Chapter 3: Electronic Structure and Periodic Properties of Elements

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Energy and Energy Changes

Energy is the capacity to do work or transfer heat.

All forms of energy are either kinetic or potential.

Kinetic energy **(E_k)** is the energy of motion.

$$E_{\mathrm{k}} = \frac{1}{2}mu^2$$

m is the mass of the object
u is its velocity

One form of kinetic energy of interest to chemists is **thermal energy**, which is the energy associated with the random motion of atoms and molecules.

Potential energy is the energy possessed by an object by virtue of its position.

There are two forms of potential energy of great interest to chemists:

- **Chemical energy** is energy stored within the structural units of chemical substances.
- **Electrostatic energy** is potential energy that results from the interaction of charged particles.

$$E_{\mathrm{el}} = \frac{Q_1 Q_2}{d}$$

Q_1 and **Q_2** represent two charges separated by the distance, **d**.

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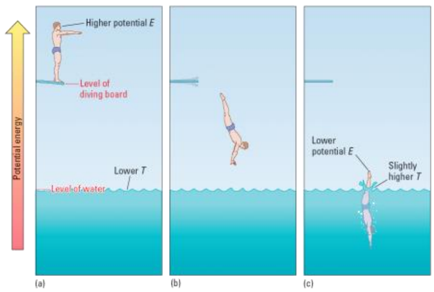
Energy and Energy Changes

Kinetic and potential energy are interchangeable – one can be converted to the other.

Although energy can assume many forms, the total energy of the universe is constant.
- Energy can neither be created nor destroyed.
- When energy of one form disappears, the same amount of energy reappears in another form or forms.
- This is known as the law of conservation of energy.



A diver:

Has E_p due to macroscale position.

Converts E_p to macroscale E_k.

Converts $E_{k,macroscale}$ to $E_{k,nanoscale}$ (motion of water, heat)

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Practice

Water in a damned-up lake :

Potential

Water rushing through turbines:

Kinetic

Moving baseball:

Kinetic

Diver standing on a cliff:

Potential

Gallon of gas:

Potential (chemical)

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Units of Energy

The SI unit of energy is the **joule (J)**, named for the English physicist James Joule. A Joule is the amount of energy possessed by a 2–kg mass moving at a speed of 1 m/s.

$$E_k = \frac{1}{2}mu^2 = \frac{1}{2}(2\ \text{kg})\left(\frac{1\ \text{m}}{\text{s}}\right)^2 = \frac{1\ \text{kg}\cdot\text{m}^2}{\text{s}^2} = 1\ \text{J}$$

The joule can also be defined as the amount of energy exerted when a force of 1 newton (N) is applied over 1 meter.

1 J = 1 N ·m

Because the magnitude of a joule is so small, we often express large amounts of energy using the unit kilojoule (kJ).

1 kJ = 1000 J

calorie (cal)

Originally: "The energy needed to heat of 1g of water from 1°C."

Now: 1 cal = 4.184 J (exactly)

Dietary Calorie (Cal) – the "big C" calorie. Used on food products.

1 Cal = 1000 cal = 1 kcal

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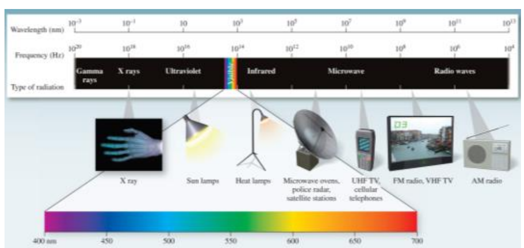
The Nature of Light



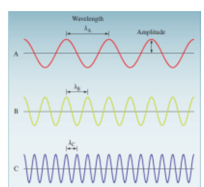
Visible light is only a small component of the continuum of radiant energy known as the **electromagnetic spectrum**.

All forms of electromagnetic radiation travel in waves. Waves are characterized by:

Wavelength (λ) – the distance between identical points on successive waves

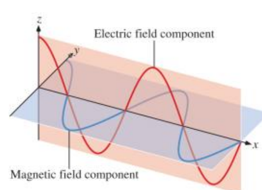
Frequency (ν) – the number of waves that pass through a point in 1 second.

Amplitude – the vertical distance from the midline of a wave to the top of the peak or the bottom of the trough.



An **electromagnetic wave** has both an electric field component and a magnetic component.

The electric and magnetic components have the same frequency and wavelength.



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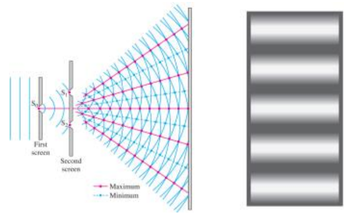
The Double–Slit Experiment

When light passes through two closely spaced slits, an interference pattern is produced.

Constructive interference is a result of adding waves that are in phase.

Destructive interference is a result of adding waves that are out of phase.



This type of interference is typical of waves and demonstrates the wave nature of light.

The speed of light (c) through a vacuum is a constant: $c = 2.998 \times 10^8$ m s^{-1}.
Speed of light, frequency and wavelength are related:

$$c = \lambda \nu$$

λ is expressed in meters
ν is expressed in reciprocal seconds (s^{-1})
s^{-1} is also known as hertz (Hz)

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Practice

(a) What is the frequency of radiation with a wavelength of 280 nm? (b) What is the wavelength of light with a frequency of 5.65×10^{14} Hz?

What is the frequency for 500. nm light?

Assume a microwave oven operates at a frequency of 1.80×10^{11} s^{-1}. What is the wavelength?

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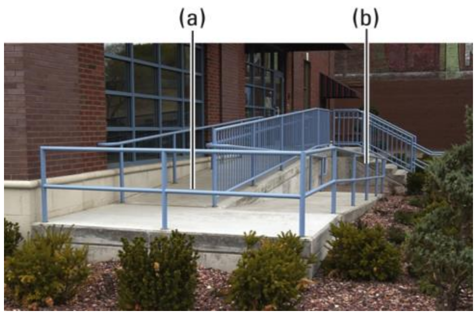
Quantum Theory

Early attempts by nineteenth-century physicists to figure out the structure of the atom met with only limited success. They were using the laws of classical physics. These laws describe the behavior of macroscopic objects.

Over time, the realization and acceptance was the behavior of subatomic particles is **NOT** governed by the same physical laws as larger objects. This became known as Quantum Mechanics.



Ramp ("classical") & stairs (quantized)

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Quantization of Energy

When a solid is heated, it emits electromagnetic radiation, known as **blackbody radiation**, over a wide range of wavelengths. The amount of energy given off at a certain temperature depends on the wavelength. Classical physics assumed that radiant energy was continuous; that is, could be emitted or absorbed in any amount.

Max Planck suggested that radiant energy is only emitted or absorbed in discrete quantities, like small packages or bundles. A **quantum** of energy is the smallest quantity of energy that can be emitted (or absorbed).

The energy E of a single quantum of energy is

$E = h\nu$ $\quad$ *h* : Planck's constant: **6.626×10^{-34} J·s**

The idea that energy is quantized rather than continuous is like walking up a staircase or playing the piano. You cannot step or play anywhere (continuous), you can only step on a stair or play on a key (quantized).

Einstein proposed that the beam of light is really a stream of particles. These "particles" of light are now called **photons**.

$c = \lambda\nu \qquad \nu = \frac{c}{\lambda} \qquad E = h\nu \qquad E = \frac{hc}{\lambda}$

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Practice

Calculate the energy (in joules) of (a) a photon with a wavelength of 501 nm and (b) a photon with a wavelength of 50.1 nm.

What is the energy of a photon at 379. nm?

What is the energy of a photon of frequency 4.86×10^{11} s^{-1}?

What is the frequency of light having an energy of 1.93×10^{-17} J

The nitrogen laser emits light at 337.1 nm. What is the energy of this light?

