ELECTRONS IN ATOMS AND THE PERIODIC TABLE

Chapter Nine

Light and Energy

- Electromagnetic radiation (EM) is an especially important form of energy for scientific study.
  - Many types of "radiant" energy are included under this description, including visible light, X-rays, and radio waves.
  - EM can be described as waves, which can be characterized by their wavelengths (λ), the distance between the peaks of each wave.
  - We also may describe light as a particle, called a photon

Wavelength and Frequency

- The frequency (ν) of waves is measured as the number of waves which occur in a period of time, usually a second.
  - For example, there are 445 peaks in a second, we would indicate this as 445 s^{-1}.
  - Alternatively, the Hertz(Hz) may be used
    - 1 Hz = 1 s^{-1}
- The frequency and the wavelength are *inversely* proportional
  - That is, as the wavelength increases, the frequency decreases, and vice versa.

The Mathematical Relationship Between Wavelength and Frequency

$$\nu = \frac{c}{\lambda}$$

Where c is the speed of light

$c = 3.00 \times 10^{8}$ m/s

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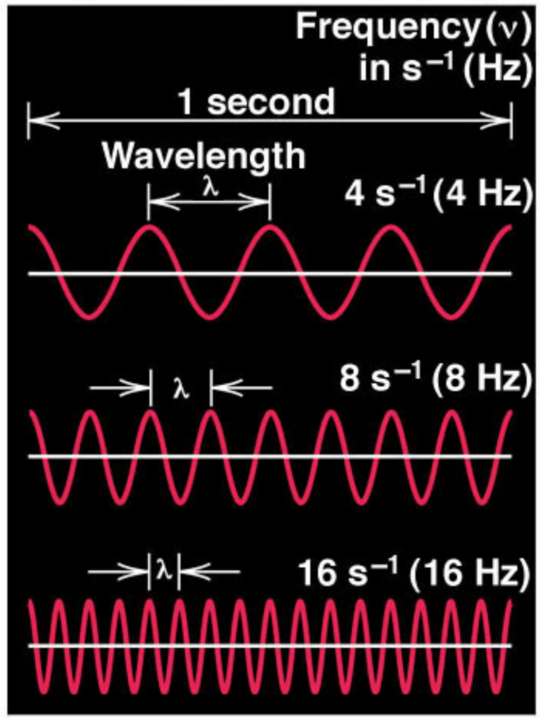
Frequency and Wavelength



Energy of EM Radiation

- The total energy of a single photon depends on the frequency (or wavelength) which that photon is associated with.
- This is described by the equation

  $$E = h\nu$$

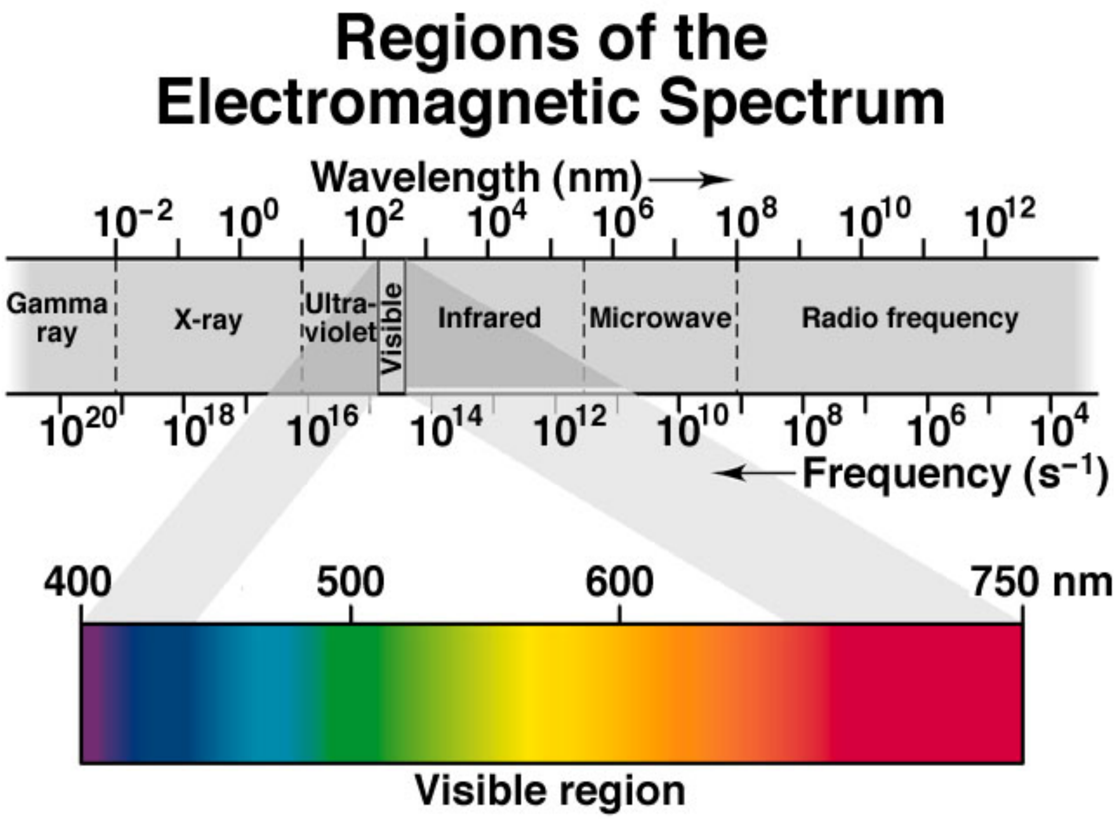
  where E is the energy (in J), ν is the frequency (in s^{-1}), and *h* is *Planck's Constant* (6.626×10^{-34} J·s).
- Greater frequency (and shorter wavelengths) indicate higher energy photons.
- *Provide a formula relating energy to wavelength rather than frequency:*

Energy, Wavelength, and Frequency

- What is the mathematic relationship (i.e. directly or inversely proportional) between each of the following?
  - Energy and Frequency
  - Energy and Wavelength

The Electromagnetic Spectrum

- EM radiation can be classified into different regions based on its wavelength or its frequency.
  - The longest wavelenths (smallest frequencies) correspond to radio waves.
  - The shortest wavelengths (greatest frequencies) correspond to gamma rays.



