Chapter 8

Electrons in Atoms

- 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

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

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).

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)

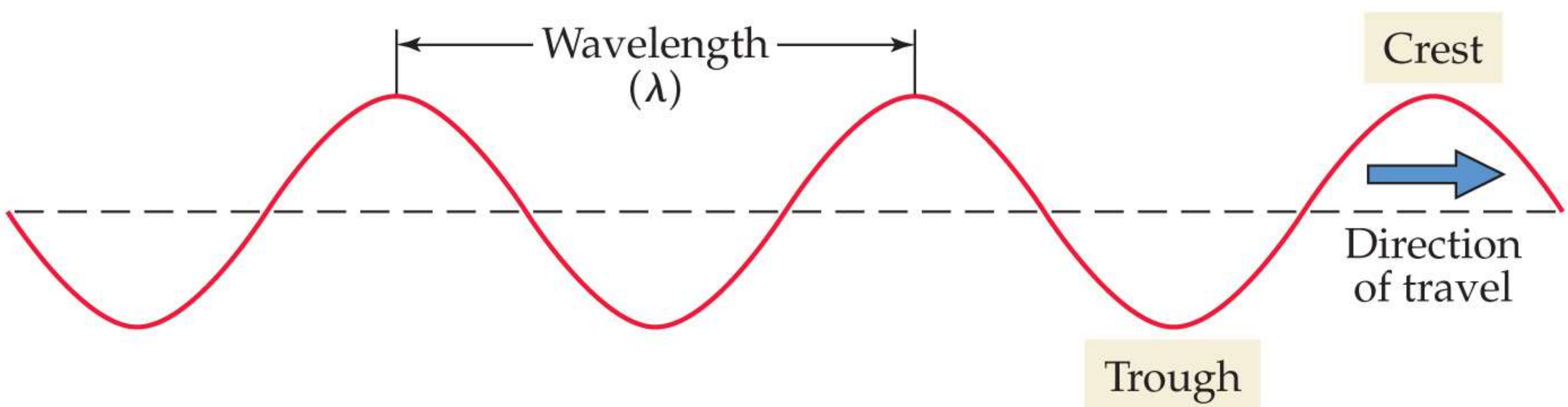
- "counts", "cycles" or "number of waves" is not a physical unit, and doesn't show up

Speed (v) – speed of propagation

Wavelength

Symbol: **λ** (lambda)

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



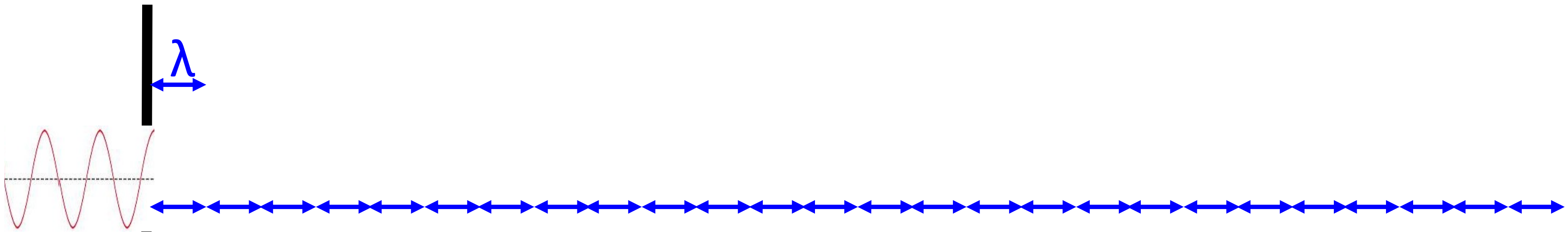
Frequency

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)

$$\text{Wave speed} = \nu\ \lambda$$

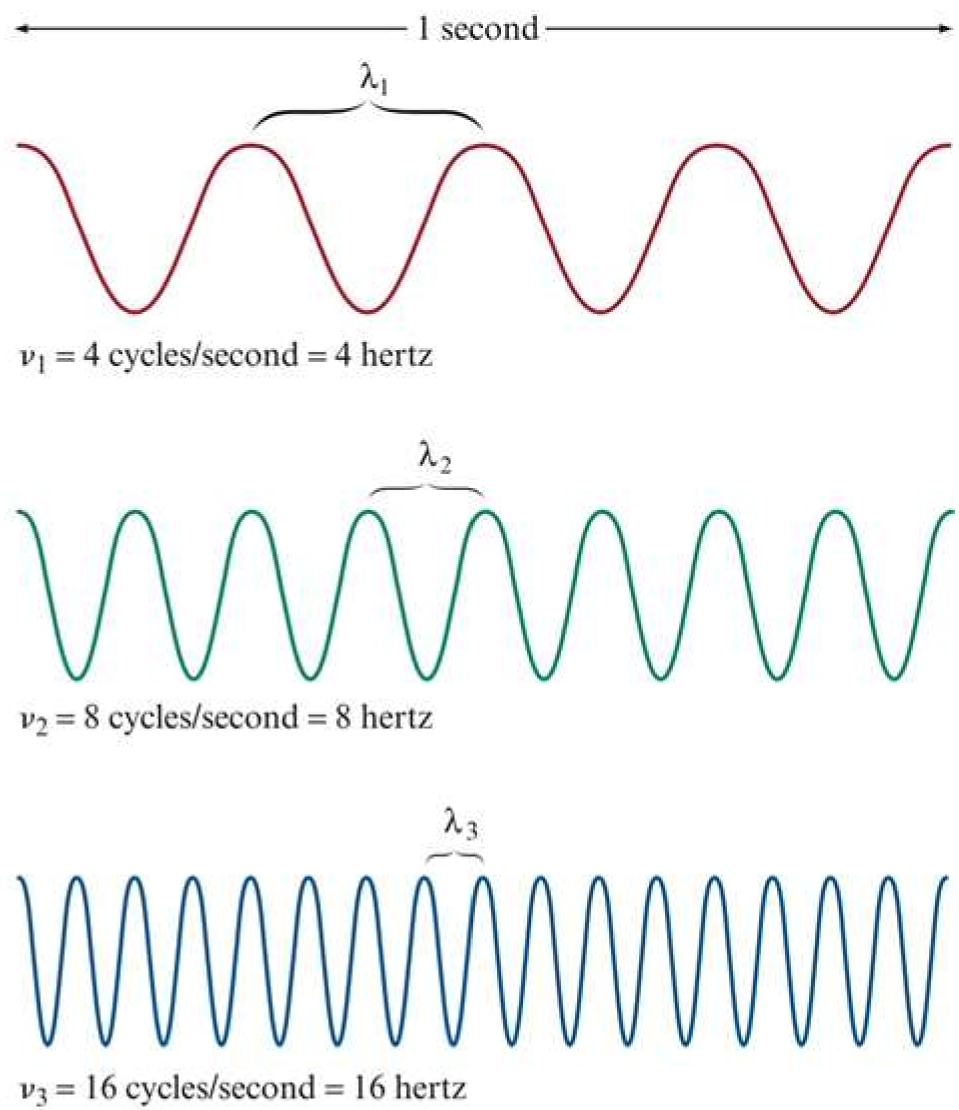
$$v = \lambda \nu$$

- 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 <u>electromagnetic</u> radiation (including <u>light</u>):

$$c = \nu \lambda$$

Speed of light

c = speed of light

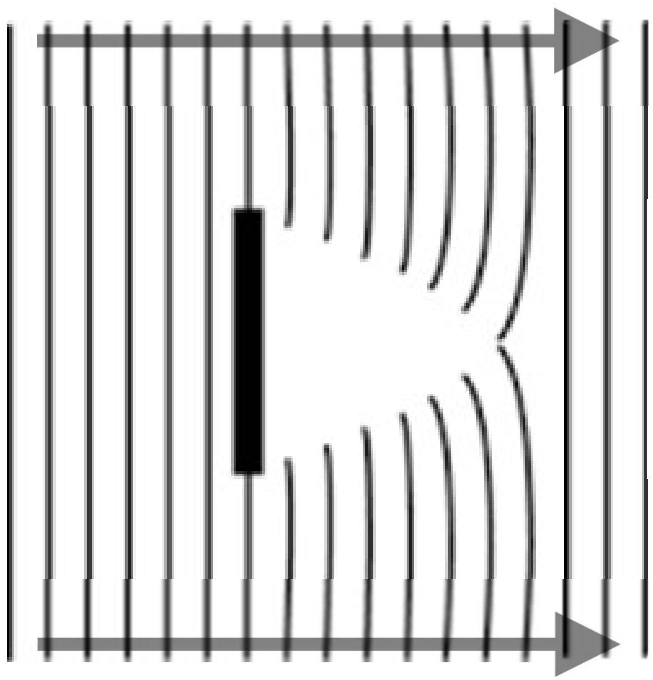
= 2.99792458×10^8 m/s

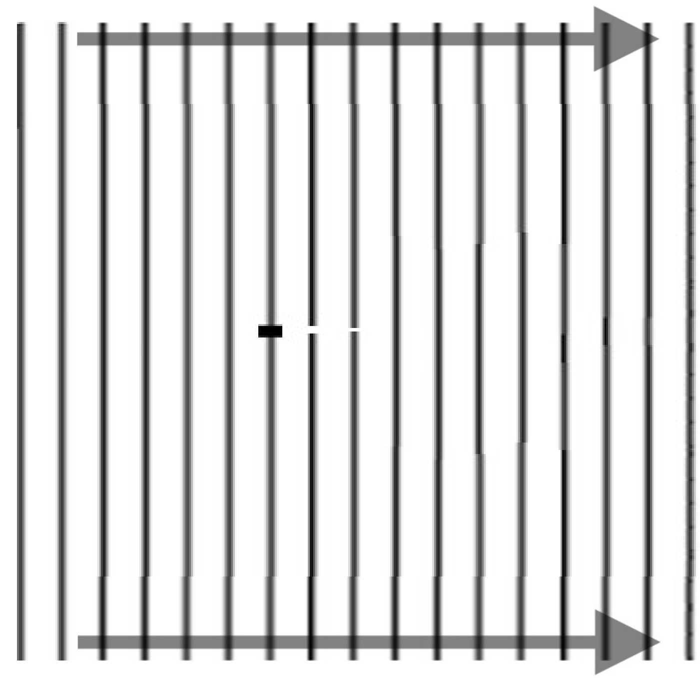
Defined exactly now.

But often used with only 3 or 4 sig. figs.

Waves diffract

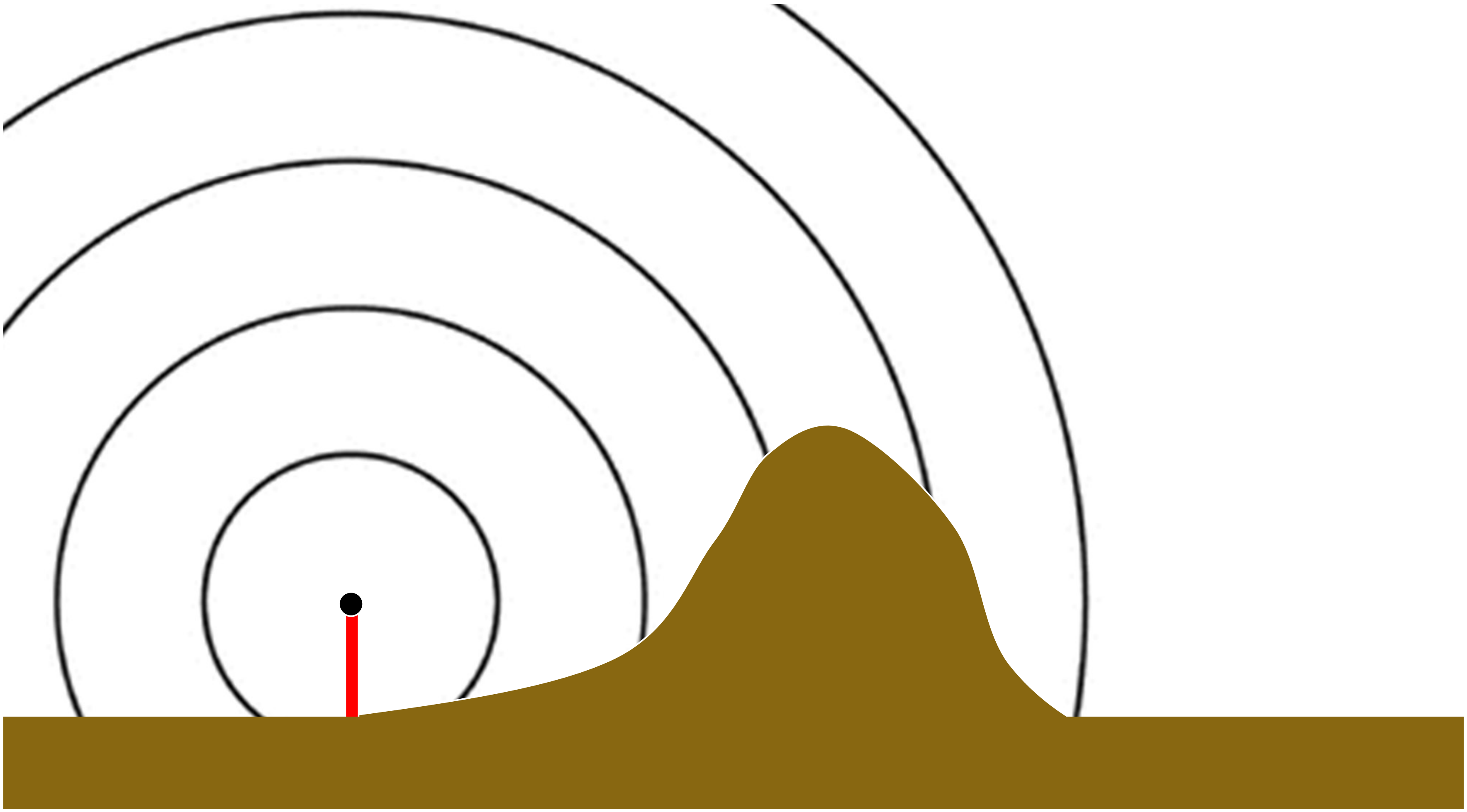
Waves bend around obstacles.
Moving into the region where there was supposed to be a "shadow"





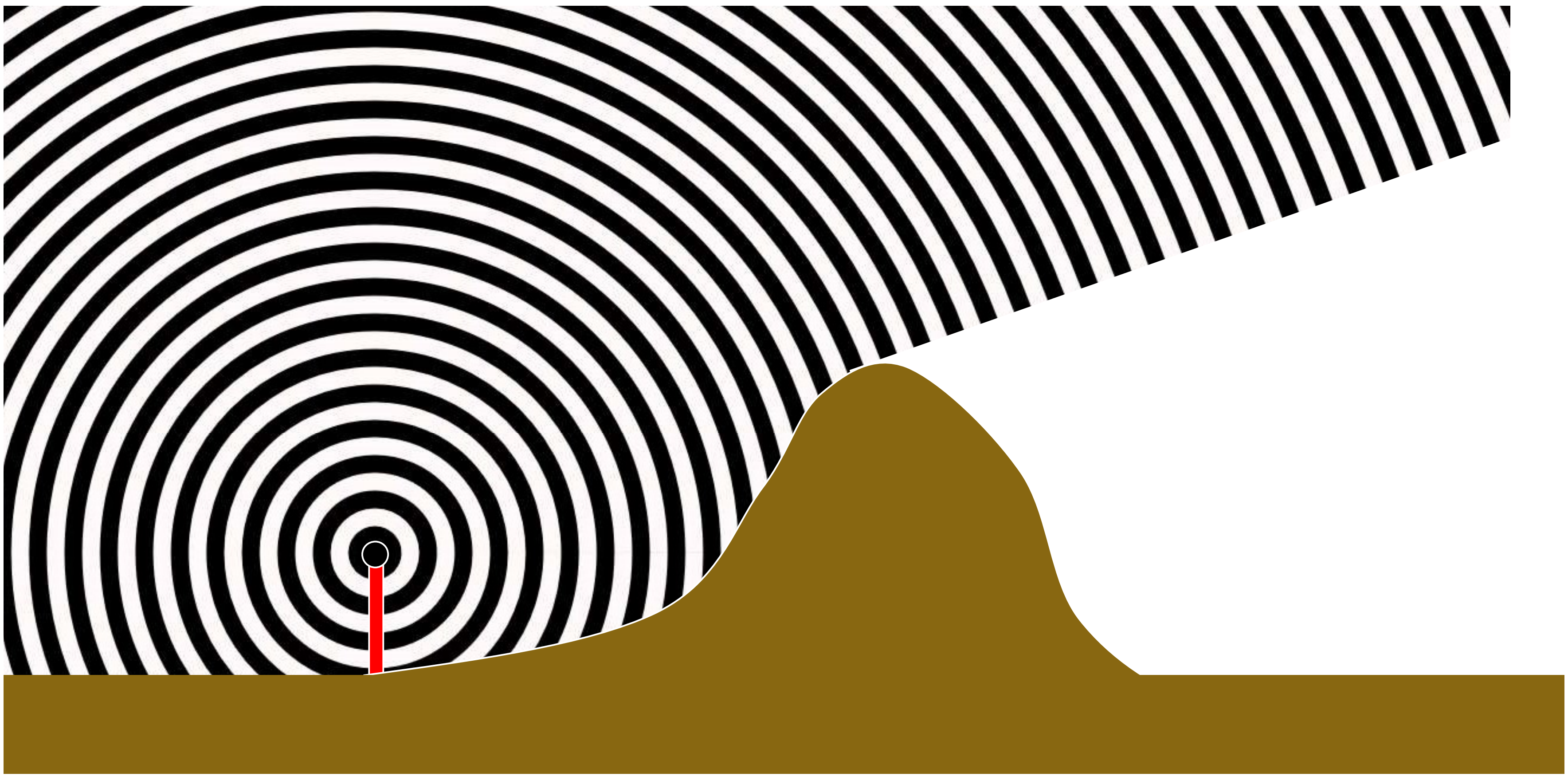
If the obstacle is a lot smaller than the wavelength, it's basically "invisible" to the wave

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



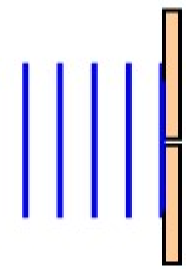
Radio waves with long wavelengths can be received behind hills, but shorter wavelengths can't.

