Light

We can use different terms to describe light:

- Color
- Wavelength
- Frequency

Light is composed of electromagnetic waves that travel through some medium.

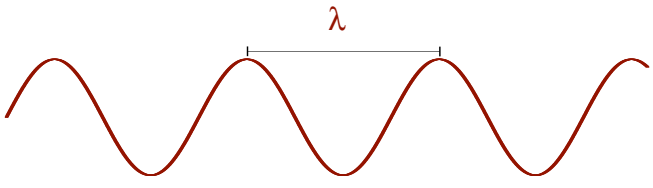
The properties of the medium determine how light travels through it.

In a vacuum, light waves travel at a speed of 3.00×10^8 m/s or 186,000 miles/s.

The speed of light in a vacuum is a constant that is tremendously important in nature and science—it is given the symbol, c.

Light (con't.)

Because light behaves like a wave, we can describe it in one of two ways—by its wavelength or by its frequency.



λ = wavelength—distance between two adjacent wave crests. λ has units of distance—frequently nanometers (nm).

ν = frequency—how many times the wave goes up and down in a period of time. ν has units of inverse time (1/s ≡ Hz[hertz]).

Light (con't.)

If you know either the frequency or the wavelength, you can calculate the other quantity through the relationship:

$$c = \lambda \bullet \nu$$

c = speed of light (3.00×10^8 m/s)
λ = wavelength (m)
ν = frequency (s^{-1})

A "particle" of light is called a photon.

Examples

Diode laser pointer: λ = 670 nm

670 nm = 670×10^{-9} m

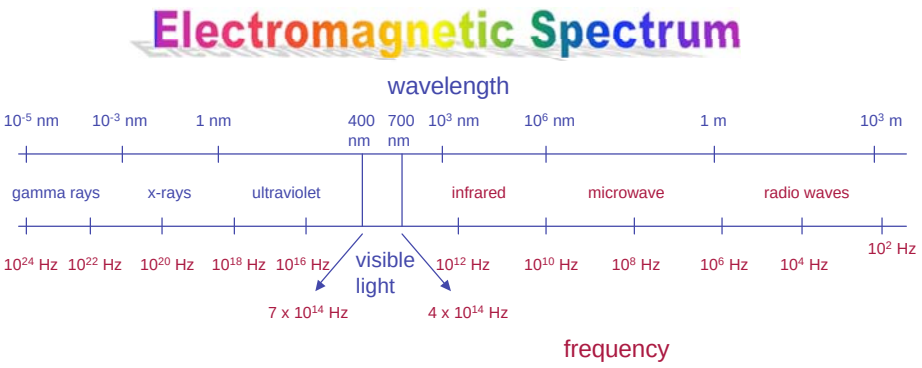
$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{670 \times 10^{-9} \text{ m}} = 4.48 \times 10^{14} \text{ Hz}$$

$\nu = 4.3 \times 10^{13}$ Hz

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{4.3 \times 10^{13} \text{ s}^{-1}} = 6.98 \times 10^{-6} \text{ m} = 6.98 \ \mu\text{m} = 6980 \text{ nm}$$

Light (con't.)

The type of light (ultraviolet, visible, infrared, x-ray, etc.) is defined by either its frequency or wavelength:



Light (con't.)

The energy of light can be determined either from its wavelength or frequency:

$$E = \frac{h\,c}{\lambda} \qquad \text{or} \qquad E = h\,\nu$$

Planck's constant: $h = 6.626 \times 10^{-34}$ J s

Examples

4.3×10^{13} Hz (ν) light:

$E = (6.626 \times 10^{-34}\ \text{J s})(4.3 \times 10^{13}\ \text{s}^{-1}) = 2.85 \times 10^{-20}\ \text{J}$

$= (2.85 \times 10^{-20}\ \text{J})\ (6.022 \times 10^{23}\ \text{mol}^{-1}) = 17.2\ \text{kJ mol}^{-1}$

1 mole = 6.022×10^{23} things (atoms, molecules, photons, etc.)

670 nm (λ) diode laser:

$$E = \frac{(6.626 \times 10^{-34}\ \text{J s})(3.00 \times 10^{8}\ \text{m s}^{-1})}{(670 \times 10^{-9}\ \text{m})} = 2.97 \times 10^{-19}\ \text{J}$$

$= (2.97 \times 10^{-19}\ \text{J})\ (6.022 \times 10^{23}\ \text{mol}^{-1}) = 179\ \text{kJ mol}^{-1}$

- Atoms and molecules absorb and emit light in the ultraviolet (UV), visible (vis), infrared (IR), and microwave (μwave) regions of the electromagnetic spectrum.
- Absorption or emission of light in the UV and visible regions involves movement of electrons in the atom or molecule.
  - One reason UV light is so damaging is that the light has enough energy to break chemical bonds—biological and chemical systems
    - E (λ = 300 nm) = 399 kJ mol
    - Average bond energy = 380 kJ mol^{-1}

Hydrogen Atom Spectrum

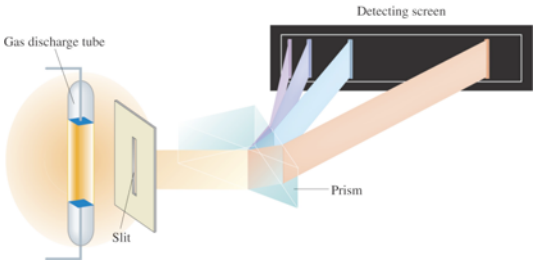
It was known for a long time that the spectrum of the hydrogen atom displayed a series of discrete lines:

The Balmer Series was found to obey the formula:

$$\frac{1}{\lambda} = \frac{\nu}{c} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$$R_H = 1.0974 \times 10^7 \text{ m}^{-1}$$

$$n = 3, 4, 5, \ldots$$



Hydrogen Atom Spectrum

The Lyman Series was found to obey the formula:

$$\frac{1}{\lambda} = \frac{\nu}{c} = R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \quad R_H = 1.0974 \times 10^7 \text{ m}^{-1}, \quad n = 2, 3, 4, \ldots$$

