Chapter 7

Atomic Structure and Periodicity

- To understand the Periodic Table, we need to understand atoms
- To understand atoms, we need to understand the nature of matter at very very small length scales.
- Quantum Mechanics rules the very very small length scales.
  - But its effects definitely show up at large length scales

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Quantum Mechanics is weird and counterintuitive.

The world at atomic and sub-atomic scale is sort of like Alice in Wonderland

Wave-particle duality

Matter is made of particles

but …

Particles can also act as waves. The smaller and lighter they are, the more wave-like they are.

We cannot understand matter at atomic scale without understanding waves

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Waves

Most waves involves the propagation of a disturbance in a medium.

Water waves propagate by the up-down motion of water.

Sound waves propagate by the rapid compression-decompression of air (or the liquid or solid through which they are traveling).

Waves

Light is also a wave. It is a form of electromagnetic wave ("electromagnetic radiation").

Electromagnetic waves do not need a medium to travel. They kind of carry themselves through space!

All waves are characterized by

Wavelength (λ) – distance between two consecutive peaks or troughs in a wave.

Frequency (ν) – number of waves (cycles) per second that pass a given point in space

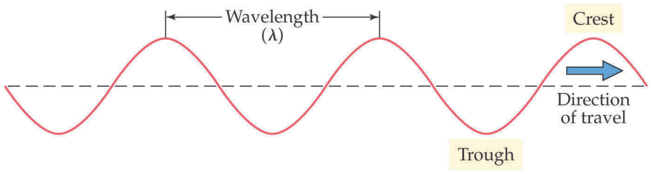
- Frequency has the unit of reciprocal time
  s^{-1} = “Hertz” (Hz)
- “counts”, “cycles” or “number of waves” is not a physical unit, and doesn’t show up

Speed (v) – speed of propagation

Wavelength

Symbol: **λ** (lambda)

The distance between adjacent wave crests (or troughs, or any two equivalent points).



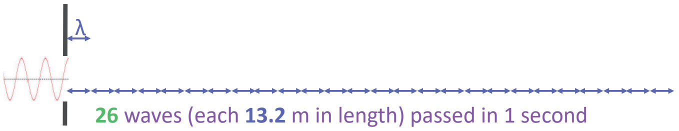
Frequency

Distance travelled in 1 sec. = **26** wave/s

Symbol: **ν** (“nu”) (yes, not “vee”)

Number of waves passing through a point per unit of time

Observing a sound wave for 1 second



26 waves (each **13.2** m in length) passed in 1 second

➡ frequency = **26** s^{-1}

$$\overbrace{\text{Distance travelled in 1 sec.}}^{\text{Wave speed}} = \overbrace{\mathbf{26}\ \text{wave/s}}^{\nu} \times \overbrace{\mathbf{13.2}\ \text{m/wave}}^{\lambda} = 343\ \text{m/s}$$

Wave speed = (number of waves per second)(length of each wave)

Wave speed = $\nu\ \lambda$

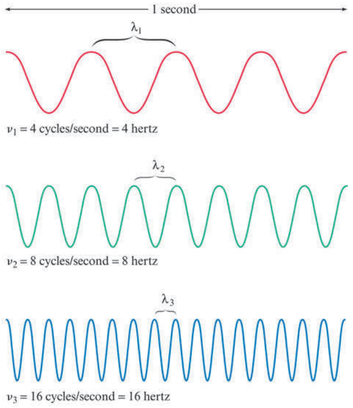
$$v = \lambda\ \nu$$

- Make sure you use consistent units.
- If v is in m/s, λ should be in m (not, say, in nm)
- If v is in km/hours, λ should be in km and

  ν should be in hours^{-1}

Frequency and wavelength are inversely related

Lower frequency
Longer wavelength



Higher frequency
Shorter wavelength

For electromagnetic radiation (including light):

$$c = \nu\ \lambda$$

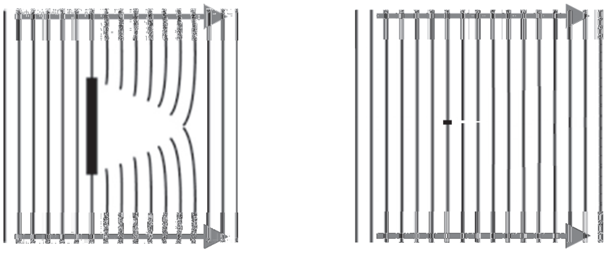
Speed of light

c = speed of light
= 2.99792458×10^{8} m/s
Defined exactly now.
But often used with only 3 or 4 sig. figs.

Waves diffract

Waves bend around obstacles.

Moving into the region where there was supposed to be a "shadow"



If the obstacle is a lot smaller than the wavelength, it's basically "invisible" to the wave

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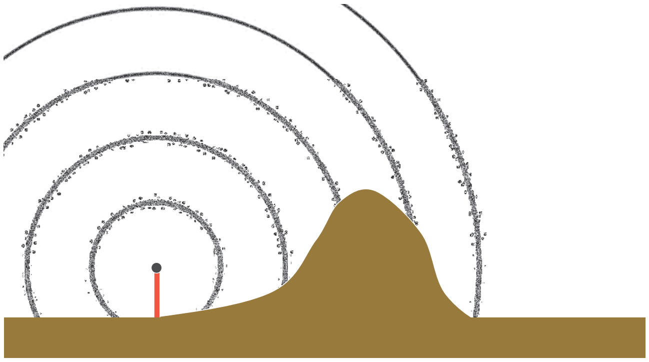
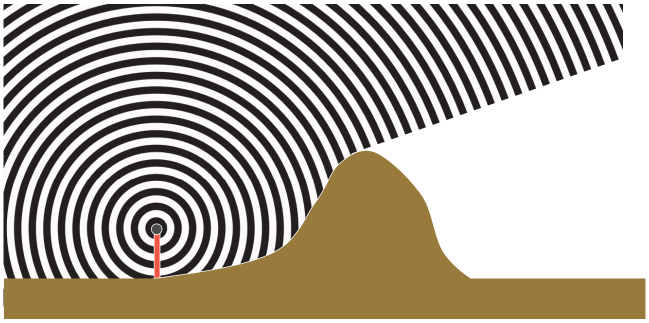
To observe appreciable diffraction, wavelength should not be much smaller than the feature it hits

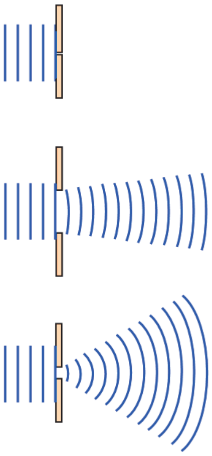


Radio waves with long wavelengths can be received behind hills, but shorter wavelengths can't.

If the wavelength is a lot smaller than the obstacle, the wave doesn't bend much and acts more like a bunch of particles; it gets blocked.



Radio waves with long wavelengths can be received behind hills, but shorter wavelengths can't.



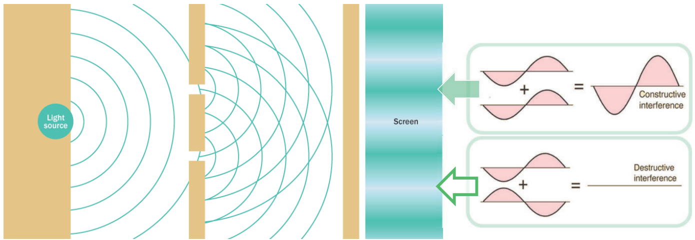
If a hole is much smaller than the wavelength, the wave is blocked -- it can't "see" the hole

If a hole is much larger than the wavelength, the diffraction (the bending effect) will be small.

If a hole is about the same size as the wavelength, it will act as a **point source** (waves will come out of it, with the hole at the center)

Waves on water diffract too!

Diffraction by multiple features cause "interference"



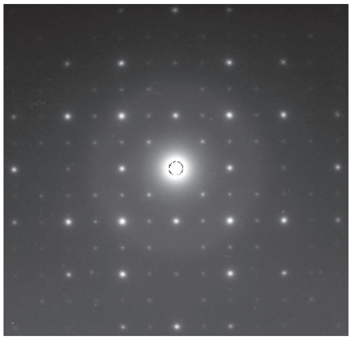
E. Otwell, sciencenews.org

Diffraction of the same wave by multiple features cause "**diffraction interference**"

- Where wave peaks coincide, amplitudes add up
- Where a wave peak coincides with another wave's trough, amplitudes cancel
- Creating an "interference pattern"

Diffraction of X-rays by atoms in a crystal lattice also form a diffraction pattern

Distance ("hole") between atoms : Angstroms (10^{-10} m)
X-ray wavelengths: Angstroms (10^{-10} m)



Crystal structures and structures of molecules in a crystal are discovered by analyzing the X-ray diffraction patterns

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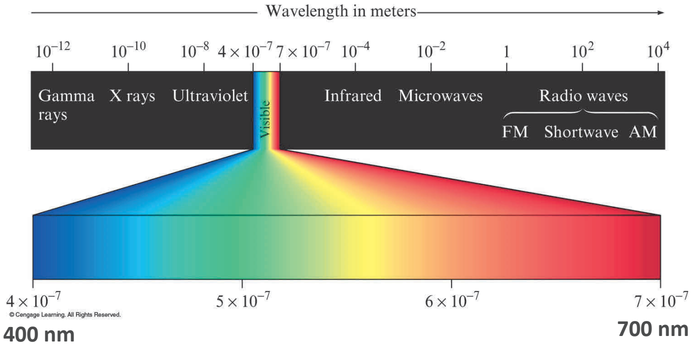
Classification of Electromagnetic Radiation



We said earlier:

Electromagnetic waves do not need a medium to travel. They kind of carry themselves through space!

- That's because they also are "particles", called photons.
- Photons are basically a "packet" of energy.
- A photon has no "rest mass". Its mass is due to its energy, because $E=mc^2$
- We cannot stop a photon. If we could, it would have no mass.
- Put another way, if we "stop" a photon it gives up its energy, and therefore its mass. It disappears.

So,

- **Electromagnetic radiation** exhibits wave properties and particulate properties.