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.

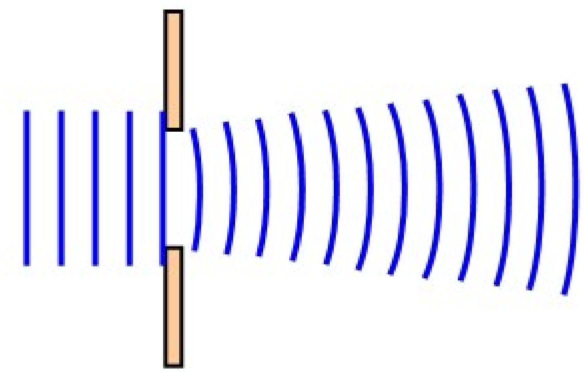


Radio waves with long wavelengths can be received behind hills, but shorter wavelengths can’t.

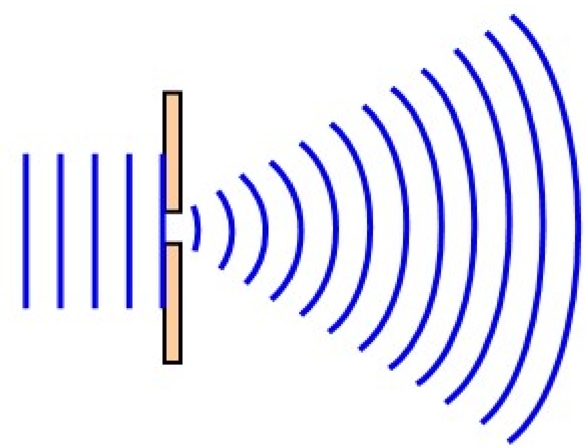
If a hole is much smaller than the wavelength, the wave is blocked -- it can't "see" the hole



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

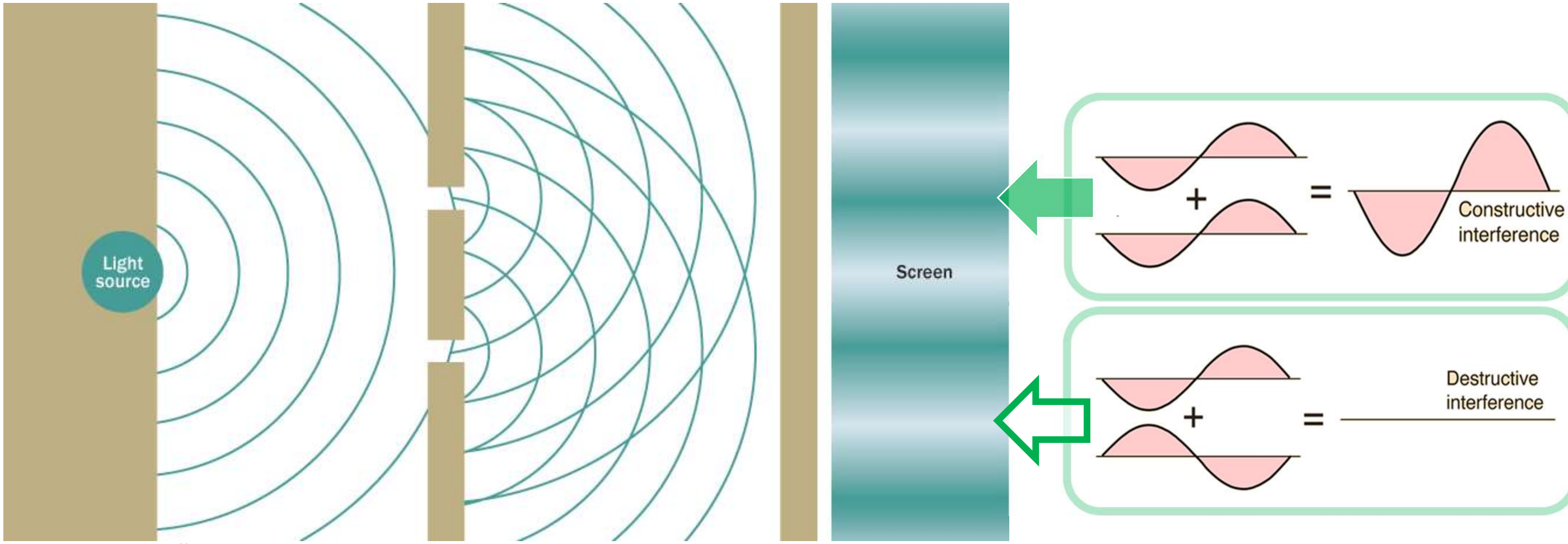


If a hole is about the same size as the wavelength, it will act as a **point source** (waves will come out of it, with the hole at the center)



Waves on water diffract too!

Diffraction by multiple features cause “interference”



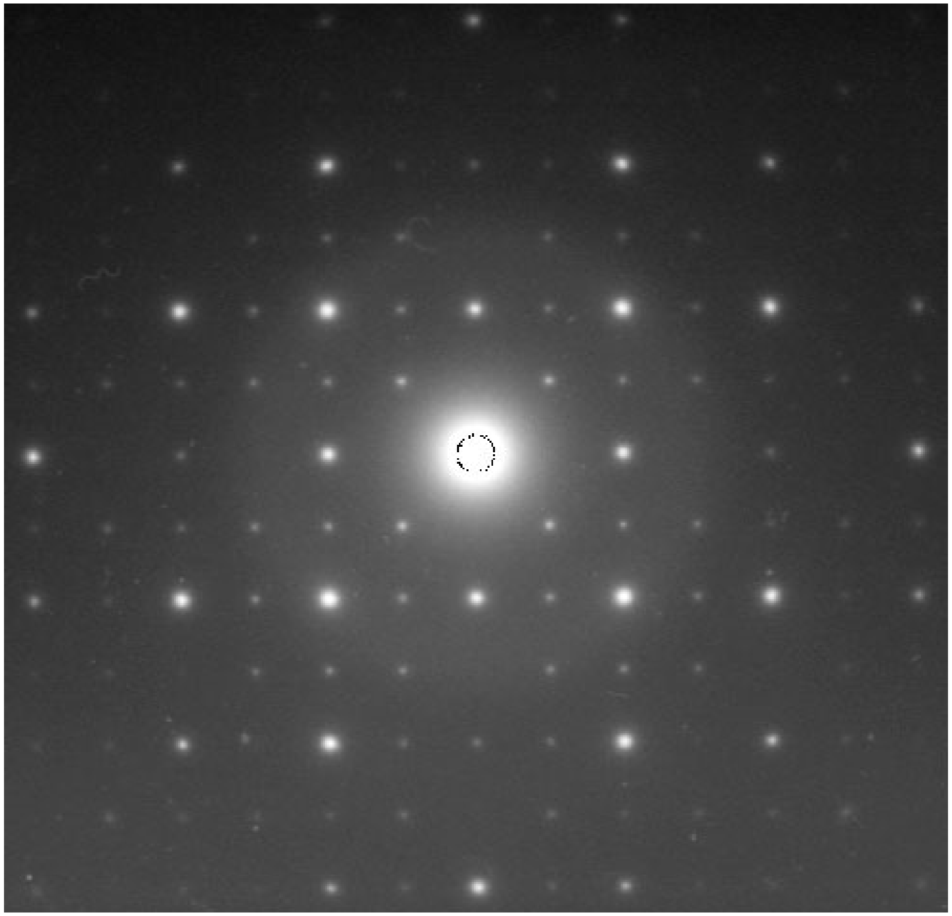
E. Otwell, sciencenews.org

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”

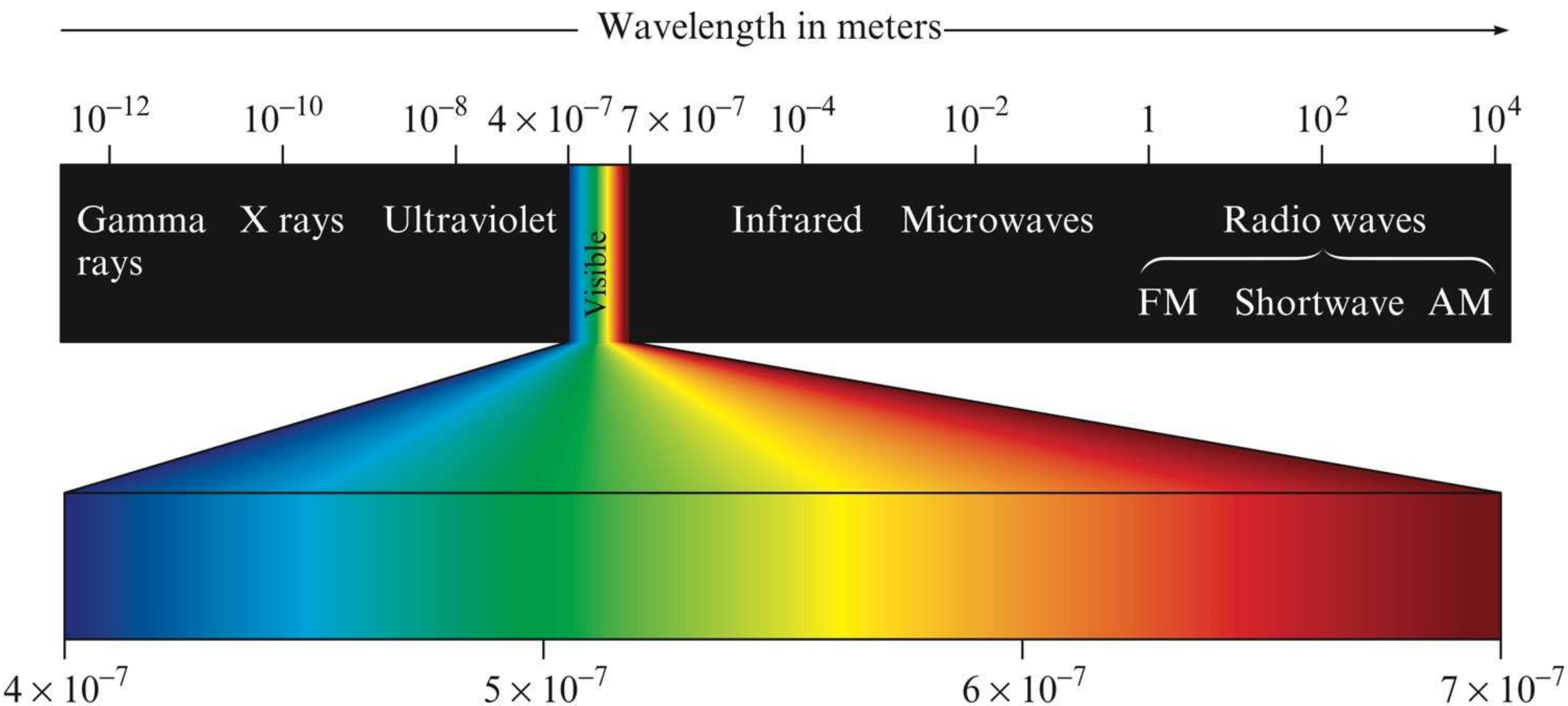
Diffraction of X-rays by atoms in a crystal lattice also form a diffraction pattern

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

Classification of Electromagnetic Radiation



400 nm **700 nm**

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

Light

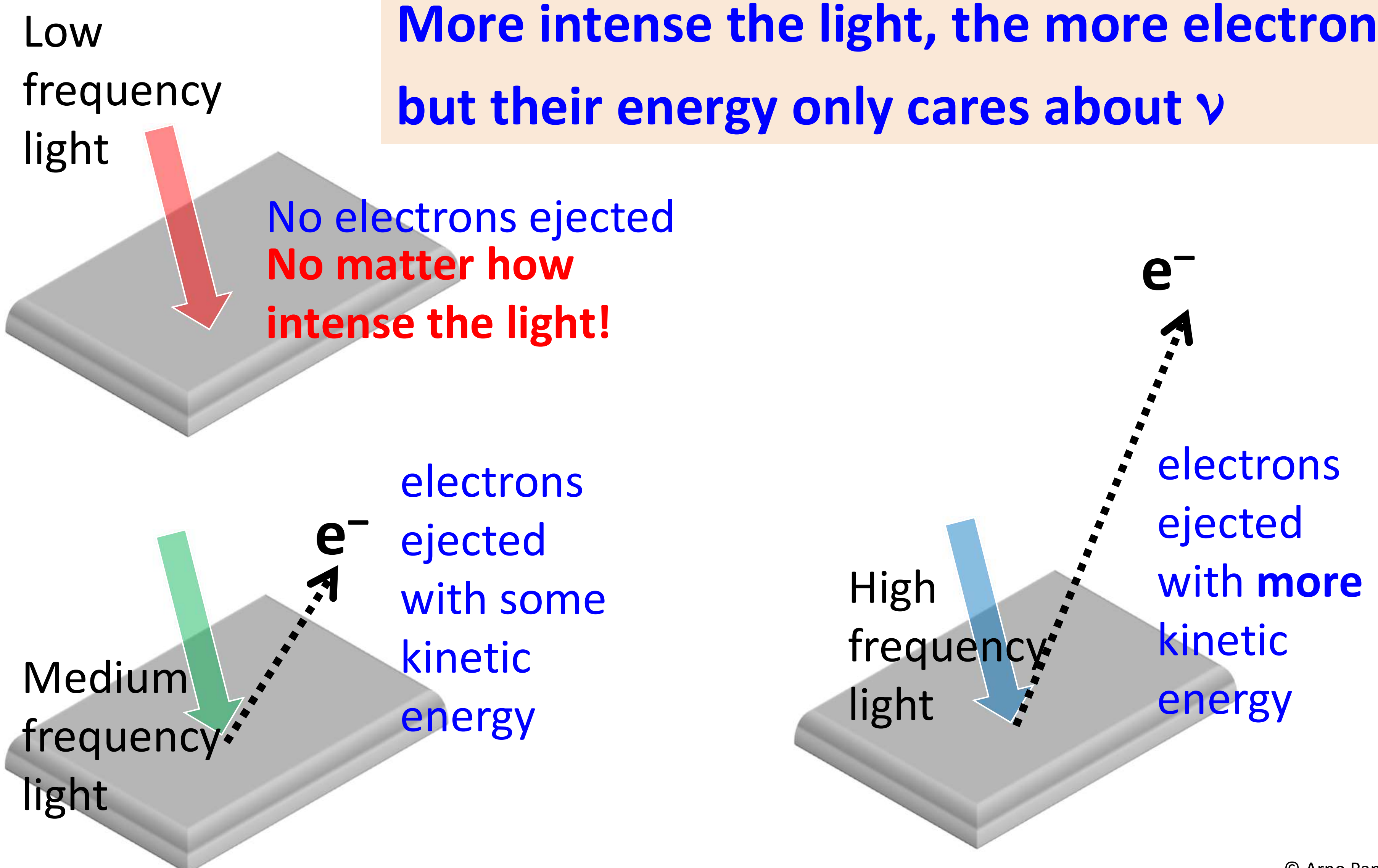
It turns out that the energy of a photon is directly proportional to frequency of the light.

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

"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



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 = $h\nu - W$

Photon energy

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

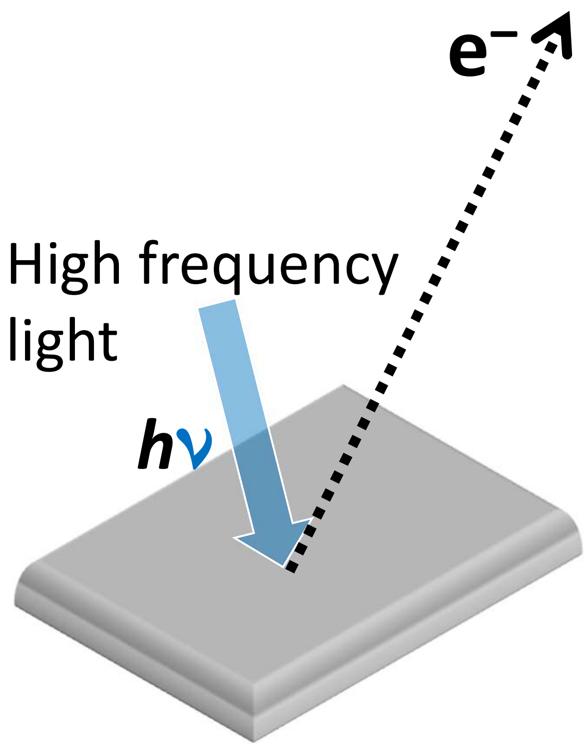
Leftover energy

$h\nu > W$

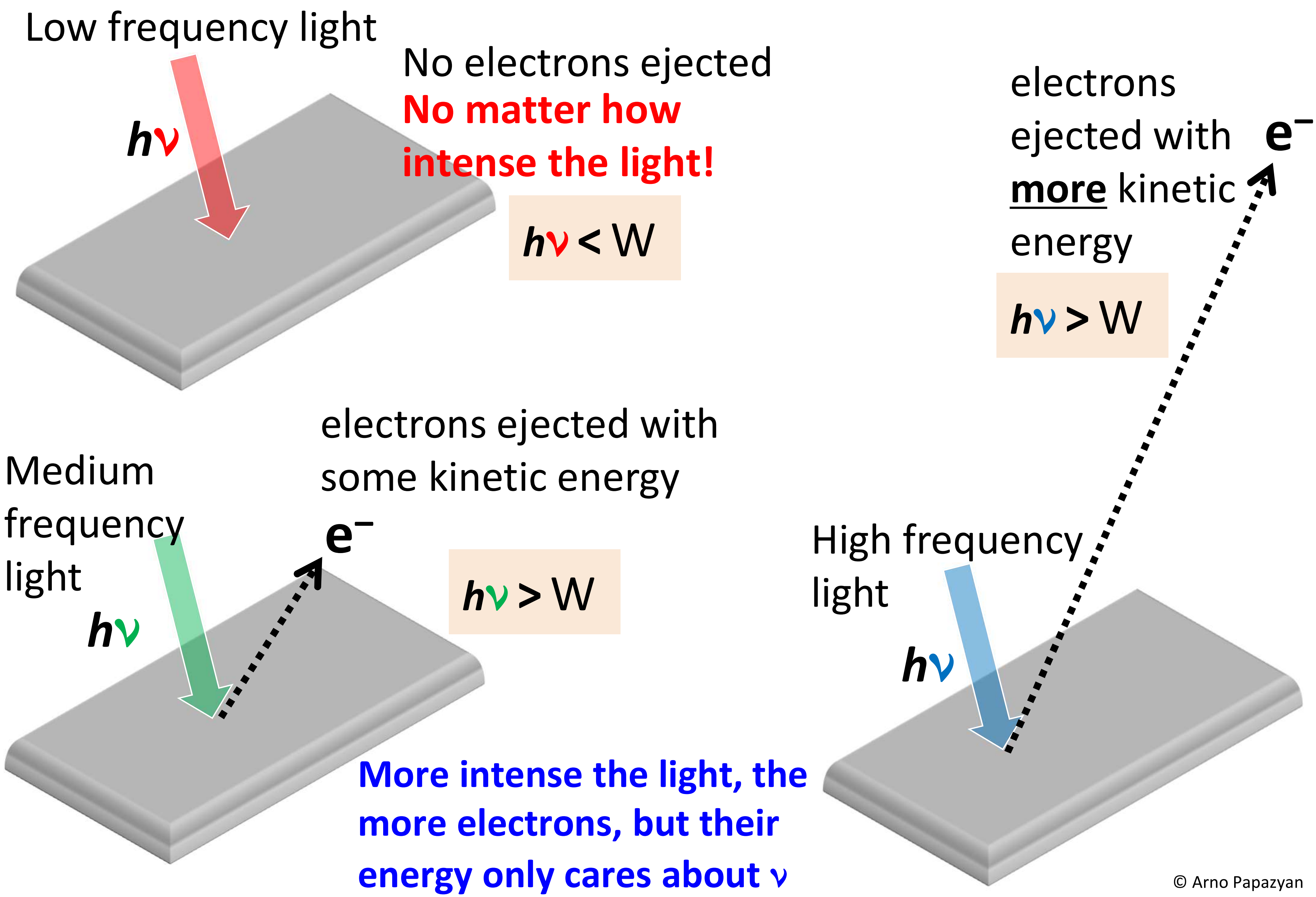
$$\text{kinetic energy of } \mathbf{e^-} = h\nu - W > 0$$