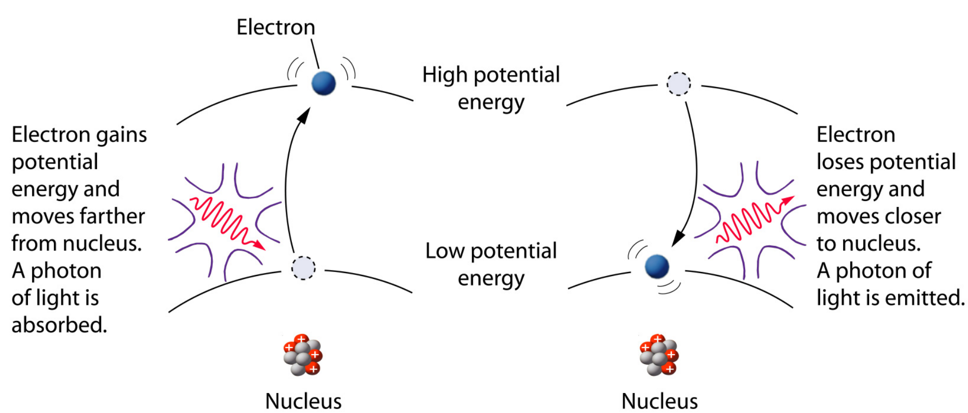
Electrons & Energy Levels

- Evidence suggested to scientists studying atomic structure that electrons "orbit" around the nucleus in specific energy levels (also called shells).
  - The farther the energy level is from the nucleus, the higher the energy of its electrons.
- Normally, electrons "fill up" the lower energy levels first, and as new electrons are added they go into higher and higher energy levels.
  - An atom is said to be in the ground state when this is true.
- An energy source, such as light or heat, can give electrons the energy necessary to "jump" from its energy level to a higher one.
  - In this situation, the atom is said to be in an excited state.

Emission of Light

- An atom in the excited state is unstable and must release the energy it gained in the first place to return to the ground state.
  - According to the Law of Conservation of Energy, this extra energy cannot simply *disappear*
- One way in which this is accomplished is for the atom to give off this energy as light. This process is called <u>emission.</u>
  - The released light is called a <u>photon</u>.
- Excited electrons return to lower energy levels.
  - Depending on the atom itself and which energy levels are involved, EM radiation of different wavelengths are given off.

Absorption vs. Emission



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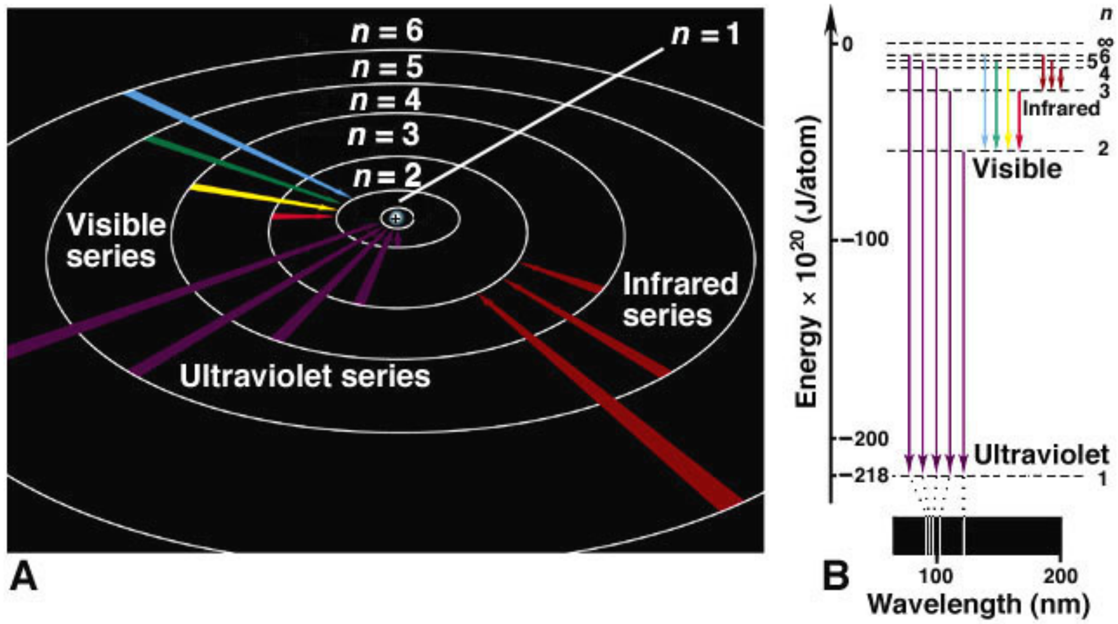
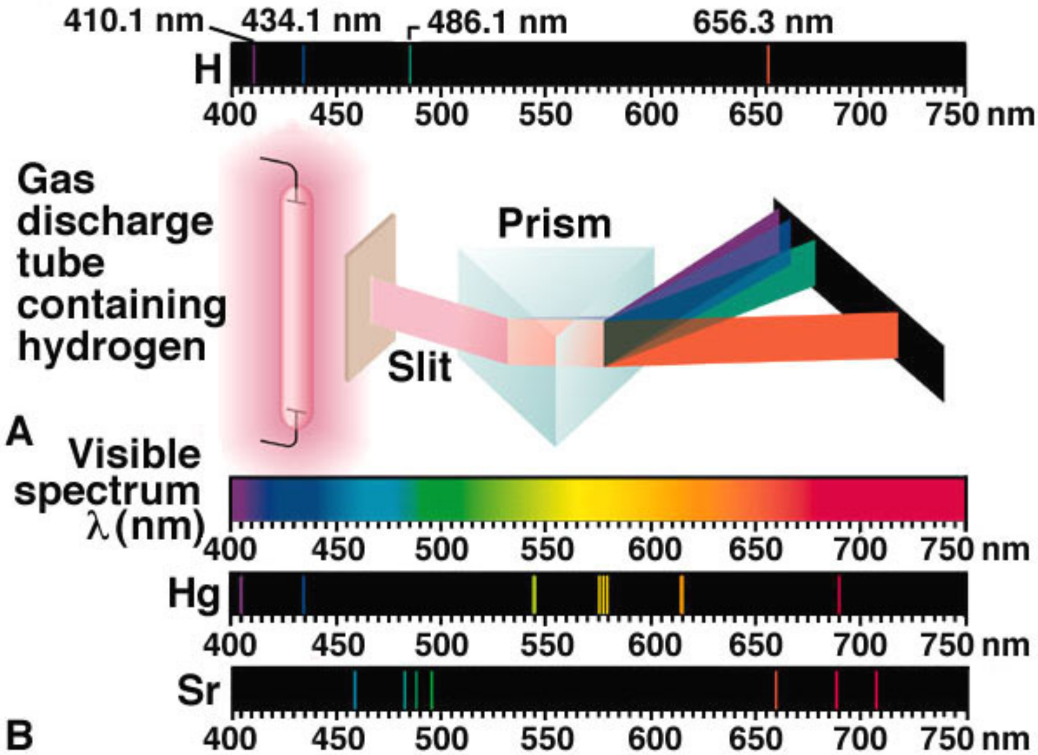
The Bohr Model Explanation of the Three Series of Spectral Lines



The Line Spectra of Several Elements



So What is Light, *Really*?