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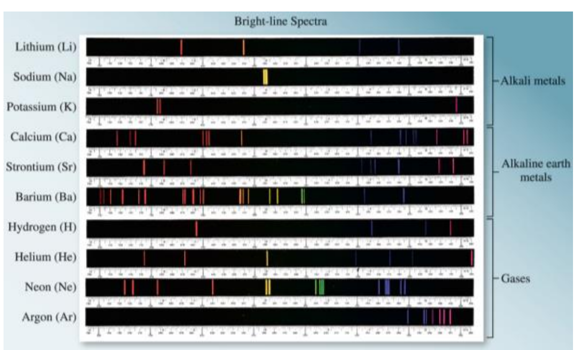
Bohr's Theory of the Hydrogen Atom

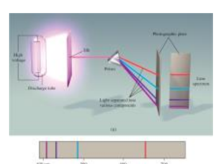
The **emission spectrum** of a substance can be seen by energizing a sample of material with some form of energy.

The "red hot" or "white hot" glow of an iron bar removed from a fire is the visible portion of its emission spectrum.

The emission spectrum of both sunlight and a heated solid are continuous; all wavelengths of visible light are present.

Line spectra are the emission of light only at specific wavelengths. Every element has its own unique emission spectrum.





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Atomic Line Spectra

The Rydberg equation can be used to calculate the wavelengths of the four visible lines in the emission spectrum of HYDROGEN.

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = -2.18\ x\ 10^{-18} J\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

R_∞ :Rydberg constant (1.09737317×10^7 m^{-1})
λ the wavelength of a line in the spectrum of hydrogen
n_1 and n_2 are positive integers where $n_2 > n_1$.
n_i (initial state) and n_f (final state)
ΔE negative (photon emitted: energy lost to surroundings); positive (photon absorbed)

Bohr's theory explains the line spectrum of the hydrogen atom. Radiant energy absorbed by the atom causes the electron to move from the ground state (n = 1) to an excited state (n > 1).

Conversely, radiant energy is emitted when the electron moves from a higher–energy state to a lower–energy excited state or the ground state.

The quantized movement of the electron from one energy state to another is analogous to a ball moving and down steps.

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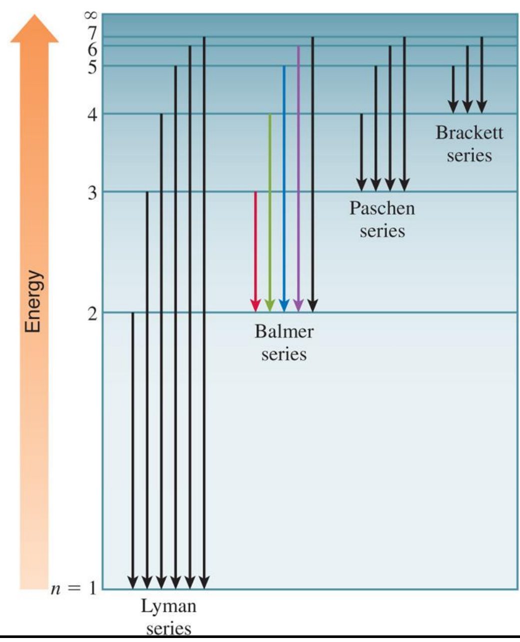
Atomic Line Spectra

The quantized movement of the electron from one energy state to another is analogous to a ball moving and down steps.



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The Line Spectrum of Hydrogen

Neils Bohr attributed the emission of radiation by an energized hydrogen atom to the electron dropping from a higher–energy orbit to a lower one.

As the electron dropped, it gave up a quantum of energy in the form of light.

Bohr showed that the energies of the electron in a hydrogen atom are given by the equation:

$$E_n = -2.18 \, x \, 10^{-18} \mathrm{J} \left(\frac{1}{n^2}\right)$$

E_n energy
n a positive integer

As an electron gets closer to the nucleus, n decreases. **E_n becomes larger in absolute value (more negative) as n gets smaller.**

E_n is most negative when n = 1.
Called the **ground state**, the lowest energy state of the atom
For hydrogen, this is the most stable state

The stability of the electron decreases as n increases.
Each energy state in which n > 1 is called an **excited state**.

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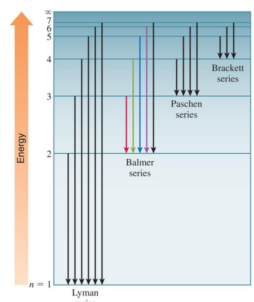
The Line Spectrum of Hydrogen

$$\Delta E = -2.18 \, x \, 10^{-18} \mathrm{J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Emission Series in the Hydrogen Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2,3,4,….	Ultraviolet (UV)
Balmer	2	3,4,5,….	Visible and UV
Paschen	3	4,5,6,….	Infrared
Brackett	4	5,6,7….	Infrared



Calculate the wavelength (in nm) of the photon emitted when an electron transitions from the *n* = 4 state to the *n* = 3 state in a hydrogen atom.

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Practice

Calculate the ΔE and wavelength (in nm) for an H–atom undergoing an n = 4 to n = 2 transition.

Calculate the wavelength emitted with an electron changes from n = 6 to n = 2 in the H atom. What is the Energy for that photon?

What is energy (in kJ) for 1 mole of those photons?

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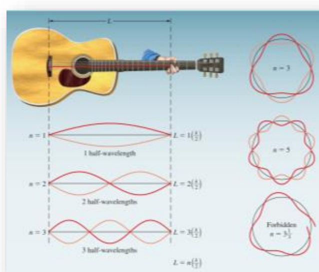
Wave Properties of Matter

Louis de Broglie reasoned that if light can behave like a stream of particles (photons), then electrons could exhibit wavelike properties.

According to de Broglie, electrons behave like standing waves.



Only certain wavelengths are allowed.

At a **node**, the amplitude of the wave is zero.

De Broglie deduced that the particle and wave properties are related by the following expression:

$$\lambda = \frac{h}{mu}$$

λ is the wavelength associated with the particle
m is the mass (in kg)
u is the velocity (in m/s)

The wavelength calculated from this equation is known as the **de Broglie wavelength**.

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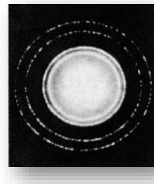
Diffraction of Electrons

Electron diffraction pattern of aluminum foil.



Experiments have shown that electrons do indeed possess wavelike properties:

The **Heisenberg uncertainty principle** states that it is impossible to know simultaneously both the momentum p and the position x of a particle with certainty.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Δx is the uncertainty in position in meters
Δp is the uncertainty in momentum

$$\Delta x \cdot m\Delta u \geq \frac{h}{4\pi}$$

Δu is the uncertainty in velocity in m/s
m is the mass in kg

An electron in a hydrogen atom is known to have a velocity of 4.99×10^6 m/s $\pm$ 5 percent. Using the uncertainty principle, calculate the minimum uncertainty in the position of the electron. (the mass of an electron is 9.11×10^{-31} kg)

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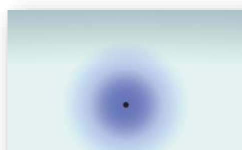
The Schrödinger Equation and The Quantum Mechanical Description of the H–Atom

Erwin Schrödinger derived a complex mathematical formula to incorporate the wave and particle characteristics of electrons. Wave behaviour is described with the **wave function** ψ.

The probability of finding an electron in a certain area of space is proportional to ψ^2 and is called **electron density**.

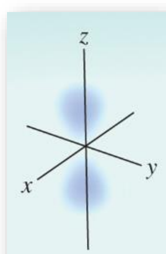
Quantum Mechanics defines the region where the electron is most likely to be at a given time


Probability map of an electron in an H atom

The Schrödinger equation specifies possible energy states an electron can occupy in a hydrogen atom.

The energy states and wave functions are characterized by a set of quantum numbers.

Instead of referring to orbits as in the Bohr model, quantum numbers and wave functions describe **atomic orbitals**.



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Quantum Numbers

Quantum numbers are required to describe the distribution of electron density in an atom (location of the electron.)

There are three quantum numbers necessary to describe an **atomic orbital**.