Energy brought by the photon

Energy spent to break away from the metal surface



Photoelectric effect



$h = 6.626 \times 10^{-34}$ 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. He regarded his work basically as a mathematical trick.
- Einstein clarified that there must be actual light particles, "photons" which were really carrying the energy in and out of discrete energy levels

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*

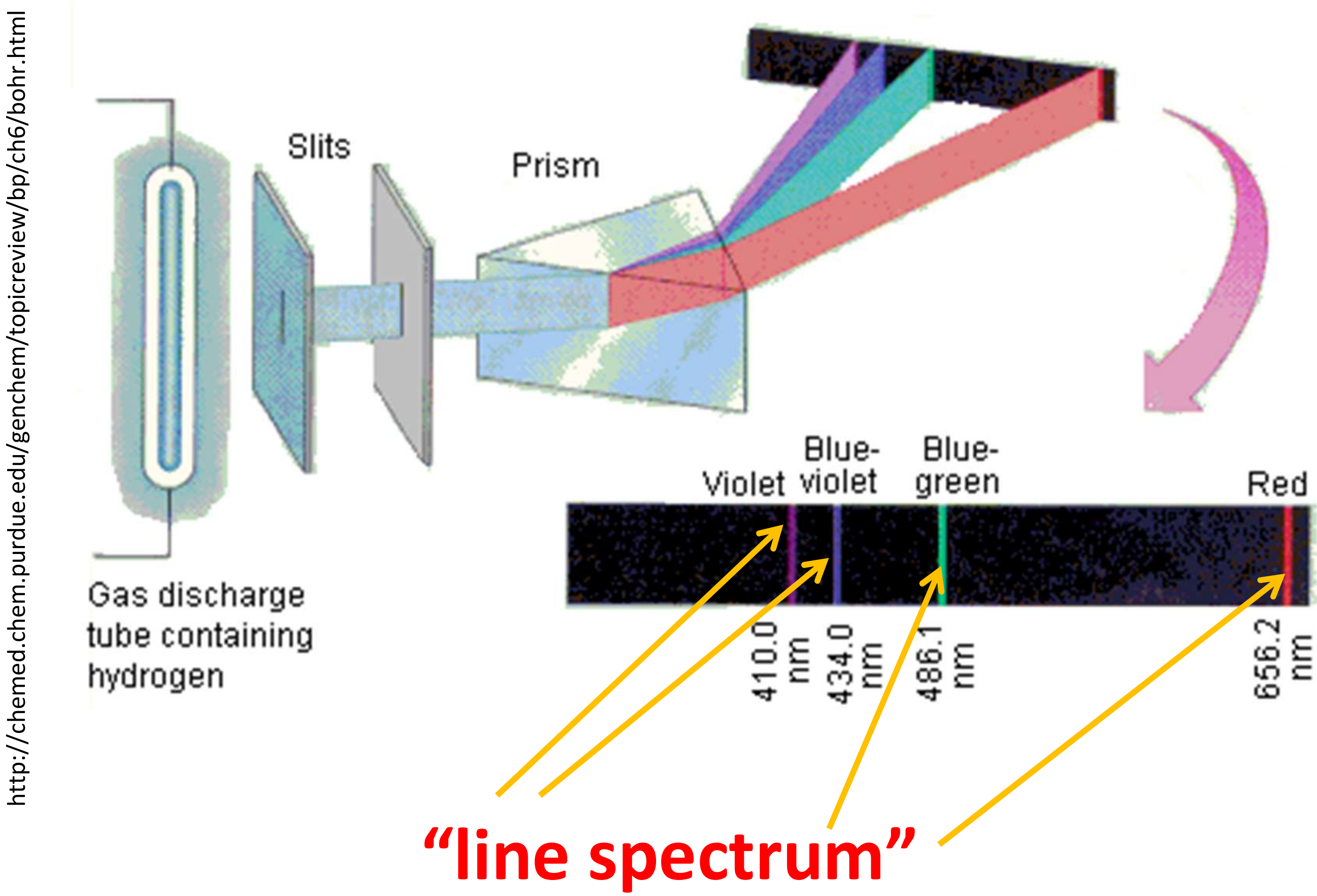
$$E_{photon} = |\Delta E| = h\nu$$

Atoms exchanging energy

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

For an atom in the gas phase:

- 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.



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**”.

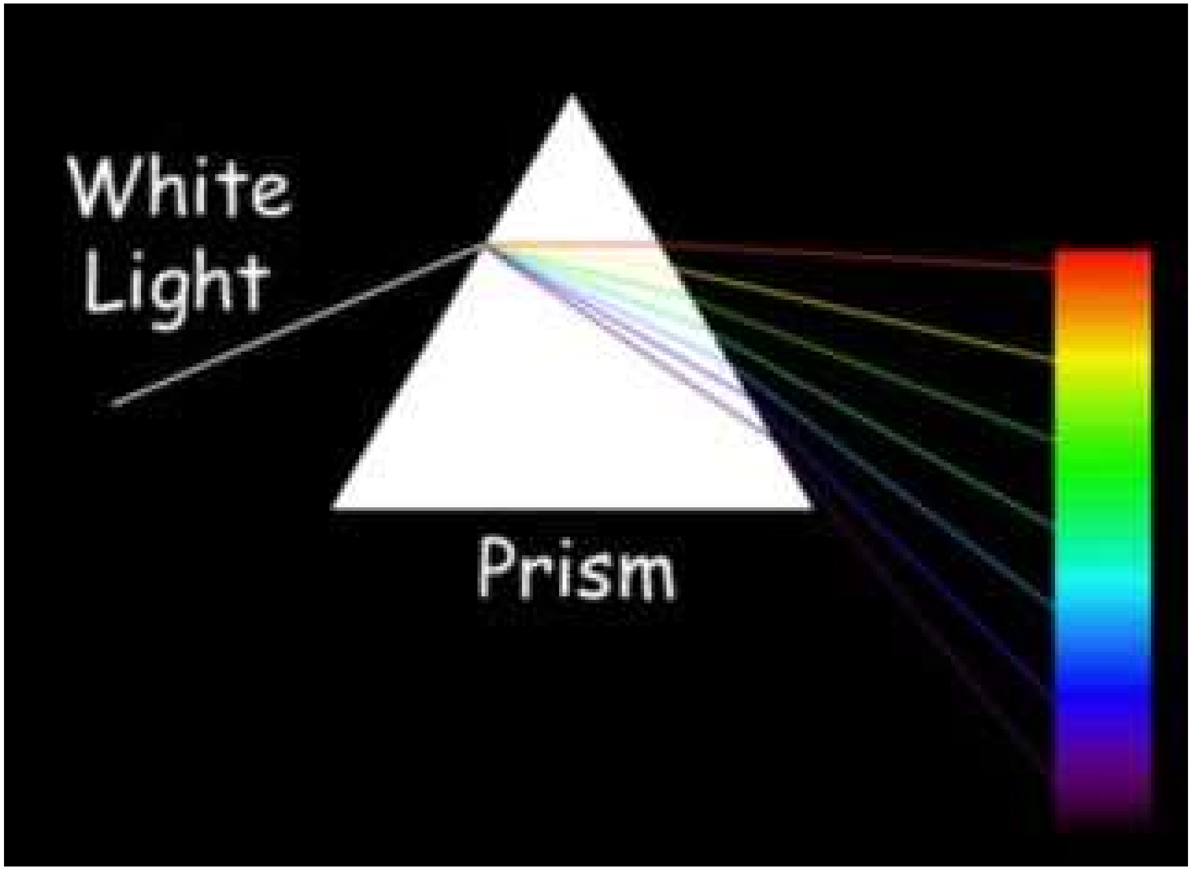
A “black body” absorbs all light and emits light with a distribution of wavelengths determined only by its temperature.

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.

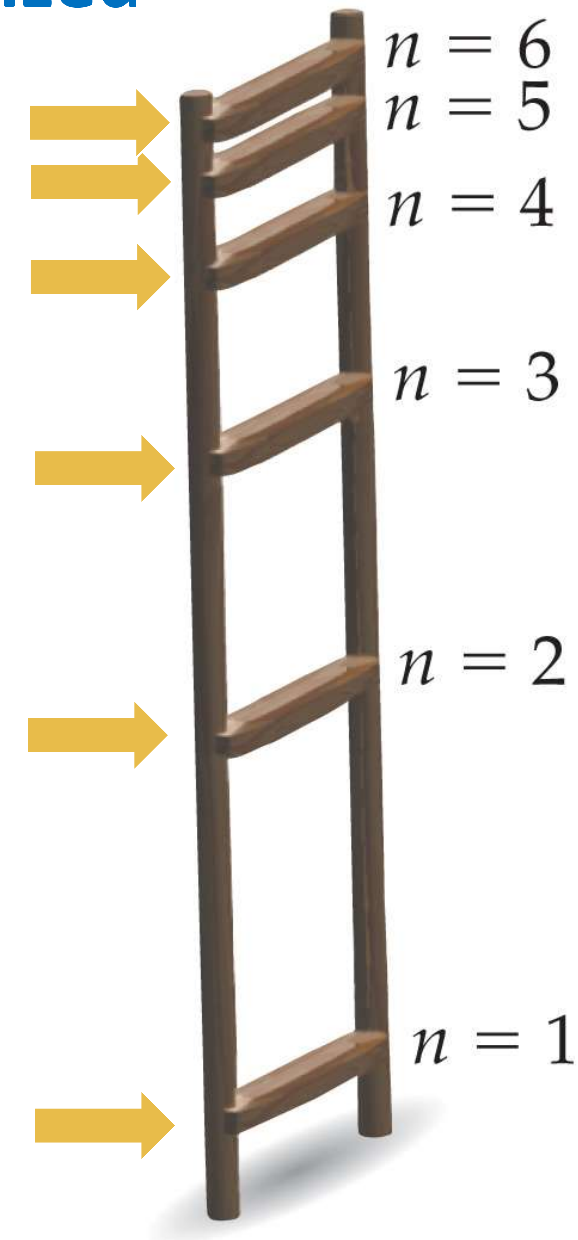
In other words:

Line spectrum → Quantized energy levels

Energy levels in an atom are quantized

- Discrete, distinct energy levels
- No other levels

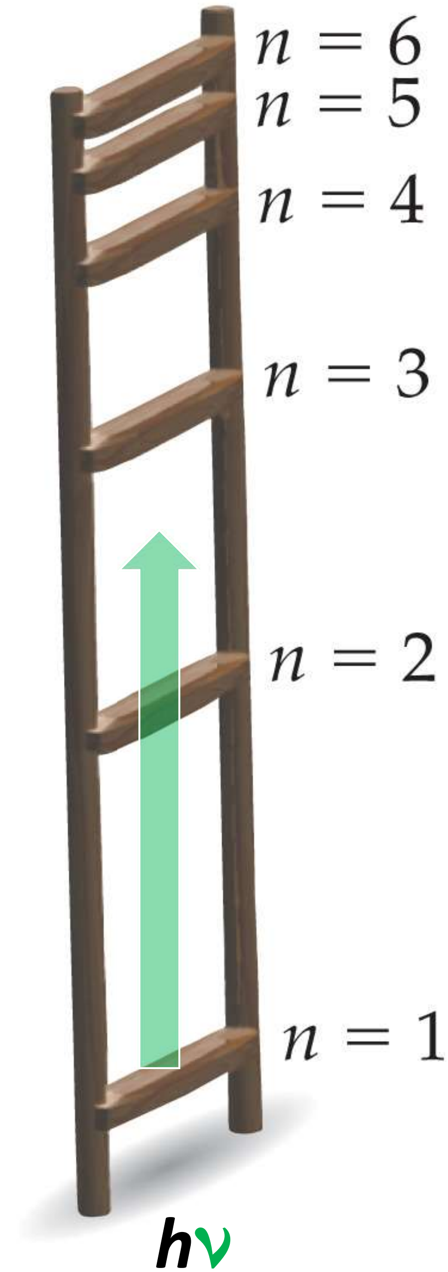
Just as we can only step on the individual levels on a ladder, the **electrons in an atom can only exist at certain energy levels** and not in between.



Energy levels in an atom are quantized

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!



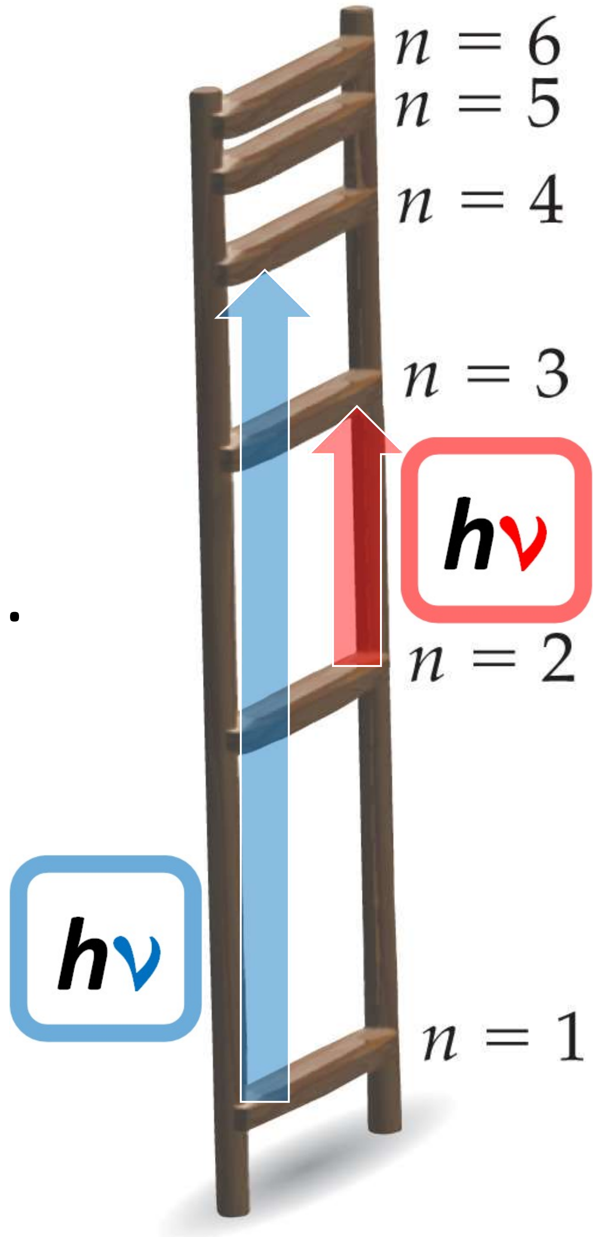
If the energy of the photon matches a difference between two levels **exactly**, it can be absorbed.

Not more, not less, exactly the same.

$E_{photon} = \Delta E_{electron}$

↑

$h\nu$



By the way …

Consider the statement we just made:

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

... Even if the it has more than enough energy

How does this compare with the situation in the photoelectric effect?

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)

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

for photons

?

$$\lambda = \frac{h}{m\,\mathbf{v}}$$

for any particle

See if it applies to everything.