The Paschen Series was found to obey the formula:

$$\frac{1}{\lambda} = \frac{\nu}{c} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \quad R_H = 1.0974 \times 10^7 \text{ m}^{-1}, \quad n = 2, 3, 4, \ldots$$

The Brackett Series was found to obey the formula:

$$\frac{1}{\lambda} = \frac{\nu}{c} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \quad R_H = 1.0974 \times 10^7 \text{ m}^{-1}, \quad n = 2, 3, 4, \ldots$$

Hydrogen Atom Spectrum

In general, the observed lines in the hydrogen atom spectrum can be described by the formula:

$$\frac{1}{\lambda} = \frac{\nu}{c} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

$R_H = 1.0974 \times 10^7\ m^{-1}$ Rydberg constant

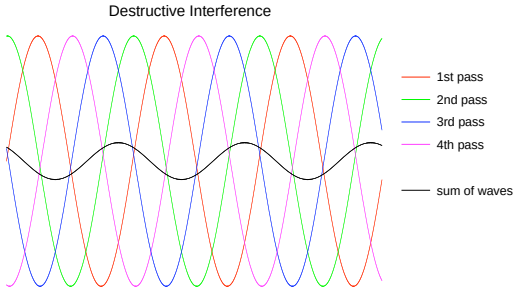
$m = 1, 2, 3, \ldots$

$n = m+1, m+2, m+3, \ldots$

Atomic Models

The Bohr Model—Niels Bohr (1913)

- Electrons behave like waves—as they circle the nucleus, the distance traveled in their orbit must be equal to an integral number of wavelengths to prevent “destructive” interference and undergo constructive interference.



Atomic Models

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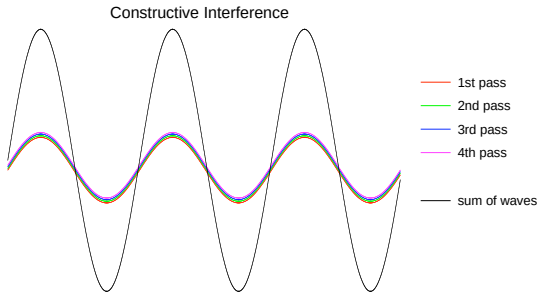
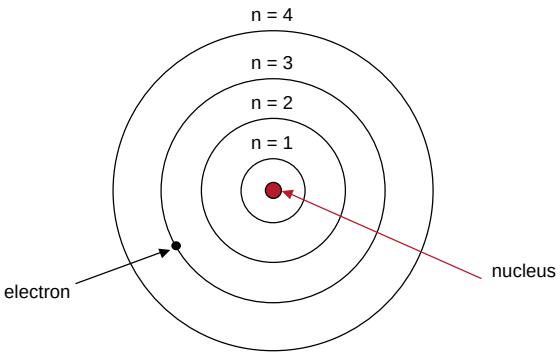


Bohr Model of the Atom

The specific energy level of the electron in a hydrogen atom was “quantized”—it was restricted to only certain “allowed” values determined by the size of the orbit of the electron about the nucleus.

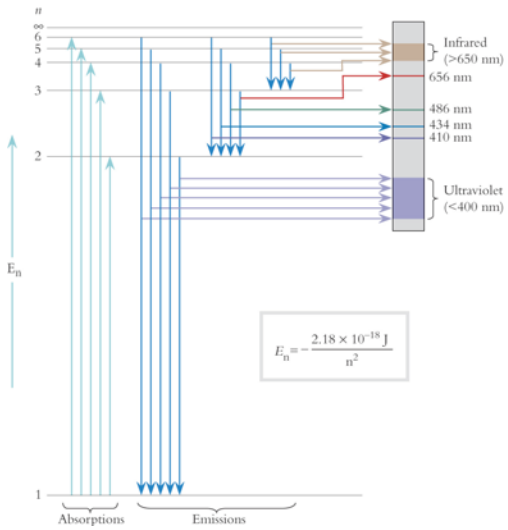


Bohr Model of the Atom

- Bohr's model of the atom is based on the *principal quantum number, n*. n denotes the energy level of the electron *orbital* (path taken by the electron as it moves about the nucleus) and is related to the size of the orbital.
- n ranges from 1 to ° in integer values:

  n = 1, 2, 3, …

Bohr Model of the Atom



Modern Model of the Atom

- Bohr's model of the atom described the observed behavior of the hydrogen atom, but could not adequately explain the spectra observed for all other elements like helium, lithium, or any other of the larger atoms.
- In order to describe the observed spectra, additional quantum numbers were necessary:

Modern Model of the Atom

- Azimuthal quantum number (ℓ) describes the shape of the orbital.

  ℓ = 0, 1, 2, …, n-1

  The value of ℓ corresponds to a specific *orbital letter* and associated orbital shape:

  ℓ = 0 *s*

  ℓ = 1 *p*

  ℓ = 2 *d*

  ℓ = 3 *f*

Modern Model of the Atom

- Magnetic quantum number (m_ℓ) describes the orientation of the orbital in space (usually along xyz axes).

  $m_\ell = -\ell, -\ell+1, \ldots, 0, 1, 2, \ldots, \ell$

  If: $\ell = 0$, $m_\ell = 0$

  $\ell = 1$, $m_\ell = -1, 0, 1$

  $\ell = 2$, $m_\ell = -2, -1, 0, 1, 2$

  $\ell = 3$, $m_\ell = -3, -2, -1, 0, 1, 2, 3$

Modern Model of the Atom

- Spin quantum number (m_s) describes the spin orientation of the electron in space. The spin can point either up or down.