The **principal quantum number (n)** – designates **size**

Larger values of n correspond to larger orbitals (higher energy).
The allowed values of n are integral numbers: 1, 2, 3 and so forth.
The value of n corresponds to the value of n in Bohr's model of the hydrogen atom.
A **collection of orbitals with the same value of n is frequently called a shell.**

The **angular moment quantum number (ℓ)** – describes **shape**

The values of ℓ are integers that depend on the value of the principal quantum number
The allowed values of ℓ range from 0 to n – 1. Example: If n = 2, ℓ can be 0 or 1.

ℓ	**0**	**1**	**2**	**3**
Orbital Designation (Shape)	*s*	*p*	*d*	*f*

A collection of orbitals with the same value of n and l is referred to as a subshell.

The **magnetic quantum number (m_ℓ)** – specifies **orientation/direction**

The values of m_ℓ are integers that depend on the value of the angular moment quantum number:
– l,…0,…+l

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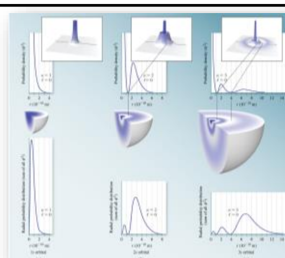
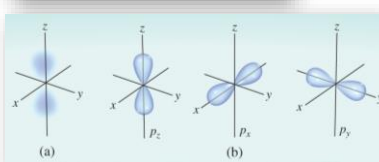
Atomic Orbitals

All **s orbitals** are spherical: One orientation:
ℓ=0
m_ℓ=0

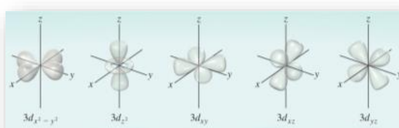
principal quantum number (n = 2) → 2*s* ← angular momentum quantum number (ℓ = 0)
m_ℓ = 0; only 1 orientation possible



p orbitals are dumbbell shaped: Three orientations:
ℓ=1
m_ℓ= –1, 0, +1



d orbitals: Five orientations:
ℓ=2
m_ℓ= *–2, –1, 0, +1, or +2*



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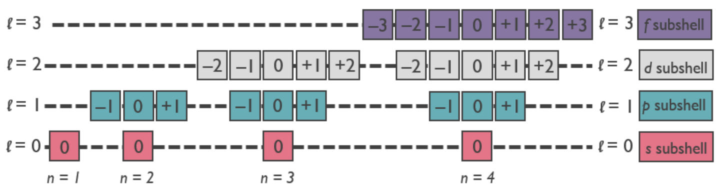
Quantum Numbers

Allowed Values of the Quantum Numbers n, ℓ, and m_ℓ			
n	ℓ can be	When ℓ is	m_ℓ can be
1	Only 0	0	Only 0
2	0 or 1	0	Only 0
		1	−1, 0, or +1
3	0, 1, or 2	0	Only 0
		1	−1, 0, or +1
		2	−2, −1, 0, +1, +2
4	0, 1, 2, or 3	0	Only 0
		1	−1, 0, or +1
		2	−2, −1, 0, +1, +2
		3	−3, −2, −1, 0, +1, +2, +3

Quantum numbers designate shells, subshells, and orbitals.



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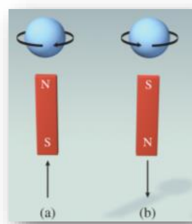
Atomic Orbitals

The **electron spin quantum number** (m_s) is used to specify an electron's spin. There are two possible directions of spin. Allowed values of m_s are +½ and −½.



To summarize quantum numbers:

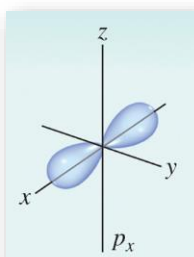
principal (n) – size
angular (ℓ) – shape
magnetic (m_ℓ) – orientation
electron spin (m_s) direction of spin

Principal (n=2)

Angular Momentum (ℓ = 1)

$2p_x$

Related to the Magnetic Quantum (m_ℓ=1)



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Practice

What are the possible values for the magnetic quantum number (m_l) when the principal quantum number (*n*) is 2 and the angular quantum number (l) is 0?

List the values of *n*, l, and m_l for each of the orbitals in a 2p subshell.

Which of the following is a legitimate set of quantum numbers for *n*, *ℓ*, and m_ℓ respectively, which corresponds to an 5*f* orbital?

A. 5, 4, –4 B. 3, 3, – 1 C. 5, 4, 0 D. 5, 3, 0

Which of the following is a list of allowed quantum numbers for an electron?

A. $n = 1, \ell = 1, m_\ell = 0, m_s = ½$

B. $n = 2, \ell = 0, m_\ell = 1, m_s = ½$

C. $n = 3, \ell = 0, m_\ell = 0, m_s = ½$

D. $n = 4, \ell = 3, m_\ell = 4, m_s = –½$

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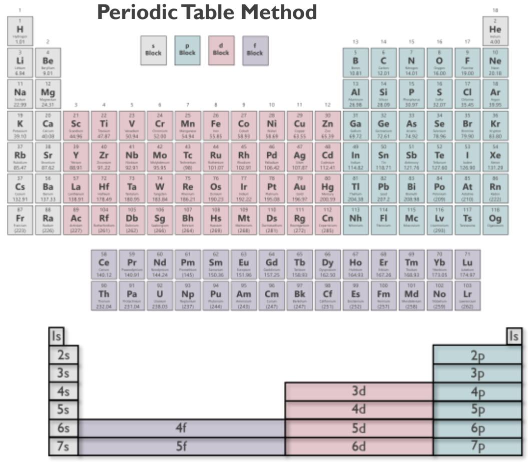
Electron Configurations

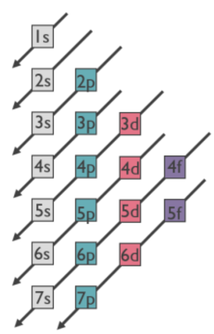
General rules for writing electron configurations:

1. Electrons will reside in the available orbitals of the lowest possible energy.
2. Each orbital can accommodate a maximum of two electrons.
3. Electrons will not pair in degenerate orbitals if an empty orbital is available.
4. Orbitals will fill in the order indicated in the figure.

Periodic Table Method



Up-Side Down Christmas Tree



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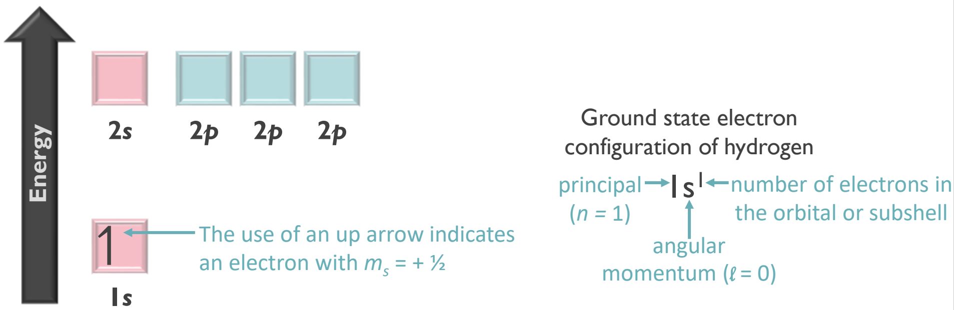
Electron Configurations

The **electron configuration** describes how the electrons are distributed in the various atomic orbitals.

In a ground state hydrogen atom, the electron is found in the 1s orbital.



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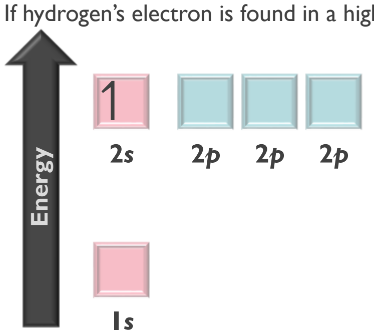
Electron Configurations

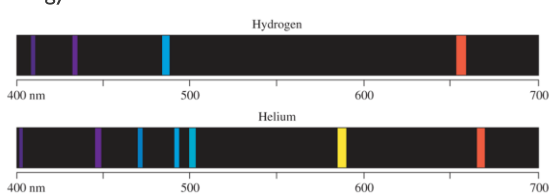
If hydrogen's electron is found in a higher energy orbital, the atom is in an *excited state.*



Possible excited state electron configuration of hydrogen.