- The answer to this is not as simple as you might think
- Light (EM in general) is correctly described as both
  - Particles (photons)
  - Waves
- Light is *not* one or the other; it is both *simultaneously!*

Quantization

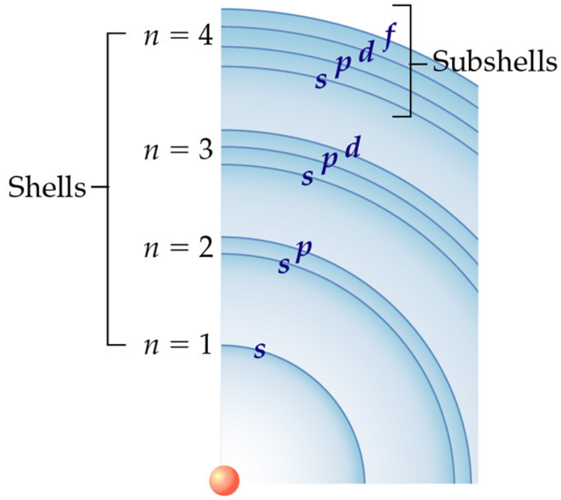
- Notice that, for a given atom, electrons are only allowed to jump to *discrete* energy levels.
  - In other words, an electron in the third level may fall to the first or second level, but not “in between” the levels.
- As a result, only specific energy changes are allowed and can be observed for each atom.
  - We say that these energy changes are “quantized” since only specific quantities of energy can be emitted,
- As an analogy, compare a ball moving down a set of stairs (step-by-step) to one moving down a ramp.
  - Which corresponds to “quantized” energy values?

Matter as Waves

- As with light, matter can be described both as particles and as waves
- The wave description of matter is only useful at very small scales (molecules, atoms, and subatomic particles)
- At the smallest scales it is not generally possible to deal with absolute ideas of location
- Instead, we must content ourselves with relative probabilities as described by complex mathematics

Orbitals & Subshells

- In truth, electrons do not simply rotate about the nucleus in simple patterns.
- Instead, electrons are mostly contained in orbitals, which are shapes which describe the regions where an electron is likely to be found.
- We will call a complete "set" of orbitals in a given energy level a subshell.
- Four orbital types are commonly encountered in modern chemistry.
  - These are designated *s*, *p*, *d*, and *f*, and are listed here from lowest energy orbital type to highest.
- Each individual orbital can hold, at most, two electrons in its ground state.

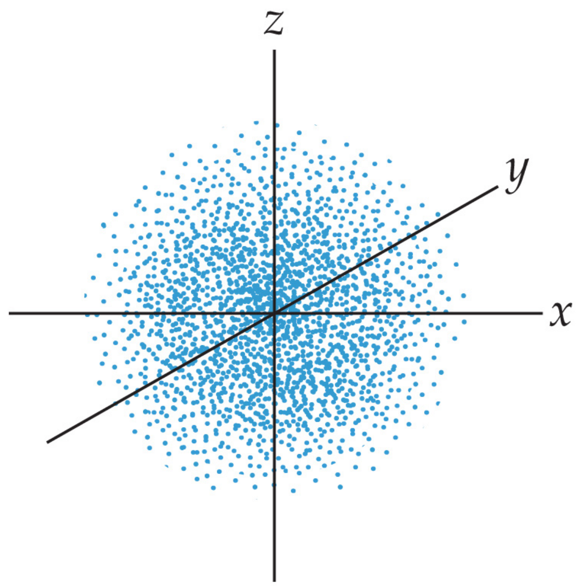


The principal quantum number n tells you the number of subshells in a shell. The $n = 1$ shell has one subshell, the $n = 2$ shell has two subshells, and so on. All subshells in a given shell are close to one another both in size and in energy.

The *s* Orbital

- The *s* orbital is the least energetic of the orbitals, and, as a sphere, is also the most simple-looking.
- All energy levels have exactly one *s* orbital.
  - Since any orbital can only hold two electrons, each *s* orbital is limited to this.

Dot representation of 1*s* orbital



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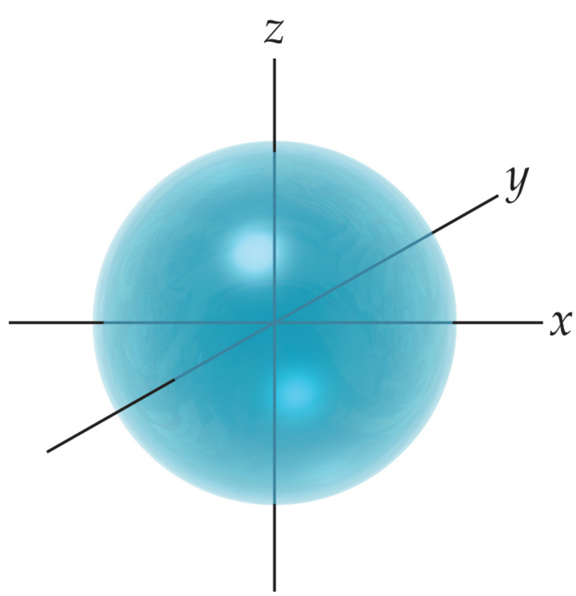
Shape representation of 1*s* orbital



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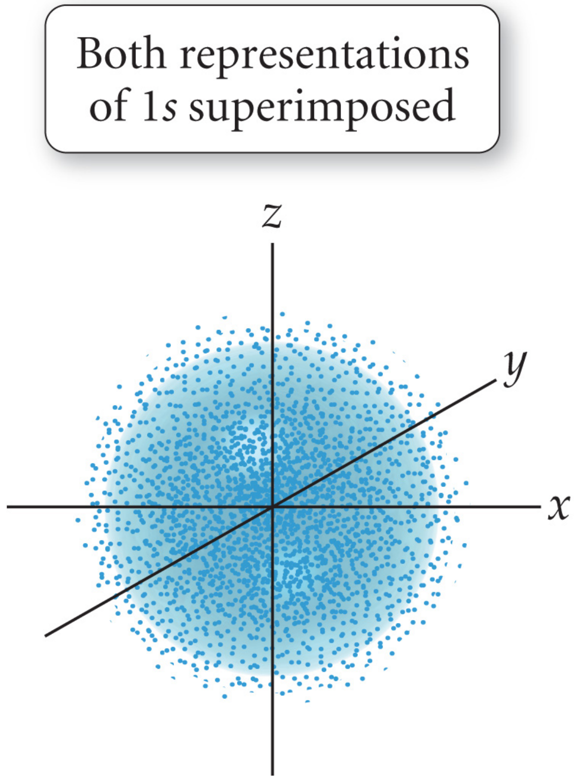

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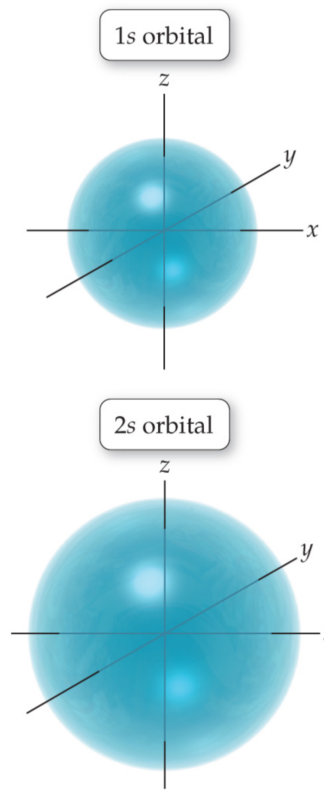