It does!

$$\boxed{\lambda = \frac{h}{m\mathrm{v}}}$$

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

“Particle in a box”

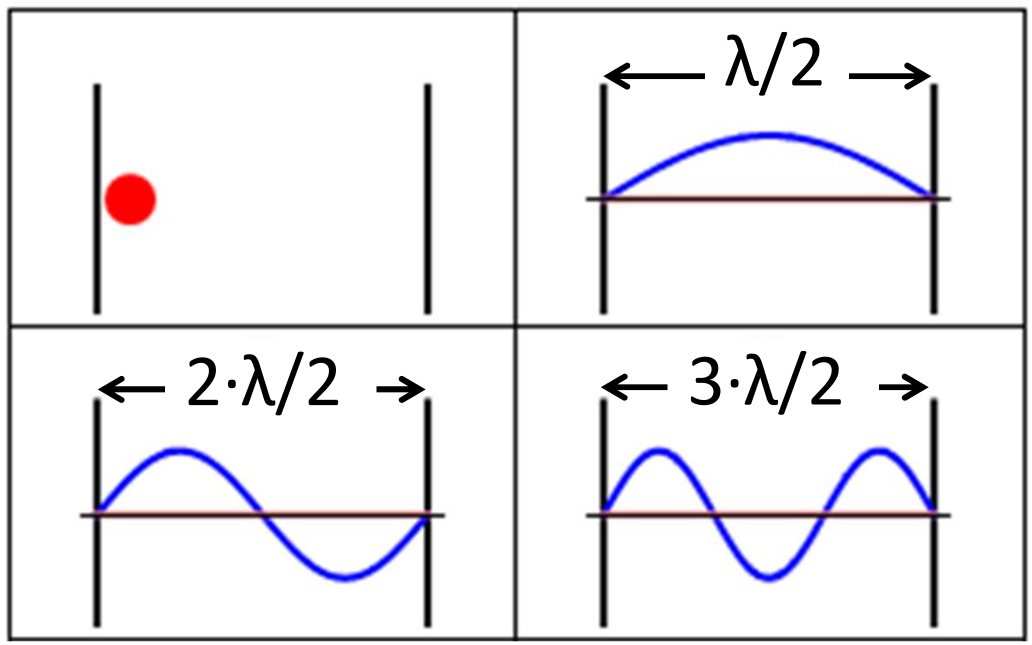
A particle is a wave with a de Broglie wavelength of λ

It fits in a “box” if box’s length is a multiple of λ/2

So only certain λ values are allowed

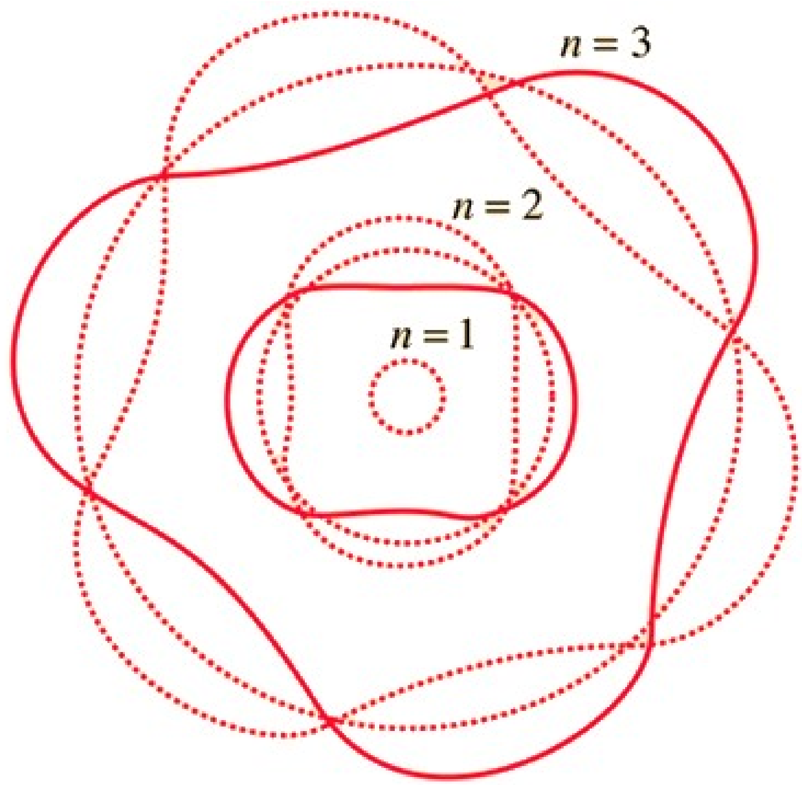
Therefore only certain particle speeds are allowed.

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

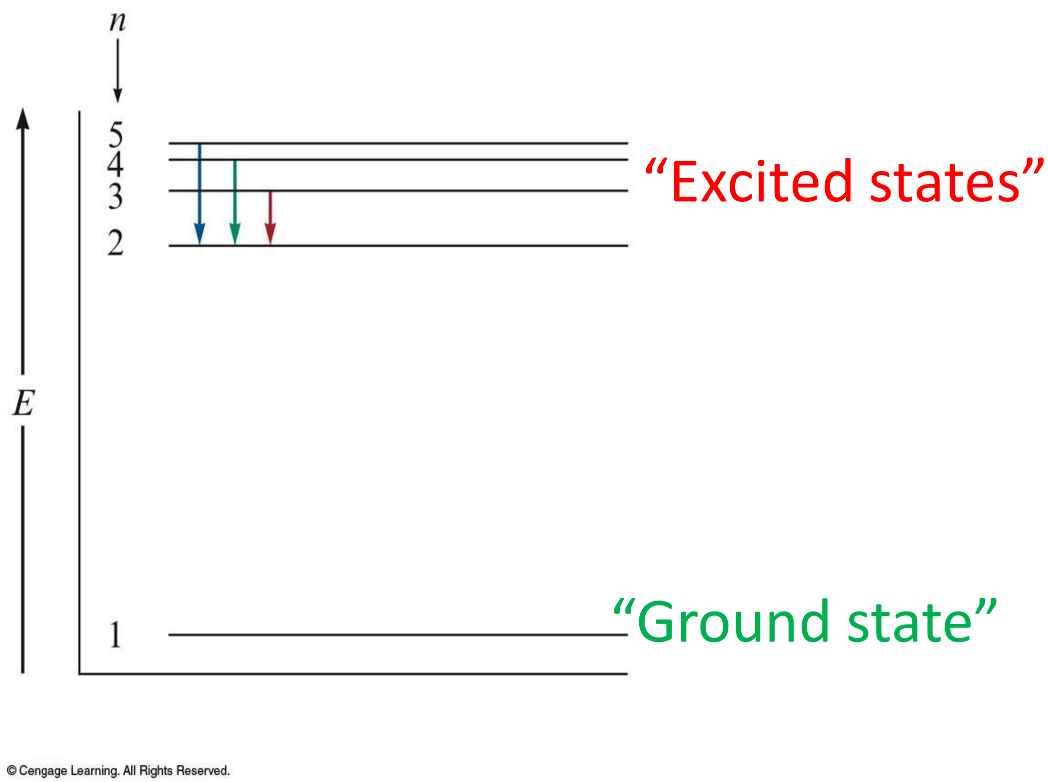
- Before de Broglie derived his result, Bohr came up with a model for Hydrogen atom.
  - Later explained by the de Broglie wavelength
- Electrons “orbit” around the nucleus, the (+)/(–) attractions balanced by the centrifugal forces
- A simple but <u>unexplained</u> assumption is made about the allowed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

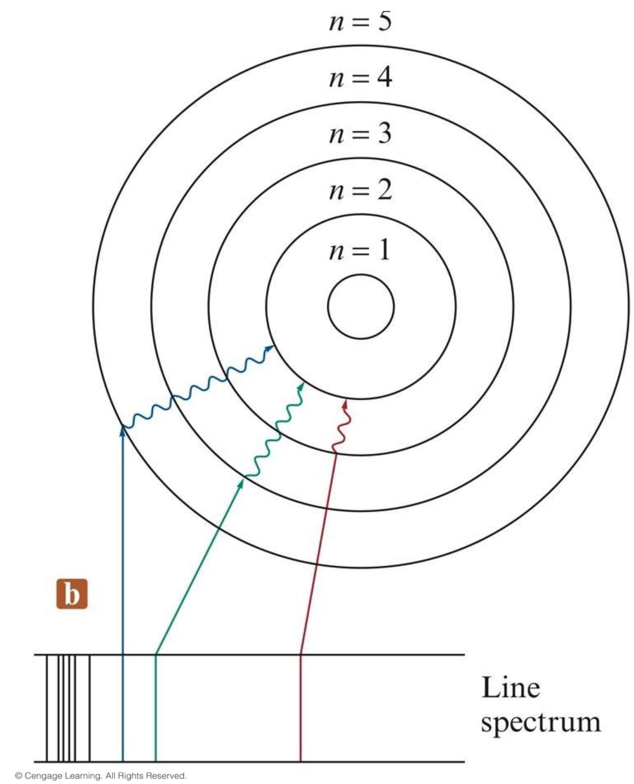
Bohr’s model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum.

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.

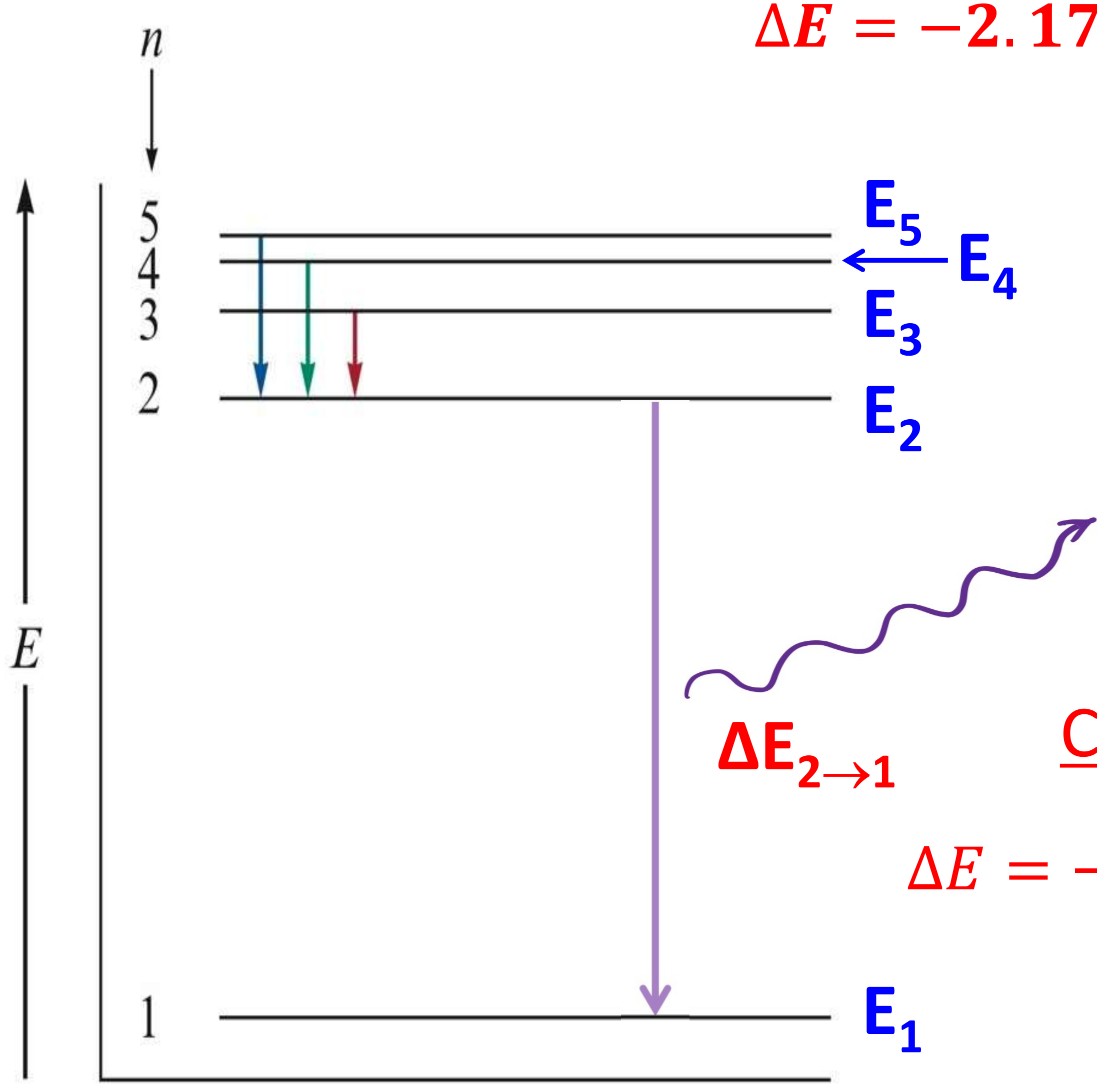
Energy levels & electronic transitions in the Bohr model





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

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



$h\nu = |\Delta E_{2\rightarrow1}|$

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

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

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

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

Applying these thoughts:

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

$E_{photon} = |-4.574\text{x}10-19\ \text{J}\,| = 4.574\text{x}10-19\ \text{J}$

$\lambda = (6.626\text{x}10^{-34}\ \text{J}\cdot\text{s})(3.00\text{x}10^{8}\ \text{m/s}) / (4.574\text{x}10^{-19}\ \text{J}) = 4.34\text{x}10^{-7}\ \text{m}$

$\lambda = (4.34\text{x}10^{-7}\ \text{m})(1\ \text{nm} / 10^{-9}\ \text{m}) = 434\ \text{nm}$

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.**

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

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

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

Same transition in two hydrogen-like species

For a given n: $E \propto Z^2$

For a given transition: $\Delta E \propto Z^2$

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

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

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

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

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

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 <u>where the electron is most likely to be found</u>, and the <u>energy</u> 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**" (<u>**not**</u> "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

Orbital Size

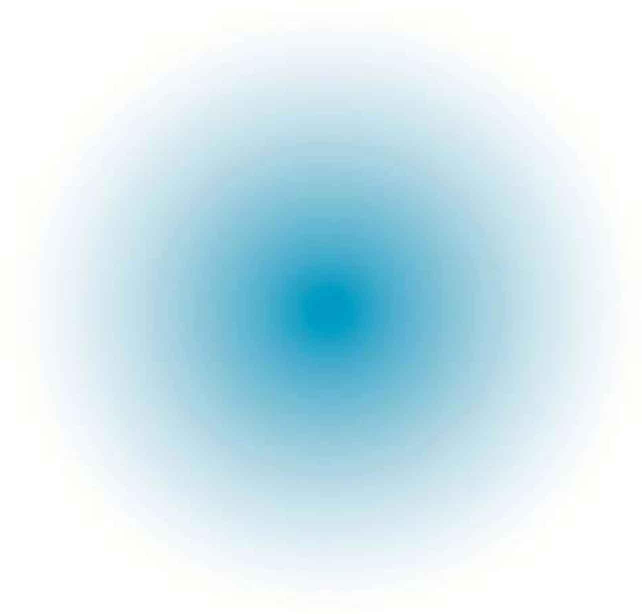
- Difficult to define precisely.
- Picture an orbital as a three-dimensional electron density "fog"

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

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

shells n starts from 1

Has n subshells

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

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

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

Quantum numbers

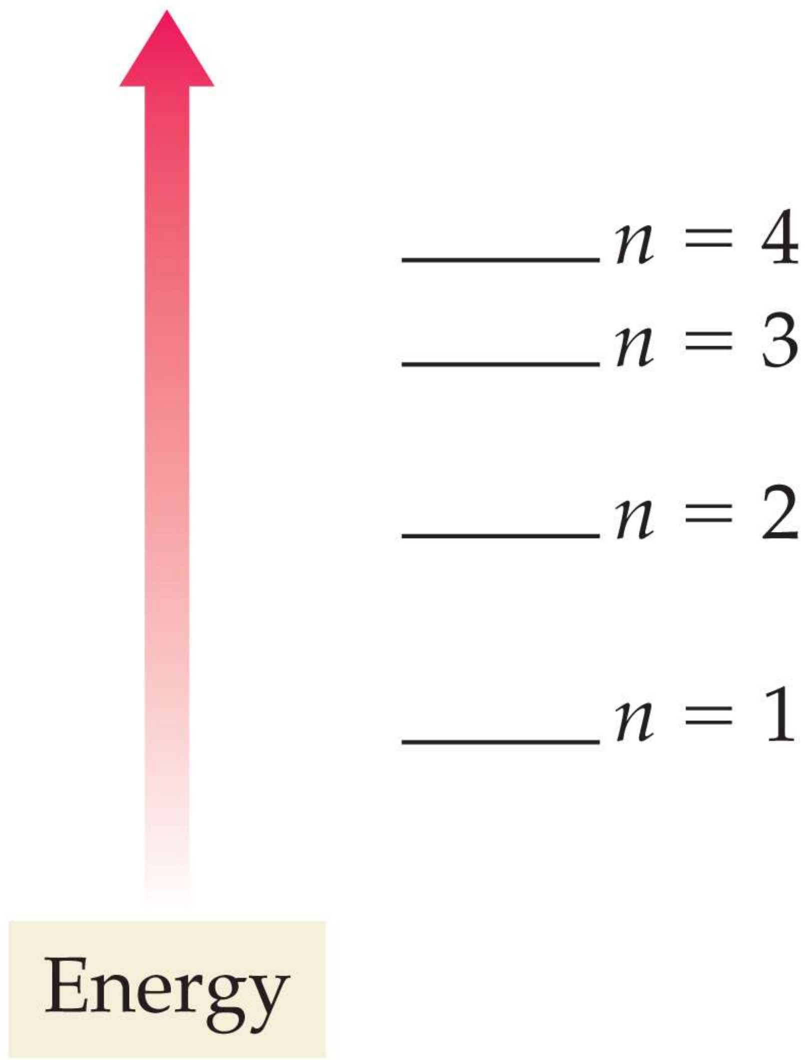
Symbol	Name	Determines	Corresponds to	Allowed Values
n	Principal	**Energy** and **Distance** from nucleus	**Shell** ***Has n sub-shells***	1,2,3,4,5, . . .
l	Angular momentum	**Shape** of the electron density **Energy** for *non-Hydrogen* atoms	**Sub-shell** ***Each subshell has 2l+1 orbitals***	0 to $n-1$ 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 $\boldsymbol{n}$ is the street name
- Then $\boldsymbol{l}$ is the number of the house. It only has a tangible meaning given a certain $\boldsymbol{n}$
- $\boldsymbol{m_l}$ has a tangible meaning given a specific $\boldsymbol{l}$, like a particular room in the house
- $\boldsymbol{m_s}$ 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
  $n = 1, 2, 3 \ldots$
- 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

