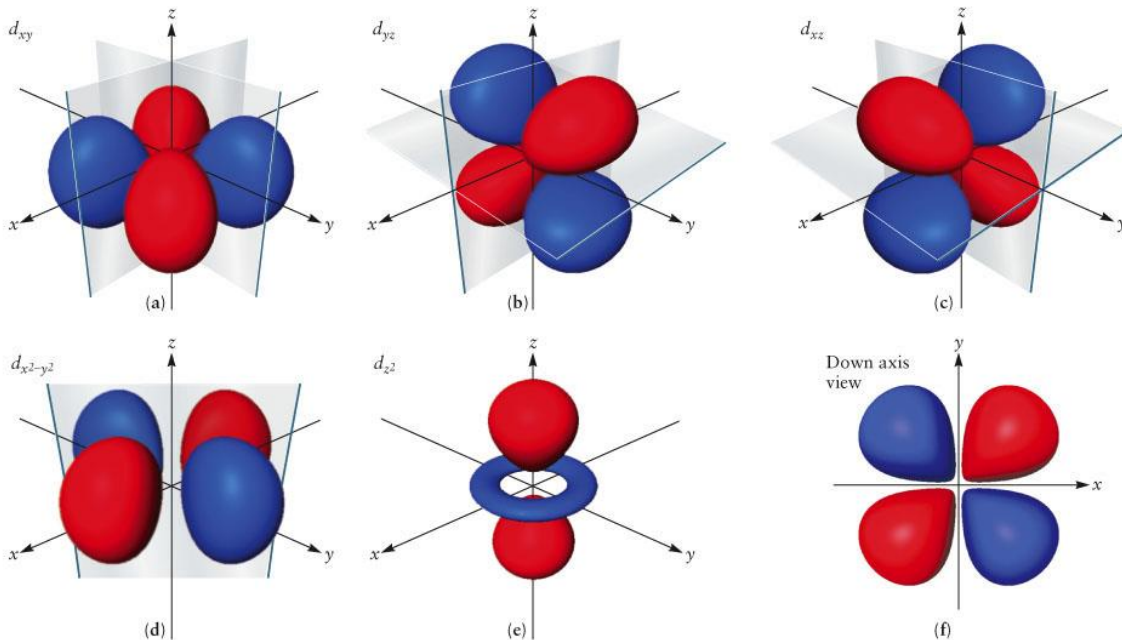| (a) Radial wavefunctions, $R_{nl}(r)$			(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$		
n	l	$R_{nl}(r)$	l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
1	0	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
2	0	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2-\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	1	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$		y	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3	0	$\dfrac{1}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(3-\dfrac{2Zr}{a_0}+\dfrac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$		z	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
	1	$\dfrac{2}{27\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2-\dfrac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$
	2	$\dfrac{4}{81\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$
				zx	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$
				x^2-y^2	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$
				z^2	$\left(\dfrac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$

1.10. Electron Spin

m_s: spin magnetic quantum number

$(m_s = +1/2, -1/2)$

→ related to the **spin** of electron

$$m_s = +\tfrac{1}{2}$$

$$m_s = -\tfrac{1}{2}$$
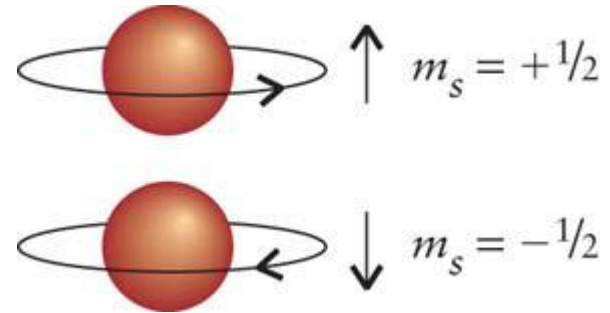
Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	0, 1, . . ., $n - 1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ s, p, d, f, g, . . .	shape
magnetic	m_l	$l, l - 1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\tfrac{1}{2}, -\tfrac{1}{2}$	spin state	spin direction

- Initially, Schrodinger's theory did not exactly match the observed spectral lines because he did not account for "spin".

1.11. The Electronic Structure of Hydrogen Atom

In the ground state,

→ $n = 1$, $l = 0$, $m_l = 0$, $m_s = +1/2$ or $-1/2$

In the excited state

→ $n = 2$ (four orbitals), $n = 3$ (nine orbitals), $n = k$ (k^2 orbitals)

    n = infinite (ionization)

Degeneracy: same energy for all orbitals in the same n

Shell

E

$3s$ — $3p$ — — — $3d$ — — — — —

$2s$ — $2p$ — — —

$1s$ ●

Electron in 1s state (ground)