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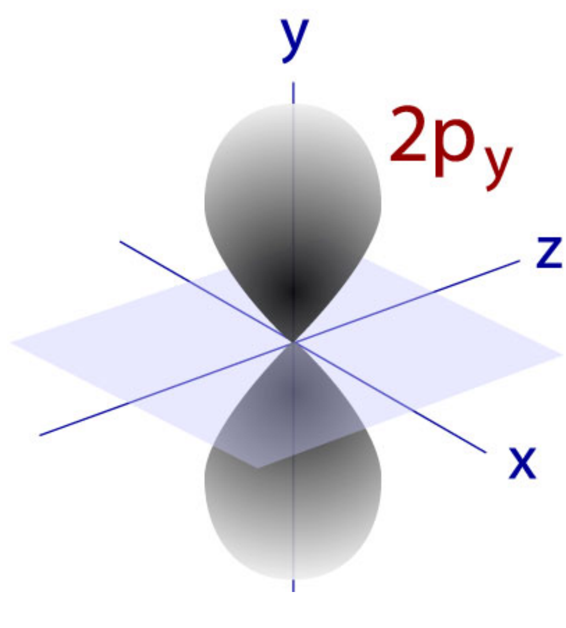
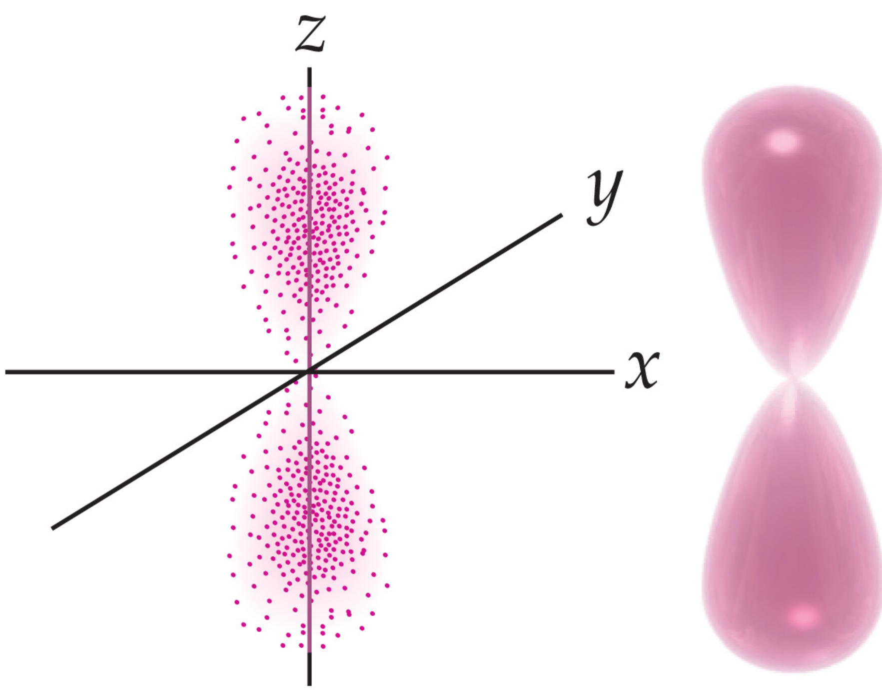
The *p* Orbital

- Starting with the 2nd energy level, each level possesses <u>three</u> "sets" of *p* orbitals.
  - There are three 2*p* orbitals, three 3*p* orbitals, etc.
- Recall that each orbital can hold up to two electrons, so the three orbitals combined will hold up to six electrons.
- The *p* orbitals are more complex in shape than the *s* orbital, and electrons residing in them typically have greater energy than those in an *s* orbital.

One of the three 2*p* orbitals





(c) p_z

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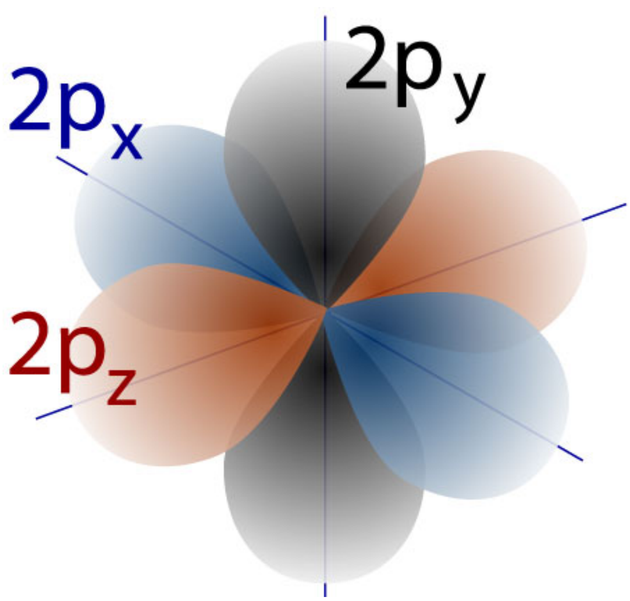
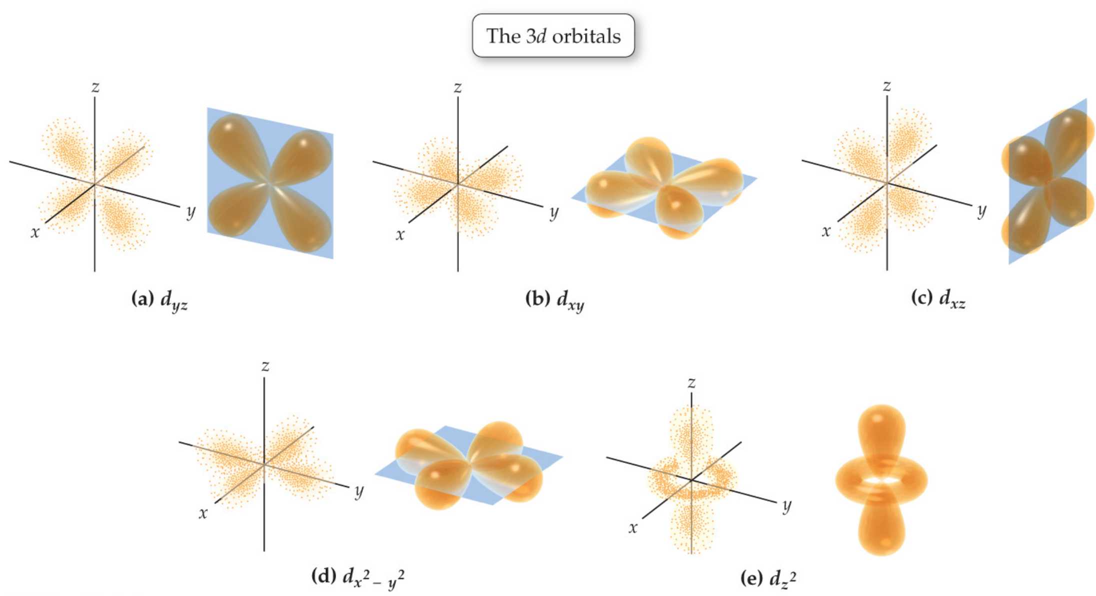
The complete 2*p* subshell



d and *f* Orbitals

- Energy levels three and higher have a total of *5* sets of *d* orbitals.
  - A full set of *d* orbitals can therefore hold up to_____electrons.
- Energy levels four and higher have a total of *7* sets of *f* orbitals.
  - A full set of *f* orbitals can therefore hold up to_____electrons.