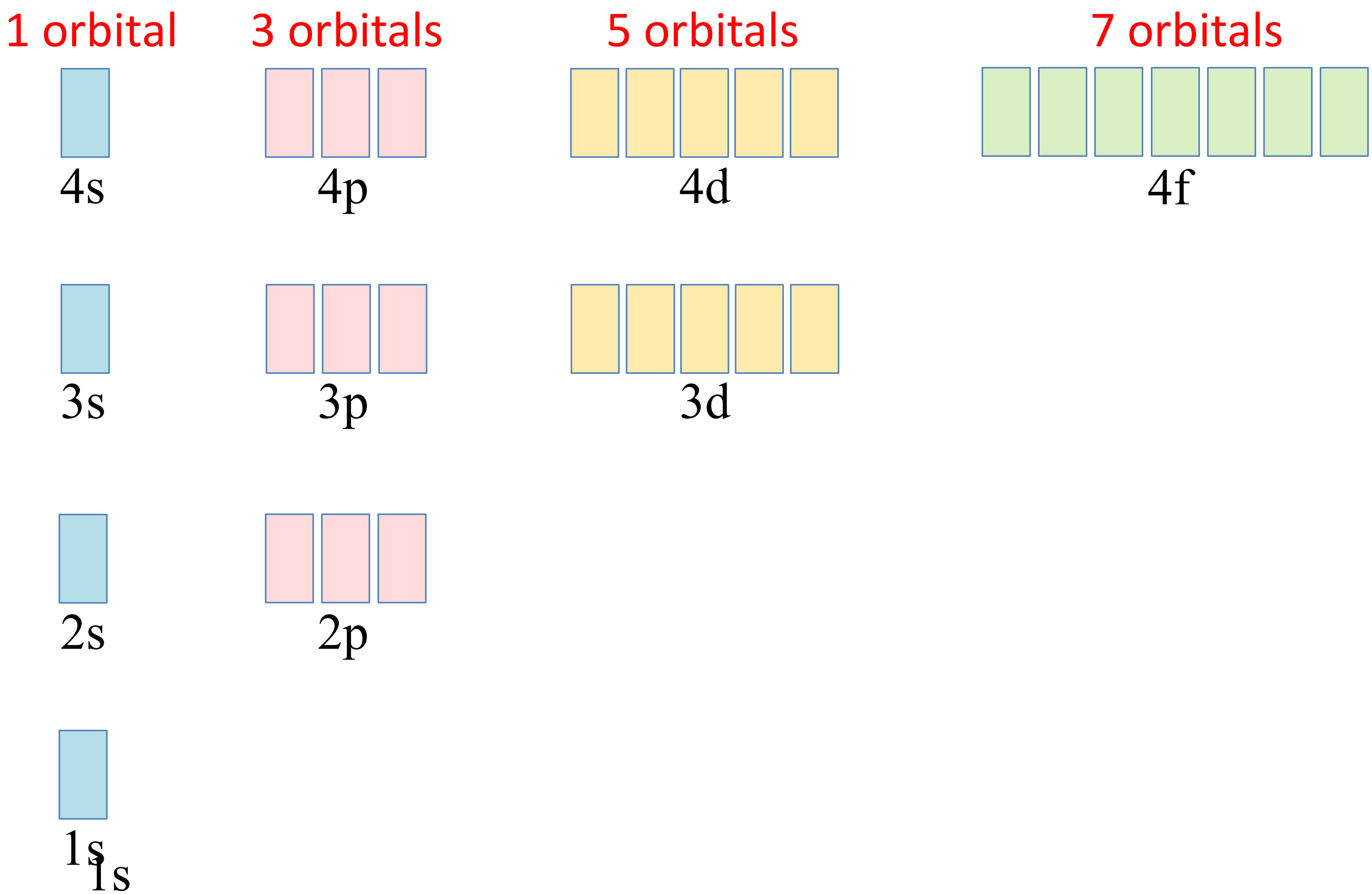
Within each shell, the **same letters** *s, p, d, f,* etc. are used to designate <u>subshells</u>

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

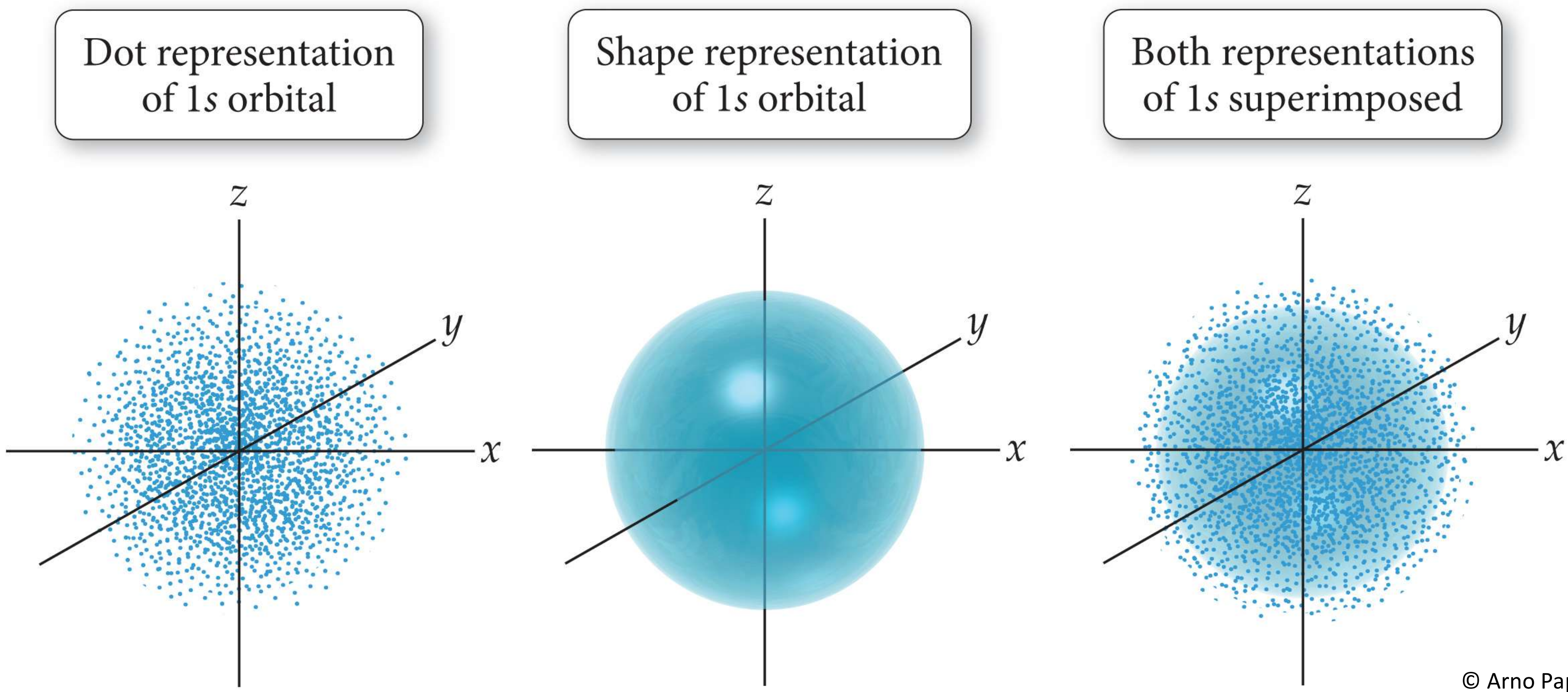
"2p orbitals" are in the "2p subshell"
"3d orbitals" are in the "3d subshell", etc.

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

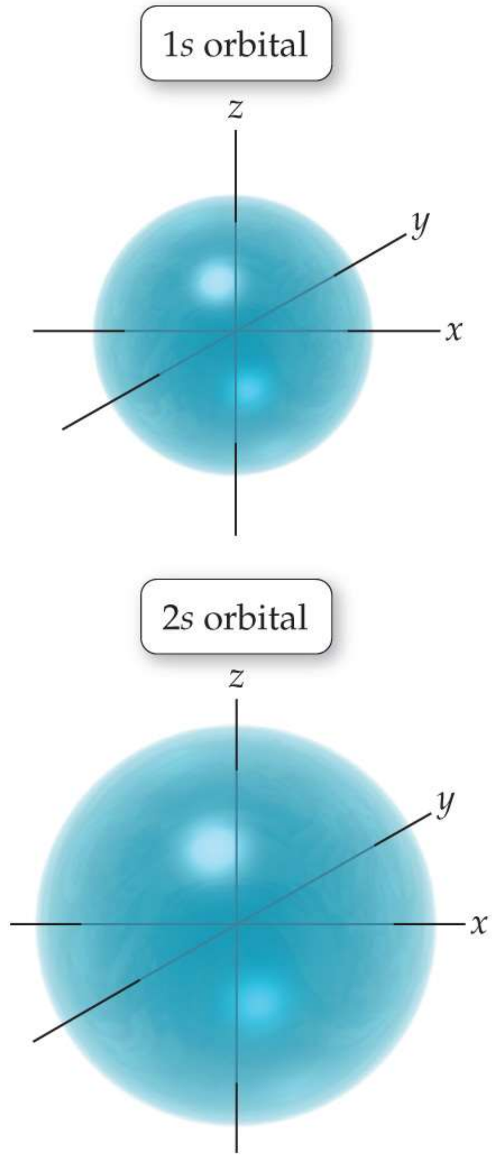
e.g. $2p_x$, $2p_y$, $2p_z$

"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.

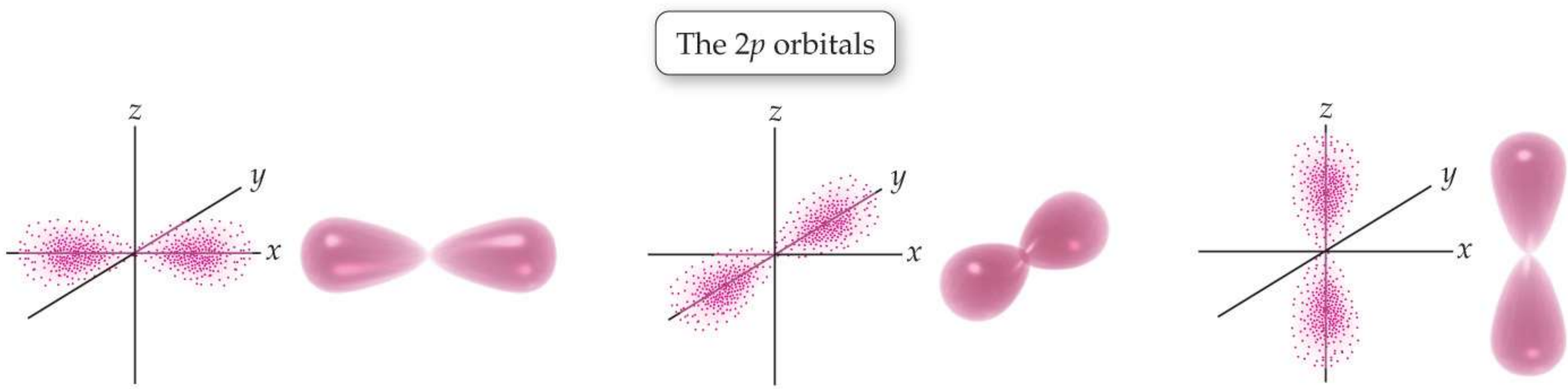


The 2*s* Orbital Is Similar to the 1*s* Orbital, but Larger in Size



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

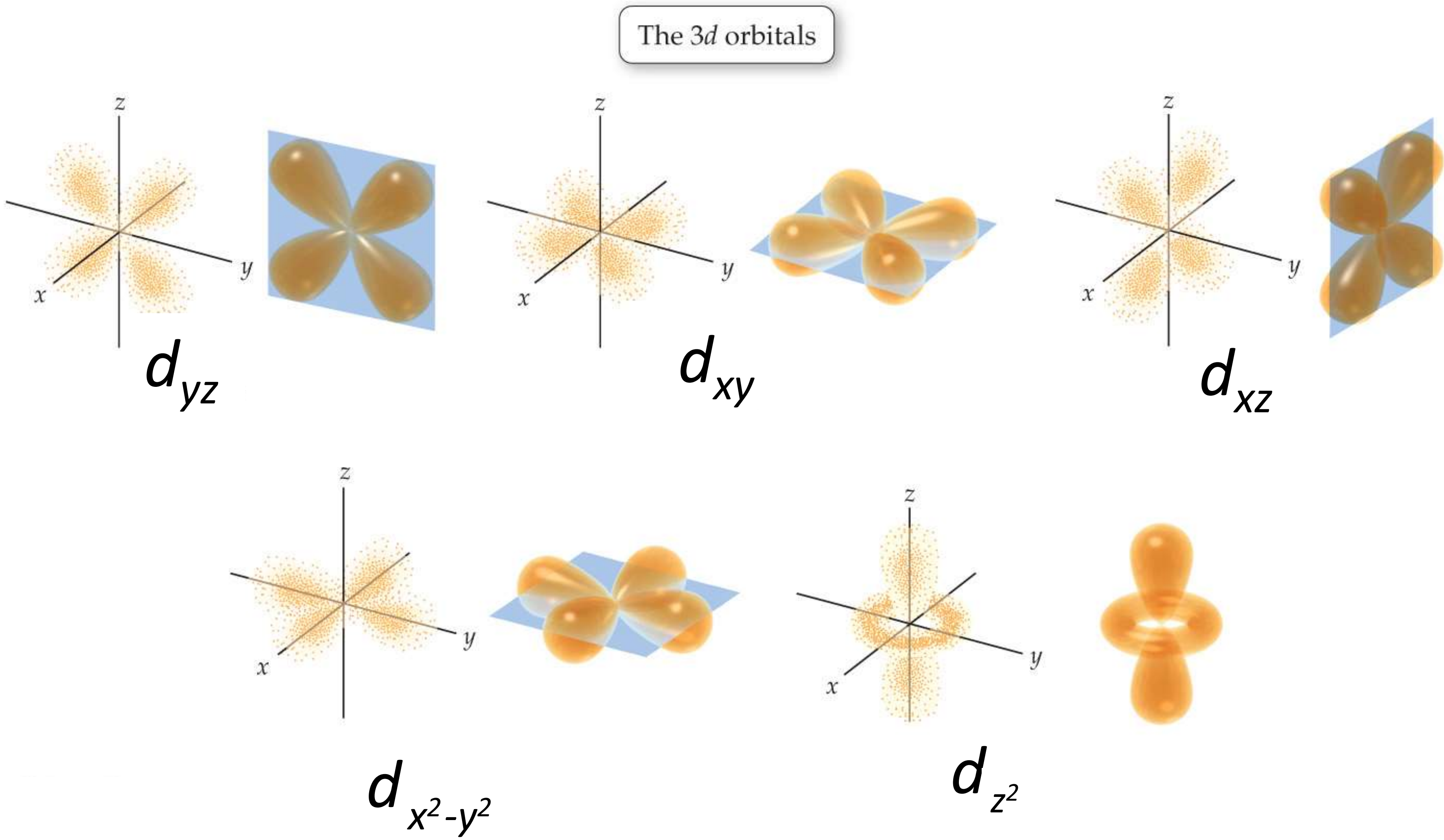
Orbitals in the 3rd shell (n = 3)

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

  3*s*, 3*p*, and 3*d*

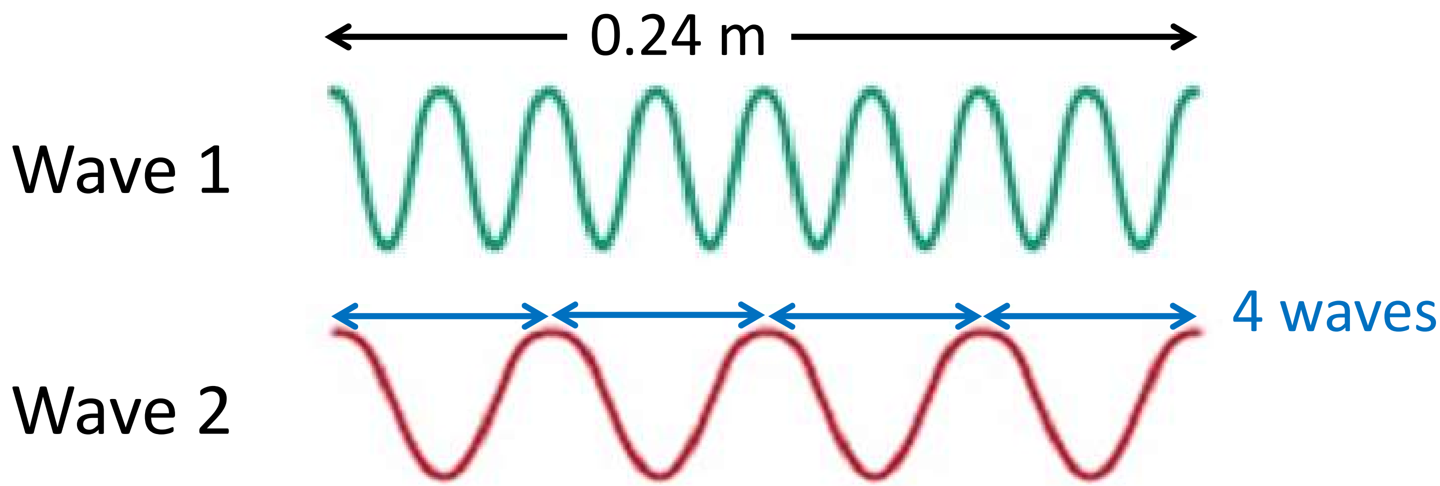
- Orbitals in 3*s* and 3*p* subshells are similar in shape to the 2*s* and 2*p* orbitals, but slightly larger and higher in energy.
- Again, one orbital in 3*s*, and three orbitals in 3*p*
- The *d* subshell contains five *d* orbitals.