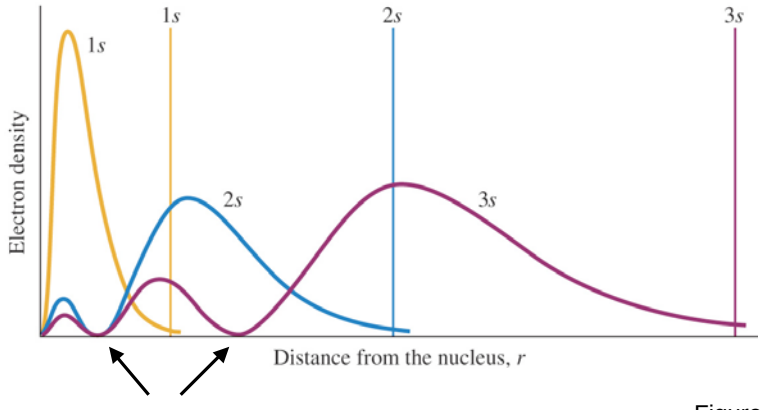
  $m_s = -\frac{1}{2}, +\frac{1}{2}$

Electron Orbital Shapes

- Because of the Uncertainty Principle and the wave-like behavior of electrons in the atom, it is incorrect to think of electrons as being found at a specific location at a specific time while orbiting the nucleus.
- We think instead in terms of the probability of finding the electron at a specific location. The probability of finding the electron as a function of radius and angle is often referred to as its *electron density*. Typically, the electron density designates that region surrounding the nucleus with a 90% probability of finding the electron.

Electron Orbital Size

- The size of an orbital increases with increasing principle quantum number, n.



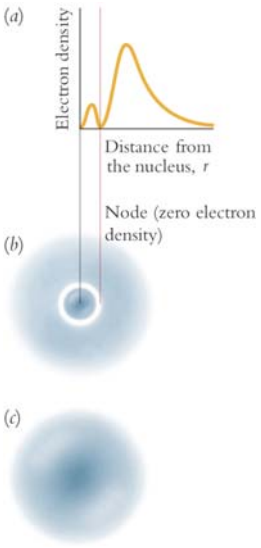
nodes: region with zero probability

Figure 6-21

Electron Orbital Shape

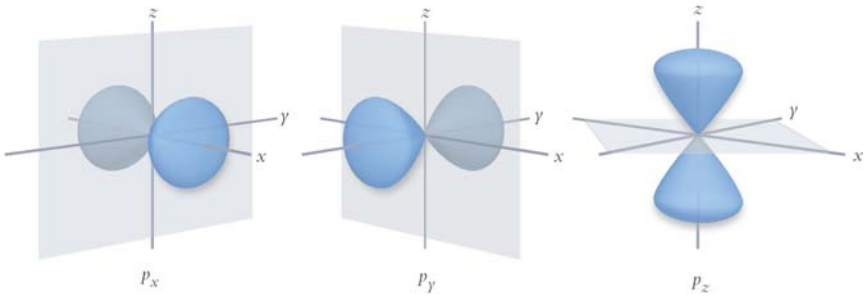
- The shape of an orbital depends on its azimuthal quantum number, ℓ :

  s orbitals (ℓ = 0) are spherical in shape. There is only one s orbital in a given principle quantum number level.



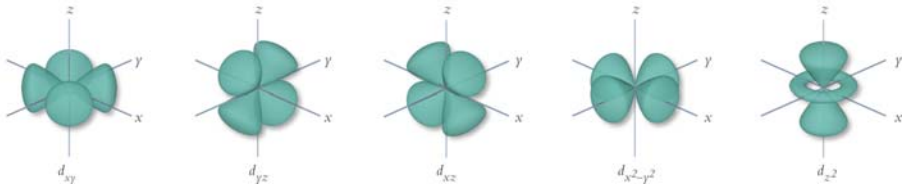
Electron Orbital Shape

p orbitals (ℓ = 1) have two lobes separated by a node at the nucleus of the atom. There are three p orbitals pointing in orthogonal directions: p_x, p_y, p_z.



Electron Orbital Shape

d orbitals (ℓ = 2) have four lobes (except d_{z^2}). There are five d orbitals pointing in orthogonal directions: d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}.



Electron Orbital Shape

f orbitals (ℓ = 3) have eight lobes. There are seven f orbitals pointing in orthogonal directions.

- Pneumonic for orbitals:

  s = spherical

  p = peanut

  d = daisy

  f = fancy flower

Electron Orbitals

Examples

What orbitals can an atom with n = 1 contain?

Remember:

ℓ = 0, 1, 2, …, n-1

m_ℓ = -ℓ , -ℓ +1, …, 0, 1, 2, …, ℓ

For n = 1, ℓ can only have the value ℓ = 0, and m_ℓ can only have the m_ℓ = 0.

The only possible orbital for n = 1 is a 1s orbital.

Electron Orbitals

Examples

What orbitals can an atom with n = 3 contain?

For n = 3, ℓ can have the values ℓ = 0, 1, 2.

For ℓ = 0, m_ℓ = 0 $\Rightarrow$ 3s orbital

For ℓ = 1, m_ℓ = -1, 0, 1 $\Rightarrow$ 3 3p orbitals

For ℓ = 2, m_ℓ = -2, -1, 0, 1, 2 $\Rightarrow$ 5 3d orbitals

Electron Orbitals

Examples

What are the possible quantum numbers for an f orbital in the fourth principle quantum number level?

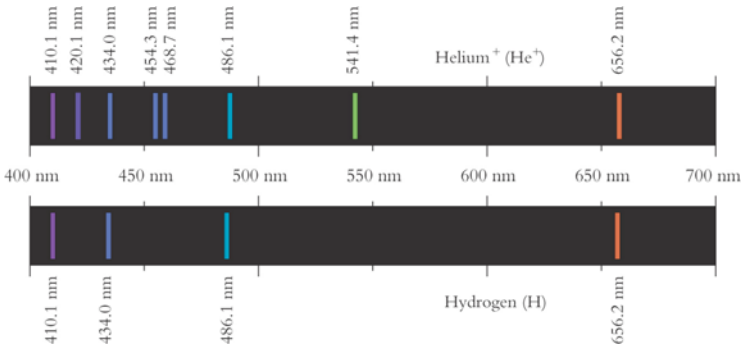
n = 4 because the question states the orbital is in the fourth principle quantum number level.