E

$3s$ — $3p$ — — — $3d$ — — — — —

$2s$ — $2p$ —●—

$1s$ —

Electron in 2p state
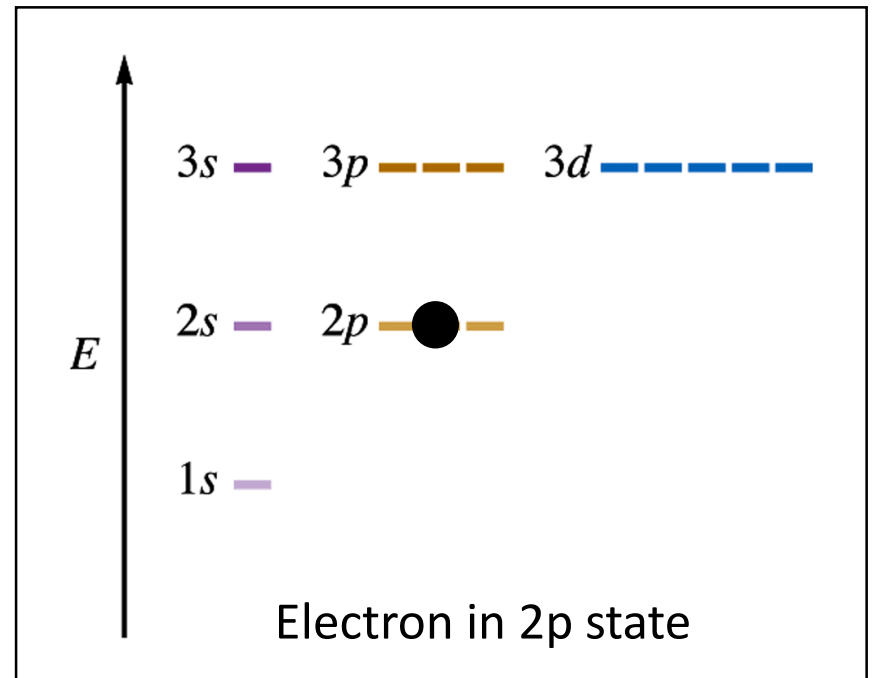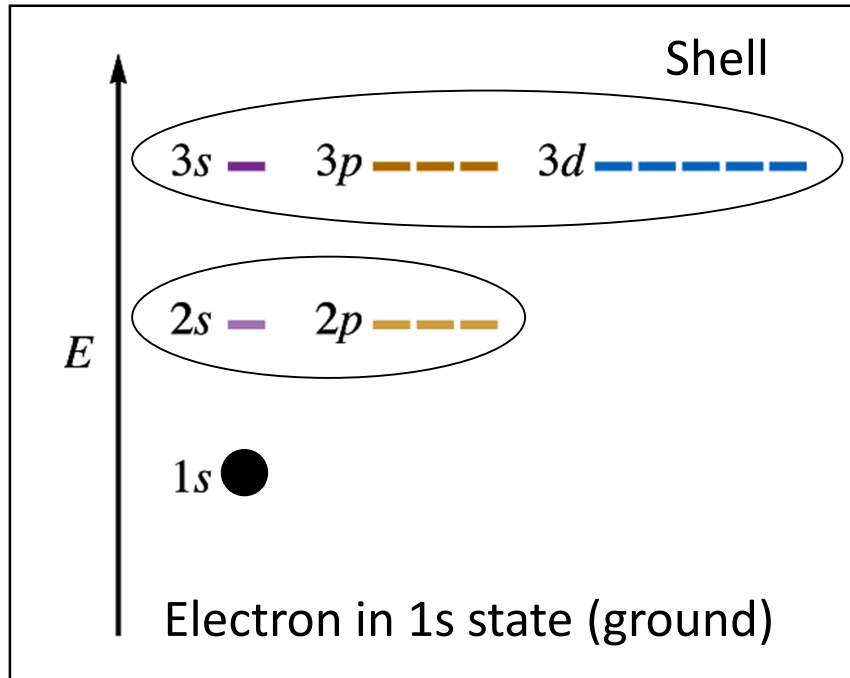
1.12. Orbital Energies

Coulomb potential for **many-electron atoms**

For poly-electronic atoms, electron-electron repulsion: Slightly change the energy level structure:

Electron 1

r_1

r_{12}

r_2

Electron 2

+Ze
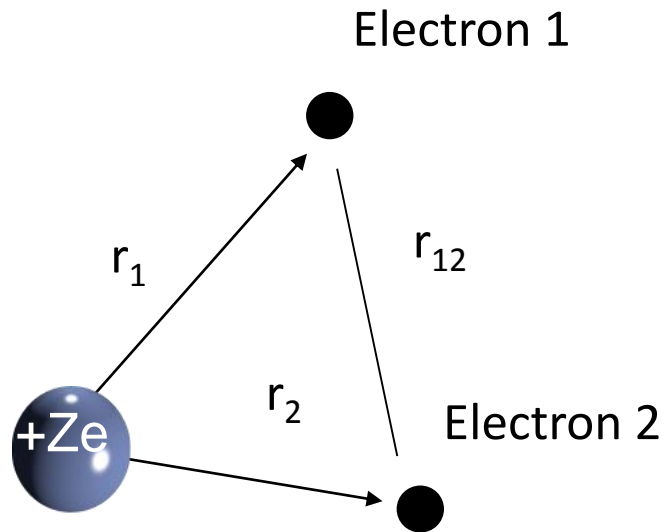
We can't obtain analytical solution to this:
→ Approximate solution exists.