The 3*d* Orbitals:



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 = (3.00×10^8 m s^{-1})/(0.060 m) = 5.0×10^9 s^{-1} (Hz)

Example

One electromagnetic radiation (let's call it EM1) has a:

frequency of 89.3 MHz (Hz = s^{-1} ; MHz = 10^6 Hz = 10^6 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: $E_{photon} = h\nu = (6.626 \times 10^{-34}\ J{\cdot}s)(89.3 \times 10^{6}\ s^{-1}) = 5.92 \times 10^{-26}\ J$

EM2: $E_{photon} = h\nu = hc/\lambda = (6.626 \times 10^{-34}\ J{\cdot}s)(3.00 \times 10^{8}\ m/s) / (31.0\ m)$

$= 6.41 \times 10^{-27}\ J$

EM3: $E_{photon} = 4.42 \times 10^{-19}\ J$

EM2 , EM1 , EM3

Example

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

$E_{photon} = 4.42\text{x}10^{-19}$ J $\qquad$ $E_{photon} = hc/\lambda \Rightarrow \lambda = hc/ E_{photon}$

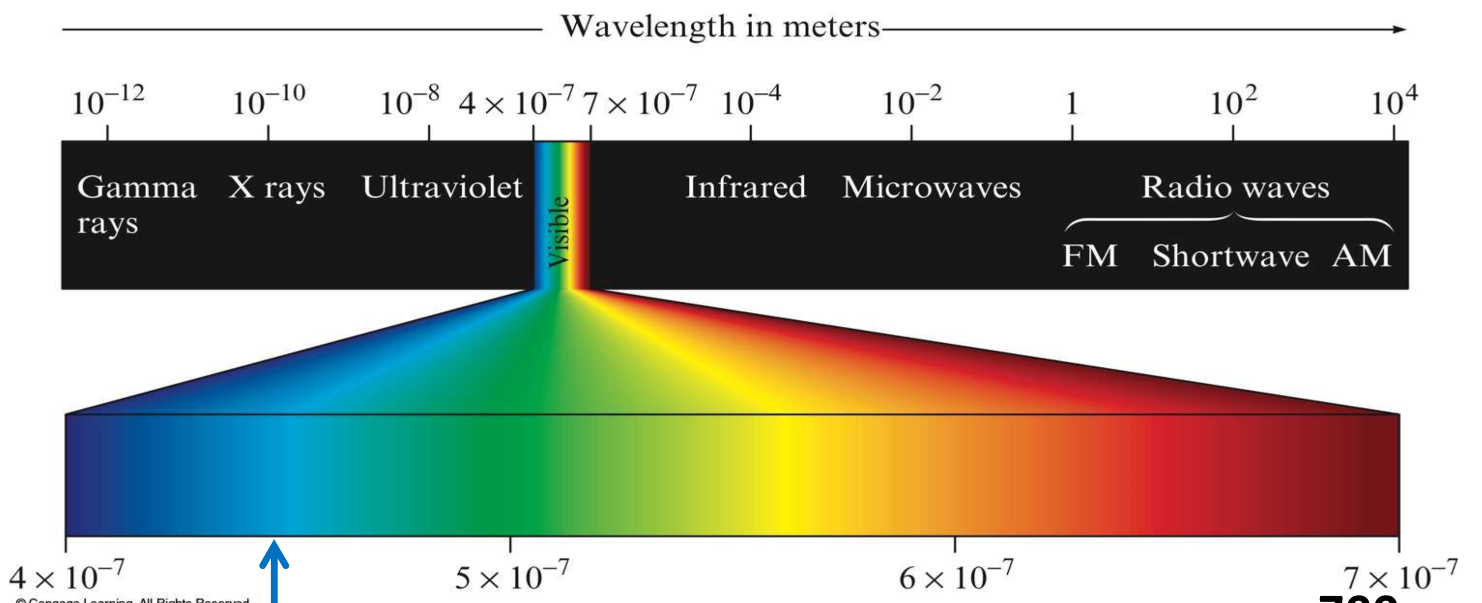
$\lambda = (6.626\text{x}10^{-34}\ \text{J·s})(3.00\text{x}10^{8}\ \text{m/s}) / (4.42\text{x}10^{-19}\ \text{J}) = 4.50\text{x}10^{-7}$ m

$\lambda = (4.50\text{x}10^{-7}\ \text{m})(1\ \text{nm} / 10^{-9}\ \text{m}) = 450.$ nm

Example

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

λ = 450. nm



400 nm

700 nm

Visible; blue

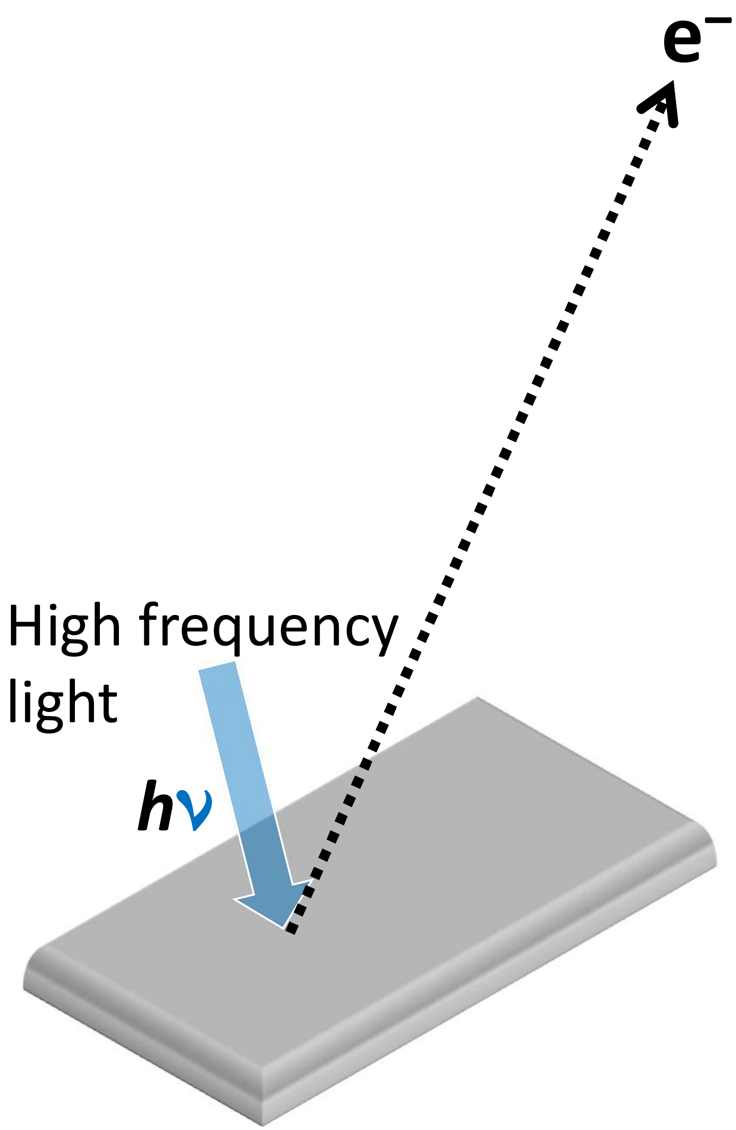
Example

The energy (W) required to free an electron from the surface of solid Cesium metal is 3.37×10^{-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?

Remember Photoelectric effect



Leftover energy

kinetic energy of $\mathbf{e}^-$ = $h\nu$ – 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 3.37×10^{-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?

$$E_{photon} = 4.42 \times 10^{-19} \text{ J}$$

$$E_{electron} = E_{photon} - W = (4.42 \times 10^{-19} \text{ J}) - (3.37 \times 10^{-19} \text{ J}) = 1.05 \times 10^{-19} \text{ J}$$

Energy of the <u>free</u> 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 **4.42×10^{-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:

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

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

$$4.42 \times 10^{-19}\ \mathrm{J} > 3.025 \times 10^{-19}\ \mathrm{J}$$

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 $\boldsymbol{n}$, $\boldsymbol{l}$, $\boldsymbol{m_l}$, and $\boldsymbol{m_s}$ 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 $\boldsymbol{n}$, $\boldsymbol{l}$, and $\boldsymbol{m_l}$
- The fourth quantum number, $\boldsymbol{m_s}$, 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 $\boldsymbol{m_s}$.
- But $\boldsymbol{m_s}$ can only be +½ or -½
- Therefore:

An orbital can hold a maximum of <u>two</u> electrons

And if there are two electrons in the same orbital, they <u>must</u> have <u>opposite</u> 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 …

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"

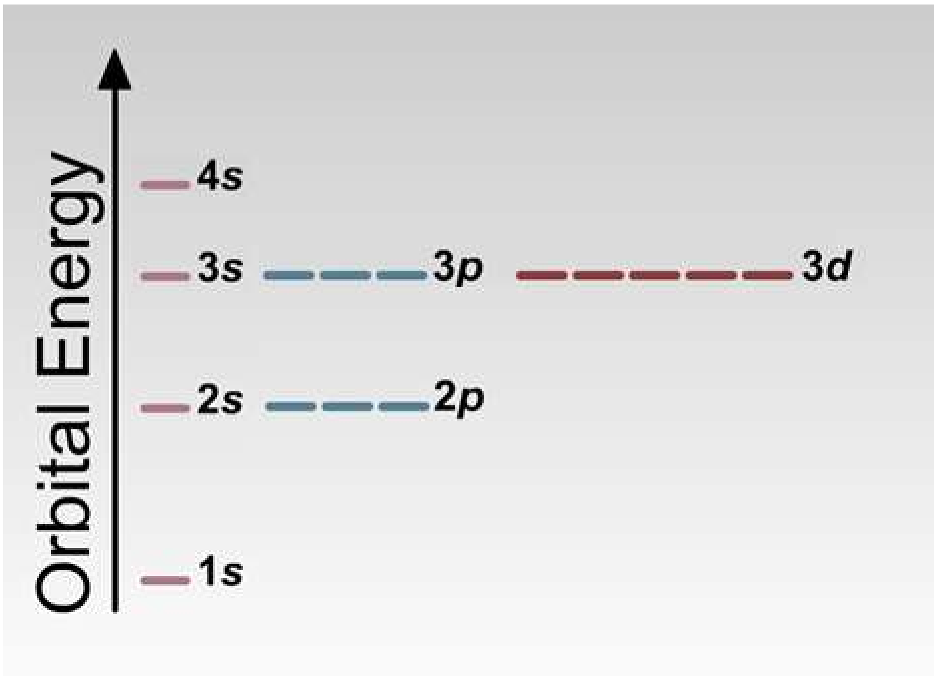
For Hydrogen there is only one electron around the nucleus, and all subshells in a given shell have the same energy (called “degenerate”; long story)

<u>For atoms with more than one electron</u>:

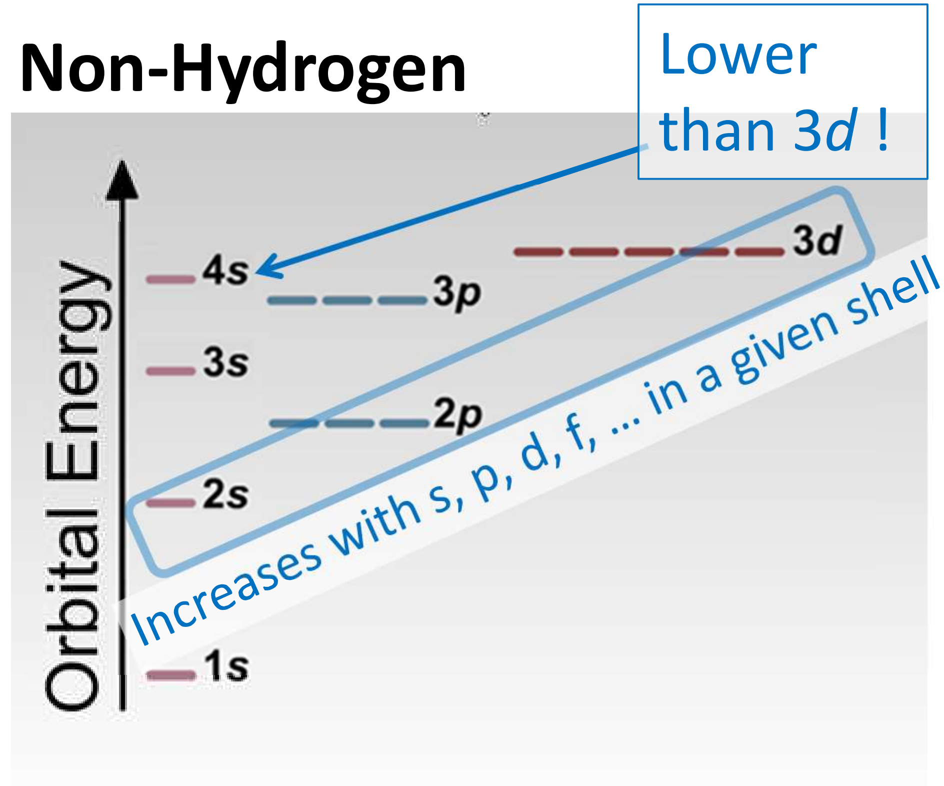
- Electron-electron repulsions affect subshell energies
- Subshell number (or letter) affects energy:
  - In a particular shell, energy of subshells follow the order *s*, *p*, *d*, *f*, …

Subshell energies

Hydrogen



Non-Hydrogen



<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

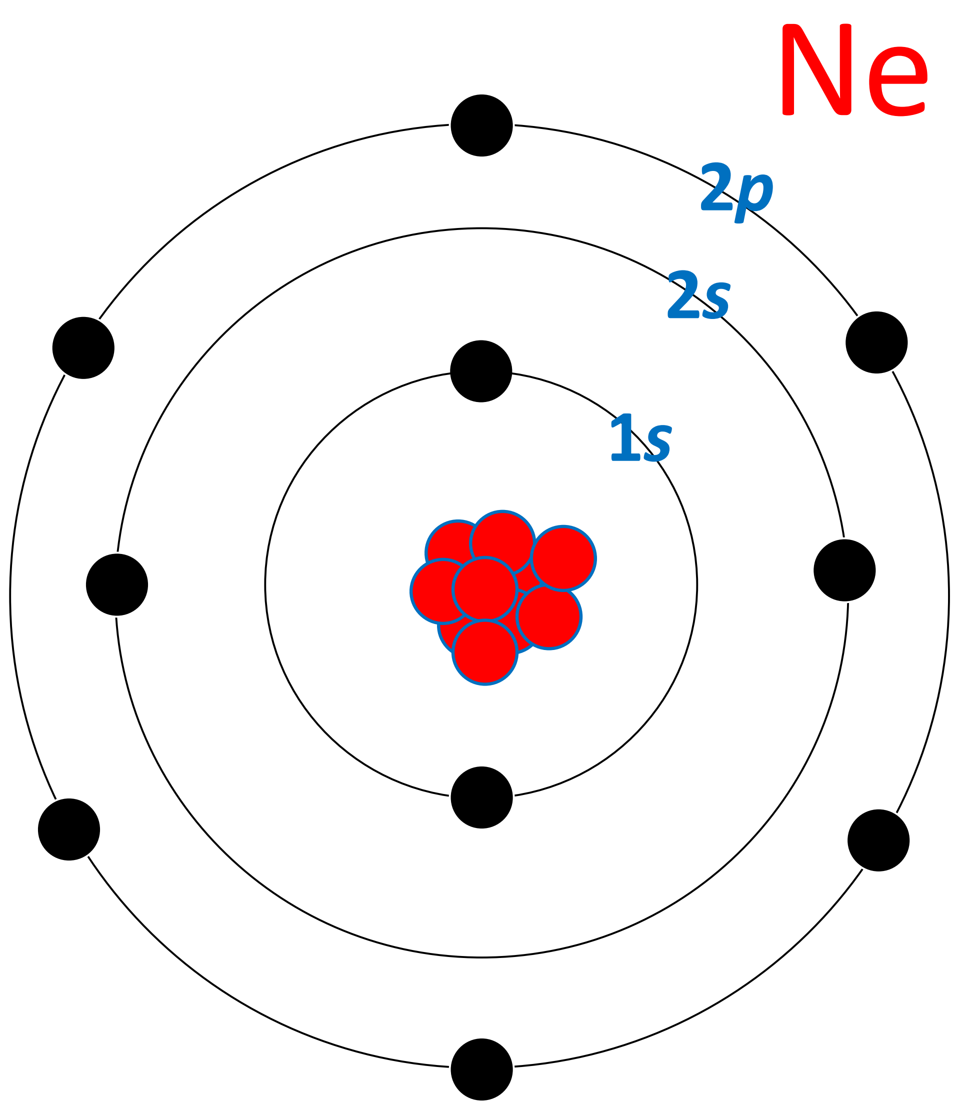
To build-up the next element, and then the next ….

- 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 lowest unfilled subshell



- 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 **not** “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?

