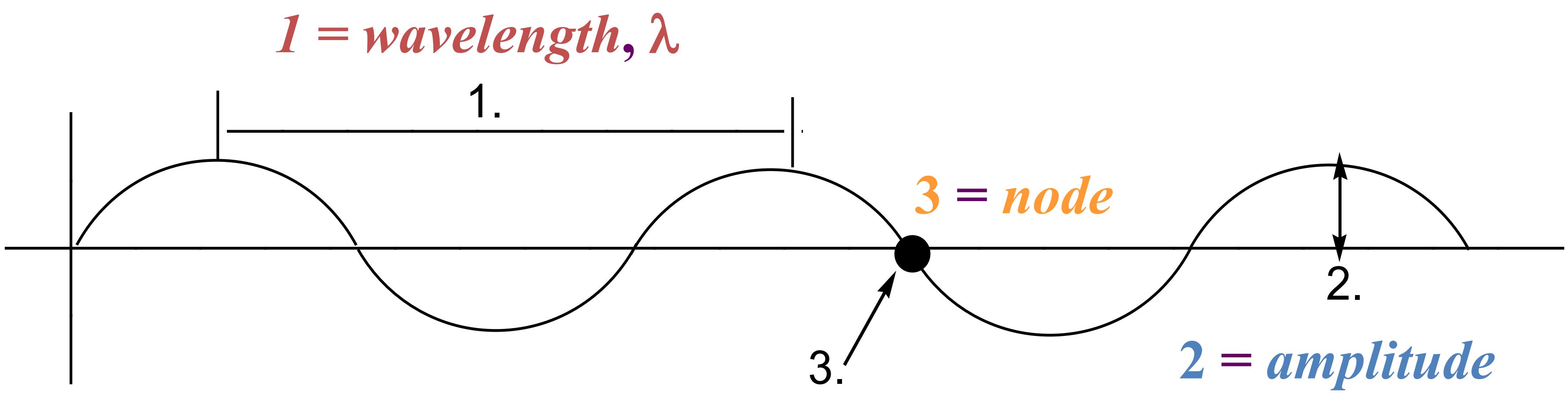
CHAPTER 6

LIGHT & the ATOM

LIGHT or Electromagnetic Radiation: An Introduction

Electromagnetic radiation exhibits wavelike properties which can be depicted in the following representation below:



ν (frequency) describes how many waves in time

Definitions

The ***wavelength***, **λ** **(lower-case Greek letter lambda), is represented by number 1, or the peak-to-peak distance, and is generally in units of meters (although usually converted to nm).**

The number 2 represents the *amplitude*, or the height of the wave above/below the center line.

Finally, the number 3 represents the *node*, or the point at which an electron occupying an orbital will NOT be found (to be discussed in more detail later).

The number of cycles per second is called the *frequency*, denoted with the symbol ν (the Greek letter nu), and expressed in units of s^{-1} of Hz (Hertz).