1.12. Orbital Energies

Coulomb potential for **many-electron atoms**

$$V = -\frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

| Attraction of electron 1 to the nucleus | Attraction electron 2 to the nucleus | Repulsion between the two electrons |

$$V(r) = \frac{(-e)(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

For **one**-electron atom

$$E_n = -\frac{h\mathcal{R}}{n^2} \qquad \mathcal{R} = \frac{m_e e^4}{8h^3\varepsilon_0^2}$$

$$E_n = -\frac{Z^2 h\mathcal{R}}{n^2}$$

For example, in a helium atom, r_1: e_1~nucleus; r_2: e_2~nucleus; r_{12}: e_1~e_2

Z = +2

Shielding and Penetration effect

: Each electron is shielded by the other (e⁻)s.

$$E_n = -\frac{Z_{eff}^2 h\mathcal{R}}{n^2}$$ Z_{eff}: effective nuclear charge ➡ **energy split**

- (e⁻)s in p orbital penetrate less than (e–)s in s orbital → $E_s < E_p$

Hydrogenic atom
(no e-e repulsion)

E

3s 3p 3d

2s 2p

1s

(Usual) Energy Ordering

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p
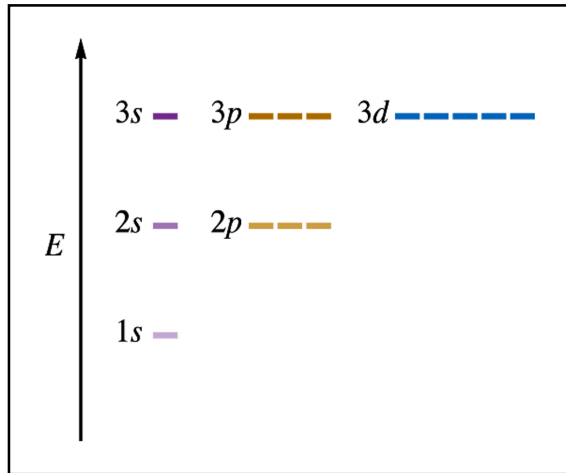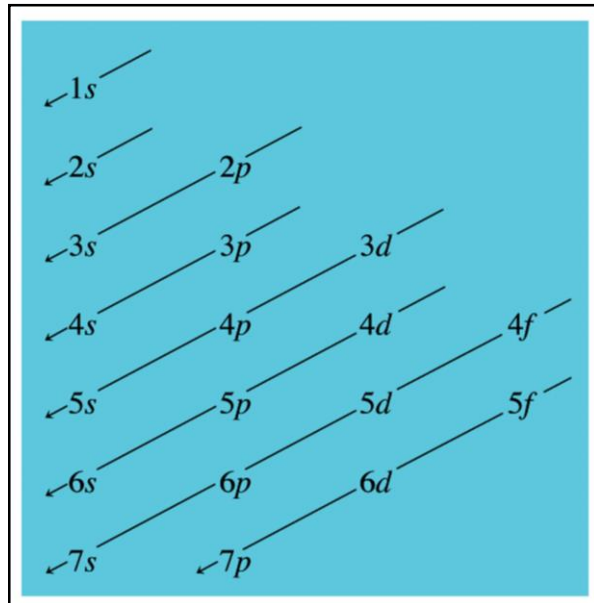
Polyelectronic atom

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

E

3d

3p

3s

2p

2s

1s
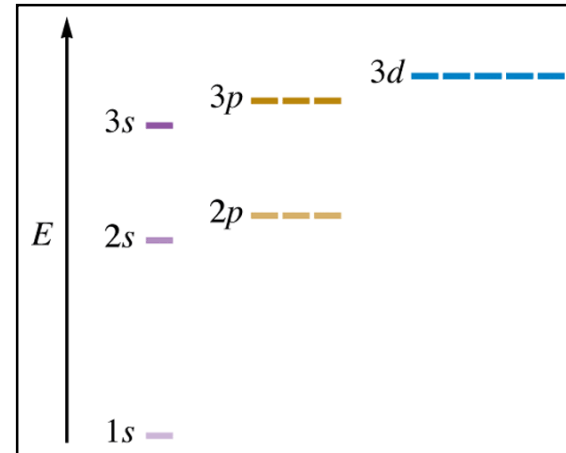
1.13. The Building-Up Principles

→ no more than 2 (e⁻)s in any given orbital: no two electrons in an atom can have the same set of 4 quantum numbers (n, l, m_l, m_s)