It's much more than an "example":

- Its fundamental properties led to the leaps of intuition that developed Quantum Mechanics
  - Wave-particle duality extended to all matter
- And its essential role in an atom's gaining or losing energy allows the actual measurements of energy changes

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Light

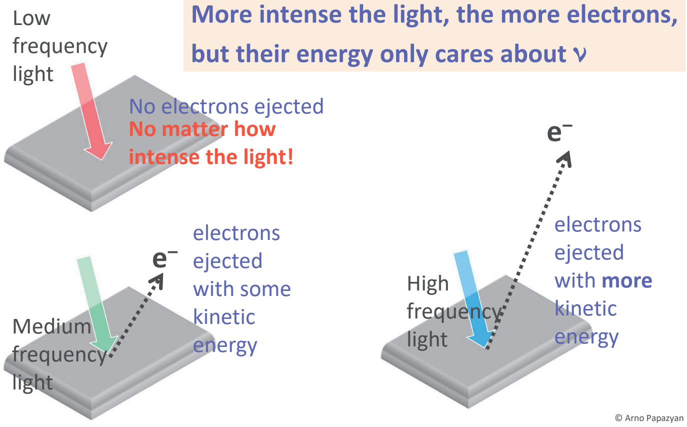
It turns out that the energy of a photon is directly proportional to frequency of the light.

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

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

Photoelectric effect (freeing electrons from a metal surface by shining light on it) surprised scientists

More intense the light, the more electrons, but their energy only cares about ν



Low frequency light

No electrons ejected
No matter how intense the light!

Medium frequency light

e^-

electrons ejected with some kinetic energy

High frequency light

e^-

electrons ejected with **more** kinetic energy

Einstein received the Nobel Prize for figuring out:

- Light is made of individual energy “quanta”
  - ➢ Called **photons**
- Each photon carries a quantity of energy proportional to the frequency of light

$$E_{photon} = h\nu$$

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

Energy can be gained or lost only in whole number multiples of $h\nu$

A system can transfer energy only in whole quanta (or “packets”)

Each “packet” contains an energy equal to $h\nu$

Photoelectric effect showed that photons transfer all of their energy or none at all

Electrons are emitted from a metal’s surface when struck by light

Kinetic energy of ejected electron = $\underbrace{h\nu}_{\text{Photon energy}} - \underbrace{W}_{\text{Photon energy required to remove the electron from the metal's surface}}$

If photon energy $h\nu$ < W, electrons are not emitted, no matter how many photons we send.

If photon energy $h\nu$ < W, electrons are not emitted, no matter how many photons we send.

This means that it’s the individual photon’s energy that is important in dislodging the electrons, not the intensity of the light (how many photons we send).

Photoelectric effect

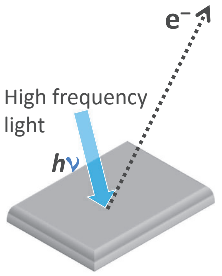
Leftover energy

$h\nu > W$

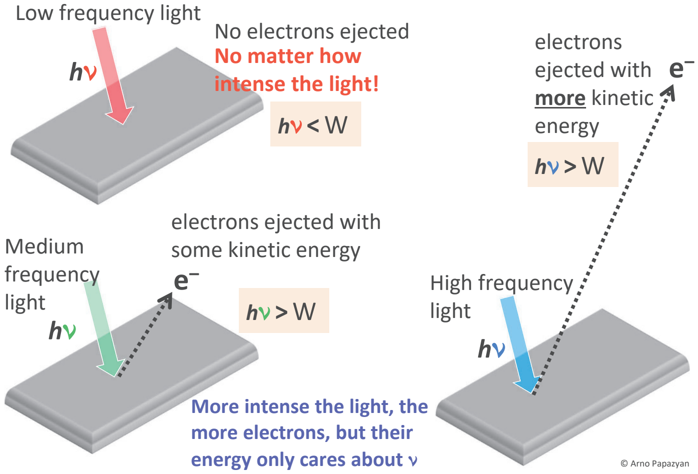
$$\text{kinetic energy of } e^- = h\nu - W > 0$$

Energy brought by the photon

Energy spent to break away from the metal surface



Photoelectric effect



No electrons ejected

No matter how intense the light!

$h\nu < W$

electrons ejected with some kinetic energy

$h\nu > W$

electrons ejected with **more** kinetic energy

$h\nu > W$

More intense the light, the more electrons, but their energy only cares about ν

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

Why not "Einstein's constant"?

- Max Planck had theorized that the energy gained or lost via light was proportional to the light frequency ($|\Delta E| = h\nu$), to explain the light emitted by objects at a given temperature, but was not convinced that it corresponded to actual particles. The fact that he needed to hypothesize discrete energy levels in matter was weird enough for him.
- Einstein clarified that <u>photons</u> were <u>really</u> carrying the energy in and out of discrete energy levels

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Photon's discovery allowed us to know:

- The "currency" of energy exchange involving electromagnetic radiation: photon
- The energy value of that "currency" (by measuring frequency or wavelength)
- We then knew that a light of certain frequency corresponded to an energy loss of that exact same energy by *something*

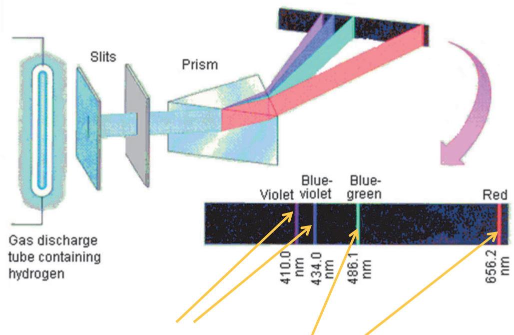
$$E_{photon} = |\Delta E| = h\nu$$

Atoms exchanging energy

When an atom gets extra energy above its most stable, "ground" level, it eventually releases the energy by emitting a photon.

<u>For an atom in the gas phase:</u>

- When "alone" in the gas phase, there are no other atoms to exchange energy with, or have many different configurations with different energy levels.
- Whatever energy levels are allowed in the isolated atom are the only levels available to its electrons.



http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/bohr.html

"line spectrum"

Hydrogen atoms in the gas phase emit light with **only several discrete wavelengths**

When an atom is in a dense environment like a liquid, or a solid, or a dense plasma like the sun, its energy levels are modified by collisions, and also numerous new levels of energy are created for electrons to be at.

So, in a **dense environment**:

There are basically an **infinite variety of energy levels** an electron can jump to (there is an appropriate ΔE for every photon that comes along), and an infinite variety of energy levels to relax down to, emitting photons with an infinite variety of energies (therefore wavelengths).

The theoretical distribution of wavelengths emitted by dense objects is well known, and is called "**black body radiation**".

A "black body" absorbs all light and emits light with a distribution of wavelengths determined only by its temperature.

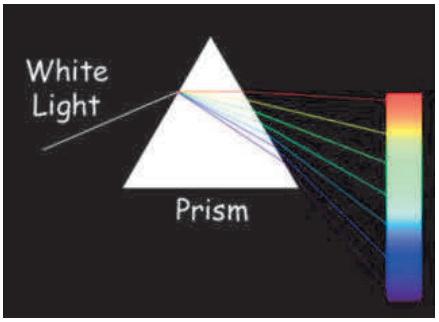
The higher the temperature, the higher the average frequency (and shorter the average wavelength) of the light emitted by a "black body".

That's how non-contact thermometers measure T

Sun is a "black body"!

—more or less

Sunlight contains a continuous distribution of wavelengths (therefore photon energies)



(Image: © NASA)

Credit Marina Shemesh / Public Domain Pictures

Back to the line spectrum of a gas:

The "line spectrum" of hydrogen, and gases of other elements, implied:

Since there are only certain ΔE values allowed for the electron in the atom, then it must have only certain E values, and not others.

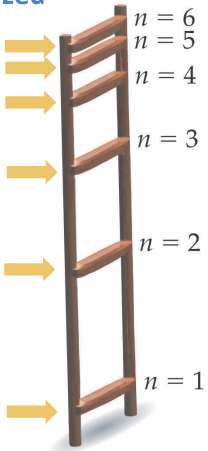
In other words:

Line spectrum → Quantized energy levels

Energy levels in an atom are quantized

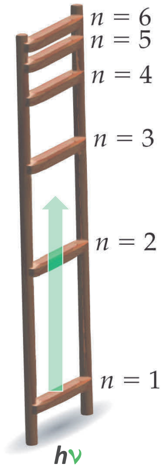
- Discrete, distinct energy levels
- No other levels

Just as we can only step on the individual levels on a ladder, the **electrons in an atom can only exist at certain energy levels** and not in between.



If the energy of the photon doesn't match an energy difference between two levels in an atom, it's not absorbed.

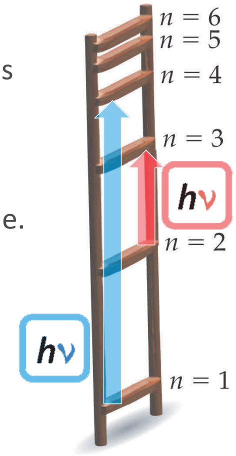
Even if it has more than enough energy!



If the energy of the photon matches a difference between two levels **exactly**, it can be absorbed.

Not more, not less, exactly the same.

$$\underset{\overset{\uparrow}{h\nu}}{E_{photon}} = \Delta E_{electron}$$



But why are energy levels in atoms quantized?

Particles as waves

De Broglie's leap of faith:

Take $E_{photon} = h\nu = \frac{hc}{\lambda}$ (applies to photons)

Combine it with $E = mc^2$ (applies to everything)

$$\Rightarrow m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{\lambda\, c} \Rightarrow \lambda = \frac{h}{m\,c}$$ **for photons**

?

$$\lambda = \frac{h}{m\,v}$$ **for any particle**

See if it applies to everything.

It does!

$$\boxed{\lambda = \frac{h}{mv}}$$

De Broglie wavelength

Wavelength of a particle!

- A stable state for a wave in a confined space is a "standing wave"
  - Like the vibrations of a guitar string
- So when we confine a particle into a limited space, the standing wave requirement allows only certain wavelengths and excludes all others

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"Particle in a box"

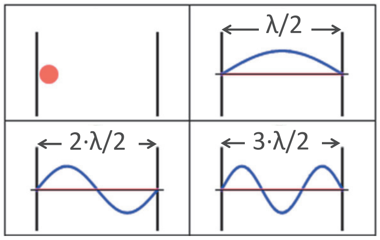
A particle is a wave with a de Broglie wavelength of λ

It fits in a "box" if box's length is a multiple of λ/2

So only certain λ values are allowed

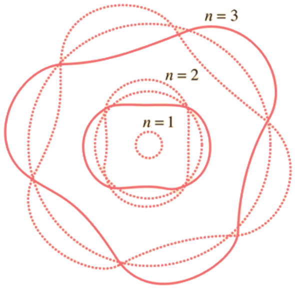
Therefore only certain particle speeds are allowed.