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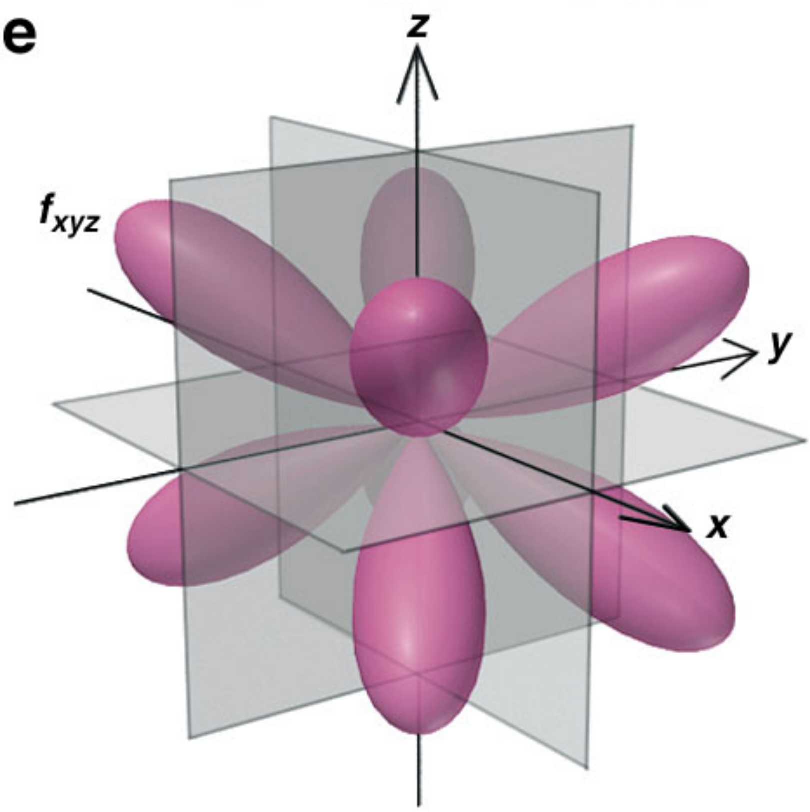
One of the Seven Possible 4*f* Orbitals

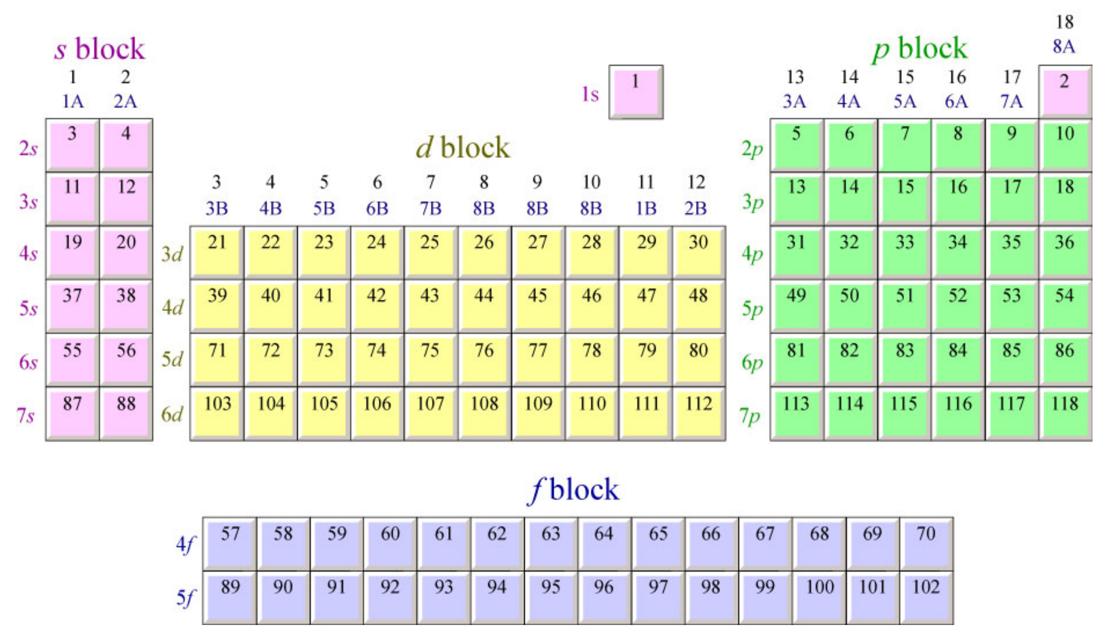


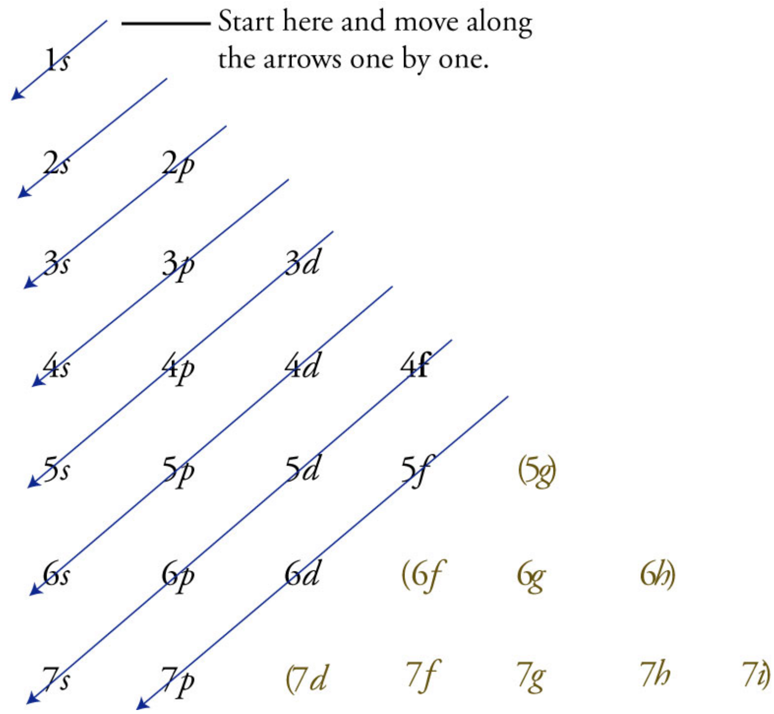
Electron Configurations

- Each element has its own unique electron configuration which describes which subshells have electrons in them and how many.
  - For example, the electron configuration of boron is $1s^22s^22p^1$, which means that there are
    - 2 electrons in an *s* orbital on the first energy level (called the 1*s* subshell)
    - 2 electrons in the 2*s* orbital (the 2*s* subshell)
    - 1 electron in a 2*p* orbital (three *p* orbitals collectively make up the 2*p* subshell)

Electron Configurations

- Atoms always fill their lowest energy orbitals first, and successively higher ones as more electrons are added.
  - This is known as the <u>Aufbau principle</u>; *aufbau* is German for "building up"
- The order in which the electrons fill can be found on the periodic table.
  - Notice that the periodic table is broken up into 4 distinct "blocks," each of which indicates where the highest energy electrons are.