→ parallel spin rather than paired

H: $1s^1$

He: $1s^2$

Li: $1s^2 2s^1$

Be: $1s^2 2s^2$

B: $1s^2 2s^2 2p^1$

C: $1s^2 2s^2 2p^2$

N: $1s^2 2s^2 2p^3$

O: $1s^2 2s^2 2p^4$

F: $1s^2 2s^2 2p^5$
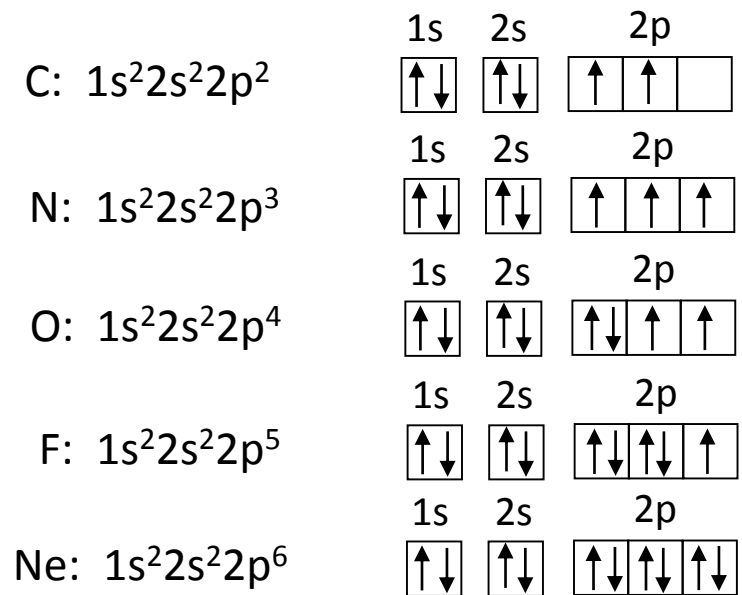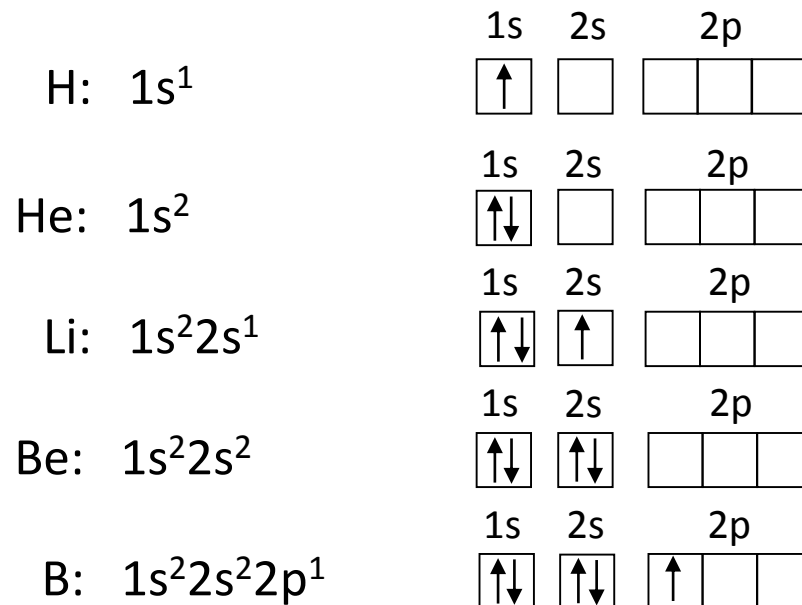
Ne: $1s^2 2s^2 2p^6$

Shell: all of the orbitals with the same *n*.

Na $1s^22s^22p^63s^1$ [Ne]$3s^1$

Mg $1s^22s^22p^63s^2$ [Ne]$3s^2$

Al $1s^22s^22p^63s^23p^1$ [Ne]$3s^23p^1$

.

.

.

Ar $1s^22s^22p^63s^23p^6$ [Ne]$3s^23p^6$

Core electrons Valence electrons

closed shell

valence shell

core electron

valence electron

	1s	2s	$2p_x$	$2p_y$	$2p_z$
H: $1s^1$	↑				
He: $1s^2$	↑↓				
Li: $1s^22s^1$	↑↓	↑			
Be: $1s^22s^2$	↑↓	↑↓			
B: $1s^22s^22p_x^1$	↑↓	↑↓	↑		
C: $1s^22s^22p_x^12p_y^1$	↑↓	↑↓	↑	↑	
N: $1s^22s^22p_x^12p_y^12p_z^1$	↑↓	↑↓	↑	↑	↑
O: $1s^22s^22p_x^22p_y^12p_z^1$	↑↓	↑↓	↑↓	↑	↑
F: $1s^22s^22p_x^22p_y^22p_z^1$	↑↓	↑↓	↑↓	↑↓	↑
Ne: $1s^22s^22p_x^22p_y^22p_z^2$	↑↓	↑↓	↑↓	↑↓	↑↓

1.14. Periodic trends in atomic properties

Atoms want to have "filled electronic shell".

F

1s 2s   2p

Unfilled n=2 shell

Filled n=1 shell
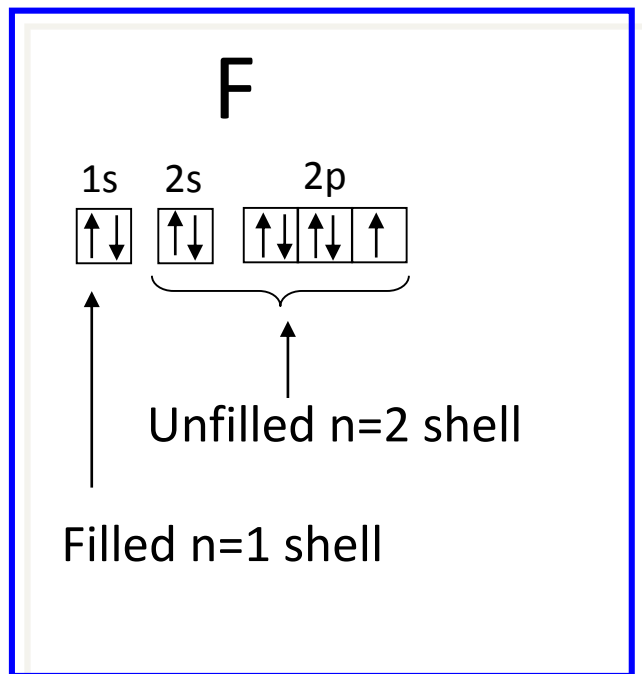
Chemically unstable,
Highly reactive