Therefore only certain particle energies are allowed.



en.wikipedia.org/wiki/Particle_in_a_box

- An electron constrained to be around the nucleus (because of the electrostatic attraction to the nucleus) is also in a kind of circular "box"
- The circle length still needs to be a multiple of λ/2



Bohr Model of the Hydrogen Atom

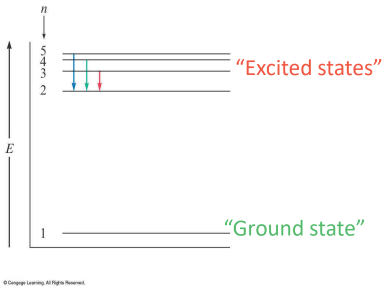
- Before de Broglie derived his result, Bohr came up with a model for Hydrogen atom.
  - ➢Later explained by the de Broglie wavelength
- Electrons "orbit" around the nucleus, the (+)/(–) attractions balanced by the centrifugal forces
- A simple but unexplained assumption is made about the allowed angular speeds of the electrons. And ta-da!

Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum.

Bohr Model of the Hydrogen Atom

- It gives a "caricature" picture of a hydrogen atom
- Electrons can be imagined to "jump" between orbits, which correspond to different energy levels.
- An electron can jump up between levels when supplied with just the right amount of energy between two levels
- When an electron jumps down between levels, the energy is lost in the form of an emitted photon.

Energy levels & electronic transitions in the Bohr model



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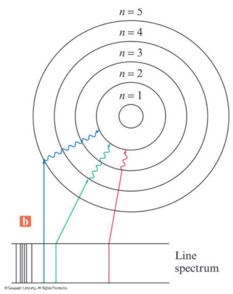

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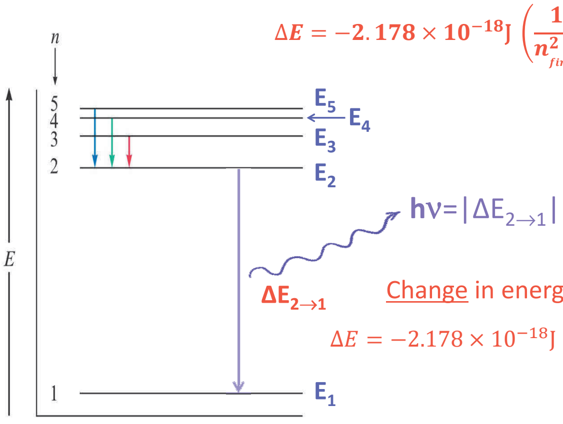
$$E_n = -2.178 \times 10^{-18}\text{J}\,\frac{1}{n^2}$$

$$\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{\text{initial}}}\right)$$



Change in energy

$$\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

Energy levels and "transitions" for the electron in an atom

- Ground state: lowest possible energy state (n = 1)
- Electrons can be "excited" to higher levels (n=2, 3, 4, …) by absorbing a photon with an energy that equals the energy difference between levels

E_{photon} is always positive

$$E_{\text{photon}} = |\Delta E_{\text{transition}}|$$

For any electronic transition, we have:

$$|\Delta E_{transition}| = E_{photon} = h\nu = \frac{hc}{\lambda}$$

Frequency and wavelength of light corresponding to the transition are given by the energy change in the transition

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Practice

Calculate the wavelength of light emitted when an excited electron in the hydrogen atom falls from n = 5 to n = 2

The energy of the transition is given by: $\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{\text{initial}}^2}\right)$

whose magnitude gives the photon energy: $|\Delta E_{transition}| = E_{photon} = h\nu = \frac{hc}{\lambda}$

then λ is given by: λ = hc/ E_{photon}

Applying these thoughts:

$\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = -4.574\text{x}10^{-19}$ J

E_{photon} = |–4.574x10–19 J | = 4.574x10–19 J

λ = (6.626x10^{-34} J·s)(3.00x10^{8} m/s) / (4.574x10^{-19} J) = 4.34x10^{-7} m

λ = (4.34x10^{-7} m)(1 nm / 10^{-9} m) = 434 nm

Energy levels in Hydrogen-like ions

Bohr's model can also predict the energy levels in hydrogen-like ions like He^+ and Li^{2+}, **which have only one electron.**

$$E_n = -2.178 \times 10^{-18}\text{J}\,\frac{Z^2}{n^2}$$

Z = nuclear charge (in atomic charge units)
+1 for a H nucleus, +2 for a He nucleus, etc.

$$E_{n_i \to n_f} = -2.178 \times 10^{-18}\text{J}\; Z^2\left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right]$$

Same transition in two hydrogen-like species

For a given n: E ∝ Z^2
For a given transition: ΔE ∝ Z^2

$$\frac{\Delta E_A}{\Delta E_B} = \frac{Z_A^{\,2}}{Z_B^{\,2}}$$

$|\Delta E| = E_{photon} = h\nu$

$$\frac{\nu_A}{\nu_B} = \frac{Z_A^{\,2}}{Z_B^{\,2}}$$

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

$$\frac{\lambda_A}{\lambda_B} = \frac{Z_B^{\,2}}{Z_A^{\,2}}$$

Note the inverse relationship of λ with Z^2

For He^+ and Li^{2+}

Z = 2

$$\frac{\nu_{He^+}}{\nu_{Li^{2+}}} = \frac{2^2}{3^2}$$

Z = 3

$$\frac{\lambda_{He^+}}{\lambda_{Li^{2+}}} = \frac{3^2}{2^2}$$

Bohr model fails for atoms with more than one electron!

- Bohr model doesn't really capture the fundamental reason for the discrete, "quantized" energy levels
- It failed to predict the energy levels and the transition energies for other elements
  - When there is more than one electron
- A true explanation was provided by Quantum Mechanics, based on the wave nature of electrons.

The Quantum-Mechanical Model: Atoms with Orbitals

- Quantum mechanics revolutionized physics and chemistry because, in the quantum-mechanical model, electrons *do not* behave like particles flying through space.
- We cannot, in general, describe their exact paths.

Quantum Mechanics gives us probabilities

- Quantum mechanics only tells us probabilities, not the exact location of particles.
- “Solving” the quantum mechanical equation for an atom gives us 3-dimensional functions that describe where the electron is most likely to be found, and the energy corresponding to that particular solution
- The result is a cloud-like description of “probability density”, which is in effect “electron density” around a nucleus
- Each possible function (“**wavefunction**”) is called an “**orbital**” (not “orbit” as Bohr’s model assumed)

Quantum Mechanics of the Atom

Each distinct solution to the H atom wavefunction is called an “**orbital**”

An orbital defines where in space an electron is likely to be found.

In other words:

- The electron is smeared into a “fog”, and an orbital describes where that fog is dense.
- The region where electron density is high describes the shape and size of an orbital

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Orbital Size

- Difficult to define precisely.
- Picture an orbital as a three-dimensional electron density “fog”

Lowest energy Hydrogen orbital is a spherical cloud

Radius of the sphere that encloses 90% (or 99%, or whatever; it doesn’t change what it looks like) of the total electron probability.

Lowest energy orbital for Hydrogen

Just one of many solutions for the electron wavefunction in Hydrogen

intensity of color denotes here the probability density at any given point

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A set of “Quantum numbers” define an orbital

Consider a simple, one-dimensional function like

$y = ax^b + cx$

It has a general form, but it’s not totally specified until we specify the factors a, b, c.

- Similarly, there are “Quantum numbers” that specify the exact form of the 3-dimensional orbital function. Their allowed values are determined when the quantum mechanical equation is solved.

A set of “Quantum numbers” define the “address” of an electron

The quantum numbers form a hierarchy

The “principal” quantum number defines a “**shell**”

Within each shell there are “**subshells**”

Within each subshell there are **orbitals**

Each orbital can contain up to two **electrons**

A set of “Quantum numbers” define the “address” of an electron

Now thinking in the opposite direction,

- An electron in an atom can be alone in an orbital, or share it with another electron.
- That orbital is in a subshell
- That subshell is in a shell

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shells n starts from 1

Has n subshells

subshells l ranges from 0 to n-1 for a given n

- It has letter designations *s, p, d, f, . . .*
- Has $2l+1$ orbitals

orbitals m_l ranges from $-l$ to $+l$

Quantum numbers

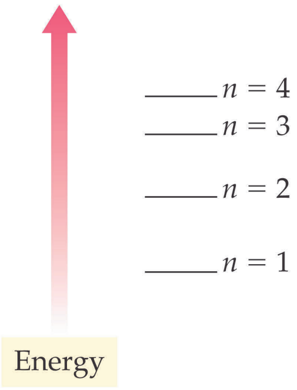
Symbol	Name	Determines	Corresponds to	Allowed Values
n	Principal	**Energy** and **Distance** from nucleus	**Shell** ***Has n sub-shells***	1,2,3,4,5, . . .
l	Angular momentum	**Shape** of the electron density **Energy** for *non-Hydrogen* atoms	**Sub-shell** ***Each subshell has 2l+1 orbitals***	0 to $n-1$ l = 0, 1, 2, 3, 4, 5, … have designations s, p, d, f, g, h, . . . If n=4: 0,1,2,3 (s,p,d,f)
m_l	Magnetic	**Orientation** of the electron density determined by l	**Orbital** ***Each orbital can have 2 electrons***	$-l$ to $+l$ For l=2: -2,-1,0,+1,+2
m_s	Spin	Direction of electron’s **magnetic field**	**Up/Down magnetic field** ***Distinguishes the 2 electrons in an orbital***	$-½$ or $+½$

Consider quantum numbers as parts of an electron’s “address”

- If n is the street name
- Then l is the number of the house. It only has a tangible meaning given a certain n
- m_l has a tangible meaning given a specific l, like a particular room in the house
- m_s then would be which of the two beds in a bunk bed the electron sleeps in
  - — appropriately, “up” or “down”

Energy Increases with Principal Quantum Number

- The higher the principal quantum number, the higher the energy of the orbital.
- The possible principal quantum numbers are
  n = 1, 2, 3 …
- Energy increases with n
- Distance from nucleus also increases with n



The number of subshells in n^{th} shell = n

Each shell is composed of subshells

Conveniently, number of subshells in a shell is equal to the “shell number” (principal quantum number)