General properties of Light
Electromagnetic Radiation

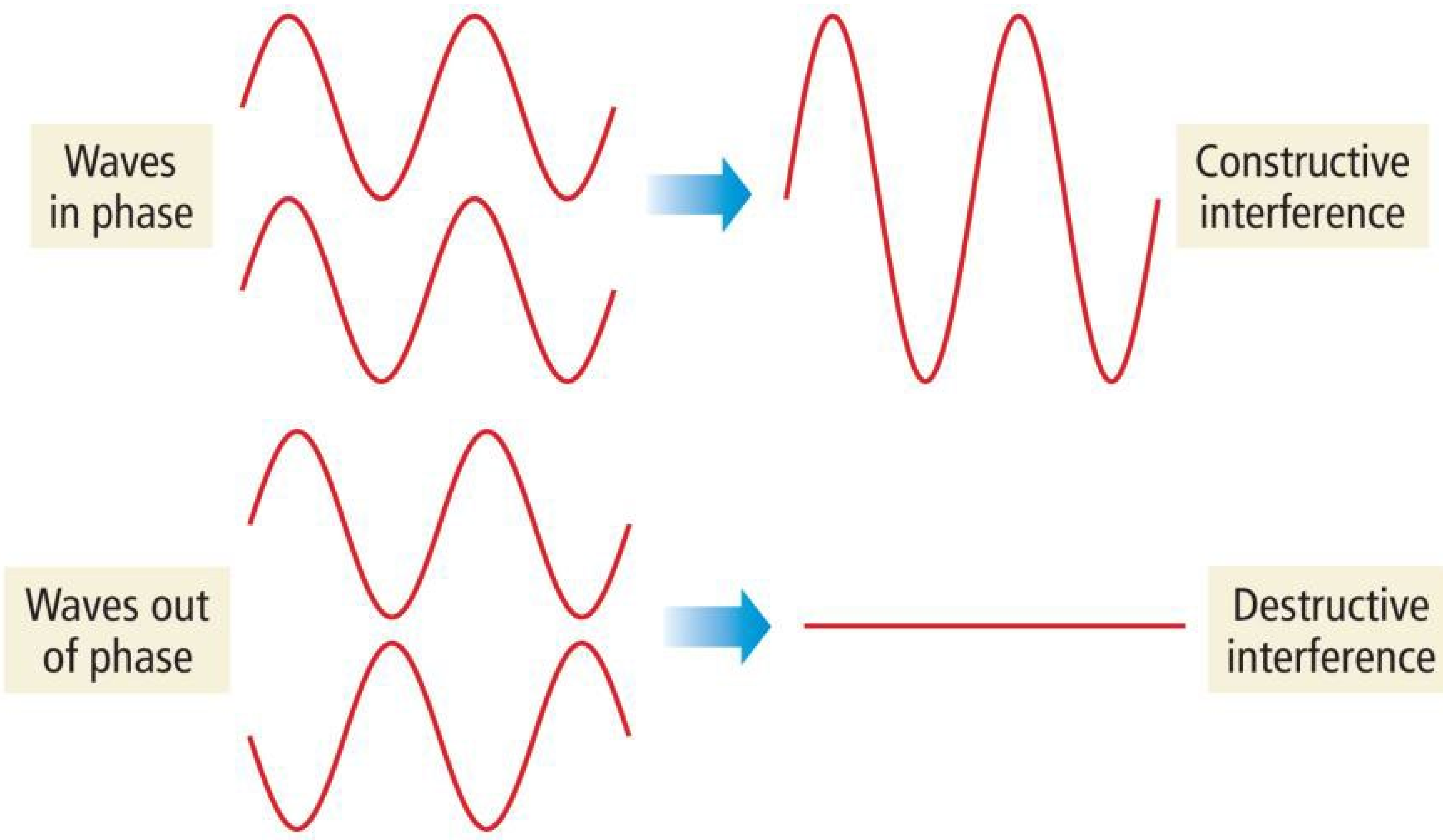
Interference
&
Diffraction

Descriptive wave-like properties

Interference

- the interaction between waves is called **interference**
- when waves interact so that they add to make a larger wave it is called **constructive interference**
  - waves are **in-phase**
- when waves interact so they cancel each other it is called **destructive interference**
  - waves are **out-of-phase**