$2s^1$

The helium emission spectrum is more complex than the hydrogen spectrum. There are more possible energy transitions in a helium atom because helium has two electrons.



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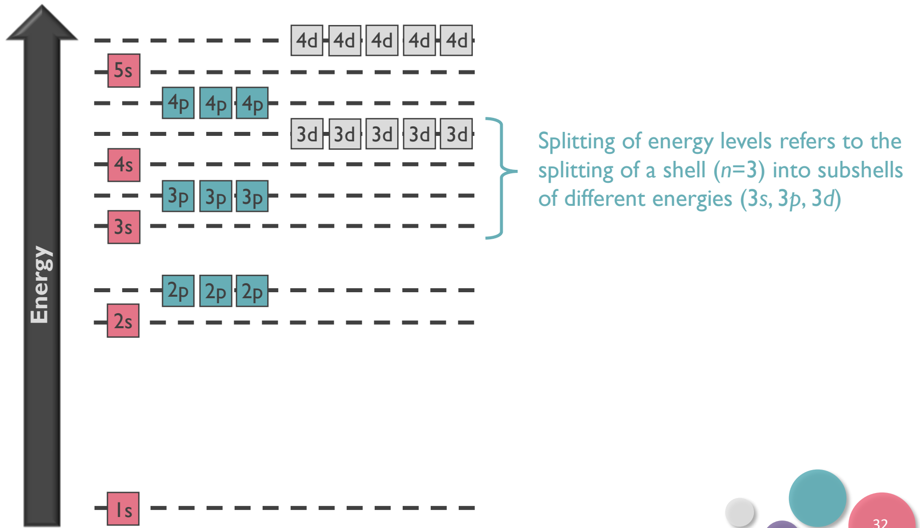
Electron Configurations

In a multi-electron atoms, the energies of the atomic orbitals are split.



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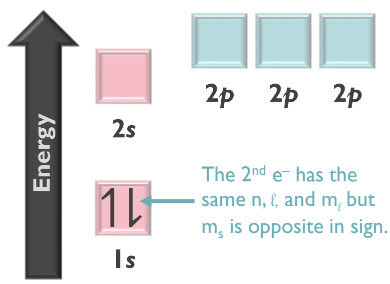
Electron Configurations

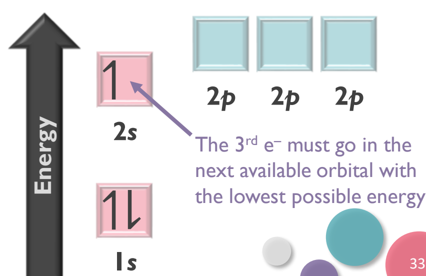
According to the **Pauli exclusion principle**, no two electrons in an atom can have the same four quantum numbers.

The **Aufbau principle** states that electrons are added to the lowest energy orbitals first before moving to higher energy orbitals.

The ground state electron configuration of He (2 e⁻)
$1s^2$



The ground state electron configuration of Li (3 e⁻)
$1s^2 2s^1$



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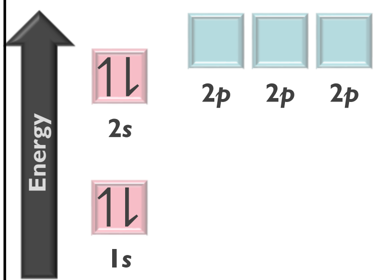
Electron Configurations

The **Aufbau principle** states that electrons are added to the lowest energy orbitals first before moving to higher energy orbitals.

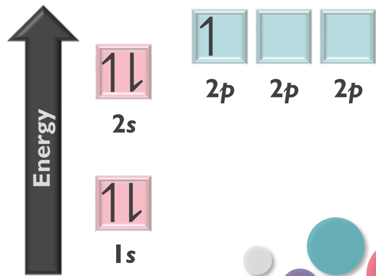
The ground state electron configuration of Be (4 e⁻)

$1s^2 2s^2$



The ground state electron configuration of B (5 e⁻)

$1s^2 2s^2 2p^1$



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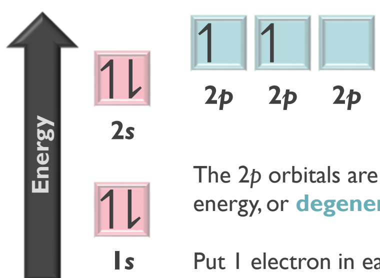
Electron Configurations

According to **Hund's rule**, the most stable arrangement of electrons is the one in which the number of electrons with the same spin is maximized.

The ground state electron configuration of C (6 e⁻)

$1s^2 2s^2 2p^2$

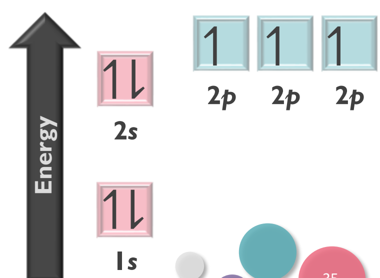


The 2*p* orbitals are of equal energy, or **degenerate**.

Put 1 electron in each before pairing (Hund's rule).

The ground state electron configuration of N (7 e⁻)

$1s^2 2s^2 2p^3$



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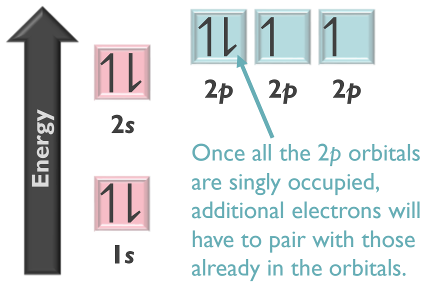
Electron Configurations

According to **Hund's rule**, the most stable arrangement of electrons is the one in which the number of electrons with the same spin is maximized.

When there are one or more unpaired electrons, as in the case of oxygen and fluorine, the atom is called **paramagnetic**.

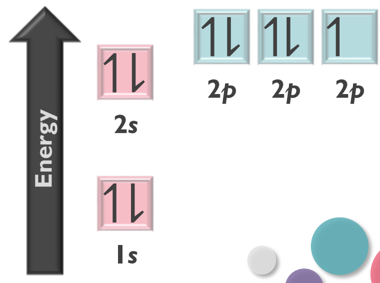
The ground state electron configuration of O (8 e^-)

$1s^2 2s^2 2p^4$



The ground state electron configuration of F (9 e^-)

$1s^2 2s^2 2p^5$



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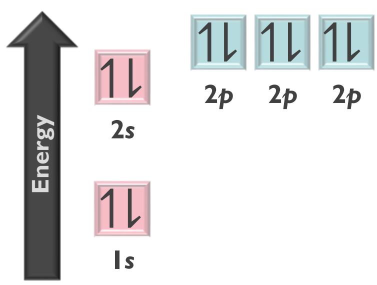
Electron Configurations

When all electrons in an atom are paired, as in neon, it is called **diamagnetic**.

The ground state electron configuration of Ne (10 e^-)

$1s^2 2s^2 2p^6$



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Practice

Write the electron configuration and give the orbital diagram of Fe (Z = 26) and Ar (Z = 18).

The 7 electrons in Nitrogen are found in the following atomic shells. List the quantum numbers for each electron.

1s (2 electrons)

2s (2 electrons)

2p (3 electrons)

Which of the following electron configurations represents silicon?

A. $1s^22s^22p^63s^33p^2$
B. $1s^22s^32p^63s^23p^2$
C. $1s^22s^22p^63s^23p^2$
D. $1s^22s^22p^63s^23p^4$

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Practice

Write the electron configuration for the following elements:

Mg	Ba
P	V
Ni	Sr
Ag	W
Pb	O

What is the correct electron configuration for sulfur?