Examples

Determine the electron configuration for each of the following atoms/ions:

Be

N

Na

V

I

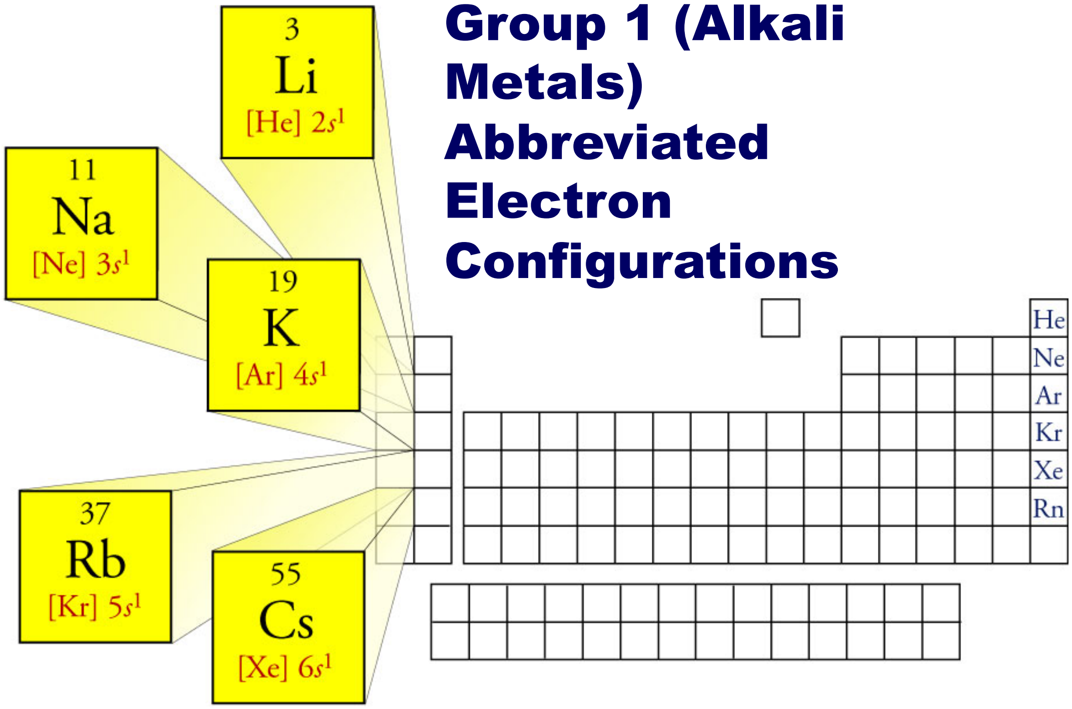
Shorthand Notation for Electron Configurations

- You can abbreviate the electron configuration with a special notation
  - Consider V for example.
  - The last noble gas before V was Ar (element 18)
  - So, we can write [Ar]$4s^2 3d^3$ as vanadium's electron configuration.
  - What is the electron configuration of antimony in shorthand notation?

Electron Configurations and Groups

- The concept of electron configurations is very useful for predicting the chemical properties of many elements
  - We will study this in detail in the coming chapters
- Notice that, with few exceptions, all elements in the same group have similar endings on their electron configurations
  - All alkali metals (Group 1A) end in s^1
  - All halogens (Group 7A) end in p^5
  - All noble gases (Group 8A) *with the exception of helium* end in p^6

Group 1 (Alkali Metals) Abbreviated Electron Configurations



Unusual Electron Configurations

- Unfortunately, the electron configurations we predict are not always correct
- For example, predict the electron configuration of copper
- The actual electron configuration is:
- There are several other elements which do not "follow the rules"; however, at this point in your study of chemistry, you do not need to be concerned with these exceptions

Spin

- Each has a property we call spin
  - This is not exactly the same thing as the spin of the earth or spin on a baseball, but this is an acceptable model
- Electrons may spin in one of two possible directions
- We refer to these as “spin up” and “spin down”

The Pauli Exclusion Principle & Hund’s Rule

- In a ground state atom, two electrons in the same orbital must have opposite spins; this is a simplified version of a rule called the Pauli Exclusion Principle
- Another important principle, Hund’s Rule, states that, for ground state atoms, electrons will fill unoccupied orbitals within a subshell before filling singularly-occupied ones
  - For example, in a nitrogen atom, with electron configuration $1s^2 2s^2 2p^3$, the three electrons in the $2p$ subshell reside in different orbitals (i.e. they do not pair up)

Orbital Diagrams

- <u>Orbital diagrams</u> are a graphical form of the electron configuration, representing electrons as arrows (up arrow for spin-up, down for spin-down) and orbitals as lines
- The lines are listed from lowest energy at the bottom (i.e. the 1*s* orbital) to highest

Symbol (#e^-)	Electron configuration	Orbital diagram: 1*s*	2*s*	2*p*
Li (3)	$1s^2 2s^1$	↑↓	↑	
Be (4)	$1s^2 2s^2$	↑↓	↑↓	
B (5)	$1s^2 2s^2 2p^1$	↑↓	↑↓	↑ | |
C (6)	$1s^2 2s^2 2p^2$	↑↓	↑↓	↑ | ↑ |
N (7)	$1s^2 2s^2 2p^3$	↑↓	↑↓	↑ | ↑ | ↑
O (8)	$1s^2 2s^2 2p^4$	↑↓	↑↓	↑↓ | ↑ | ↑
F (9)	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑↓ | ↑↓ | ↑
Ne (10)	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓ | ↑↓ | ↑↓

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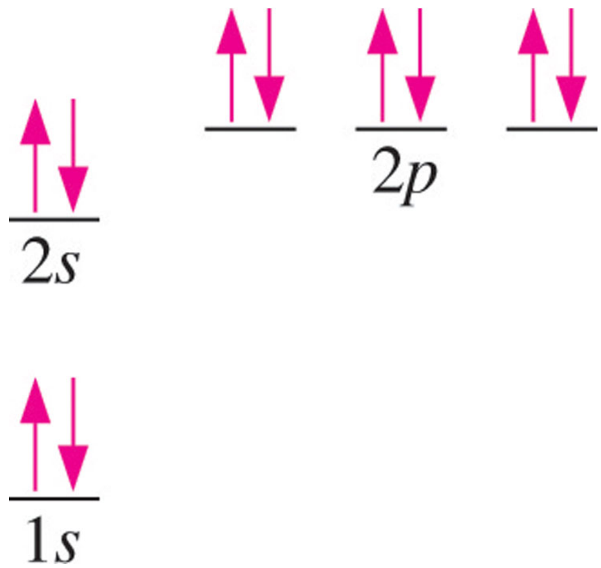
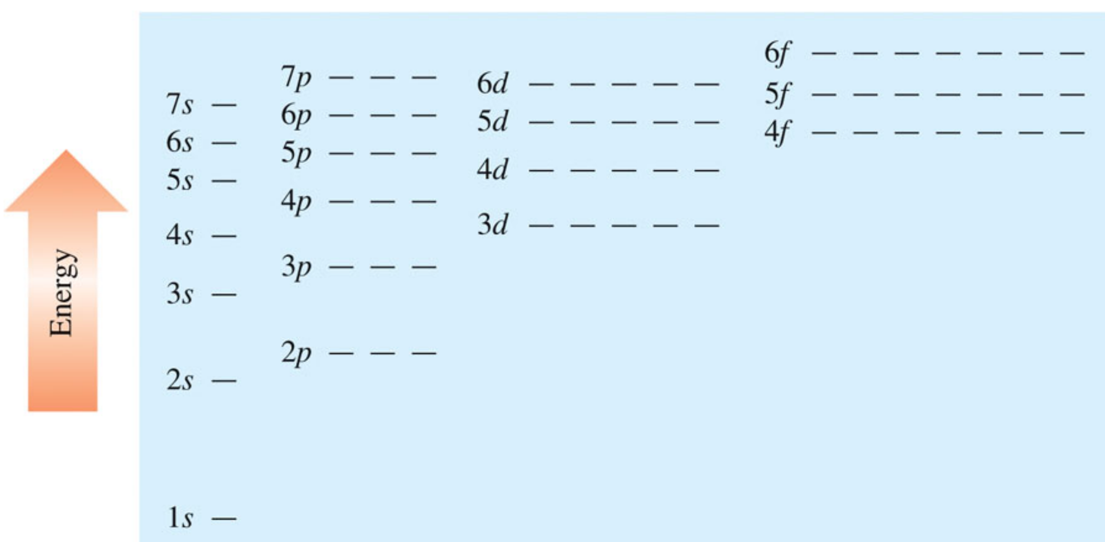