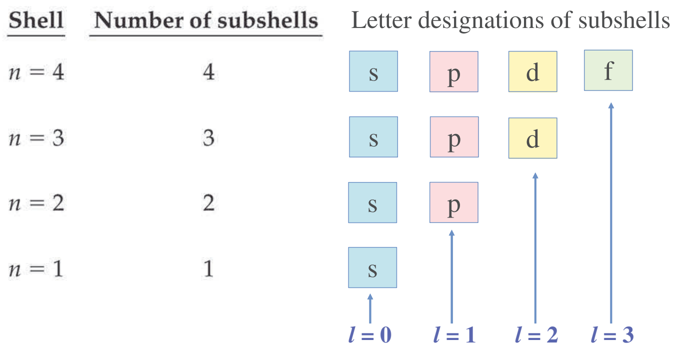
Shell	Number of subshells
$n = 4$	4
$n = 3$	3
$n = 2$	2
$n = 1$	1

Subshells are usually represented by letters

Subshell determines the shape of the orbitals within it

Each subshell has a letter designation

Within each shell, the **same letters** *s, p, d, f,* etc. are used to designate subshells

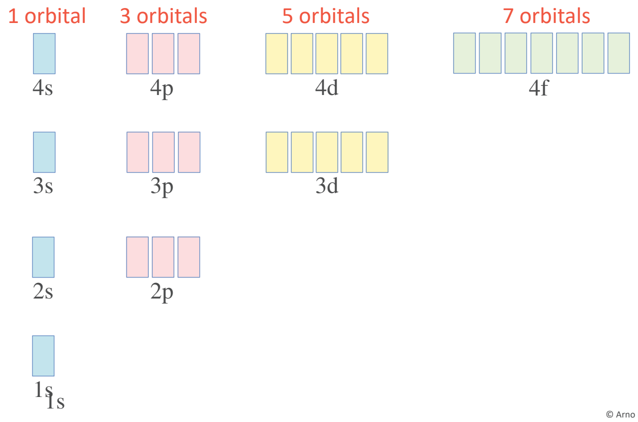


Shell	Number of subshells	Letter designations of subshells			
$n = 4$	4	s	p	d	f
$n = 3$	3	s	p	d	
$n = 2$	2	s	p		
$n = 1$	1	s			
		$l = 0$	$l = 1$	$l = 2$	$l = 3$

The full designation for a subshell includes the shell number

Shell	Number of subshells	Letter designations of subshells			
$n = 4$	4	4s	4p	4d	4f
$n = 3$	3	3s	3p	3d	
$n = 2$	2	2s	2p		
$n = 1$	1	1s			

Number of orbitals in a subshell depends only on its subshell number (i.e. letter designation)



Orbitals in a given subshell carry the same letter designation as the subshell

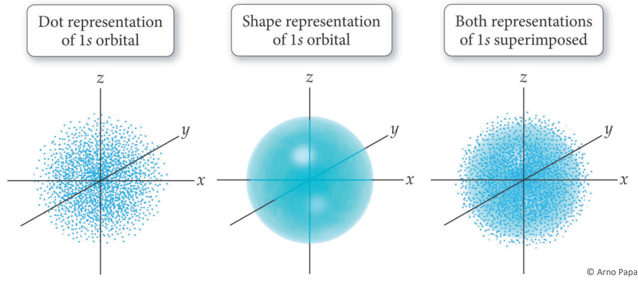
"2p orbitals" are in the "2p subshell"
"3d orbitals" are in the "3d subshell", etc.

Subscript labels are used to distinguish between orbitals in a given subshell, when needed

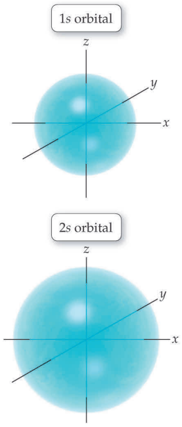
e.g. $2p_x$, $2p_y$, $2p_z$

"Shape" of an orbital indicates where the electron spends most of its time

Dot density and shape representations of the 1*s* orbital: The dot density is proportional to the probability of finding the electron. The greater dot density near the middle represents a higher probability of finding the electron near the nucleus.

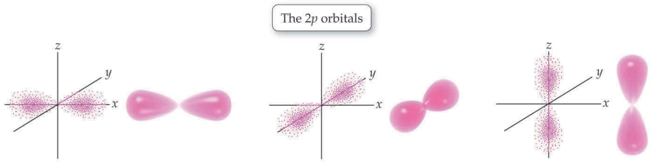


The 2*s* Orbital Is Similar to the 1*s* Orbital, but Larger in Size



The 2*p* Orbitals: The orbitals in the 2*p* subshell ($n = 2$, $l = 1$, $m_l = -1, 0, 1$)

p-orbitals are “dumbbell shaped”



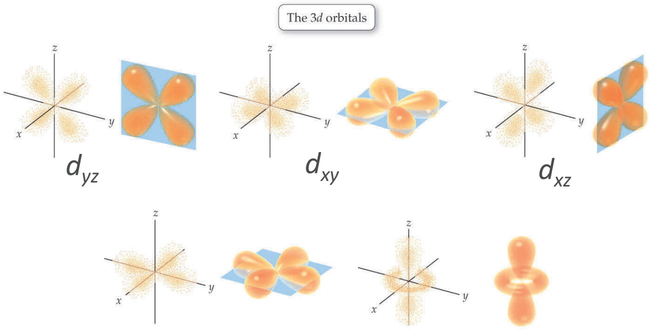
p_x p_y p_z

Orbitals in the 3rd shell (n = 3)

- 3rd shell contains three subshells specified by *s*, *p*, and *d:*

  3*s*, 3*p*, and 3*d*
- Orbitals in 3*s* and 3*p* subshells are similar in shape to the 2*s* and 2*p* orbitals, but slightly larger and higher in energy.
- Again, one orbital in 3*s*, and three orbitals in 3*p*
- The *d* subshell contains five *d* orbitals.

The 3*d* Orbitals:

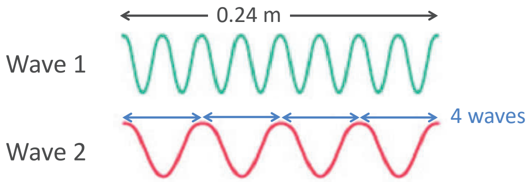


d_{yz} d_{xy} d_{xz}

$d_{x^2-y^2}$ d_{z^2}

Practice

Consider two different electromagnetic waves:



Which wave has the longer wavelength? What is its wavelength? What is its frequency?

Wavelength(λ) = (0.24 m)/4 = 0.060 m = 6.0 cm

Frequency(ν) = c/ λ = $(3.00\times10^8 \text{m s}^{-1})/(0.060 \text{ m}) = 5.0\times10^9 \text{ s}^{-1}$ (Hz)

Example

One electromagnetic radiation (let’s call it EM1) has a:
frequency of 89.3 MHz ($\text{Hz} = \text{s}^{-1}$; $\text{MHz} = 10^6 \text{ Hz} = 10^6 \text{ s}^{-1}$)

A second electromagnetic radiation (EM2) has a:
wavelength of 31.0 meters

A third electromagnetic radiation (EM3) has a:
photon energy of 4.42×10^{-19} Joules

Sort EM1, EM2, and EM3 in increasing order of photon energy.

EM1: $E_{\text{photon}} = h\nu = (6.626\times10^{-34} \text{ J·s})(89.3\times10^6 \text{ s}^{-1}) = 5.92\times10^{-26} \text{ J}$

EM2: $E_{\text{photon}} = h\nu = hc/\lambda = (6.626\times10^{-34} \text{ J·s})(3.00\times10^8 \text{ m/s}) / (31.0 \text{ m})$
$= 6.41\times10^{-27} \text{ J}$

EM3: $E_{\text{photon}} = 4.42\times10^{-19} \text{ J}$

EM2 , EM1 , EM3

Example

What is the wavelength (in nm) of the highest-energy photon in the previous question?

E_{photon} = 4.42x10^{-19} J $\qquad$ E_{photon} = hc/λ $\Longrightarrow$ λ = hc/ E_{photon}

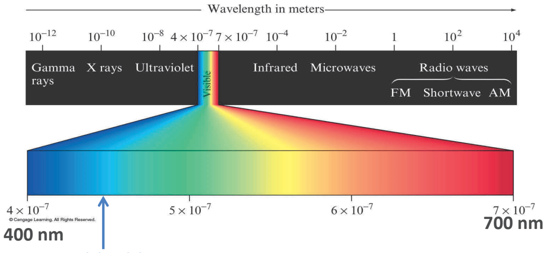
λ = (6.626x10^{-34} J·s)(3.00x10^{8} m/s) / (4.42x10^{-19} J) = 4.50x10^{-7} m

λ = (4.50x10^{-7} m)(1 nm / 10^{-9} m) = 450. nm

Example

What region of the electromagnetic spectrum does this photon the previous question belong to?

λ = 450. nm



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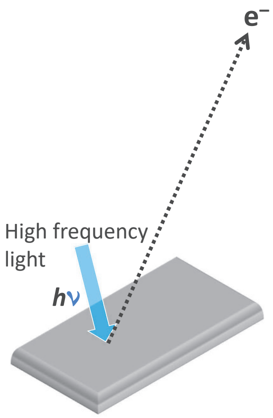
Visible; blue

Example

The energy (W) required to free an electron from the surface of solid Cesium metal is 3.37x10^{-19} J.
Does the photon in the previous question (with λ=450nm) have enough energy to display the photoelectric effect with Cesium?
If so, what would be the kinetic energy the ejected electron?

Light

Remember Photoelectric effect



Leftover energy

kinetic energy of e^- = $h\nu$ − W

Energy brought by the photon

Energy spent to break away from the metal surface

Let’s rewrite the problem here:

The energy (W) required to free an electron from the surface of solid Cesium metal is 3.37x10^{-19} J.
Does the photon in the previous question (with λ=450nm) have enough energy to display the photoelectric effect with Cesium?
If so, what would be the kinetic energy the ejected electron?

E_{photon} = 4.42x10^{-19} J

$E_{electron}$ = E_{photon} – W = (4.42x10^{-19} J) – (3.37x10^{-19} J) = 1.05x10^{-19} J

Energy of the free electron is in the form of kinetic energy since it is freed from any forces, and is now moving in vacuum.

Example

The photon in the previous question (with an energy of **4.42x10^{-19} J**) was able to free an electron from the surface of Cesium metal and give it the leftover energy in the form of kinetic energy. Could that photon excite an electron in a hydrogen atom from n=2 to n=3?