A. $1s^22s^22p^63s^23p^5$
B. $1s^22s^22p^63s^23p^4$
C. $1s^22s^22p^73s^23p^2$
D. $3s^23p^4$

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Electron Configurations and the Periodic Table

The electron configurations of all elements except hydrogen and helium can be represented using a **noble gas core**. These core electrons are highly stable. Those not in the core are considered **valence** electrons.

The electron configuration of potassium (Z = 19) is $1s^22s^22p^63s^23p^64s^1$. Ar has an electron configuration of $1s^22s^22p^63s^23p^6$, allowing us to simplify potassium's configuration to $[Ar]4s^1$.

Ground State Electron Configuration of K:

$\underbrace{1s^22s^22p^63s^23p^6}_{[Ar]}4s^1$

Noble Gas Configuration of K:

$\mathbf{[Ar]4s^1}$

Give the noble gas configuration for the following:

Ba

Hg

Fe

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Electron Configurations and the Periodic Table

There are several notable exceptions to the order of electron filling for some of the transition metals.

The reason for these anomalies is the slightly greater stability of *d* subshells that are either half-filled (d^5) or completely filled (d^{10}).

Copper (Z = 29) is $[Ar]4s^13d^{10}$ and NOT $[Ar]4s^23d^9$ as expected.

Cu:	**[Ar]**	↑	↑↓	↑↓	↑↓	↑↓	↑↓
		4s	**3d**	**3d**	**3d**	**3d**	**3d**

Chromium (Z = 24) is $[Ar]4s^13d^5$ and NOT $[Ar]4s^23d^4$ as expected.

Cr:	**[Ar]**	↑	↑	↑	↑	↑	↑
		4s	**3d**	**3d**	**3d**	**3d**	**3d**

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Diamagnetic and Paramagnetic

Spinning e^- = tiny magnet. If all e^- are paired, then the magnets cancel.

The atom is **diamagnetic** and is pushed weakly away from magnetic fields.

With unpaired e^-:

Unpaired spins point in the same direction (Hund's rule) making the magnets add together.

The atom is **paramagnetic** and are attracted to magnetic fields.

If individual atom-magnets line up in a bulk sample

A **ferromagnet** – a permanent magnet.

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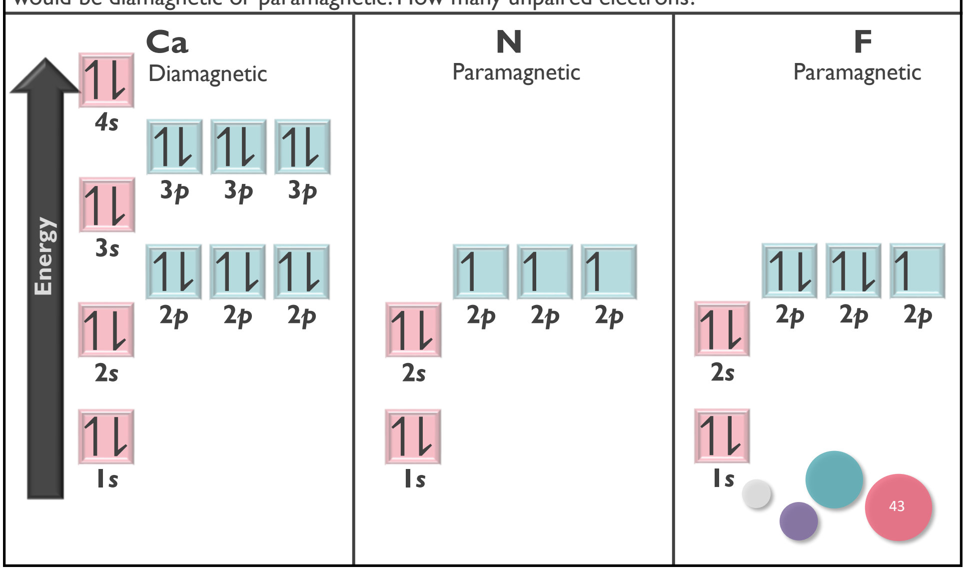
Diamagnetic and Paramagnetic

For each of the atoms/ions below, draw out the electrons with energy levels and determine if it would be diamagnetic or paramagnetic. How many unpaired electrons?



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Development of the Periodic Table

However, Mendeleev could not explain inconsistencies such as argon coming before potassium in the periodic table, despite having a higher atomic mass.

In 1913, Henry Moseley discovered the correlation between the number of protons (*atomic number*) and frequency of X-rays generated. Ordering the periodic table by atomic number instead of atomic mass enabled scientists to make sense of discrepancies. Entries today include atomic number and symbol; and are arranged according to electron configuration.

Summarizes

- Atomic numbers.
- Atomic weights.
- Physical state (solid/liquid/gas).
- Type (metal/non-metal/metalloid).

Periodicity

- Elements with similar properties are arranged in vertical groups.

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Modern Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.01																	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
37 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium (293)	117 Ts Tennessine	118 Og Oganesson

58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.05	71 Lu Lutetium 174.97
90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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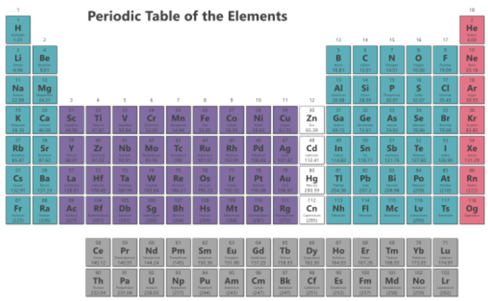
Classification of Elements

The **main group elements** (also called the representative elements) are the elements in Groups 1A through 7A.

The **noble gases** are found in Group 8A and have filled p subshells.

The transition metals are found in Group 1B and 3B through 8B.
Group 2B have filled *d* subshells and are **NOT** transition metals.

The **lanthanides** and **actinides** make up the *f*-block transition elements.



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The Modern Periodic Table

There is a distinct pattern to the electron configurations of the elements in a particular group.

For Group 1A: [noble gas]ns^1 For Group 2A: [noble gas]ns^2

Electron Configurations of Group 1A and Group 2A Elements			
Group 1A		Group 2A	
Li	[He]$2s^1$	Be	[He]$2s^2$
Na	[Ne]$3s^1$	Mg	[He]$2s^2$
K	[Ar]$4s^1$	Ca	[He]$2s^2$
Rb	[Kr]$5s^1$	Sr	[He]$2s^2$
Cs	[Xe]$6s^1$	Ba	[He]$2s^2$
Fr	[Rn]$7s^1$	Ra	[He]$2s^2$

The outermost electrons of an atom are called the **valence electrons**.
Valence electrons are involved in the formation of chemical bonds.
Similarity of valence electron configurations help predict chemical properties.
All electrons associated with the highest principle quantum number are valence

For Group 1A: [noble gas]ns^1 (core: [noble gas]; valence: ns^1)

For Group 7A: [noble gas]ns^2np^5 (core: [noble gas]; valence: ns^2np^5)

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Practice

Determine the number of valence electrons for the following elements:

K	Cu
Mg	Mo
Se	Ni
I	Zn
Al	Fe
Si	Cr

When the d shell is filled (d^{10}), then the d electrons don't count as valence.

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Electron Configurations of Ions

To write the electron configuration of an ion formed by a main group element:

1. Write the configuration for the atom.
2. Add or remove the appropriate number of electrons. Positive ions, remove electrons; negative ions, add electrons

Na: $1s^22s^22p^63s^1 \longrightarrow$ Na^+: $1s^22s^22p^6$ 10 electrons total, **isoelectronic** with Ne

Cl: $1s^22s^22p^63s^23p^5 \longrightarrow$ Cl^-: $1s^22s^22p^63s^23p^6$ 18 electrons total, **isoelectronic** with Ar

Species with identical electron configurations to the noble gas to the right are called **isoelectronic**

Common monatomic ions arranged by their positions in the periodic table

Note that mercury(I) is a **poly**atomic ion (Hg_2^{2+})

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Practice

Write electron configurations for the following ions of main group elements: (a) N^{3-}, (b) Ba^{2+}, and (c) Be^{2+}.