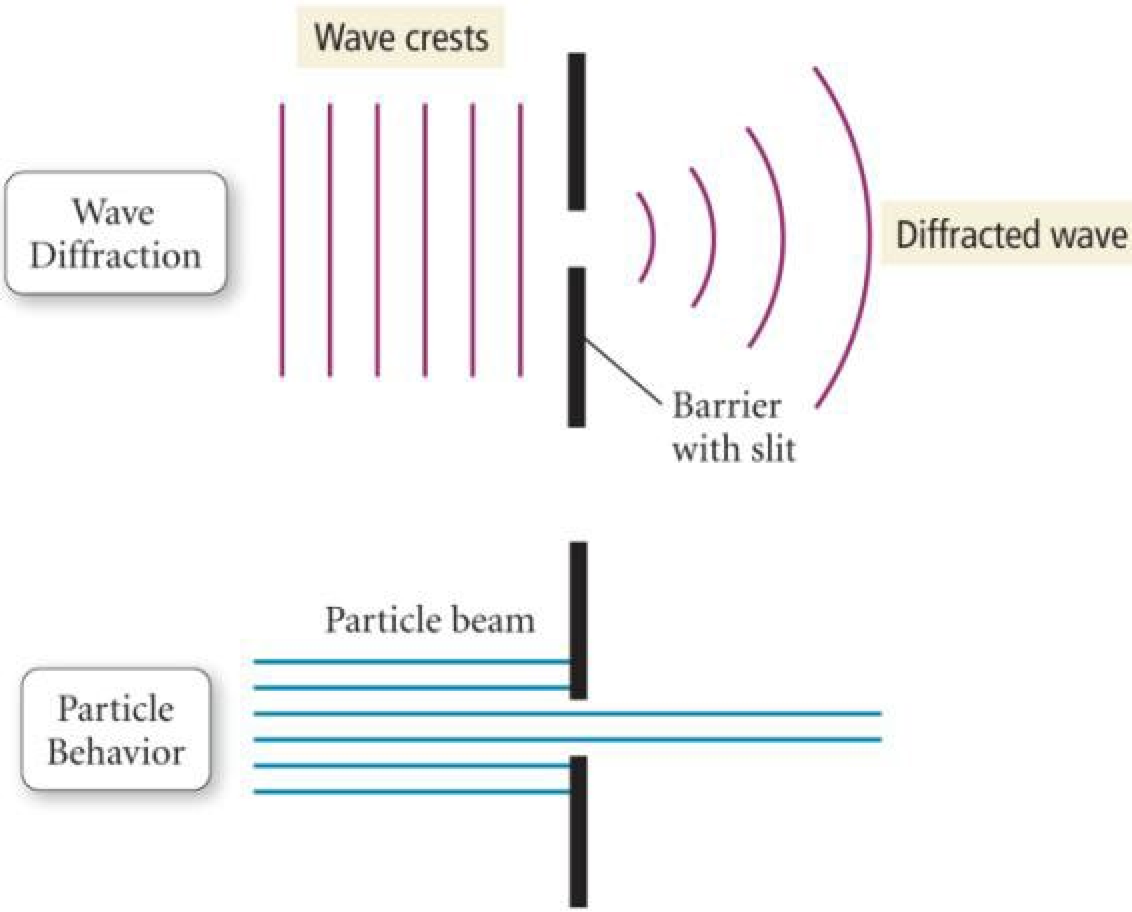
Interference



Diffraction

- when traveling waves encounter an obstacle or opening in a barrier that is about the same size as the wavelength, they bend around it – this is called **diffraction**
  - traveling particles do not diffract
- the diffraction of light through two slits separated by a distance comparable to the wavelength results in an interference pattern of the diffracted waves
- an interference pattern is a characteristic of all light waves

Diffraction



2-Slit Interference

This experiment demonstrates that light and matter can display characteristics of both classically defined waves & particles.

When monochromatic light passes through two slits it, illuminates on a distant screen, displaying a characteristic pattern of bright and dark.

This interference pattern is caused by the superposition of overlapping light waves.

- **Both light & waves can be characterized by wavelength and frequency.**

- **All electromagnetic radiation moves at the speed of light (*c*).**

- **Max Planck first analyzed data from the emission of light from hot, glowing solids. He observed that the color of the solids varied with temperature. Furthermore, Planck suggested that a relationship exists between energy of atoms in the solid and wavelength. This led to the following equation:**

$$\nu\lambda = c$$

Speed of Energy Transmission

$$\nu\lambda = c$$

This equation has multiple interpretations. If the wavelength is long, there will be fewer cycles of the wave passing a point per second; thus, the frequency will be low. Conversely, for a wave to have a high frequency, the distance between the peaks of the wave must be small (short wavelength).

In summary, an inverse relationship exists between frequency and wavelength of electromagnetic radiation as the speed of light is always constant.

Energy can be released (or absorbed) by atoms in discreet chunks (also known as quantum or photons) of some minimum size; that is, energy is quantized.

It is emitted or absorbed in whole number units of $h\nu$.

Collectively, we say that:

$$E = nh\nu = nhc/\lambda$$

where
n = *the quantum number,* h = Planck's constant (6.626×10^{-34} J s), ν = frequency, λ = wavelength, and c = speed of light (3.0×10^{8} m/s).

Energy (E) is generally expressed in units of Joules (J), where this actually implies J/atom. n = 1 for ground state

Electromagnetic Spectrum

Electromagnetic radiation is produced by the combination of electrical and magnetic fields which are at right angles to one another (i.e. perpendicular). The various types of waves (spectrum) include:

radio waves, microwaves, infrared, visible light, ultraviolet, x-rays, cosmic rays, and gamma rays.