Ne

1s 2s   2p

Filled n=2 shell

Filled n=1 shell
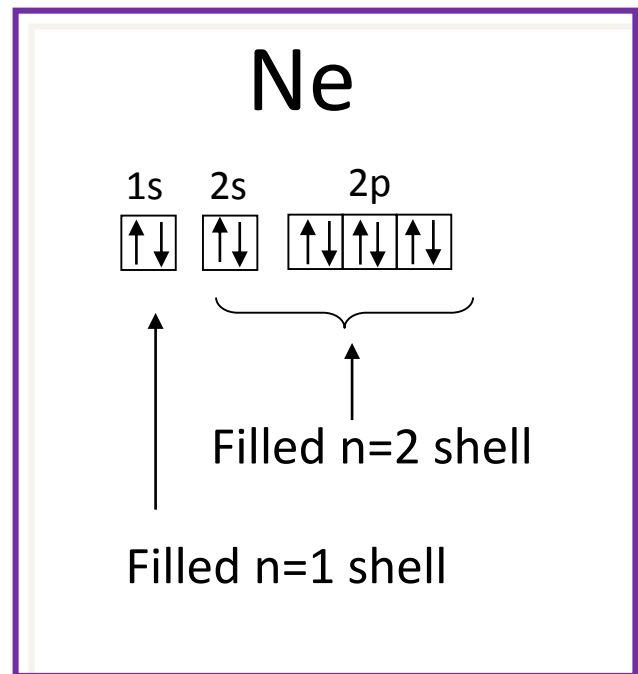
Chemically Stable,
does not react

Electron Configurations
of the first-low transition metals

d-block transition elements

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	Ac†	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub

f-block transition elements

	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
*Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ [Ar]$4s^1$

Ca: [Ar]$4s^2$

Sc: [Ar]$4s^2 3d^1$

Ti: [Ar]$4s^2 3d^2$

V: [Ar]$4s^2 3d^3$

Cr: [Ar]$4s^2 3d^4$ ➡ actually [Ar]$4s^1 3d^5$
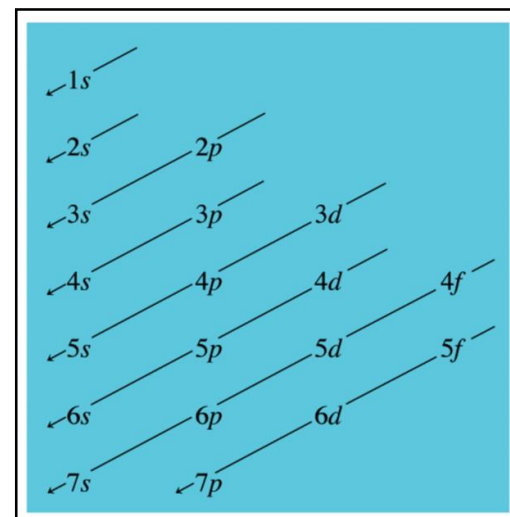
Mn: [Ar]$4s^2 3d^5$

Fe: [Ar]$4s^2 3d^6$

Co: [Ar]$4s^2 3d^7$

Ni: [Ar]$4s^2 3d^8$

Cu: [Ar]$4s^2 3d^9$ ➡ actually [Ar]$4s^1 3d^{10}$

Zn: [Ar]$4s^2 3d^{10}$

Transition elements favors half-filled and filled orbital!

$1s$
$2s$ $2p$
$3s$ $3p$ $3d$
$4s$ $4p$ $4d$ $4f$
$5s$ $5p$ $5d$ $5f$
$6s$ $6p$ $6d$
$7s$ $7p$

Partially filled d-orbitals

Filled d-orbitals + partially filled p

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$4s^1 3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$4s^1 3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$

1s																	1s
H																	He

2s–filling											2p–filling						
Li	Be										B	C	N	O	F	Ne	

3s–filling											3p–filling						
Na	Mg										Al	Si	P	S	Cl	Ar	

4s–filling		3d–filling									4p–filling						
K	Ca	Sc	Ti	V	Cr $3d^5 4s^1$	Mn	Fe	Co	Ni	Cu $3d^{10} 4s^1$	Zn	Ga	Ge	As	Se	Br	Kr

5s–filling		4d–filling									5p–filling						
Rb	Sr	Y	Zr	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10}$	Ag $4d^{10} 5s^1$	Cd	In	Sn	Sb	Te	I	Xe

6s–filling		5d–filling									6p–filling						
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt $5d^9 6s^1$	Au $5d^{10} 6s^1$	Hg	Tl	Pb	Bi	Po	At	Rn

7s–filling		6d–filling								
Fr	Ra	Lr	Rf	Ha	Sg	Ns	Hs	Mt	Uun	Uuu

4f–filling													
La $5d^1 6s^2$	Ce $4f^1 5d^1 6s^2$	Pr	Nd	Pm	Sm	Eu	Gd $4f^7 5d^1 6s^2$	Tb	Dy	Ho	Er	Tm	Yb

| 5f–filling													
Ac $6d^1 7s^2$	Th $6d^2 7s^2$	Pa $5f^2 6d^1 7s^2$	U $5f^3 6d^1 7s^2$	Np $5f^4 6d^1 7s^2$	Pu	Am	Cm $5f^7 6d^1 7s^2$	Bk	Cf	Es	Fm	Md	No

Why is this happening?