Determine the electron configuration for the following ions:

Cl^{-}

N^{3-}

K^{+}

Ca^{2+}

Are any of them isoelectronic?

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Electron Configurations of d-block Elements

Ions of d-block elements are formed by removing electrons first from the shell with the highest value of n.

For Fe to form Fe^{2+}, two electrons are lost from the 4s subshell not the 3d.

Fe: $[Ar]4s^2 3d^6 \longrightarrow Fe^{2+}$: $[Ar]3d^6$

Fe can also form Fe^{3+}, in which case the third electron is removed from the 3*d* subshell.

Fe: $[Ar]4s^2 3d^6 \longrightarrow Fe^{3+}$: $[Ar]3d^5$

Write electron configurations for the following ions of *d*-block elements: (a) Zn^{2+}, (b) Mn^{2+}, and (c) Cr^{3+}.

(a) $[Ar]3d^{10}$ (b) $[Ar]3d^5$ (c) $[Ar]3d^3$

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Practice

Determine the electron configuration for the following ions:

Fe^{+2}

Fe^{+3}

Cr^{+3}

Ti^{+2}

Ti^{+4}

Ni^{+2}

Ag^{+}

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Periodic Trends and Properties of Elements

Atomic radius is the distance between the nucleus of an atom and its valence shell.

(a) Atomic radius in metals, or **metallic radius**, is half the distance between the nuclei of two adjacent, identical metal atoms.
(b) Atomic radius in nonmetals, or **covalent radius**, is half the distance between adjacent, identical nuclei connected by a chemical bond.

Effective nuclear charge **(Z_{eff})** is the actual magnitude of positive charge that is "experienced" by an electron in the atom.
In a multi-electron atom, electrons are simultaneously attracted to the nucleus and repelled by one another.

This results in **shielding**, where an electron is partially shielded from the positive charge of the nucleus by the other electrons.
Although all electrons shield one another to some extent, the most effective are the core electrons.

As a result, the value of Z_{eff} increases steadily from left to right because the core electrons remain the same but Z increases.

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Effective Nuclear Charge

Z_{eff} increases steadily from left to right because the core electrons remain the same but Z increases.

	Li	Be	B	C	N	O	F
Z	3	4	5	6	7	8	9
Z_{eff}	1.28	1.91	2.42	3.14	3.83	4.45	5.10

In general, the effective nuclear charge is given by: $Z_{eff} = Z - \sigma$

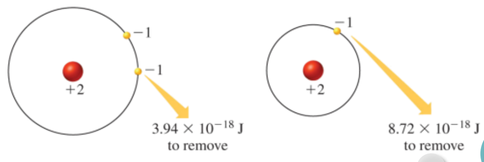
Z is the nuclear charge, the number of protons in the nucleus.

σ is the shielding constant.

Z_{eff} increases from left to right across a period; changes very little down a column.

Example of He:

Removal of 1[st] e⁻ requires less energy than removal of the second e⁻ due to shielding



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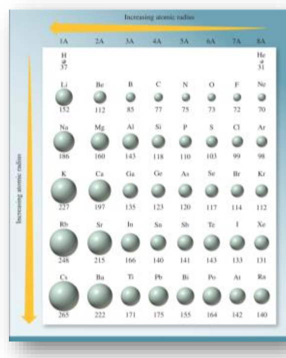
Atomic Radius



The atomic radius increases from top to bottom down a group.

Increasing n, so outermost shell lies farther from the nucleus

Atomic radius decreases from left to right across a period.

Increasing Z_{eff} which draws the valence shell closer to the nucleus

Atomic radius decreases left to right across a period due to increased electrostatic attraction between the effective nuclear charge and the charge on the valence shell.

	Li	Be	B	C	N	O	F
Z_{eff}	1.28	1.91	2.42	3.14	3.83	4.45	5.10
Charge on valence shell	−1	−2	−3	−4	−5	−6	−7
$F \propto$	$\frac{(+1.28)(-1)}{d^2}$	$\frac{(+1.91)(-2)}{d^2}$	$\frac{(+2.42)(-3)}{d^2}$	$\frac{(+3.14)(-4)}{d^2}$	$\frac{(+3.83)(-5)}{d^2}$	$\frac{(+4.45)(-6)}{d^2}$	$\frac{(+5.10)(-7)}{d^2}$

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Practice

Increasing
ATOMIC RADIUS

Referring only to a periodic table, arrange the elements P, S, and O in order of increasing atomic radius.

Using only the periodic table arrange the following elements in order of increasing atomic radius: **Astatine, Bromine, Chlorine, Fluorine, Iodine**

Which is the largest atom below?

A. O
B. N
C. Al
D. S
E. Mg

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Ionization Energy

Ionization energy (IE) is the minimum energy required to remove an electron from an atom in the gas phase.
The result is an **ion**, a chemical species with a net charge.

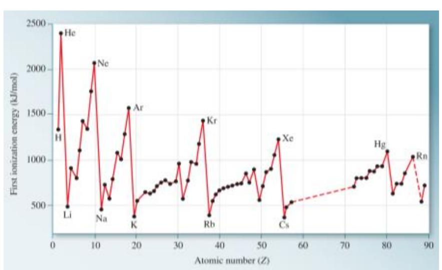
$$Na(g) \longrightarrow Na^{+}(g) + e^{-}$$

Sodium has an ionization energy of 495.8 kJ/mol. Specifically, 495.8 kJ mol^{-1} is the first ionization energy of sodium, IE_1(Na), which corresponds to the removal of the most loosely held electron.

In general, as Z_{eff} increases, ionization energy also increases. Thus, IE_1 increases from left to right across a period.

1A 1	2A 2	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
H 1312							He 2372
Li 520	Be 899	B 800	C 1086	N 1402	O 1314	F 1681	Ne 2080
Na 496	Mg 738	Al 577	Si 786	P 1012	S 999	Cl 1256	Ar 1520
K 419	Ca 590	Ga 579	Ge 761	As 947	Se 941	Br 1143	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	Te 869	I 1009	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 813	At (926)	Rn 1037

IE_1 values for main group elements (kJ/mol)



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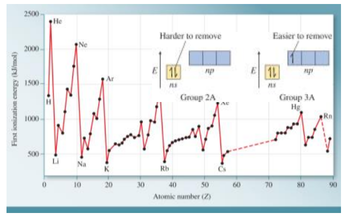
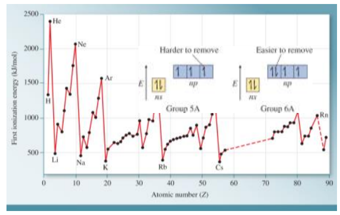
Ionization Energy

Within a given shell, electrons with a higher value of *l* are higher in energy and thus, easier to remove.



Removing a paired electron is easier because of the repulsive forces between two electrons in the same orbital.



It is possible to remove additional electrons in subsequent ionizations, giving IE_1, IE_2, and so on.

$Na(g) \longrightarrow Na^{+}(g) + e^{-}$
$IE_1(Na) = 496$ kJ/mol

$Na^{+}(g) \longrightarrow Na^{+2}(g) + e^{-}$
$IE_2(Na) = 4562$ kJ/mol

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Ionization Energy

It takes more energy to remove the 2nd, 3rd, 4th, etc. electrons because it is harder to remove an electron from a cation than an atom.

It takes much more energy to remove core electrons than valence.

- Core electrons are closer to nucleus.
- Core electrons experience greater Z_{eff} because of fewer filled shells shielding them from the nucleus.

<u>Increasing</u>
Ionization Energy

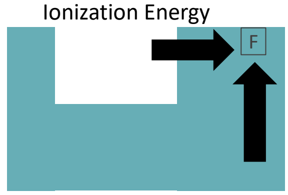

TABLE 4.2 Ionization Energies (in kJ/mol) for Elements 3 through 11*

	Z	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
Li	3	520	7,298	11,815							
Be	4	899	1,757	14,848	21,007						
B	5	800	2,427	3,660	25,026	32,827					
C	6	1,086	2,353	4,621	6,223	37,831	47,277				
N	7	1,402	2,856	4,578	7,475	9,445	53,267	64,360			
O	8	1,314	3,388	5,301	7,469	10,990	13,327	71,330	84,078		
F	9	1,681	3,374	6,050	8,408	11,023	15,164	17,868	92,038	106,434	
Ne	10	2,080	3,952	6,122	9,371	12,177	15,238	19,999	23,069	115,380	131,432
Na	11	496	4,562	6,910	9,543	13,354	16,613	20,117	25,496	28,932	141,362

*Cells shaded with blue represent the removal of core electrons.