Energy change in electronic transitions in a hydrogen atom is given by:

$$\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{\text{initial}}}\right)$$

$$\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = \mathbf{3.025x10^{-19}\ J}$$

4.42x10^{-19} J **>** 3.025x10^{-19} J

The photon has more energy than required to make the electron jump from n=2 to n=3.

But its energy doesn’t match the transition energy!
It **cannot** excite the electron even if it has **more than enough** energy!

The number of cycles of a wave that passes a stationary point in one second is called its:

A) trough.

B) frequency.

C) wavelength.

D) crest.

E) none of the above

Which among the following statements is TRUE?

A) The wavelength of light is inversely related to its energy.

B) As the energy increases, the frequency of radiation decreases.

C) Red light has a shorter wavelength than violet light.

D) As the wavelength increases, the frequency also increases.

E) none of the above

Which color of the visible spectrum has the shortest wavelength (400 nm)?

A) violet

B) yellow

C) red

D) green

What is the correct order of the electromagnetic spectrum from shortest wavelength to longest?

A) GammaRays, X–rays, Visible Light, Ultraviolet Radiation, Infrared Radiation , Microwaves, Radio Waves

B) Gamma Rays, X–rays, Infrared Radiation, Visible Light, Ultraviolet Radiation, Microwaves, Radio Waves

C) Gamma Rays, X–rays, Ultraviolet Radiation, Visible Light, Infrared Radiation, Microwaves, Radio Waves

D) Visible Light, Infrared Radiation, Microwaves , Radio Waves, Gamma Rays, X–rays, Ultraviolet Radiation

E) Radio Waves, X–rays, Ultraviolet Radiation, Visible Light, Infrared Radiation, Microwaves, Gamma Rays

---

Which form of electromagnetic radiation has photons with the highest energy?

A) Radio Waves

B) Microwaves

C) X - rays

D) Gamma Rays

E) Infrared Radiation

The energy level diagram for a hydrogen atom is:

Which of the following transitions produces light with the longest wavelength?

A) 1→2

B) 1→5

C) 5→4

D) 5→1

E) 2→1

Which statement below does NOT follow the Bohr Model?

A) When an atom emits light, electrons fall from a higher orbit into a lower orbit.

B) When energy is absorbed by atoms, the electrons are promoted to higher - energy orbits.

C) Electrons exist in specific, quantized orbits.

D) The energy emitted from a relaxing electron can have any wavelength.

E) none of the above

Which of the following statements about the quantum - mechanical model is FALSE?

A) Orbitals are specific paths electrons follow.

B) Orbitals are a probability map of finding electrons.

C) Electrons cannot have arbitrary energies when confined.

D) Electron paths cannot be described exactly.

E) All of the above are correct statements.

The subshell letter:

A) specifies the maximum number of electrons.

B) specifies the 3 - D shape of the orbital.

C) specifies the principal shell of the orbital.

D) specifies the principal quantum number of the orbital.

E) none of the above

How many subshells are there in the n = 4 principal shell?

A) 1

B) 2

C) 3

D) 4

E) not enough information

The n = ________ principal shell is the lowest that may contain a d - subshell.

A) 1

B) 2

C) 3

D) 4

E) not enough information

Which subshell letter corresponds to a spherical orbital?

A) p

B) s

C) f

D) d

E) not enough information

Which statement is NOT true about "p" orbitals?

A) A 3p orbital has a higher energy than a 2p orbital.

B) A p-subshell contains three "p-orbitals”.

C) These orbitals are shaped like dumbbells.

D) All three of these statements are true.

E) none of the above

Origin of widely different elements, with periodically varying properties

Elements are the way they are, and they differ from one another as much as they do, and their properties vary periodically, because of a natural law called:
The **“Pauli Exclusion Principle”**.

> No two electrons in the same atom can have the same set of quantum numbers.

That means **we can’t keep stuffing electrons in the same orbital**. Otherwise, all the electrons would have the same n, l, m_l, and m_s with no problem. Actually they would all have gone into the 1*s* orbital. After all, it is the lowest energy orbital.

Electron Spin and the Pauli Exclusion Principle

- An orbital is defined by n, l, and m_l
- The fourth quantum number, m_s, i.e. the “spin” is the remaining number to make each electron unique
- If there were no limitations on the values it could take on, we could put all the electrons in the same orbital. Each electron would still have a different m_s.
- But m_s can only be +½ or -½
- Therefore:

An orbital can hold a maximum of two electrons

And if there are two electrons in the same orbital, they must have opposite spins: “up” (↑) and “down” (↓)
i.e. They must be “paired”

Aufbau (build-up) Principle

So, the “Pauli Exclusion Principle”, combined with the fact that m_s can only have two values, imposes a capacity of two electrons per orbital.

This forces electrons to populate higher energy subshells as they fill and run out of unfilled orbitals in a subshell.

We now turn our attention to the energy order of those subshells …

Aufbau (build-up) Principle

All the quantum numbers, shells, subshells, orbitals we have seen are derived for the Hydrogen atom:
1 electron
They technically apply only to Hydrogen

Other atoms have more than one electron, and the solutions to quantum mechanical equations don’t give us expressions with quantum numbers. The intuition is lost.

But it turns out:
- We can apply the concepts developed from H atom to other atoms,
- But there are “complications”

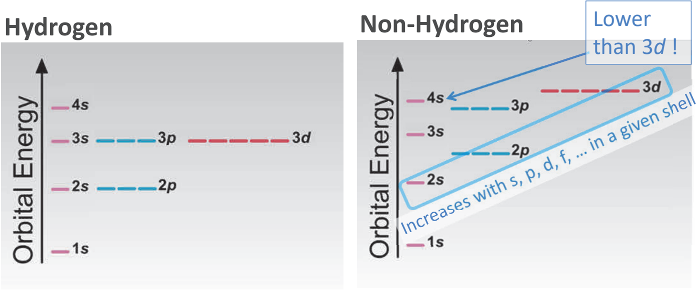
Aufbau (build-up) Principle

For Hydrogen there is only one electron around the nucleus, and all subshells in a given shell have the same energy (called “degenerate”; long story)

For atoms with more than one electron:

- Electron-electron repulsions affect subshell energies
- Subshell number (or letter) affects energy:
  - In a particular shell, energy of subshells follow the order *s*, *p*, *d*, *f*, …

Subshell energies



<u>In non-hydrogen atoms</u>:

- Subshells in a shell are **not of equal energy**
- A subshell in a higher shell can have a lower energy than one in a lower shell

---

Electrons in an atom are “built up” by adding them into the available orbitals in subshells in the order of increasing energy.

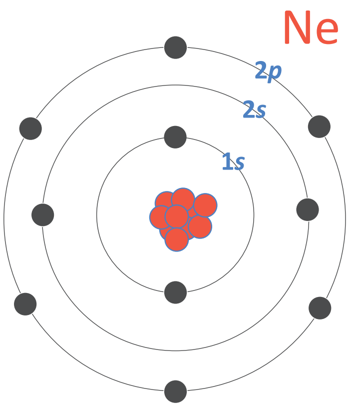
A lower energy subshell is filled first, followed by higher energy subshells

To build-up the next element, and then the next ….

- For each proton added to the nucleus:
  --- Electrons are added to hydrogen-like orbitals (which are in subshells designated by *s, p, d, f*, …).

Building up an atom

For each proton we add to the nucleus to make the next atom, we add an **electron** into the <u>lowest unfilled subshell</u>



- The neutrons needed to keep the protons together are not shown
- Relative size of the nucleus is much, much smaller than shown
- Electrons are actually **<u>not</u>** “dots” on a fixed orbit

---

For example,

An oxygen atom has 8 protons and **8** electrons.

- **2** electrons are added to the **1*s*** subshell
- Then **2** electrons to the **2*s*** subshell
- And finally **4** electrons to the **2*p*** subshell
- In increasing order of energy

We show the population of each subshell with a superscript:

2 electrons in 1s

2 electrons in 2s

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

4 electrons in 2p

Building up the electron configurations

- Simple enough to populate the subshells until we come to 4*s*
- How do we know 4*s* electrons have lower energy than 3*d* electrons?
- How do we know other cases when a subshell in a higher shell gets populated before a subshell in a lower shell?

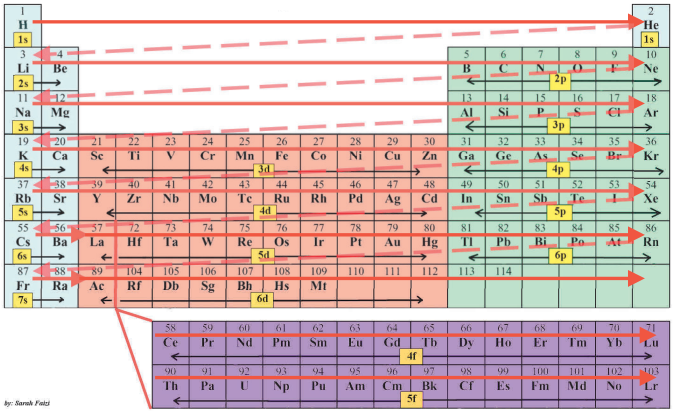
Best way: Use the **Periodic Table**

- The origin of the periodic repetition of the properties lies in the electron configurations of the elements.
- Just as the electron configurations gives rise to the periodic table, **periodic table can give us the electronic configurations of the elements**.

Applying the aufbau principle using the periodic table:

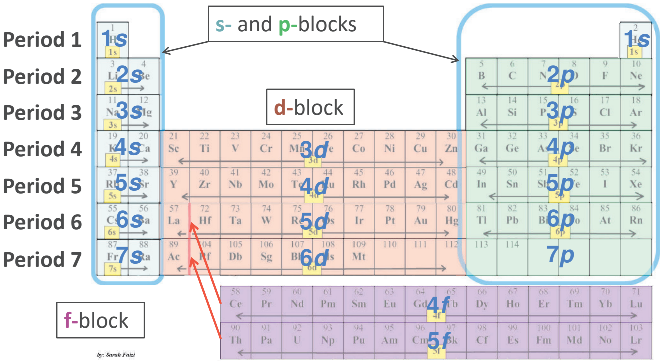
We start from the first element (H) onward and assign the electrons according to the “block” they belong to as we move from left to right and top to bottom, “reading” the table one element at a time until we arrive at the element whose configuration we want to find.