ℓ = 3 because it is an f orbital.

m_ℓ = -3, -2, -1, 0, 1, 2, 3 are all possible because the exact f orbital was not specified.

Effects of Nuclear Charge

The spectrum of He^+ can be fit by an expression similar to that of hydrogen, but using a different value for R_H.



Effects of Nuclear Charge

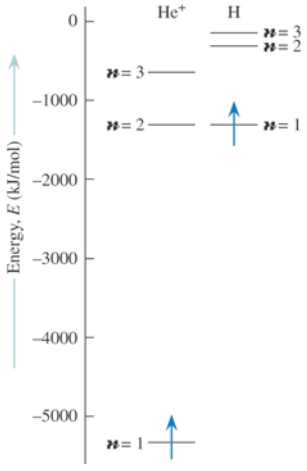
$$\frac{1}{\lambda} = \frac{\nu}{c} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

$R_H(He^+) = 4.387 \times 10^7\ m^{-1}$

$R_H(H) = 1.097 \times 10^7\ m^{-1}$

He^+ ion, like hydrogen atom, has only one electron orbiting the nucleus. The difference between the two species is that He^+ contains two protons in the nucleus instead of one for H atom. The stronger electrostatic interaction of the +2 nuclear charge hold the electron of He^+ more closely to the nucleus and shifts the spectrum of He^+.

Effects of Nuclear Charge



Orbital energies of He^+ ion and H atom relative to the ionization threshold—the point at which the e^- is no longer attached to the nucleus.

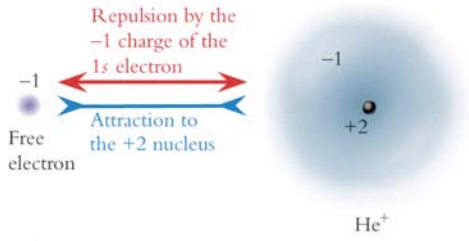
The energy required to remove the e^- is called the ionization energy, IE.

$IE(H) = 2.18 \times 10^{-18}$ J

$IE(He^+) = 8.72 \times 10^{-18}$ J

Effective Nuclear Charge

When an atom has more than one electron, the repulsion between the negatively charged e^-'s results in screening of the total charge of the nucleus—the charge an e^- sees is less than the actual total charge of the protons.



Effective Nuclear Charge

The charge an individual e^- experiences is called Z_{eff}, the effective nuclear charge.

He atom (not He^+) has two e^-'s, both in the 1s orbital. With a -1 charge, an e^- could reduce Z_{eff} by 1 unit of charge—from +2 to +1 for He. If that were the case, the remaining electron would see Z_{eff} = +1, and the IE for the second e^- would be the same as for the H atom.

Effective Nuclear Charge

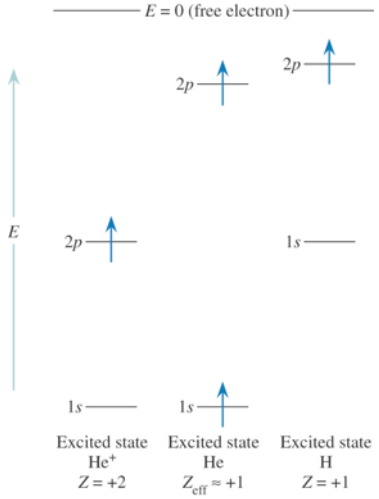
IE(He) = 3.94 x 10^{-18} J

IE(H) = 2.18 x 10^{-18} J

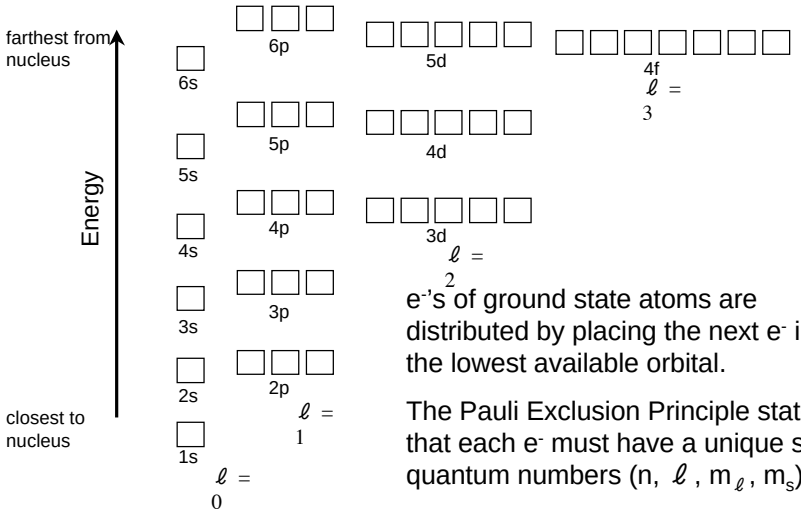
Because the IE's are different, screening by the first e^- is not complete. This is because both e^-'s occupy the same orbital, and therefore move within the same region of space—one e^- does not spend all of its time closer to the nucleus than the other e^-.

Effective Nuclear Charge

For atoms with more than two e^-'s, the e^-'s in inner orbitals are much more effective at screening nuclear charge.



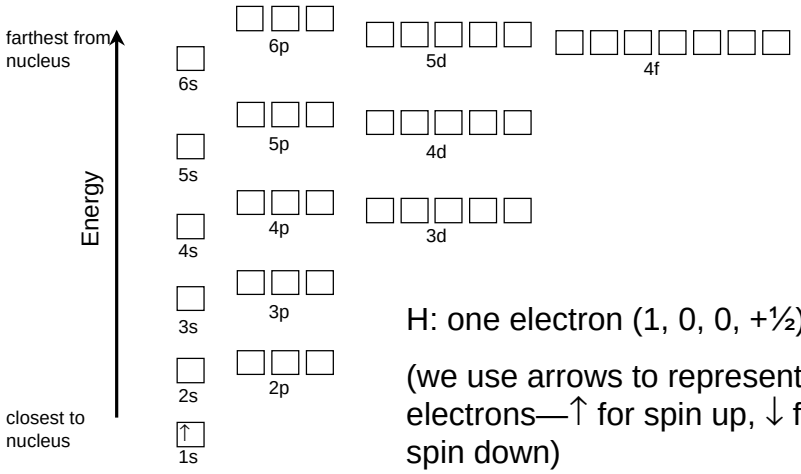
Electron Orbital Energies



e⁻'s of ground state atoms are distributed by placing the next e⁻ into the lowest available orbital.