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Practice

Would you expect Na or Mg to have the greater first ionization energy (IE_1)? Which should have the greater second ionization energy (IE_2)?

Which atom below has the greatest ionization energy?

A. Li
B. Ne
C. Na
D. Kr

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Electron Affinity

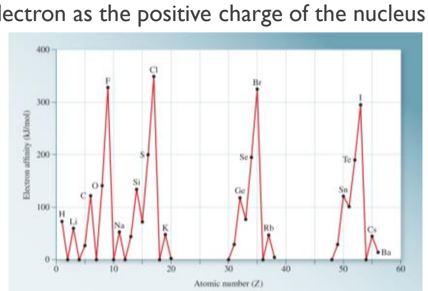
Electron affinity (EA) is the energy released when an atom in the gas phase accepts an electron.

$$Cl(g) + e^{-} \longrightarrow Cl^{-}(g)$$

1A 1	2A 2	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
H +72.8							He (0.0)
Li +59.6	Be ≤0	B +26.7	C +122	N −7	O +141	F +328	Ne (−29)
Na +52.9	Mg ≤0	Al +42.5	Si +134	P +72.0	S +200	Cl +349	Ar (−35)
K +48.4	Ca +2.37	Ga +28.9	Ge +119	As +78.2	Se +195	Br +325	Kr (−39)
Rb +46.9	Sr +5.03	In +28.9	Sn +107	Sb +103	Te +190	I +295	Xe (−41)
Cs +45.5	Ba +13.95	Tl +19.3	Pb +35.1	Bi +91.3	Po +183	At +270	Rn (−41)

Like ionization energy, electron affinity increases from left to right across a period as Z_{eff} increases.

Easier to add an electron as the positive charge of the nucleus increases.



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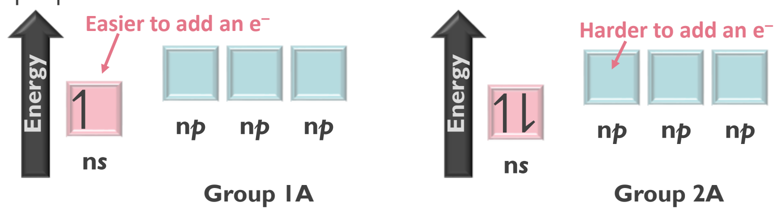
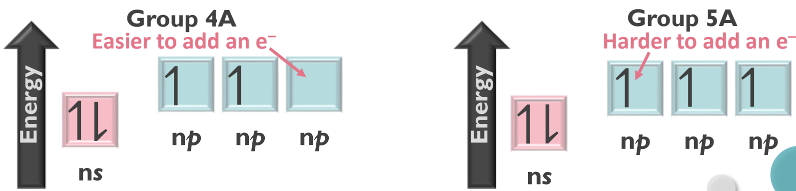
Electron Affinity

It is easier to add an electron to an *s* orbital than to add one to a *p* orbital with the same principal quantum number.



Within a *p* subshell, it is easier to add an electron to an empty orbital than to add one to an orbital that already contains an electron.



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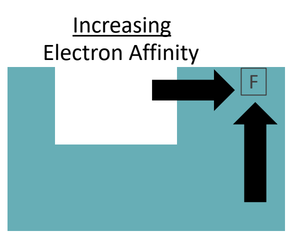
Electron Affinity

More than one electron may be added to an atom.

Process	Electron Affinity
$O(g) + e^- \longrightarrow O^-(g)$	$EA_1 = 141$ kJ mol^{-1}
$O^-(g) + e^- \longrightarrow O^{2-}(g)$	$EA_2 = -741$ kJ mol^{-1}

While many first electron affinities are positive, subsequent electron affinities are always negative.

Considerable energy is required to overcome the repulsive forces between the electron and the negatively charged ion.



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Practice

For each pair of elements, indicate which one you would expect to have the greater first electron affinity, EA_1: (a) Al or Si, (b) Si or P.

Which process illustrates electron affinity?

A. $Li \longrightarrow Li^+ + e^-$

B. $O + e^- \longrightarrow O^-$

C. $O + O \longrightarrow O_2$

D. $Na + Cl \longrightarrow Na^+ + Cl^-$

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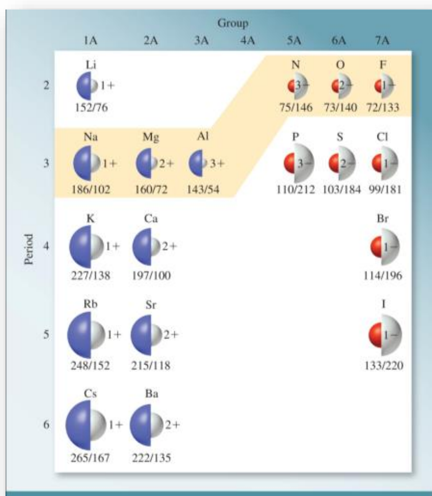
Ionic Radius

The **ionic radius** is the radius of a cation or an anion.

When an atom loses an electron to become a cation, its radius decreases due in part to a reduction in electron-electron repulsions in the valence shell.

A significant decrease in radius occurs when all of an atom's valence electrons are removed.

When an atom gains one or more electrons and becomes an anion, its radius increases due to increased electron-electron repulsions.



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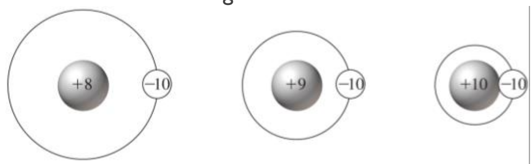
Isoelectronic Series

An **isoelectronic series** is a series of two or more species that have identical electron configurations, but different nuclear charges.



All Are Isoelectronic

O^{2-}: $1s^22s^22p^6$ F^-: $1s^22s^22p^6$ Ne: $1s^22s^22p^6$

Isoelectronic Ions	O^{2-}	F^-	Na^+	Mg^{2+}
Ionic Radius (pm)	126	119	116	86
Number of Protons	8	9	11	12
Number of Electrons	10	10	10	10

Increasing nuclear charge → decreasing size

Practice

Identify the isoelectronic series in the following group of species and arrange them in order of increasing radius: K^+, Ne, Ar, Kr, P^{3-}, S^{2-}, and Cl^-.

Which of two species below are isoelectronic?