Order of filling subshells, by reading the periodic table like a book



When building configurations:

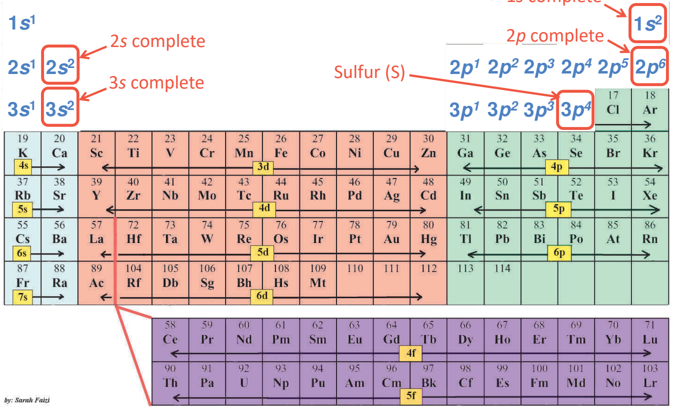
- **For s- and p-subshells:** **(Shell #) = (Period #)**
- **For d-subshells:** **(Shell #) = (Period #) – 1**
- **For f-subshells:** **(Shell #) = (Period #) – 2**



Example

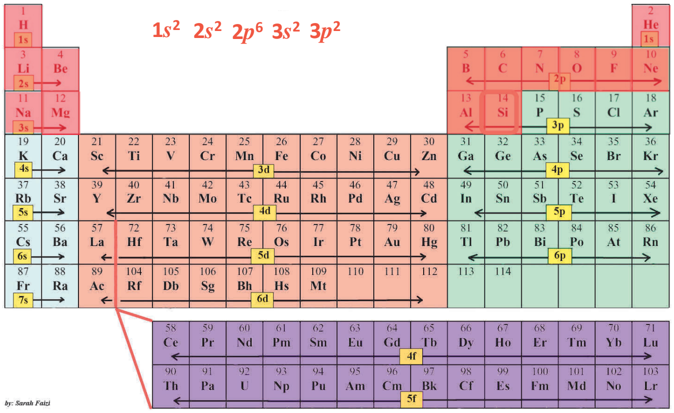
What is the electron configuration of Sulfur (S)?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$



Example: Electron configuration of Si

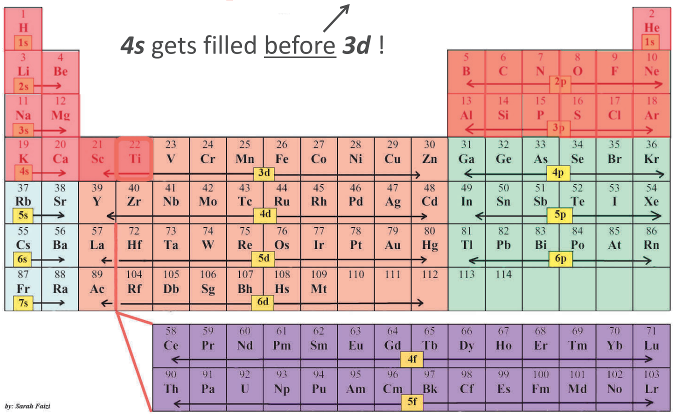
$1s^2\ \ 2s^2\ \ 2p^6\ \ 3s^2\ \ 3p^2$



Example: Electron configuration of Ti

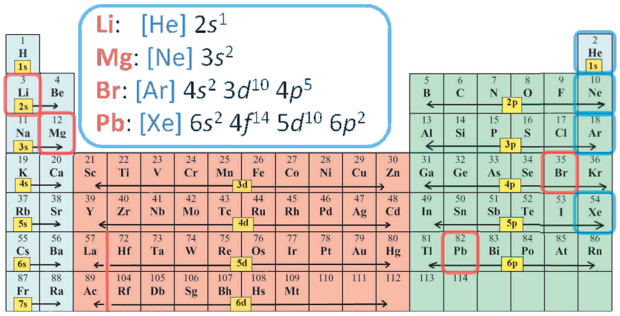
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$

4s gets filled <u>before</u> ***3d*** !



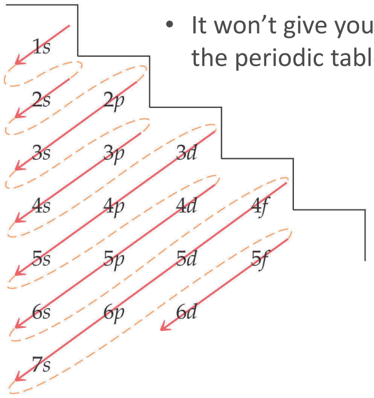
Abbreviated representation of electronic configurations

Only shows the configuration beyond the last noble gas.
-- with the last noble gas shown in square brackets



Li: [He] $2s^1$
Mg: [Ne] $3s^2$
Br: [Ar] $4s^2\ 3d^{10}\ 4p^5$
Pb: [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$

Order of filling subshells; without a periodic table



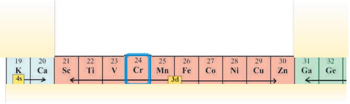
You can use this, but:

- It won't give you the insight you get by using the periodic table
- It won't contribute to your getting familiar with the periodic table
- **It actually sabotages your learning**

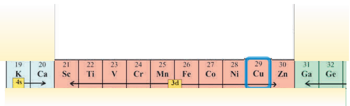
Irregularities in the buildup of electron configurations -- half-filled and filled subshells are favored

Cr and **Cu** are the important exceptions to remember

Cr:
Expected: [Ar] $4s^2\ 3d^4$
Actual: [Ar] $4s^1\ 3d^5$
Achieves half-filled *4s* and half-filled *3d* by shifting a *4s* electron to *3d*



Cu:
Expected: [Ar] $4s^2\ 3d^9$
Actual: [Ar] $4s^1\ 3d^{10}$
Achieves half-filled 4*s* & filled 3*d* by shifting a 4*s* electron to 3*d*



Electron configuration of ions

Anions:

Add electrons the same way as for neutral atoms. The configuration of an anion with **–n** charge is the same as the neutral atom whose atomic number is **larger** by **n**

O: [He] $2s^2\ 2p^4$
O^{2-}: [He] $2s^2\ 2p^6$ same as [Ne]
2 more electrons added

Electron configuration of ions

Cations:

Remove electrons from the valence shell of the neutral atom (starting with ***p*** electrons, and then ***s*** electrons)

Removed electrons are not necessarily the ones that were added last in the build-up process!

It's an issue only with d- and f-block elements.

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

3d-electrons were added last, but the *4s* electrons are lost first!

Valence Electrons

- The electrons in the outermost principal quantum level of an atom.
  $1s^2 2s^2 2p^6$ (no. of valence electrons = 8)
- The elements in the same **group** on the periodic table have the same number of valence electrons.
- Valence electrons are the "interface" of an atom
- Its chemistry is largely done (and defined) by them
- Chemical and physical properties of an element depends on them

Populating the orbitals

Remember that the orbitals in a subshell have equal energy.

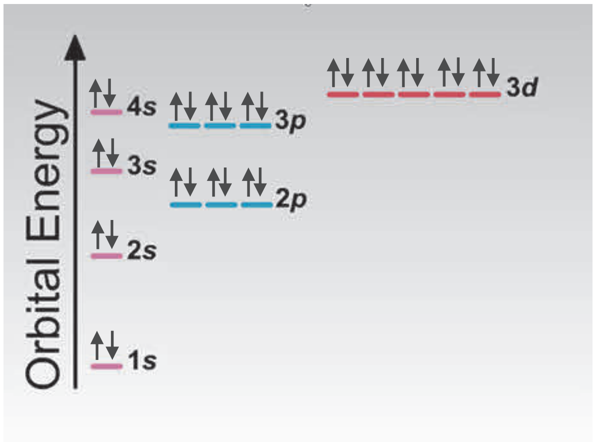
Hund’s rule is about the order of putting electrons in those orbitals.

Hund’s Rule

When putting electrons in a subshell”

- Electrons go into empty orbitals first, with parallel spins
  - —if we put the first electron with spin “up”, others must also be “up”
- After we run out of empty orbitals, the new electrons “pair up” with the electron already in an orbital, according to the “Pauli Exclusion Principle” we saw earlier (forcing paired electrons to have opposite spins)

Applying Hund’s Rule & Pauli Exclusion Principle

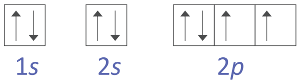


Orbital Diagrams

A notation that shows how many electrons an atom has in each of its occupied electron orbitals.

Example

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

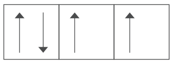


Electron Spins and Magnetic Properties

- The spin quantum number m_s gives the electron the ability to interact with magnetic fields.
- The electron acts as a tiny magnet, and it aligns its spin so that there is an attractive force between the source of the magnetic field and the electron.

Paramagnetism

If an atom has one or more unpaired electrons (at least one orbital occupied by a single electron)



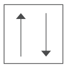
2 unpaired electrons

it is **attracted to a magnetic field**.

Then the atom is **paramagnetic**.

Diamagnetism

If all the electrons in an atom are paired (all orbitals are occupied by two electrons of opposite spins)



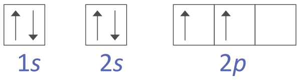
their spins cancel out, and the atom is **repelled by a magnetic field**.

Then the atom is **diamagnetic**.

Example

Determine if a gas-phase carbon atom is paramagnetic

Carbon: $1s^22s^22p^2$

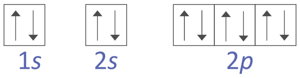


Carbon has 2 unpaired electrons in 2p orbitals, therefore it is paramagnetic.

Example

Determine if atoms of neon gas is paramagnetic

Neon: $1s^22s^22p^6$



Neon has no unpaired electrons, therefore it is diamagnetic.

Electron configurations and paramagnetism/diamagnetism discussed here are for isolated atoms.

When bonded, even to another atom of the same element, electron configurations and the resulting paramagnetism/diamagnetism change.

Practice

In a given atom, what is the maximum number of electrons that can have the quantum numbers n=2 and l=1?

For n = 2, l can be 0 or 1. So l = 1 is allowed
i.e. the number of electrons is not zero

Number of orbitals in an l = 1 ("p") subshell is 2(1)+1 = 3

Each orbital can hold up to 2 electrons.

Maximum number of electrons with n = 2, l = 1 is:

(2)(number of orbitals) = (2)(3) = 6

Practice

Which of the following orbital diagrams violates the Pauli Exclusion Principle?

Electrons in the same orbital (therefore the same n, l, m_l) cannot have the same spin (m_s)

Practice

Which of the following electron configurations is impossible, according to the Pauli exclusion principle?

a) $1s^2\ 2s^2\ 2p^5$

b) $1s^2\ 2s^2\ 2p^3$

[✓ c) $1s^2\ 2s^5$]

d) $1s^2\ 2s^2\ 2p^6\ 3s^1$

e) $1s^2\ 2s^2\ 2p^2$

An s-subshell has only one orbital.