The Pauli Exclusion Principle states that each e⁻ must have a unique set of quantum numbers (n, ℓ, m_ℓ, m_s)

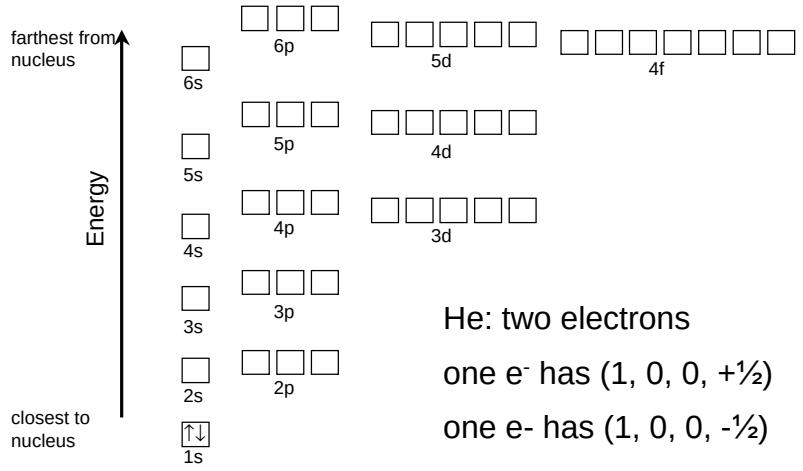
Electron Orbital Energies



H: one electron (1, 0, 0, +½)

(we use arrows to represent electrons—↑ for spin up, ↓ for spin down)

Electron Orbital Energies

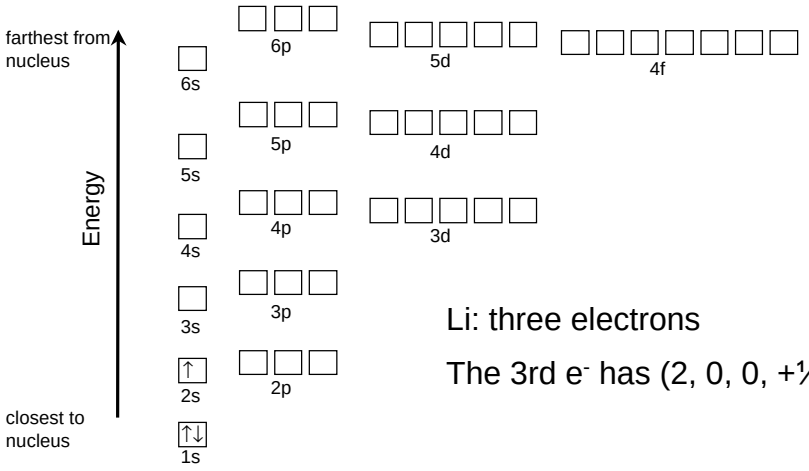


He: two electrons

one e^- has (1, 0, 0, +½)

one e- has (1, 0, 0, -½)

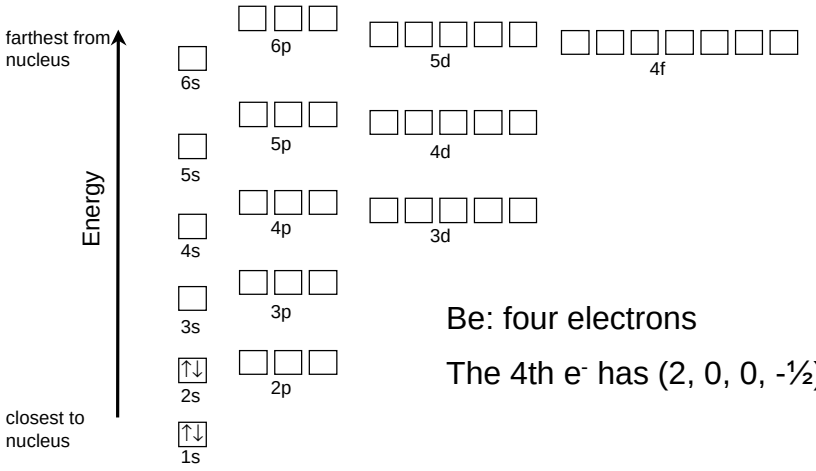
Electron Orbital Energies



Li: three electrons

The 3rd e^- has (2, 0, 0, +½)

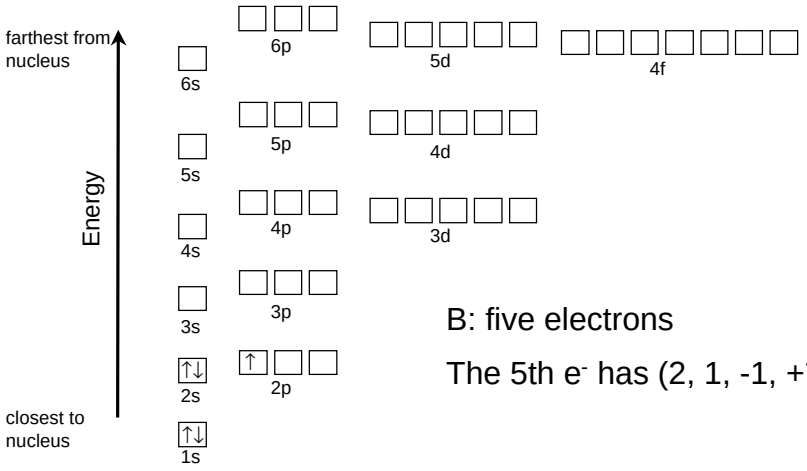
Electron Orbital Energies



Be: four electrons

The 4th e$^-$ has (2, 0, 0, -½)