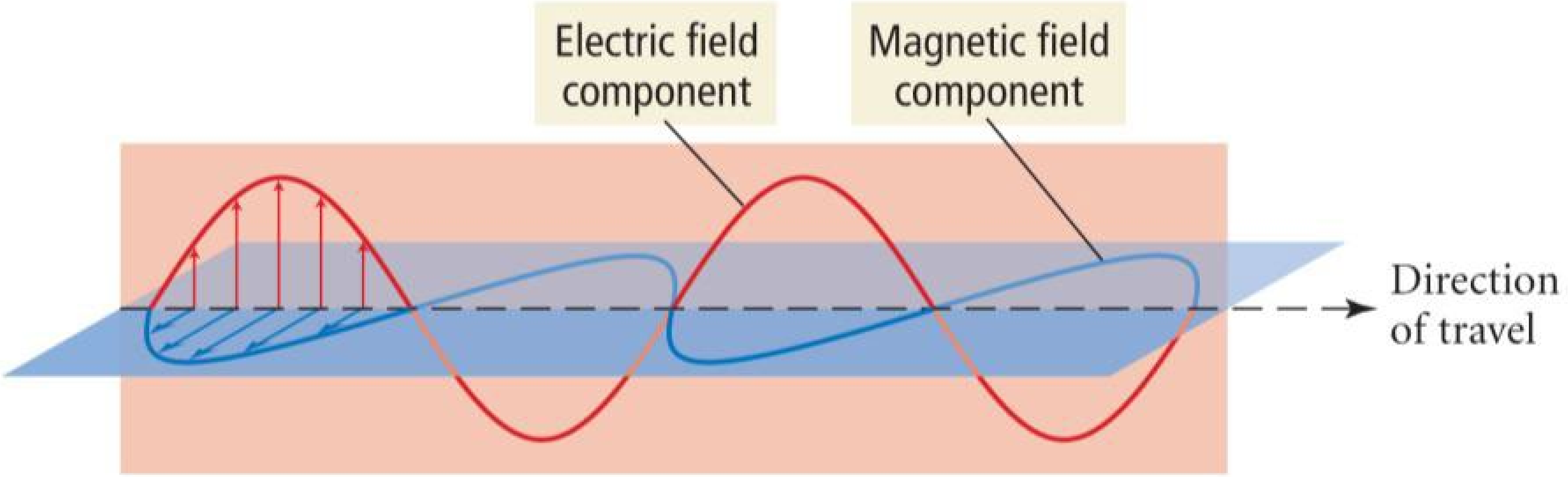
All electromagnetic waves travel at the speed of light; they differ from one another by their corresponding wavelengths and frequencies.