It can accommodate only two electrons with opposite spins.

The only way for it to have more electrons is by violating Pauli Exclusion Principle (which it can't).

Practice

What is the valence shell electron configuration for the fourth period element in Group 5A?

a) $4s^2\ 5p^5$

b) $5s^2\ 5p^5$

[✓ c) $4s^2\ 4p^3$]

d) $5s^2\ 4p^5$

e) $4s^2\ 3d^3$

Valence shell can only have s and p electrons
s- and p-subshells in the ground state configuration have the same shell number as the Period number: **4**
The "A" in Group 5A means "main group element". So the "5" is equal to the number of valence electrons.

Trends in the periodic table

We will study the periodic trends of the following:

- Ionization Energy
- Electron Affinity
- Atomic Radius

Trends in the periodic table

Why do we see trends?

- Trends across a period (left to right) can be explained by **increasing effective nuclear charge**
- Trends from top to bottom in a group can be explained by **increasing distance from the nucleus**

Ionization Energy

Energy required to remove an electron from a gaseous atom or ion.

$$X(g) \rightarrow X^+(g) + e^-$$

$$Mg(g) \rightarrow Mg^+(g) + e^- \qquad \Delta E = 735\ kJ$$

Ionization energy of Mg = 735 kJ/mol

Electron Affinity

- Energy change for an atom when it gets an electron

  $$X(g) + e^- \rightarrow X^-(g)$$

- e^- can only attach to an atom if ΔE for that process is negative (energy is released).
- If electron affinity is listed as a (+) value, it is the magnitude of the energy released.
- The extra electron is repelled by the electrons in the atom, but is attracted to the nucleus.
  —Usually favorable overall, releasing energy

Atomic Radius

- Atomic radius is the size of the largest occupied orbitals (which is in the valence shell) in an atom.
- As such, its precise value depends on how we define the “size” of the electron cloud in those orbitals.
- But the trends in the atomic radius don’t depend on the specific definition used

---

To understand trends, we need to remember:

Protons in the nucleus are (+) charged

Electrons in the surrounding shells are (–) charged

Protons and electrons attract

Stronger attraction pulls electrons closer to the nucleus (smaller radius)

Stronger attraction makes it harder to remove an electron from the atom (larger ionization energy)

Stronger attraction makes it more favorable to add an electron to the atom (larger electron affinity)

The concept of “shielding”

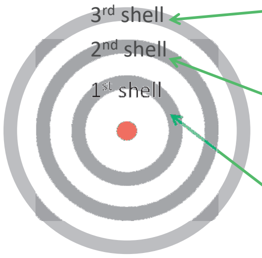
Other electrons in the same atom counteract the attractive force exerted by the nucleus on an electron, because electrons repel each other.

If an electron provides full shielding to another electron, it’s as if that second electron is feeling one less proton in the nucleus.

Each electron is “shielded” from the nucleus by other electrons to some extent.

The more of an electron’s “cloud” lies between the other electron and the nucleus, the more shielding it provides.

In order to shield another electron from the nuclear charge, an electron’s cloud must lie between the nucleus and the other electron.

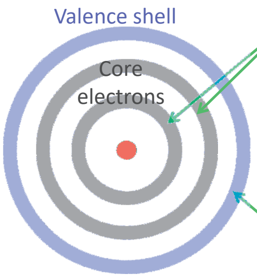


- Is shielded by the 1st and 2nd shells
- Does not shield the 1st and 2nd shells

- Shields the 3rd shell from the nucleus
- Does not shield the 1st shell
- Is shielded by the 1st shell

- Almost completely exposed to the nuclear charge
- Not shielded by the outer electrons
- Shields 2nd and 3rd shells (cancels the effect of two protons)

“Shielding” of the valence electrons



Shells closer to the nucleus (“core electrons”) almost completely shield the valence electrons from the protons that came with the core electrons.

e.g. the valence electron of Na (Z=11) feels very little of the 10 protons that came with the 10 core electrons.

Valence electrons are partially shielded by other valence electrons.

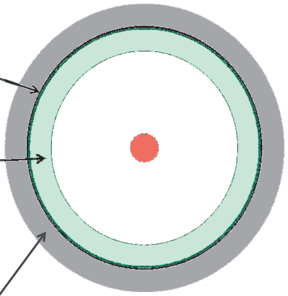
They do **<u>partially</u> feel** the protons that were added when other valence electrons were added to build the atom.

Understanding the “partial shielding” of the valence electrons by other valence electrons

For a given electron in a shell:

- Only a part (about a third) of other valence electrons’ “cloud” is closer to the nucleus than the given electron
- That part provides “shielding”
  — like the core electrons do

- Part of the other electrons’ cloud is farther out
- That part provides no shielding



Vertical trends in the periodic table

Understood in terms of:

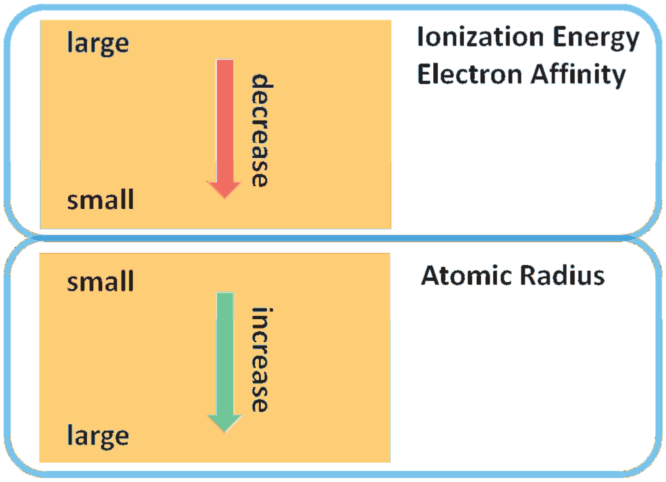
- Distance from the nucleus, and
- “Core” electrons completely canceling the effect of an equal number of protons in the nucleus
  - ➢ Outermost shell’s distance from the nucleus won’t be affected much by the protons that came with the earlier, “core” electrons
- Each time we go down in the periodic table, a new valence shell starts getting populated
- The valence shell is the farthest from the nucleus

Vertical trends in the periodic table

Going downward in a group:

- Atomic size is determined by the farthest shell. So it gets larger as we travel down the periodic table in a given group
- Removing an electron from a farther-out shell costs less energy (smaller plus-minus attraction)
  - ➢smaller ionization energy
- Adding an electron to farther-out shells releases less energy (smaller plus-minus attraction)
  - ➢ smaller electron affinity

Vertical trends in the Periodic Table



Ionization Energy
Electron Affinity

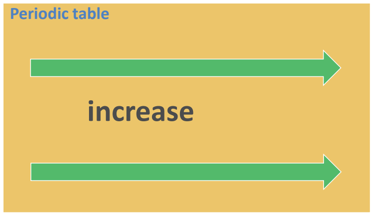
Atomic Radius

Horizontal trends in the periodic table

All horizontal trends are explained by this:

Incomplete shielding by electrons in the valence shell leads to **increasing effective nuclear charge** felt by each of them as we go from left to right across a period.

Effective nuclear charge



Understanding “increasing effective nuclear charge”

Across a period, each new atom adds a proton in the nucleus and an electron in the valence shell.

But the added electron does not fully cancel the effect of the accompanying proton on the other valence electrons.

As more valence electrons are added (going across a period), more of those “only partially shielded protons” are added with them.

Increasing number of “only partially shielded protons” lead to **increasing effective nuclear charge**.

Increasing effective nuclear charge explains all horizontal trends. Across a period:

<u>Atomic radius decreases</u>

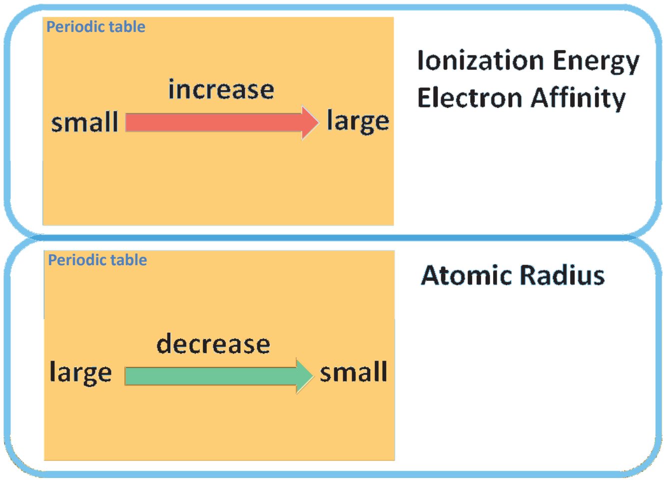
- ➢ Stronger attraction by the nucleus pulls the valence electrons closer and closer

<u>Ionization energy increases</u>

- ➢ Stronger attraction by the nucleus raises the energy cost of removing an electron

<u>Electron affinity increases</u>

- ➢ Stronger attraction by the nucleus makes the energy of the added electron lower, releasing more energy



Periodic table

small increase large

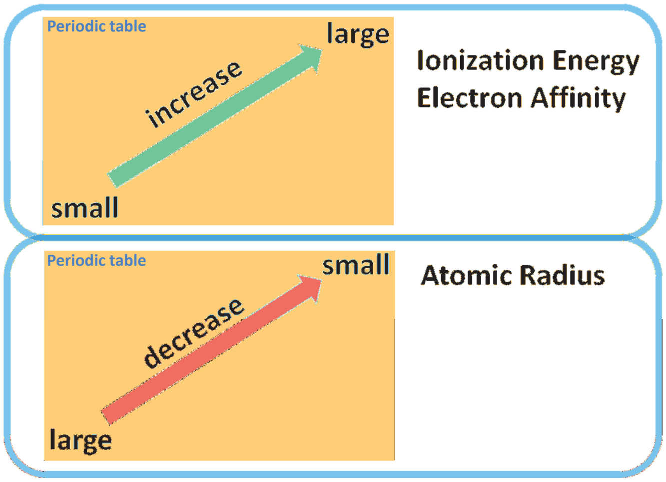
Ionization Energy
Electron Affinity

Periodic table

large decrease small

Atomic Radius

Overall trends in the Periodic Table



Periodic table

small increase large

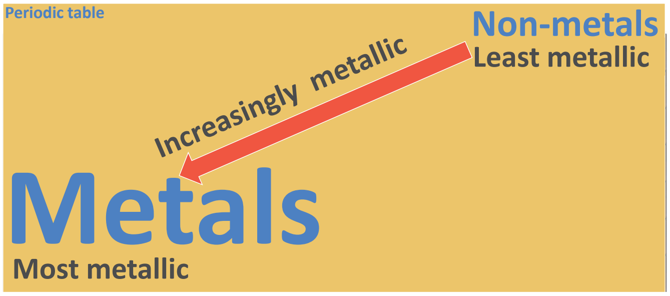
Ionization Energy
Electron Affinity

Periodic table

large decrease small

Atomic Radius

Low ionization energy (low cost for electron removal), and low electron affinity (low "reward" for accepting an electron) leads to metallic character



Periodic table

Non-metals
Least metallic

Increasingly metallic

Metals
Most metallic

"Metallic character"

Metals form cations (low energy cost to remove electrons)

- All of their chemistry is defined by this!