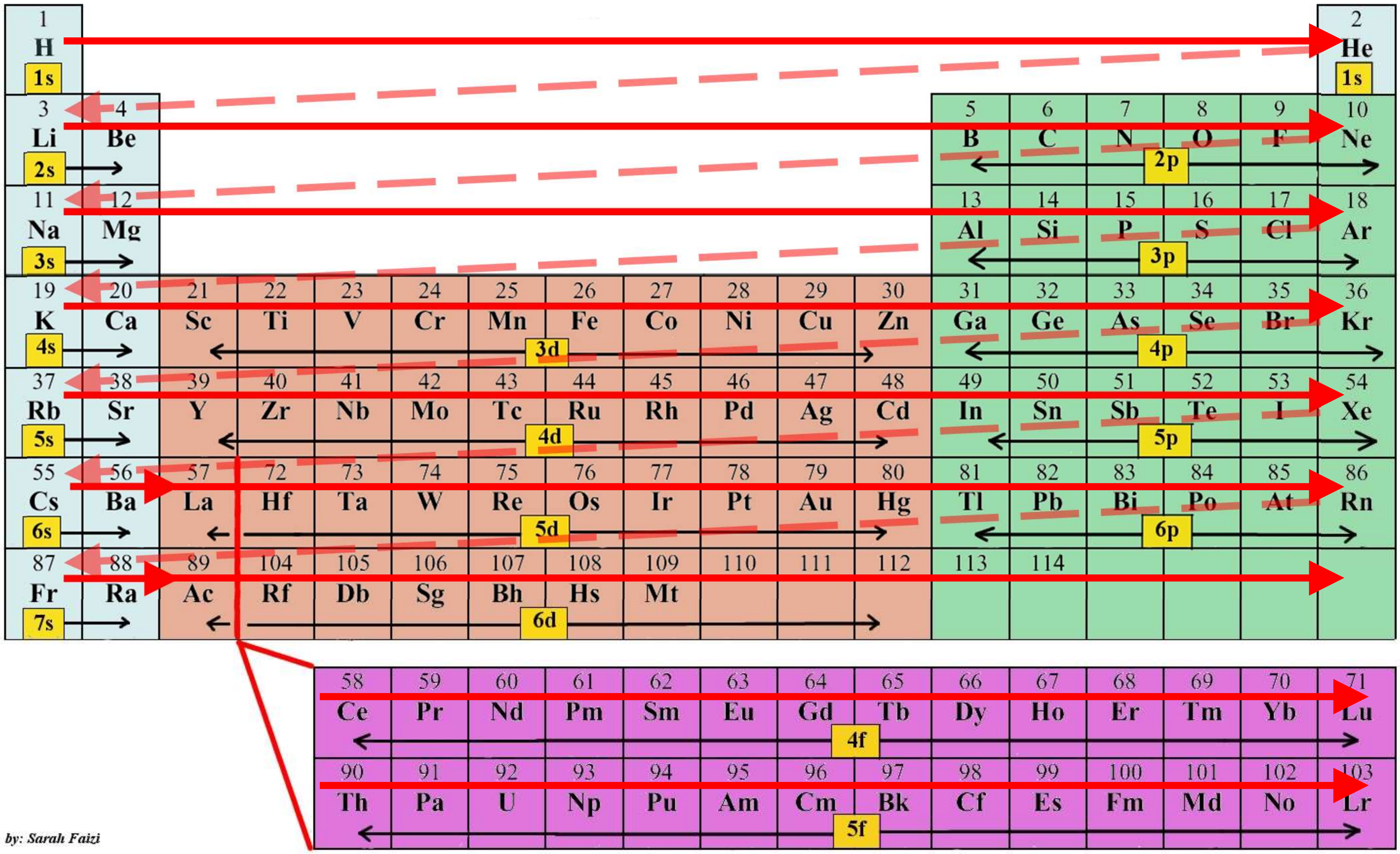
Best way: Use the **Periodic Table**

- 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.

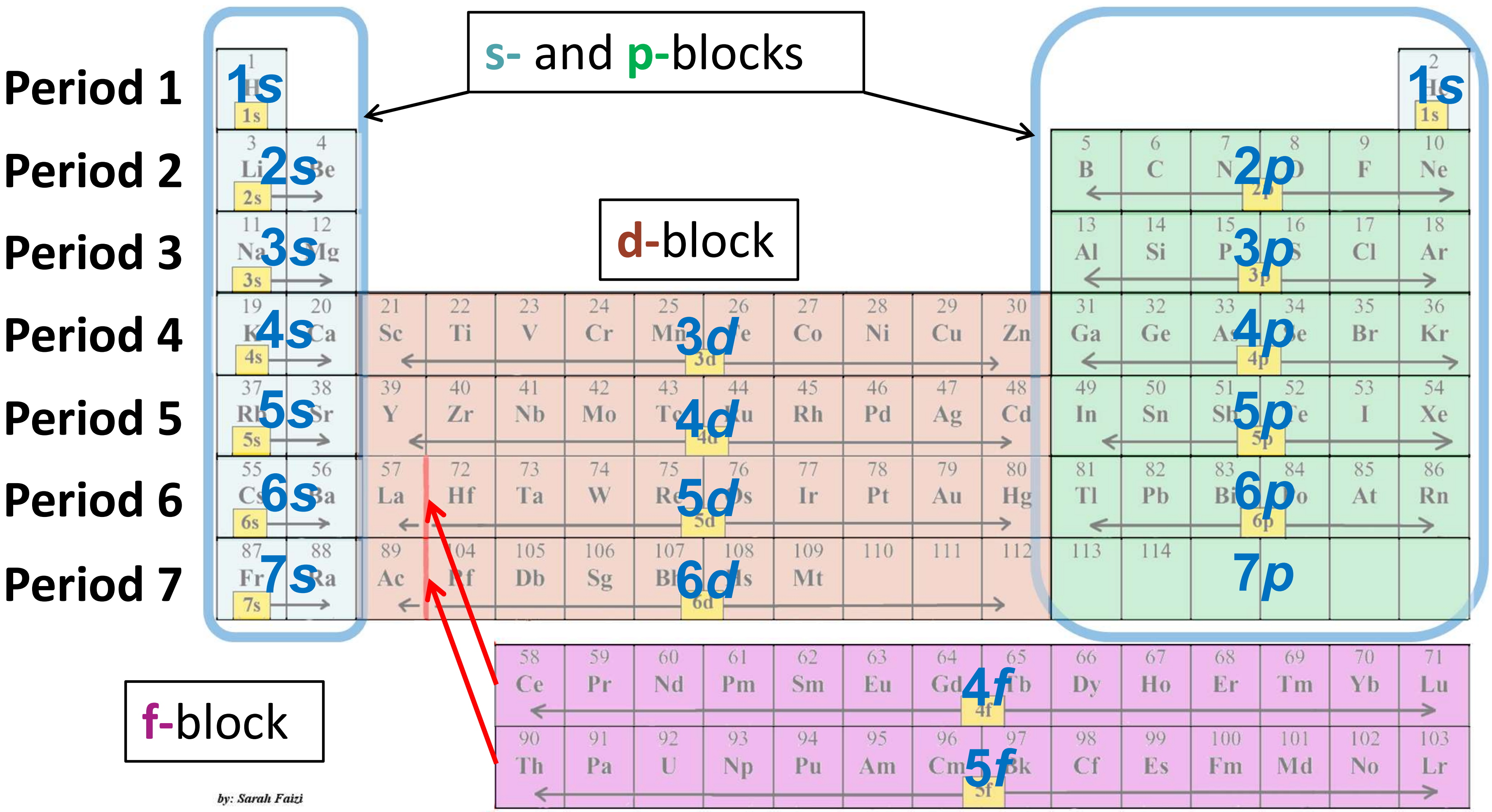
Order of filling subshells, by reading the periodic table like a book



by: Sarah Faizi

When building configurations:

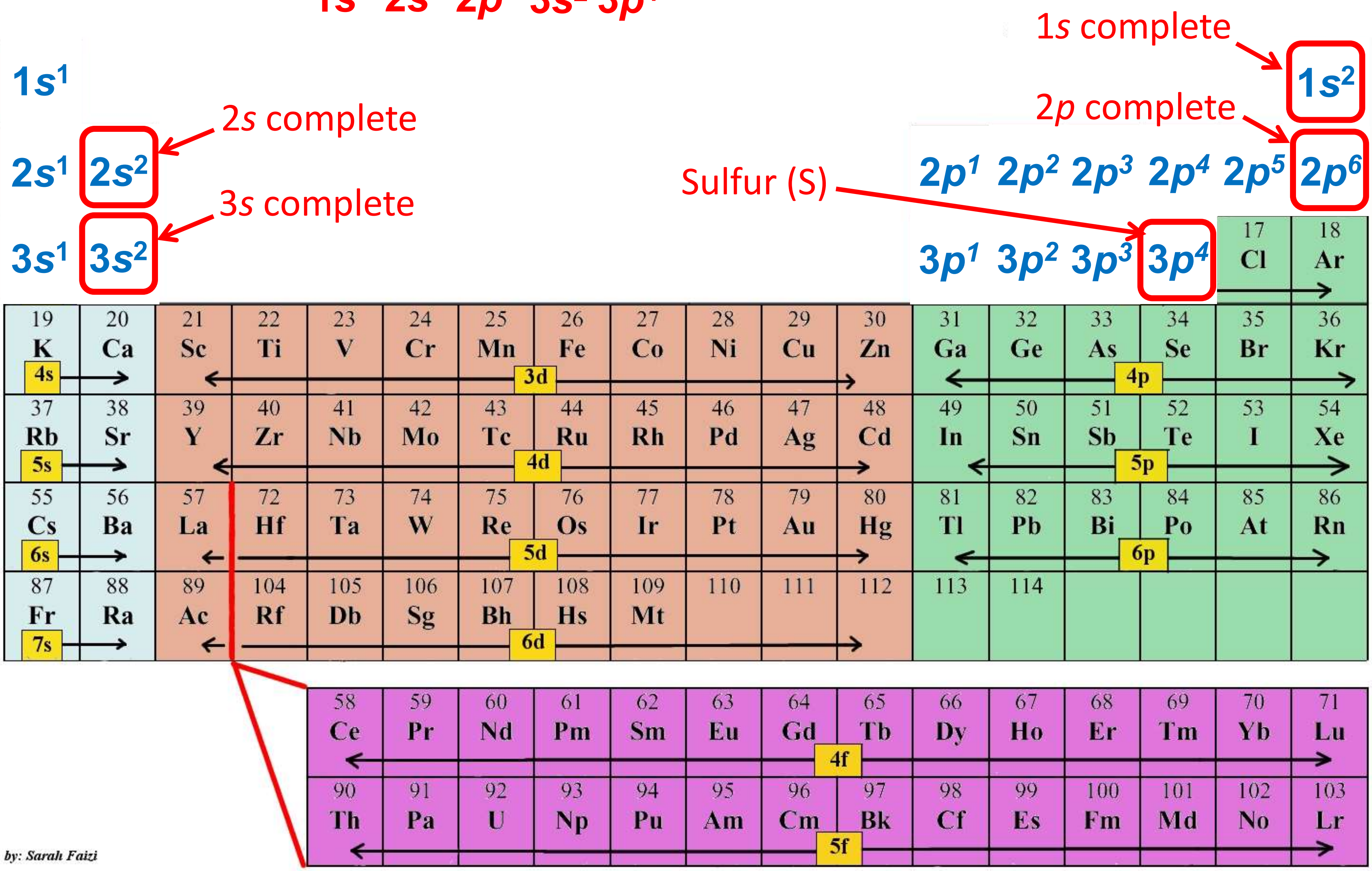
- **For s- and p-subshells:** (Shell #) = (Period #)
- **For d-subshells:** (Shell #) = (Period #) – 1
- **For f-subshells:** (Shell #) = (Period #) – 2



Example

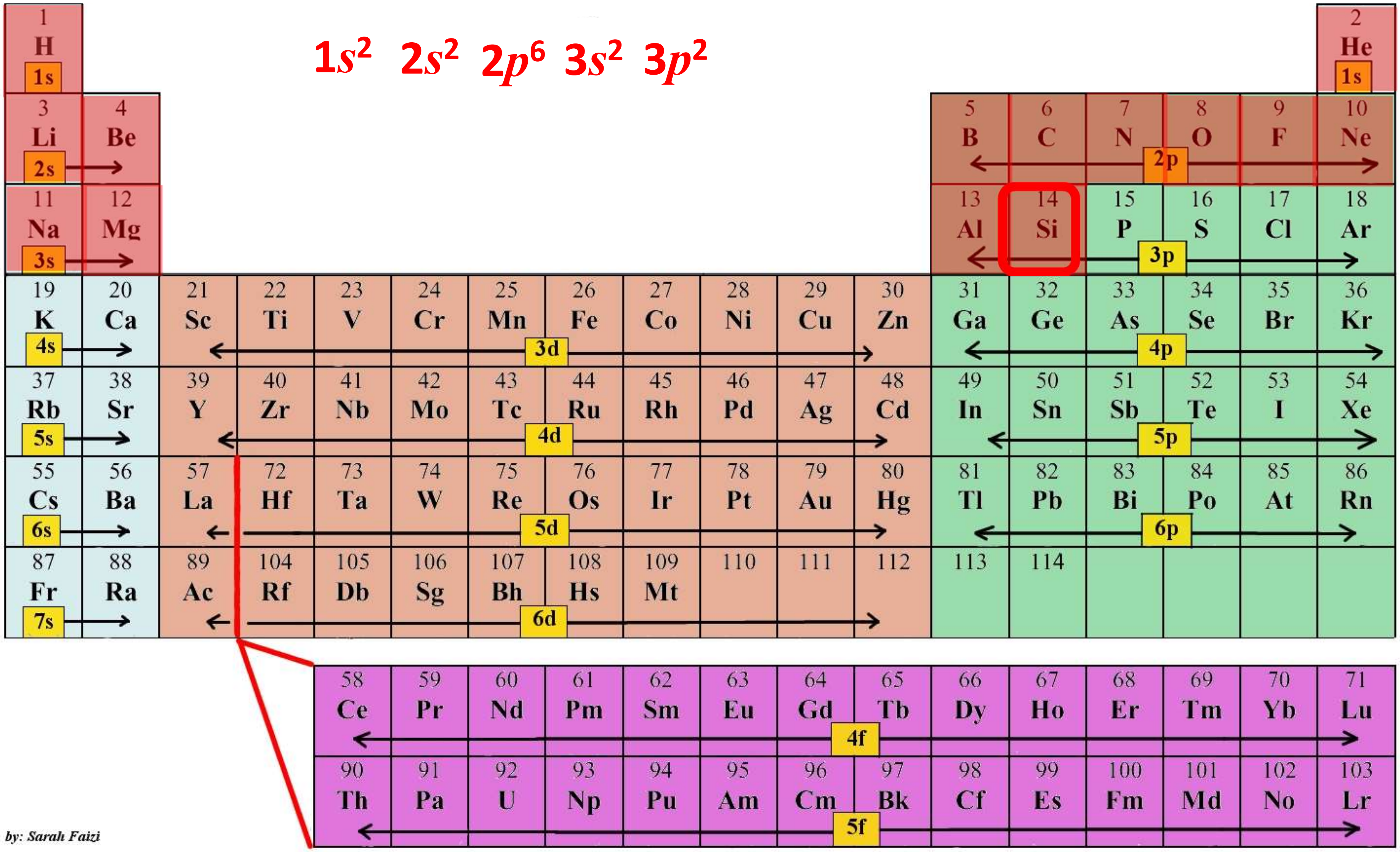
What is the electron configuration of Sulfur (S)?