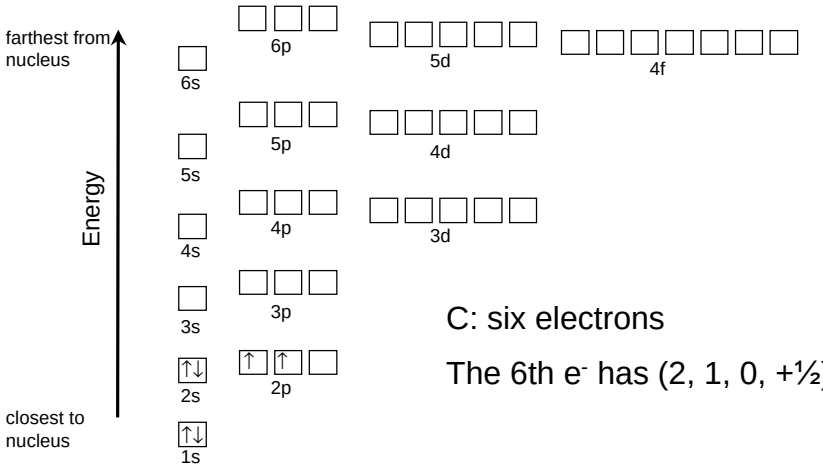
Electron Orbital Energies



B: five electrons

The 5th e$^-$ has (2, 1, -1, +½)

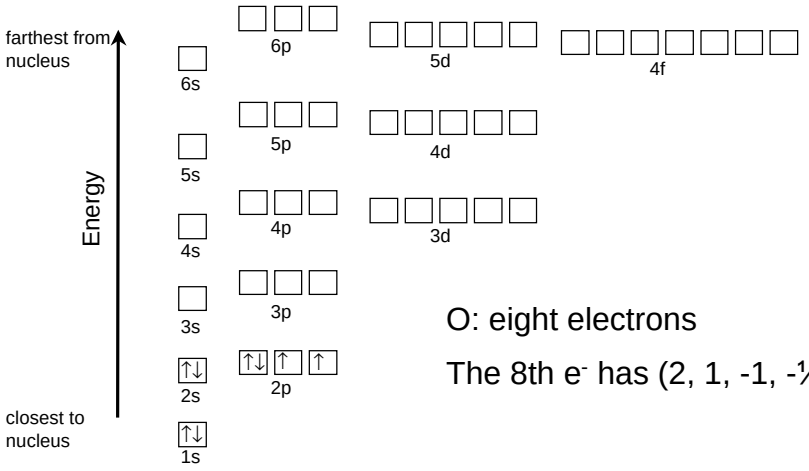
Electron Orbital Energies



C: six electrons

The 6th e$^-$ has (2, 1, 0, +½)

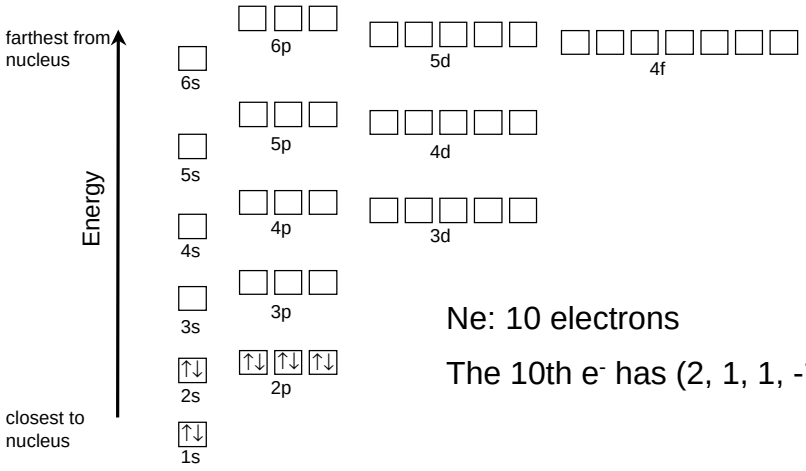
Electron Orbital Energies



O: eight electrons

The 8th e$^-$ has (2, 1, -1, -½)

Electron Orbital Energies

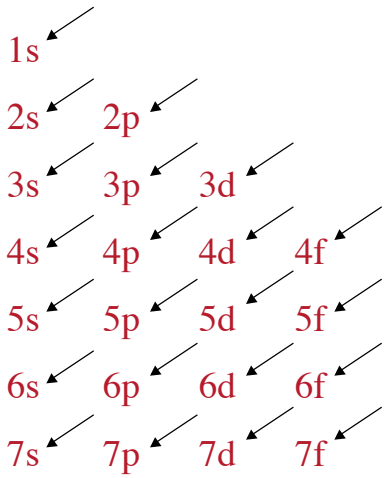


Ne: 10 electrons

The 10th e^- has (2, 1, 1, -½)

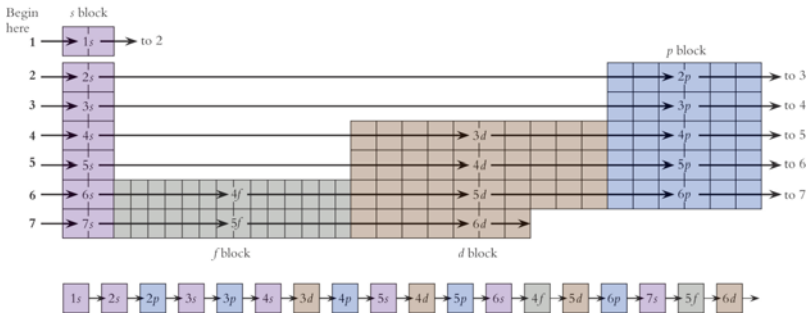
The Aufbau Principle

The order in which e^-'s are placed in orbitals may be remembered by listing the orbitals in rows by increasing principle quantum number, and moving down at a 45° angle beginning with 1s, then 2s, etc.