Valence shell electrons are "loose" enough to jump between metal atoms where they are more stable being (still weakly) attracted to the nuclei of numerous metal atoms.

- Metals conduct electricity

The "loose", conducting electrons form a glue-like non-specific, non-directional bonding between metal atoms.

- Because there are no specific bonds to break, metal atoms easily slide around
- Therefore metals tend to be easy to push and pull into shape (malleable and ductile)

Using metallic character to remember trends

We can remember the periodic trends by simply remembering where the metals are in the periodic table, and one of the most prominent features of metals: they conduct electricity

Metals conduct electricity because their valence electrons are "loose"

Using metallic character to remember trends

Electrons being "loose" means they are not strongly bound to the atom.

That means the energy cost to remove an electron from a "more metallic" atom must be lower (lower ionization energy), and less energy will be released by adding an electron (small electron affinity).

Also, a "loose" valence shell, weakly attracted by the nucleus, will not be "squeezed" smaller. It will be larger than the less metallic elements.

In the next few slides, we will take a closer look at the three properties (ionization energy, electron affinity, atomic radius) whose periodic trends we considered.

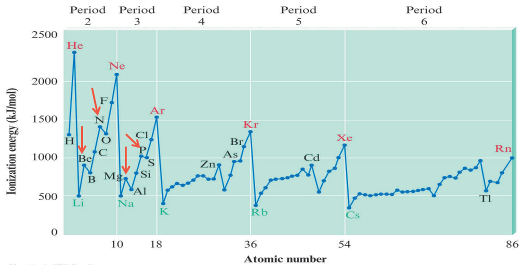
“Closer Look”

Ionization energy trends have “bumps”

Atoms with **filled or half-filled subshells** appear to have anomalously high ionization energies (**more stable than the atoms on their left or right**)

-- Half-filled or filled subshells are relatively stable

-- It takes more energy to pry away an electron



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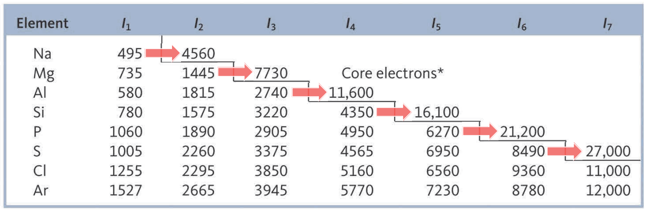
“Closer Look”

Second, third, etc. ionization energies for an element can tell us how many valence electrons it has



Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

- From the **jump** in successive ionization energies, we can tell when we are **starting to dig into the lower shell**, having to lift the electron from a lower level.
- So we can tell which periodic table group the atom belongs to.

“Closer Look”

“Ionization energy” can refer to removing an electron from entities other than a neutral atom

$X^+(g) \rightarrow X^{2+}(g) + e^-$	1st IE of X^+ 2nd IE of X 3rd IE of X^-
$X^-(g) \rightarrow X(g) + e^-$	1st IE of X^- 2nd IE of X^{2-}

etc.

“Closer Look”

More on Electron Affinity

- Adding an e^- to an atom is <u>not</u> the reverse of removing an electron from a neutral atom.
- Removing an e^- from an atom creates a charge separation that always requires energy (ionization energy)
- But adding an e^- to a neutral atom (electron affinity) doesn’t combine or separate charges.

“Closer Look”

More on Electron Affinity (cont.)

Some elements don’t have an EA because the ΔE for adding an e^- is (+). The element cannot form an anion in vacuum because there is no barrier to simply spitting out the added electron in order to attain a lower energy (basically the e^- bounces off the atom)

"Closer Look"

Electron Affinity trends have many exceptions

Atoms with filled subshells (Group 2, 12, 18) have anomalously small (or zero) electron affinities

- Added electron has to go to a higher-energy subshell

Atoms with half-filled subshells (Groups 7, 15) have anomalously small (or zero) electron affinities

- Configuration with added electron lacks the stabilization of the half-filled subshell

Second period elements have smaller (or zero)EA than the element below them, violating the trend

- Their small size makes it more difficult to squeeze in an extra electron

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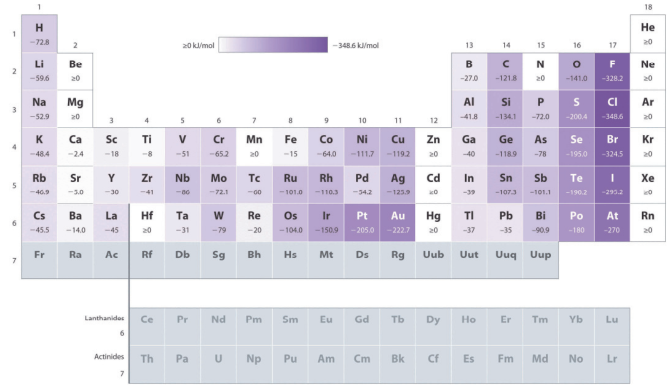
"Closer Look"

Electron Affinity trends have many exceptions



≥0 kJ/mol … −348.6 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H −72.8																	He ≥0
2	Li −59.6	Be ≥0											B −27.0	C −121.8	N ≥0	O −141.0	F −328.2	Ne ≥0
3	Na −52.9	Mg ≥0											Al −41.8	Si −134.1	P −72.0	S −200.4	Cl −348.6	Ar ≥0
4	K −48.4	Ca −2.4	Sc −18	Ti −8	V −51	Cr −65.2	Mn ≥0	Fe −15	Co −64.0	Ni −111.7	Cu −119.2	Zn ≥0	Ga −40	Ge −118.9	As −78	Se −195.0	Br −324.5	Kr ≥0
5	Rb −46.9	Sr −5.0	Y −30	Zr −41	Nb −86	Mo −72.1	Tc −60	Ru −101.0	Rh −110.3	Pd −54.2	Ag −125.9	Cd ≥0	In −39	Sn −107.3	Sb −101.1	Te −190.2	I −295.2	Xe ≥0
6	Cs −45.5	Ba −14.0	La −45	Hf ≥0	Ta −31	W −79	Re −20	Os −104.0	Ir −150.9	Pt −205.0	Au −222.7	Hg ≥0	Tl −37	Pb −35	Bi −90.9	Po −180	At −270	Rn ≥0
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
Lanthanides 6				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides 7				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

From chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/07._Periodic_Properties_of_the_Elements/7.5%3A_Electron_Affinities

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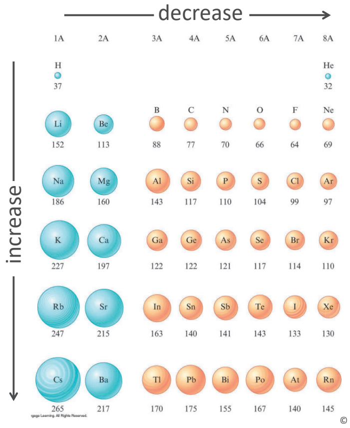
"Closer Look"

Atomic Radii trends of the main group elements have no serious exceptions



decrease →

increase ↓

1A	2A	3A	4A	5A	6A	7A	8A
H 37							He 32
Li 152	Be 113	B 88	C 77	N 70	O 66	F 64	Ne 69
Na 186	Mg 160	Al 143	Si 117	P 110	S 104	Cl 99	Ar 97
K 227	Ca 197	Ga 122	Ge 122	As 121	Se 117	Br 114	Kr 110
Rb 247	Sr 215	In 163	Sn 140	Sb 141	Te 143	I 133	Xe 130
Cs 265	Ba 217	Tl 170	Pb 175	Bi 155	Po 167	At 140	Rn 145

Practice

Which of the following elements has the smallest atomic radius?

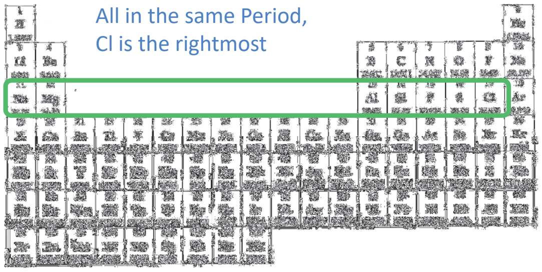
a) P

b) Cl

c) S

d) Na

e) Si



All in the same Period,
Cl is the rightmost

Practice

Which of the following elements has the highest ionization energy?

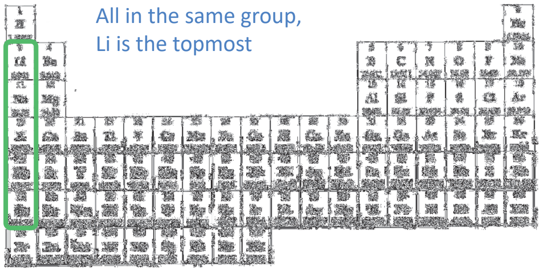
a) Li

b) Na

c) K

d) Rb

e) Cs



All in the same group,
Li is the topmost

Practice

Which of the following elements has the smallest ionization energy?

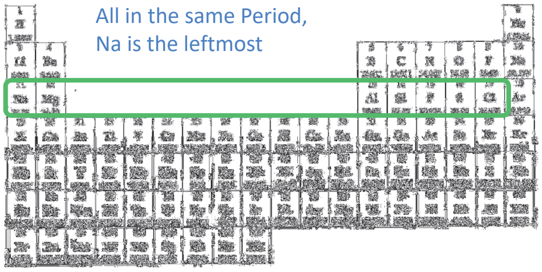
a) P

b) Cl

c) S

d) Na

e) Si



All in the same Period,
Na is the leftmost