2p
2s
1s


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

Example

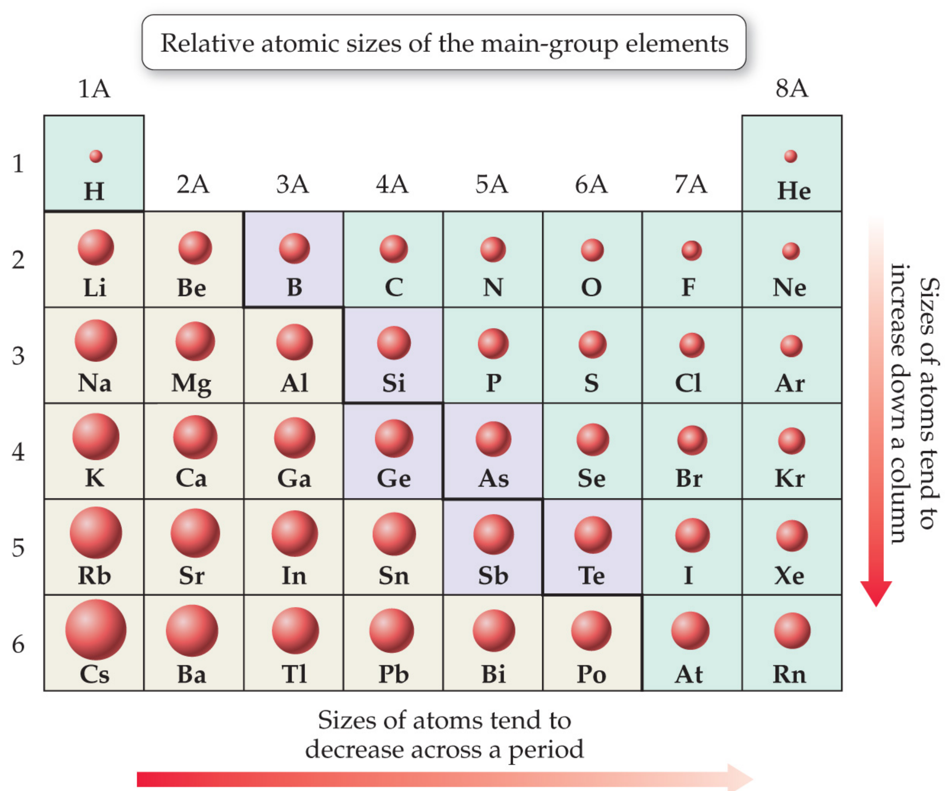
- Draw the orbital diagrams for
  a. titanium b. S^{2-}

Periodic Trends

- By comparing the position of one element to another on the periodic table, it is often possible to make comparisons between the properties of those elements; these are a result of periodic trends.
- In this class we consider four of these trends:
  - Atomic radius
  - Ionization Energy
  - Metallic Character
  - Electronegativity (discussed in Chapter 10)

Atomic Radius

- The radius of an atom tends to increase as you move down a group in the periodic table.
  - Explanation: Elements in lower groups of the periodic table have electrons in outer energy levels. These electrons are not held as tightly by the nucleus, so they can travel further away from it.
- The radius of an atom tends to decrease from left to right across a period.
  - Explanation: The valence electrons of atoms in the same period fill the same energy levels. However, the positive charge in the nucleus is increasing as we move from left to right on the periodic table as the number of protons is likewise increasing. This pulls the electrons in closer, making the radius smaller.



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Atomic Radius: Ions

- Recall that when an ion is formed, an atom gains or loses electrons, while the number of protons remains the same
- When an atom loses an electron to form a cation, the positive charge of the nucleus pulls the remaining electrons closer towards the nucleus
- A monatomic cation is smaller than the corresponding neutral atom
  - Na^+ has a smaller atomic radius than Na
  - Mg^{2+} has a smaller atomic radius that Mg

Atomic Radius: Ions

- When an atom gains an electron to form an anion, the increased repulsion of the additional electrons results in electrons moving farther from the nucleus
  - Cl^- has a larger atomic radius than Cl
  - O^{2-} has a larger atomic radius than O
- When comparing atoms and ions with the <u>same</u> number of electrons, the largest ions are those with the most negative charge