Structure of the Periodic Table

Elements in the Periodic Table are arranged by the order in which e⁻'s are placed into orbitals. This is called the *Aufbau Principle*.



Valence Electrons

Electrons available to participate in chemistry are called *valence electrons*. These are the electrons in the outermost orbitals of an atom. e⁻'s in inner orbitals are called *core electrons*—they do not participate in bonding, ionization, etc.

Examples

H atom has one e⁻ in the 1s orbital. This is the only valence e⁻ in H.

Lithium has two e⁻'s in the 1s orbital, and one e⁻ in the 2s orbital. The 2s e⁻ is the only valence e⁻ that participates in bonding, ionization, etc. The 1s e⁻'s are core e⁻'s.

Valence Electrons

Examples (con't.)

Chlorine has e^-'s in the 1s, 2s, 2p, 3s, and 3p orbitals. The 1s, 2s, and 2p e^-'s are core electrons and do not participate in chemistry. The e^-'s in n = 3 are the valence e^-'s.

Valence Electrons

Exceptions

Because energies of the ns and (n-1)d orbitals are nearly equal (degenerate), the (n-1)d e^-'s also participate in bonding: you get compounds such as $TiCl_4$ and TiO_2 instead of $TiCl_2$ or TiO.

Valence e^-'s are all those e^-'s of highest principle quantum number plus any e^-'s in partially filled d and f orbitals

Electron Configuration

The *electron configuration* of an atom or ion is a shorthand notation used to specify which orbitals are occupied with e^-'s.

$n\ \ell^{i}$

n = principle quantum number of orbital

ℓ = letter for azimuthal quantum number (s, p, d, or f)

superscript i = number of electrons in that orbital

Electron Configuration

Examples

Hydrogen: one e^- in the is orbital
electron configuration = $1s^1$

Helium: two e^-'s in the 1s orbital
electron configuration = $1s^2$

Lithium: two e^-'s in 1s orbital; one e^- in 2s orbital
electron configuration = $1s^2\ 2s^1$

Carbon: two e^-'s in 1s; two e^-'s in 2s; two e^-'s in 2p
electron configuration = $1s^2\ 2s^2\ 2p^2$

Electron Configuration

Examples

Neon: two e^-'s in 1s; two e^-'s in 2s; six e^-'s in 2p
electron configuration = $1s^2\ 2s^2\ 2p^6$

Sodium: two e^-'s in 1s; two e^-'s in 2s; six e^-'s in 2p; one e^- in 3s

electron configuration = $1s^2\ 2s^2\ 2p^6\ 3s^1$

Electron Configuration

Examples

Na electron configuration = $1s^2\ 2s^2\ 2p^6\ 3s^1$

Because Na has just one more electron than Ne, we can shorten the electron configuration by using this neon core to represent the core electrons: [Ne] = $1s^2\ 2s^2\ 3p^6$

electron configuration = [Ne] $3s^1$

where [Ne] represents the neon core

This can be done using any of the Noble gas cores.

Electron Configuration

Examples

What is the electron configuration of iodine?

I = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^5$

= [Kr] $5s^2\ 4d^{10}\ 5p^5$

Electron Configuration

Electron-electron repulsion—remember than e⁻'s prefer to be as far away from each as possible in order to minimize the energy costs from repulsion by particle with the same electrical charge.

This effects the electron configuration of elements with near-degenerate orbitals:

Electron Configuration

Chromium

For Cr, because the 4s and 3d orbitals are so close in energy, option 2 is found experimentally to be the ground state because of the lower energy achieved when the e⁻'s are unpaired.

Electron Configuration

Copper

For Cu, option 2 is found experimentally to be the ground state because atoms want to have a full valence orbital, and this configuration is lower in energy.

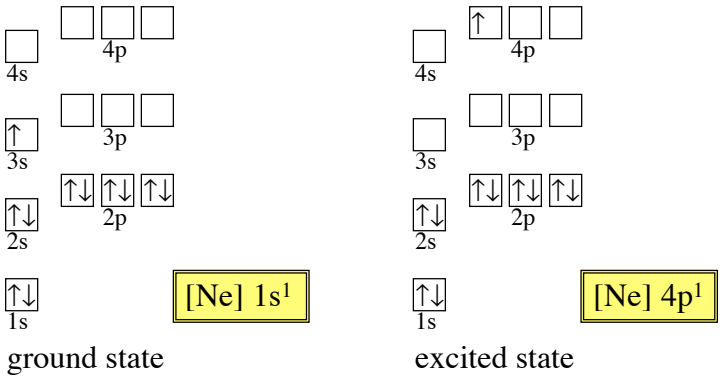
Energetics of Atoms

When the electrons in an atom are in the lowest possible energy configuration of orbitals, the atom is in its *ground state*—the ground state of any system represents the lowest energy available for the system.

If an electron is promoted to a higher orbital, it is in an *excited state*—an excited state represents some energy state higher than the ground state.

Energetics of Atoms

Sodium



Atomic Properties and the Periodic Table

- The combination of electron configuration and effective nuclear charge may be used to explain many of the observed trends in the physical properties of atoms in the Periodic Table.
- Remember that e^-'s in the same type of orbital do not screen nuclear charge as effectively as e^-'s in inner orbitals:

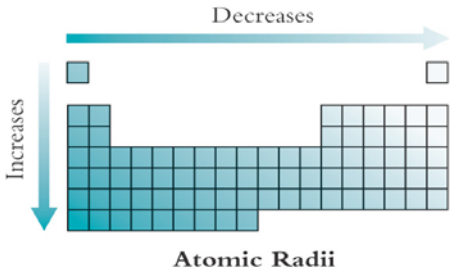
  An e^- in a 3p orbital is screened more effectively by a 3s e^- or a 2p e^- compared to another 3p e^-.

Atomic Properties and the Periodic Table

Atomic Radius

The radius of an atom determines the average volume it occupies.

Trend in atomic radii is: Atomic size increases from top to bottom and decreases from left to right of the Periodic Table.