- 4s and 3d orbitals are close in energy.
- In fact, 'orbital picture' of the electrons is an approximation
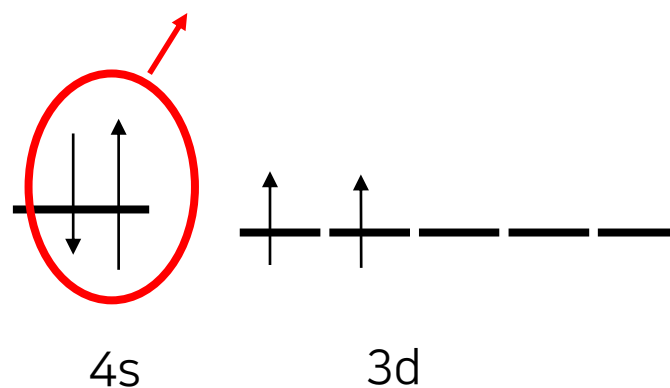- Electron-electron repulsion changes the energy level ordering.

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For transition metal,

- Ti: [Ar] $(4s)^2(3d)^2$ Ti^{3+} : $(4s)^0(3d)^1$

4s   3d   4s   3d
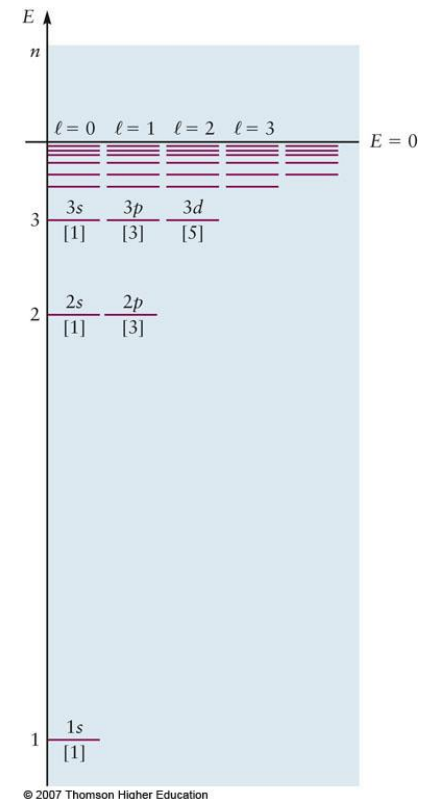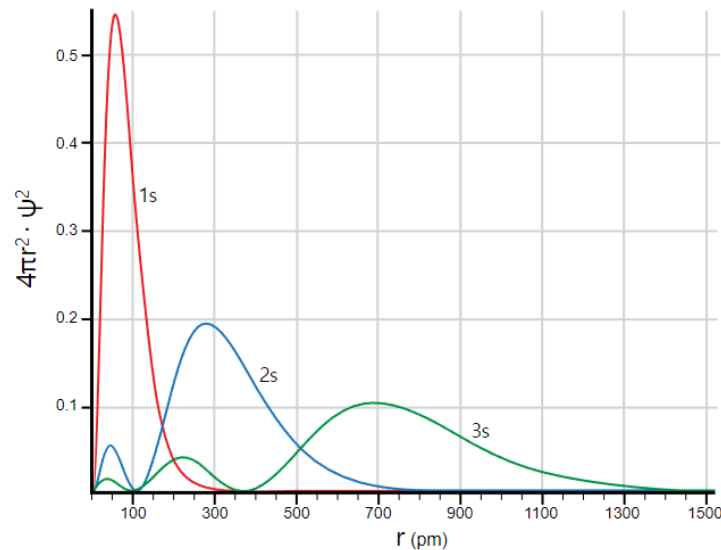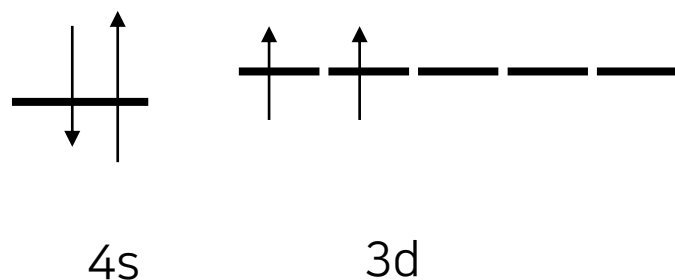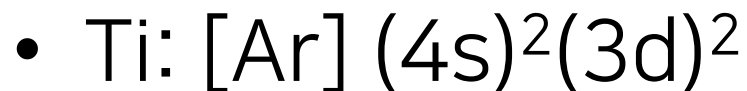
When adding electrons:

s-orbital fills first
d-orbital fills later

When losing electrons:

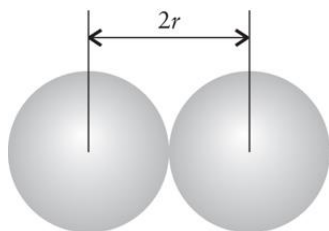s-orbital first
d-orbital later

Electronic Configuration of Ions.