Atomic Radius: Ions

Rank each of the following atoms/ions in order from largest to smallest

I. Li K N Ne Cs

II. Ne Al^{3+} O^{2-} F^- Na^+ Mg^{2+}

Ionization Energy

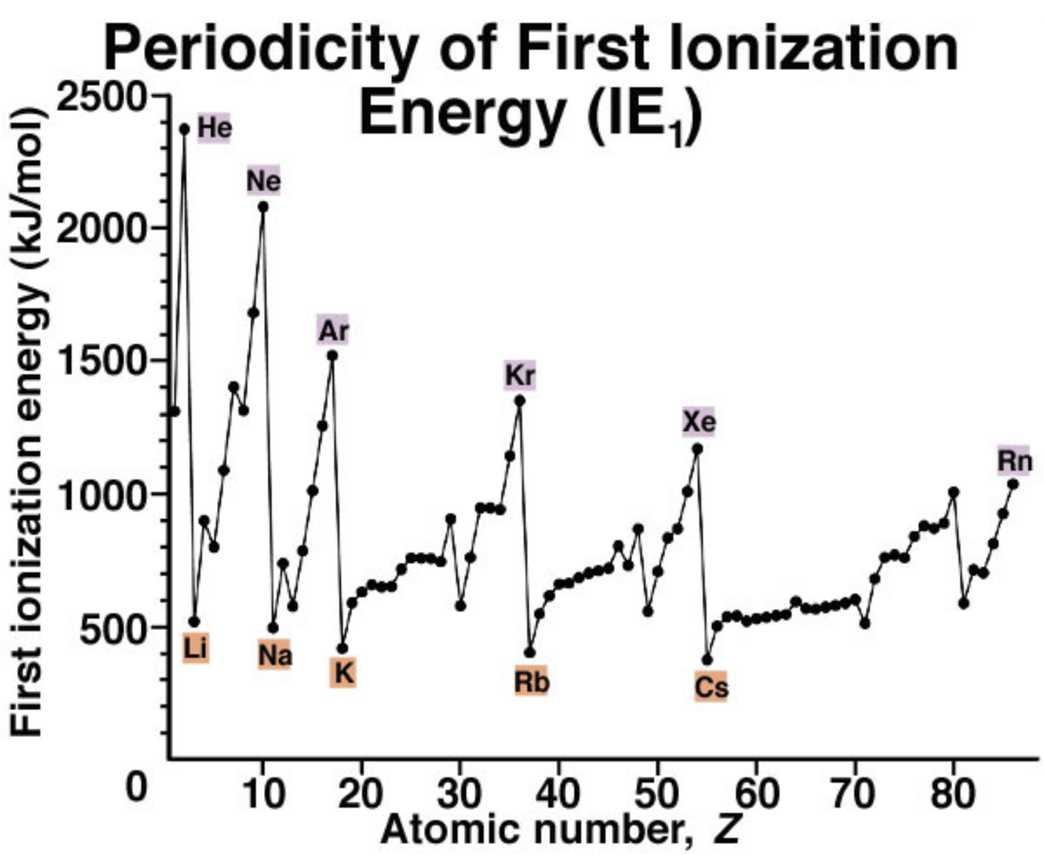
- The <u>ionization energy</u> is the amount of energy required to remove an electron from a mole of atoms in their gas state of a particular element.

$$X_{(g)} \rightarrow X^+_{(g)} + e^-$$

  - The <u>first ionization energy</u> is the amount of energy required to remove the first electron.
  - The <u>second ionization energy</u> is the amount of energy required to remove the second electron. Etc.

Ionization Energy

- Ionization energy tends to decrease down a group.
  - Explanation: Electrons in the outer shells are further from the nucleus and feel its pull less than the core electrons do. Less energy is required to remove them.
- Ionization energy *tends* to increase from left to right across a period.
  - Explanation: Protons are added to the nucleus from left to right across the table, and these protons exert a greater pull on the electrons, requiring more energy to remove them.
  - Why is the first ionization energy of oxygen less than that of nitrogen?



Comparing Ionization Energies

- Generally, the first ionization energy is less than the second, which is less than the third, etc.
- If an atom has lost enough electrons to give it an octet in its outer shell, it requires a tremendous amount of energy to remove any electrons beyond this.

The First Three Ionization Energies of Beryllium

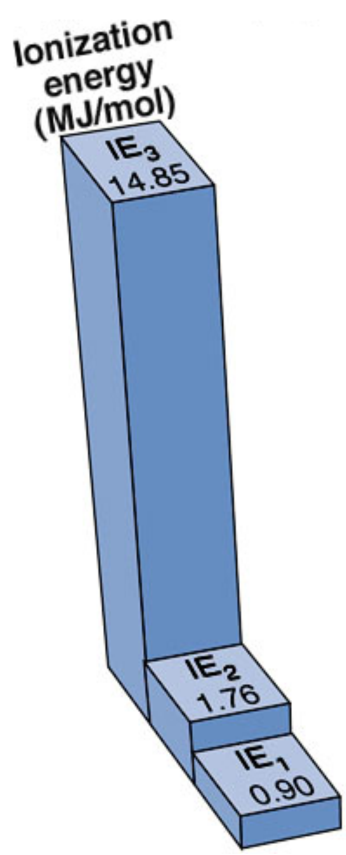


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Table 13.1 Successive Ionization Energies for Some Main Group Elements (kilojoules per mole)

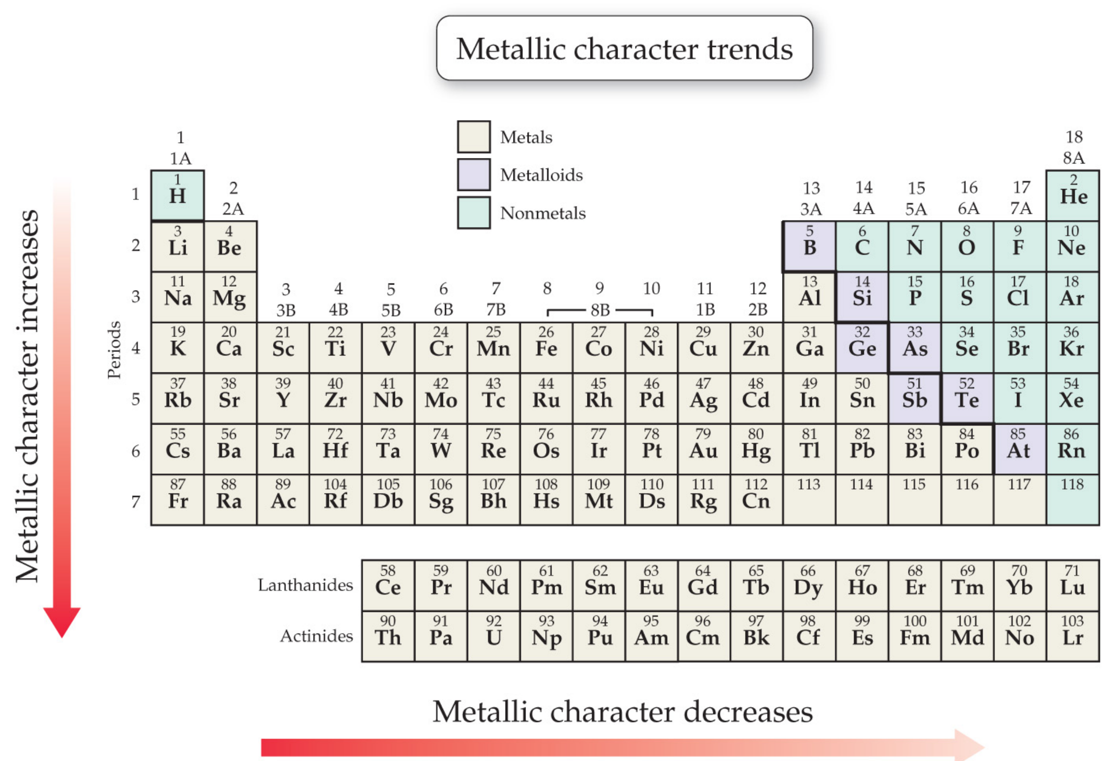
	First	Second	Third
Na	495.8	4562	6912
Mg	737.7	1451	7733
Al	577.6	1817	2745

A Atomic size

B Ionization energy

Metallic Character

- As the term implies, the <u>metallic character</u> of an element is a description of how much "like a metal" it is
- Metals tend to lose electrons in chemical reactions, while non-metals either gain or share them
- Metallic character can effectively be described as the opposite of ionization energy, so the trends in metallic character are the opposite of those for ionization energy
- Metallic character tends to increase down a group.
- Metallic character tends to decrease from left to right across a period.



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