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



Example: Electron configuration of Si

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

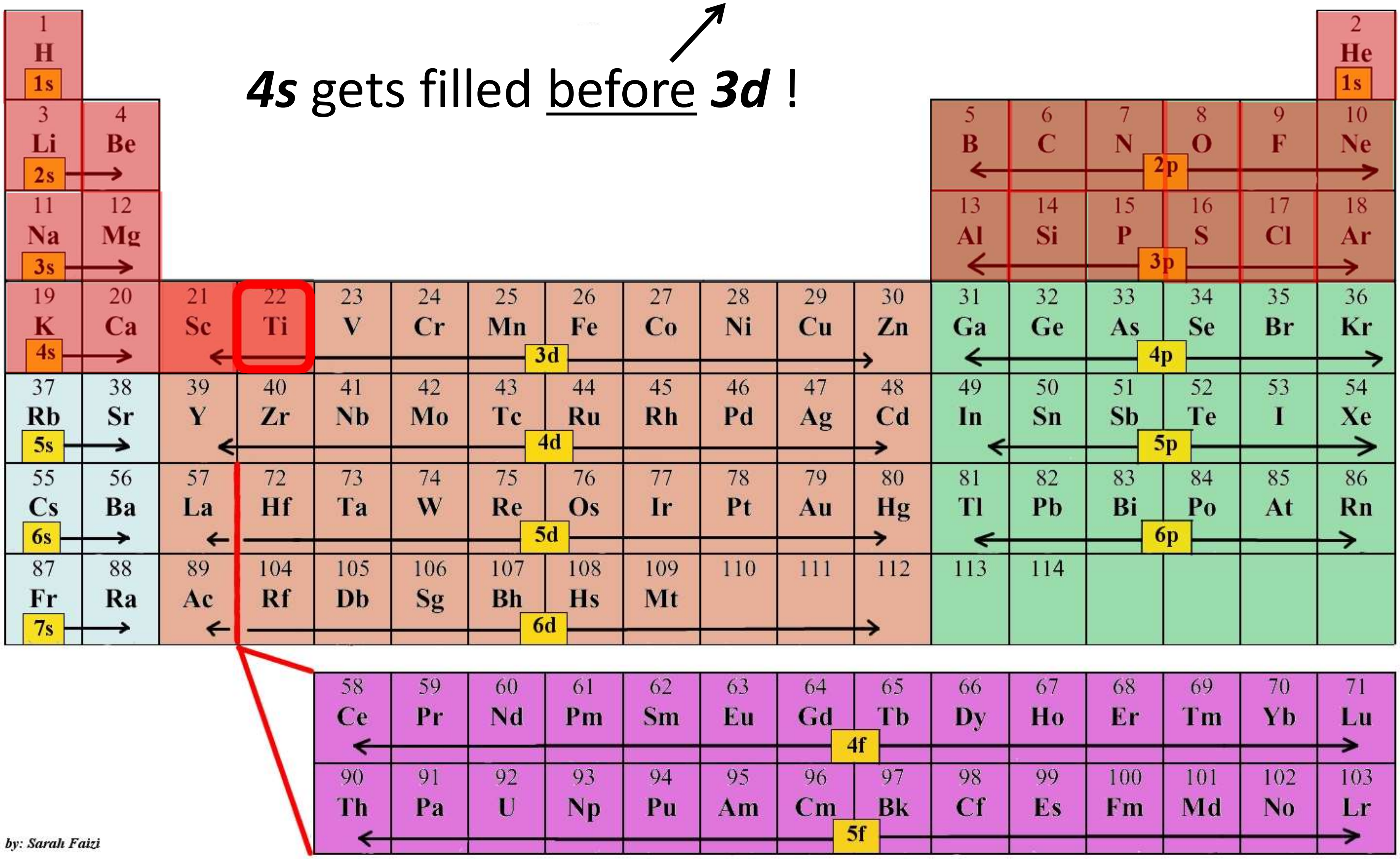


by: Sarah Faizi

Example: Electron configuration of Ti

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

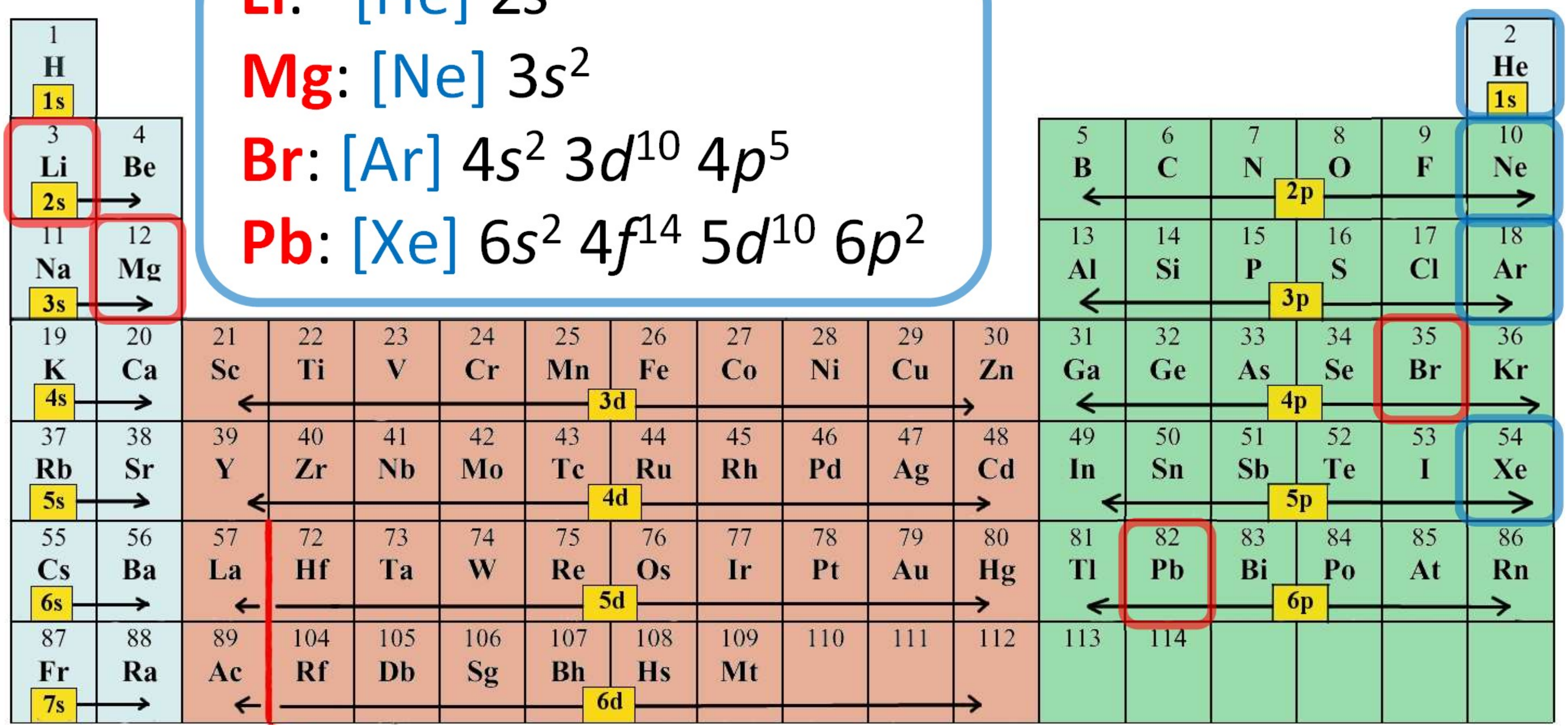
4s gets filled <u>before</u> ***3d*** !



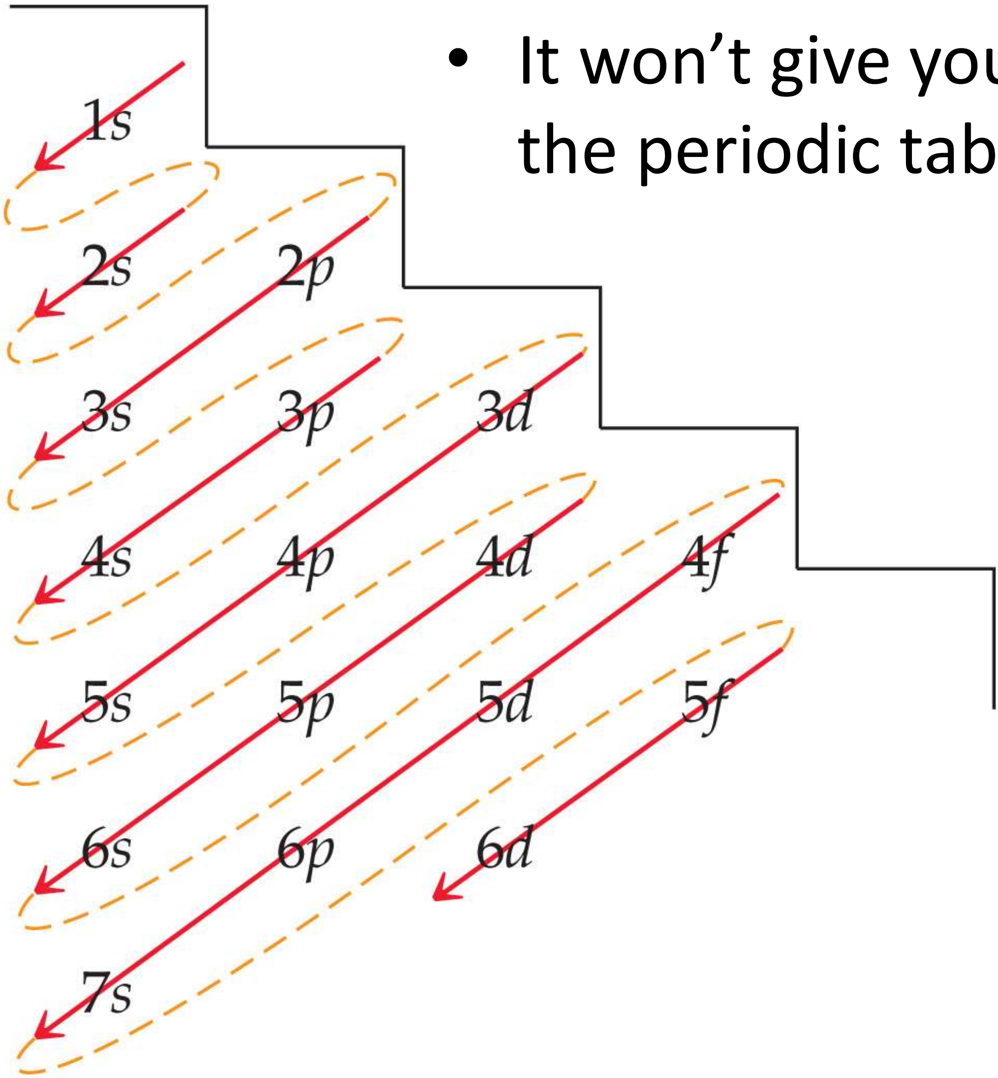
Abbreviated representation of electronic configurations

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

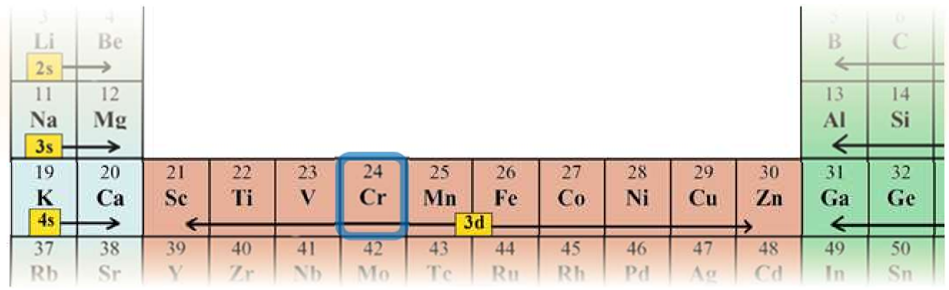


You can use this, but:

- 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

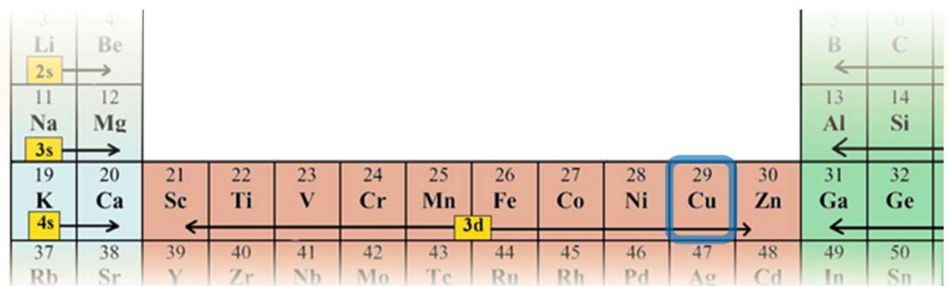


Cr:

Expected: [Ar] $4s^2\ 3d^4$

Actual: [Ar] $4s^1\ 3d^5$

Achieves <u>half-filled *4s*</u> and <u>half-filled *3d*</u> by shifting a *4s* electron to *3d*



Cu:

Expected: [Ar] $4s^2\ 3d^9$

Actual: [Ar] $4s^1\ 3d^{10}$

Achieves <u>half-filled 4*s*</u> & <u>filled 3*d*</u> 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.

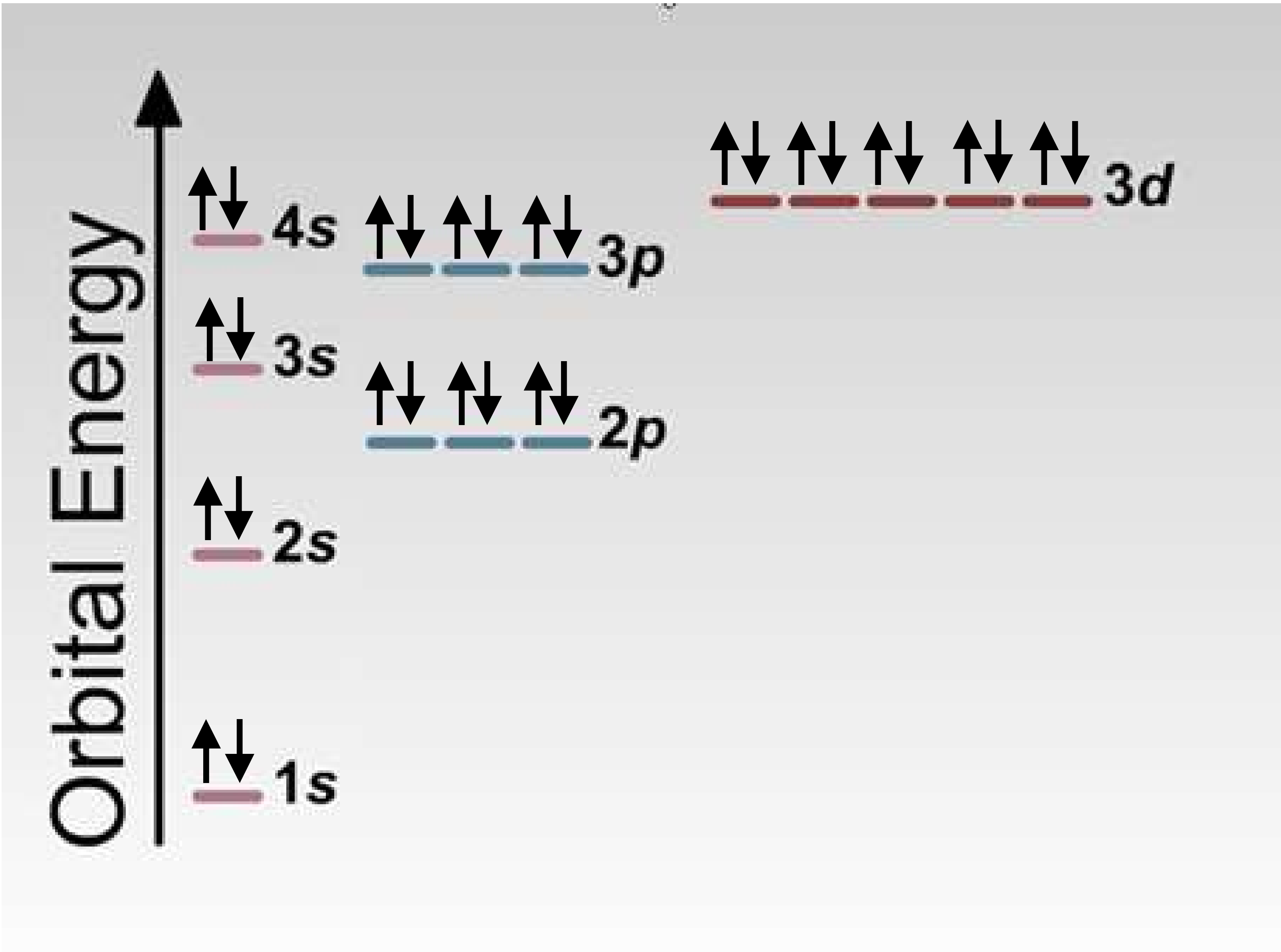
Hund's rule is about the order of putting electrons in those orbitals.

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"
- <u>After</u> 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

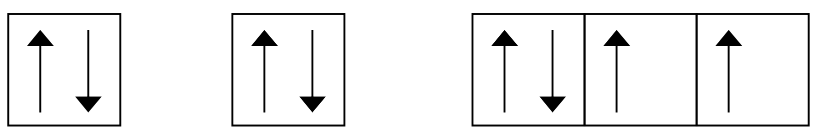


Orbital Diagrams

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

Example

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



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

The textbook covers this at the end of Ch. 9

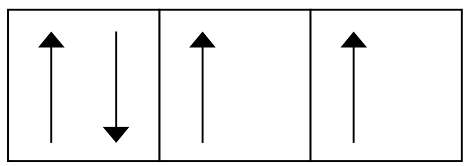
Electron Spins and Magnetic Properties

- The spin quantum number $\boldsymbol{m_s}$ 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

The textbook covers this at the end of Ch. 9

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



2 unpaired electrons

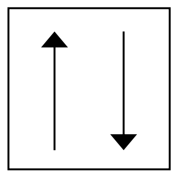
it is **attracted to a magnetic field**.

Then the atom is **<u>paramagnetic</u>**.

Diamagnetism

The textbook covers this at the end of Ch. 9

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.**

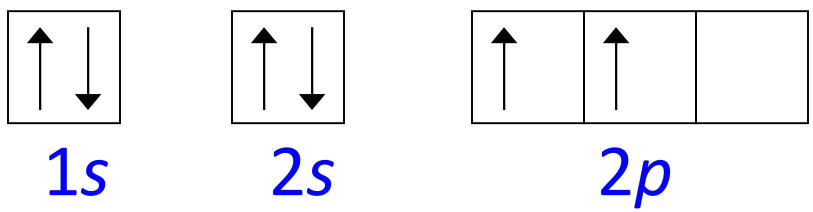
Then the atom is **diamagnetic**.

The textbook covers this at the end of Ch. 9

Example

Determine if a gas-phase carbon atom is paramagnetic

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



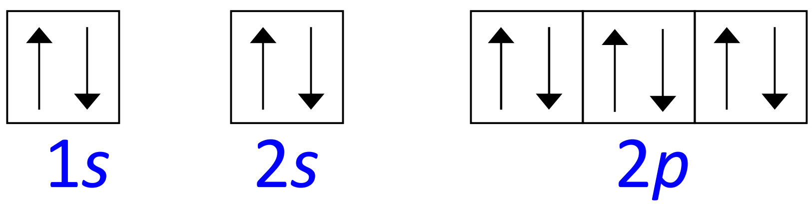
Carbon has 2 unpaired electrons in 2p orbitals, therefore it is paramagnetic.

The textbook covers this at the end of Ch. 9

Example

Determine if atoms of neon gas is paramagnetic

Neon: $1s^2 2s^2 2p^6$



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 $\boldsymbol{n}$ = 2, $\boldsymbol{l}$ can be 0 or 1. So $\boldsymbol{l}$ = 1 is allowed
i.e. the number of electrons is not zero

Number of orbitals in an $\boldsymbol{l}$ = 1 (“p”) subshell is 2(1)+1 = 3

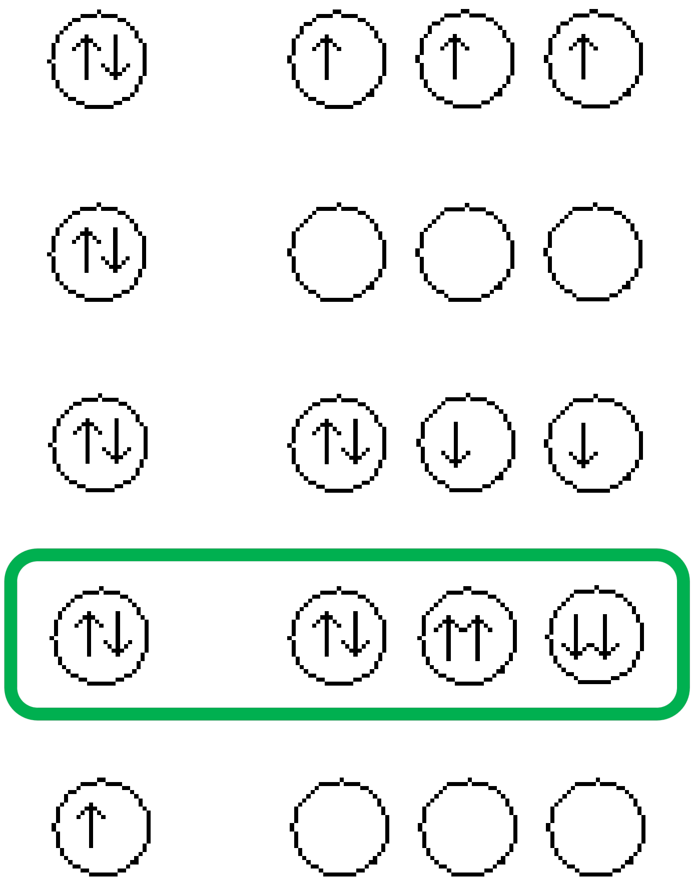
Each orbital can hold up to 2 electrons.

Maximum number of electrons with $\boldsymbol{n}$ = 2, $\boldsymbol{l}$ = 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) $\boxed{1s^2\ 2s^5}$

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) $\boxed{4s^2\ 4p^3}$

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.