- Sc^{2+}: $[Ar](4s)^0(3d)^1$
- Ti^{2+} : $[Ar](4s)^0(3d)^2$ Ti^{3+} : $(4s)^0(3d)^1$
- V^{2+} : $[Ar](4s)^0(3d)^3$
- Cr^{2+} : $[Ar](4s)^0(3d)^4$
- Mn^{2+} : $[Ar](4s)^0(3d)^5$
- Fe^{2+} : $[Ar](4s)^0(3d)^6$
- Co^{2+} : $[Ar](4s)^0(3d)^7$
- Ni^{2+} : $[Ar](4s)^0(3d)^8$
- Cu^{2+} : $[Ar](4s)^0(3d)^9$
- Zn^{2+} : $[Ar](4s)^0(3d)^{10}$

1.15. Atomic Radius

increase in effective Z (Z_{eff})

Increase in n

1.16. Ionic Radius

isoelectric ions

Sizes of atoms and their ions in pm
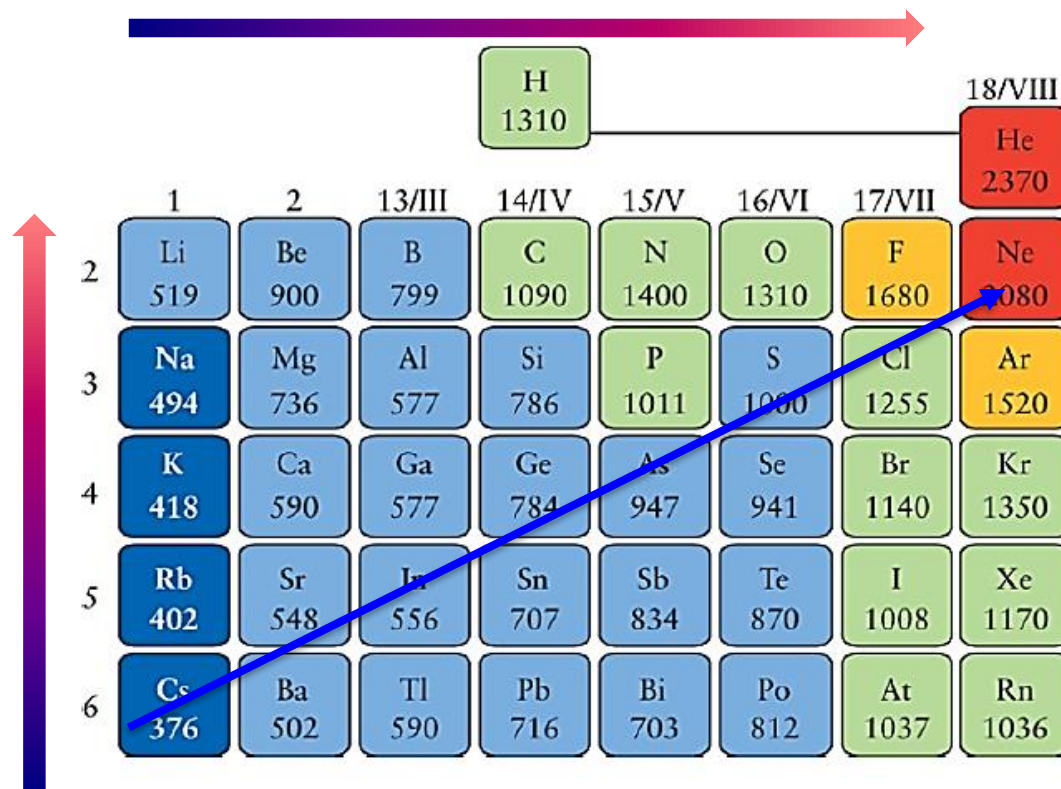
Group 1	Group 2	Group 13	Group 16	Group 17
Li⁺ 90 — Li 134	Be²⁺ 59 — Be 90	B³⁺ 41 — B 82	O 73 — O²⁻ 126	F 71 — F⁻ 119
Na⁺ 116 — Na 154	Mg²⁺ 86 — Mg 130	Al³⁺ 68 — Al 118	S 102 — S²⁻ 170	Cl 99 — Cl⁻ 167
K⁺ 152 — K 196	Ca²⁺ 114 — Ca 174	Ga³⁺ 76 — Ga 126	Se 116 — Se²⁻ 184	Br 114 — Br⁻ 182
Rb⁺ 166 — Rb 211	Sr²⁺ 132 — Sr 192	In³⁺ 94 — In 144	Te 135 — Te²⁻ 207	I 133 — I⁻ 206

1.17. Ionization Energy

The minimum E <u>need</u> to remove an electron from an atom in the gas phase.

$$X\ (g) \rightarrow X^+\ (g) + e^-\ (g) \qquad I = E(X^+) - E(X)$$
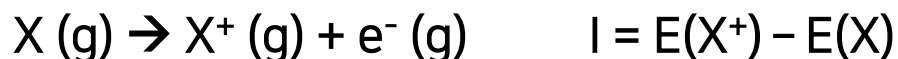
Typically, I_1 increases across a period