Atomic Properties and the Periodic Table

Atomic Radius

Top to bottom: as principle quantum number increases, the size of the outermost orbitals increases resulting in larger atoms.

H	r = 0.37 Å (37 pm)	n = 1
Li	r = 1.52 Å	n = 2
Na	r = 1.86 Å	n = 3
K	r = 2.27 Å	n = 4
Rb	r = 2.48 Å	n = 5
Cs	r = 2.65 Å	n = 6
Fr	r = 2.70 Å	n = 7

Atomic Properties and the Periodic Table

Atomic Radius

Left to right: as e^-'s are added to the same type of orbitals, the effective nuclear charge experienced by the e^-'s increases more than the screening by other e^-'s in the same type of orbital, so the outer e^-'s are pulled closer to the nucleus.

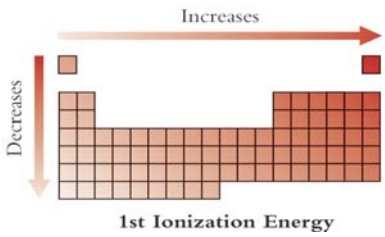
Li	r = 1.52 Å ($2s^1$)	N	r = 0.75 Å ($2s^2\ 2p^3$)
Be	r = 1.12 Å ($2s^2$)	O	r = 0.73 Å ($2s^2\ 2p^4$)
B	r = 0.85 Å ($2s^2\ 2p^1$)	F	r = 0.72 Å ($2s^2\ 2p^5$)
C	r = 0.77 Å ($2s^2\ 2p^2$)	Ne	r = 0.71 Å ($2s^2\ 2p^6$)

Atomic Properties and the Periodic Table

Ionization Energy

The first ionization energy is the energy required to pull the first electron completely away from a neutral atom.

Trend in IE_1: decreases from top to bottom and increases from left to right in the Periodic Table.



Atomic Properties and the Periodic Table

First Ionization Energy

Top to bottom: as principle quantum number increases, the outermost electron is further from the nucleus and experience lower electrostatic attraction making it easier to pull off.

F $IE_1 = 1681$ kJ mol^{-1} r = 0.72 Å

Cl $IE_1 = 1256$ kJ mol^{-1} r = 1.00 Å

Br $IE_1 = 1143$ kJ mol^{-1} r = 1.14 Å

I $IE_1 = 1009$ kJ mol^{-1} r = 1.33 Å

At $IE_1 = 926$ kJ mol^{-1} r = 1.40 Å

Atomic Properties and the Periodic Table

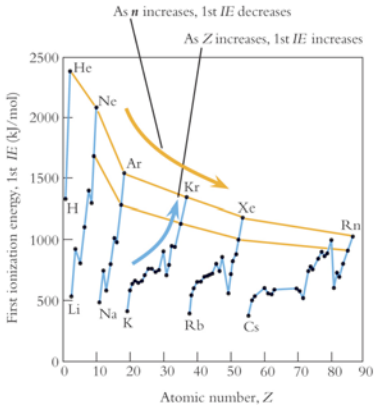
First Ionization Energy

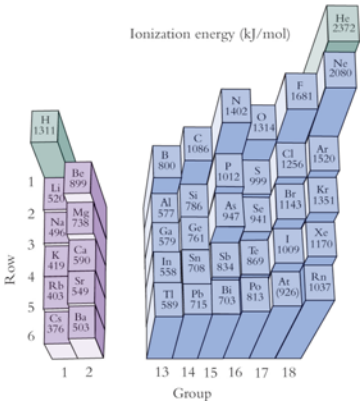
Left to right: the effective nuclear charge increases and atomic size decreases moving left to right. Both effect IE_1. Additionally, the effects of electron-electron repulsion may decrease IE_1 when beginning to pair up e^-'s in p orbitals.

Li	$IE_1 = 520$ kJ mol^{-1}	N	$IE_1 = 1402$ kJ mol^{-1}
Be	$IE_1 = 899$ kJ mol^{-1}	O	$IE_1 = 1314$ kJ mol^{-1}
B	$IE_1 = 800$ kJ mol^{-1}	F	$IE_1 = 1681$ kJ mol^{-1}
C	$IE_1 = 1086$ kJ mol^{-1}	Ne	$IE_1 = 2080$ kJ mol^{-1}

Atomic Properties and the Periodic Table

First Ionization Energy





Atomic Properties and the Periodic Table

Electron Affinity

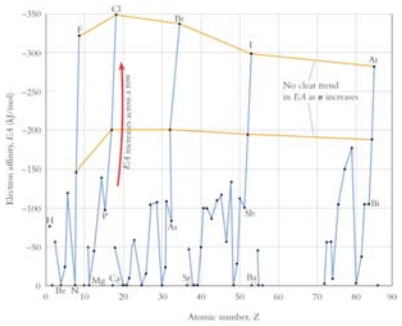
Electron affinity (EA) is, as the name suggests, a measure of how strongly a species would like to add an e^- into its valence orbitals. Whereas ionization energy measures the removal of an electron, electron affinity measures the addition of an electron. You can think of electron affinity as opposite of the energy required to ionize an anion.

$F + e^- \rightarrow F^-$ EA = -322 kJ mol^{-1}

Atomic Properties and the Periodic Table

Electron Affinity

The trend is for EA to increase from left to right in the Periodic Table.



Atomic Properties and the Periodic Table

Size of ions

Cations are always smaller than the corresponding neutral atom because they have an increased effective nuclear charge due the decrease in screening resulting from the loss of e^-'s in the valence orbitals.

Na	r = 1.86 Å	Na^+	r = 1.16 Å
Mg	r = 1.60 Å	Mg^{2+}	r = 0.86 Å

Atomic Properties and the Periodic Table

Size of ions

Anions are always larger than the corresponding neutral atom because they have a decreased effective nuclear charge due to increased screening by additional e^-'s in the valence orbitals.

Cl	r = 1.00 Å	Cl^-	r = 1.67 Å
S	r = 1.03 Å	S^{2-}	r = 1.70 Å