A. O^{2-}, C^{4-}

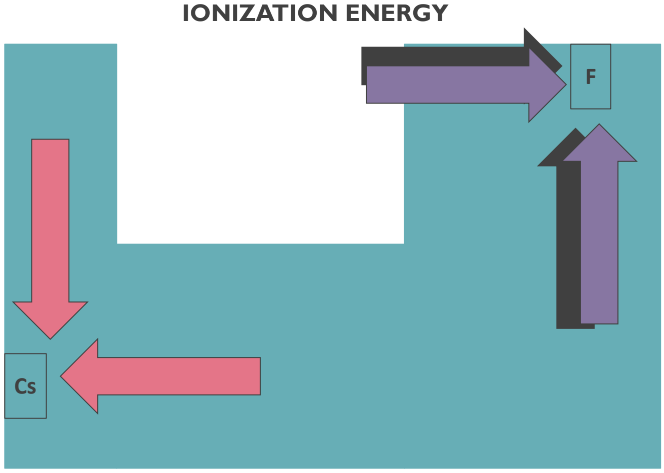
B. N^{2-}, Cl^-

C. Mg, Na

D. Li^+, Be^+

Periodic Trends Review

INCREASING ATOMIC RADIUS / ELECTRON AFFINITY / IONIZATION ENERGY



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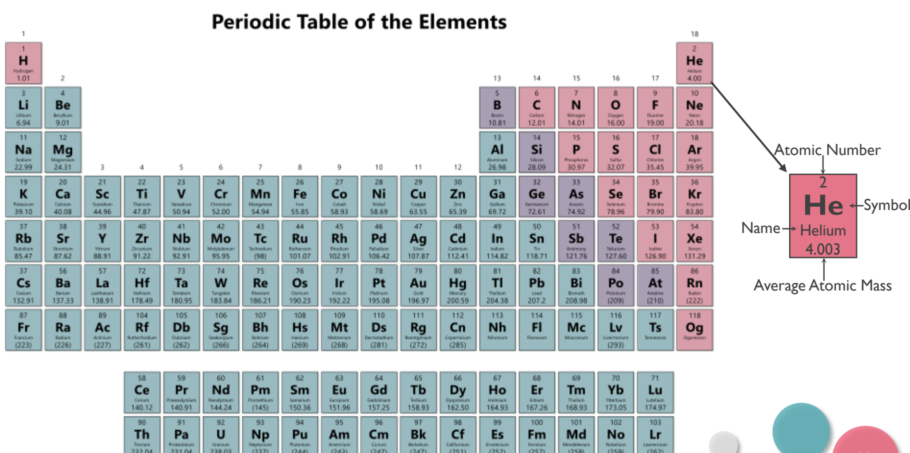
The Periodic Table

The **periodic table** is a chart in which elements having similar chemical and physical properties are grouped together.



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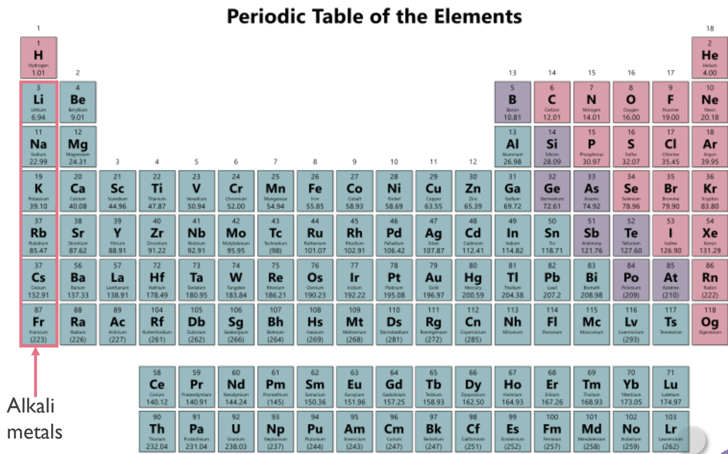
The Periodic Table

Elements are arranged in **periods**, horizontal rows, in order of increasing atomic number.

A vertical column is known as a **group**. Group 1A elements (Li, Na, K, Rb, Cs, Fr) are called **alkali metals**.



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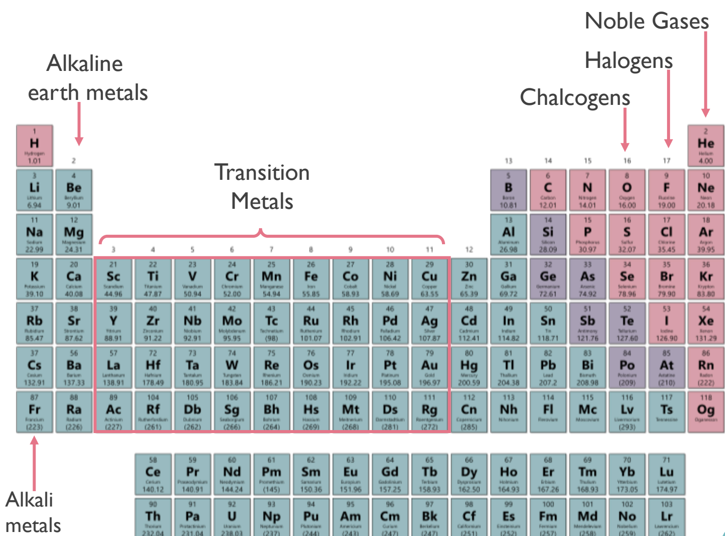
The Periodic Table



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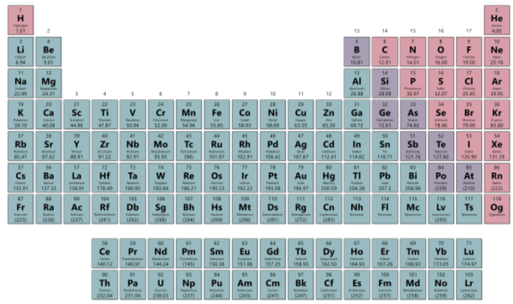
The Periodic Table

Elements can be categorized as **metals**, **nonmetals**, or **metalloids**.

Metals are good conductors of heat and electricity.
solids (except mercury – a liquid)
ductile (can be drawn into wires)
malleable (can be rolled into sheets)



Nonmetals are poor conductors of heat or electricity. (graphite is the one exception)
Occur in all physical states.

Metalloids have intermediate properties.
Boron, silicon, germanium, arsenic, antimony, tellurium, (astatine)
They exhibit metallic and nonmetallic properties:
- Conduct electricity (not as well as metals).
  - Look like metals (shiny).
    - semiconductors.

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Types of Compounds

Ionic compounds: compounds comprised of ions. These are usually formed with a metal and non-metal. These ions are **cations** (positive ion) and **anions** (negative ion). The negative and positive charges of the cations and anions form the electrostatic forces that hold the compound together. (Look for a metal and nonmetal)

$$F = k_e \frac{q_1 q_2}{r^2}$$

k_e: constant, q: scalar charge, r: distance between charges

Molecular (covalent) Compounds: Do not contain ions but are comprised of neutral molecules. These are compounds in which the electrons are shared between the two different atoms through a covalent bond. These are usually formed with two non-metals.

Acids: (for now), Release hydrogen ions (protons, H^+) when dissolved in water. Two types:
Binary Acids
Oxyacids

Hydrates: Any compound containing water in the form of H_2O molecules

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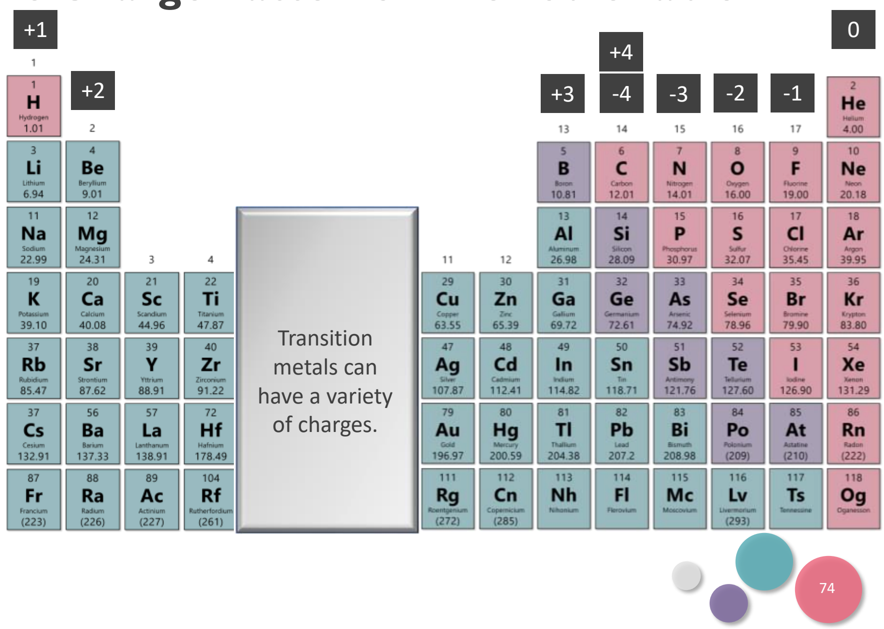
Ionic Charge Patterns in Periodic Table



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