Typically,

I_1 decreases down a group

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
							H 1310	He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

Table: the 1st I (kJ mol^{-1})

Table: the 1ˢᵗ and 2ⁿᵈ I (kJ mol⁻¹)

Table: the 1st and 2nd I (kJ mol^{-1})

N: 1s^{2}2s^{2}2p^3

1s   2s   2p

| ↑↓ | ↑↓ | ↑ | ↑ | ↑ |

1s   2s   2p

| ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ |

O: 1s^{2}2s^{2}2p^4
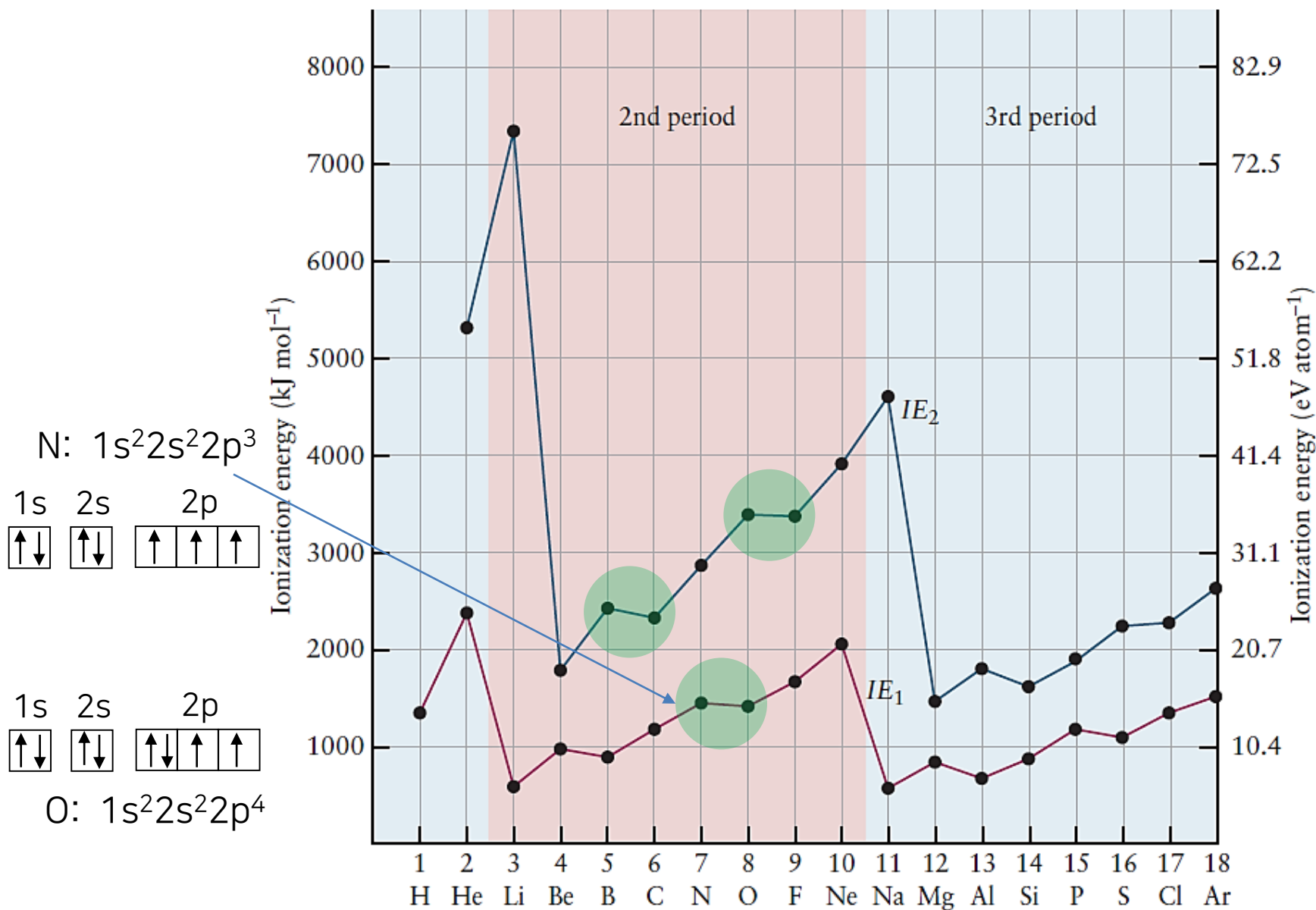
1.18. Electron Affinity

The E <u>released</u> when an electron is added to an atom in the gas phase.
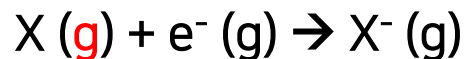
$$X\ (g) + e^-\ (g) \rightarrow X^-\ (g) \qquad\qquad E_{ea}\ (X) = E(X) - E(X^-)$$

Typically, E_{ea} increases across a period

H, Ne··· → Do not want to have one more electron

O, F, Cl,··· → Want to have more electrons

Typically,

E_{ea} decreases down a group

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
							H +73	He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200 −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0

electron affinity (kJ mol^{-1})