Increasing Frequency (ν) and Energy (E) →

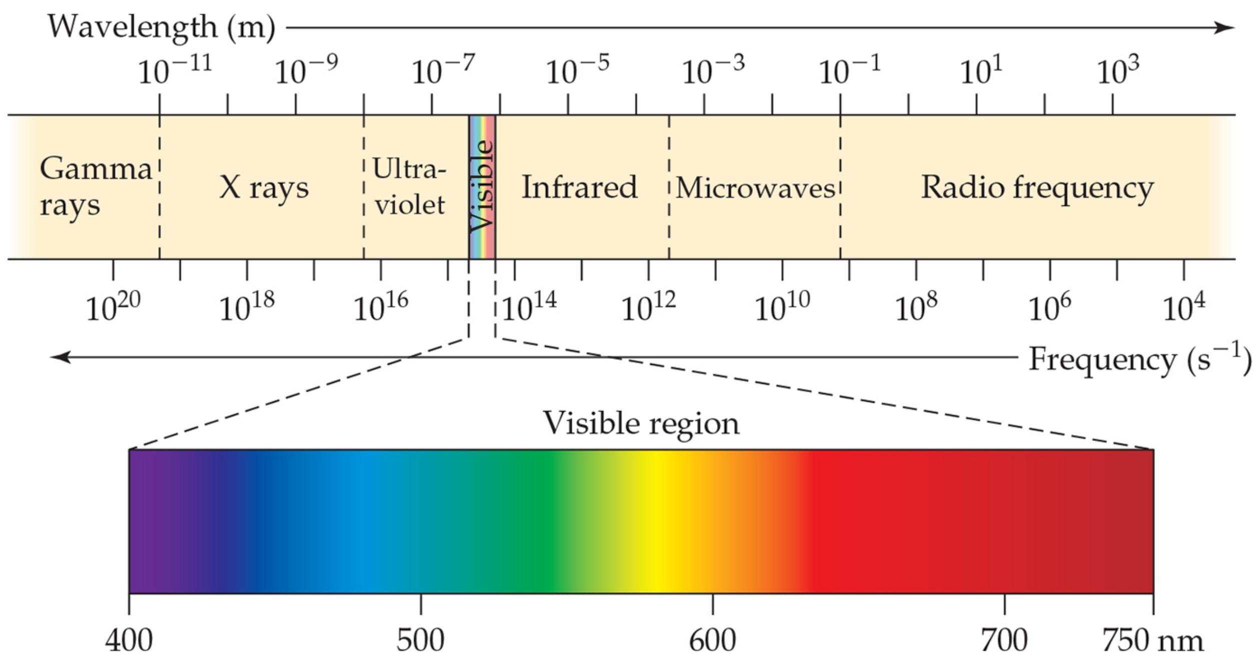
Radio Micro IR Visible UV X-ray Cosmic Gamma

← **Increasing Wavelength (λ)**

Electromagnetic Radiation



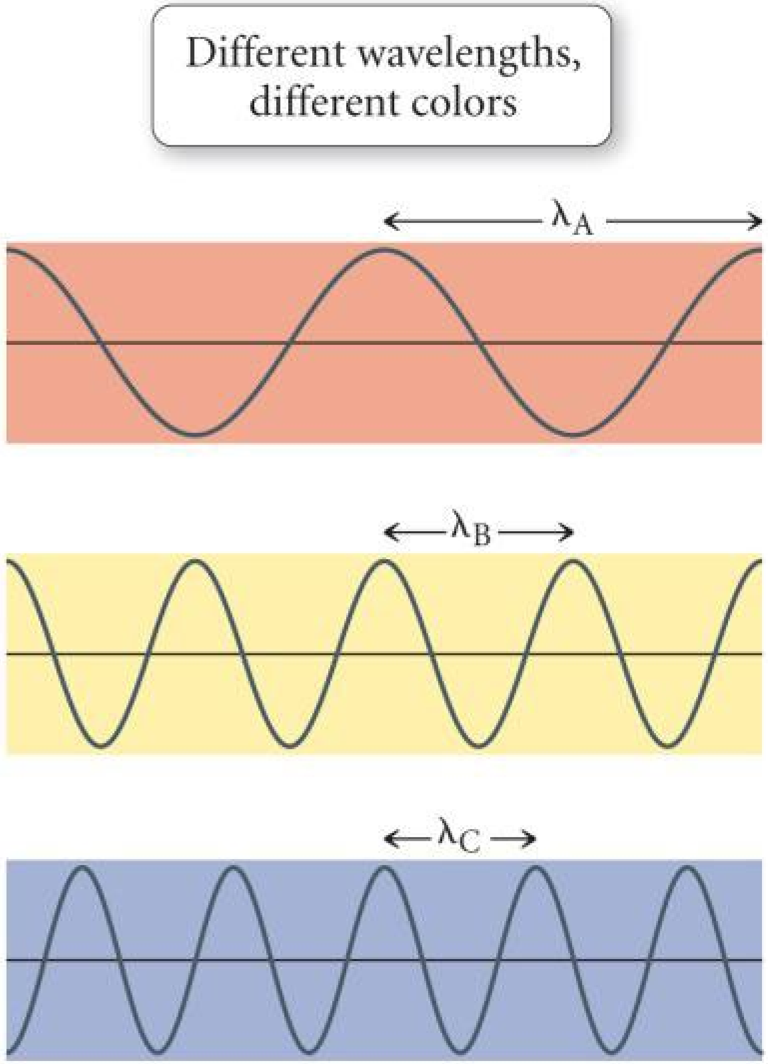
Electromagnetic Radiation [0]

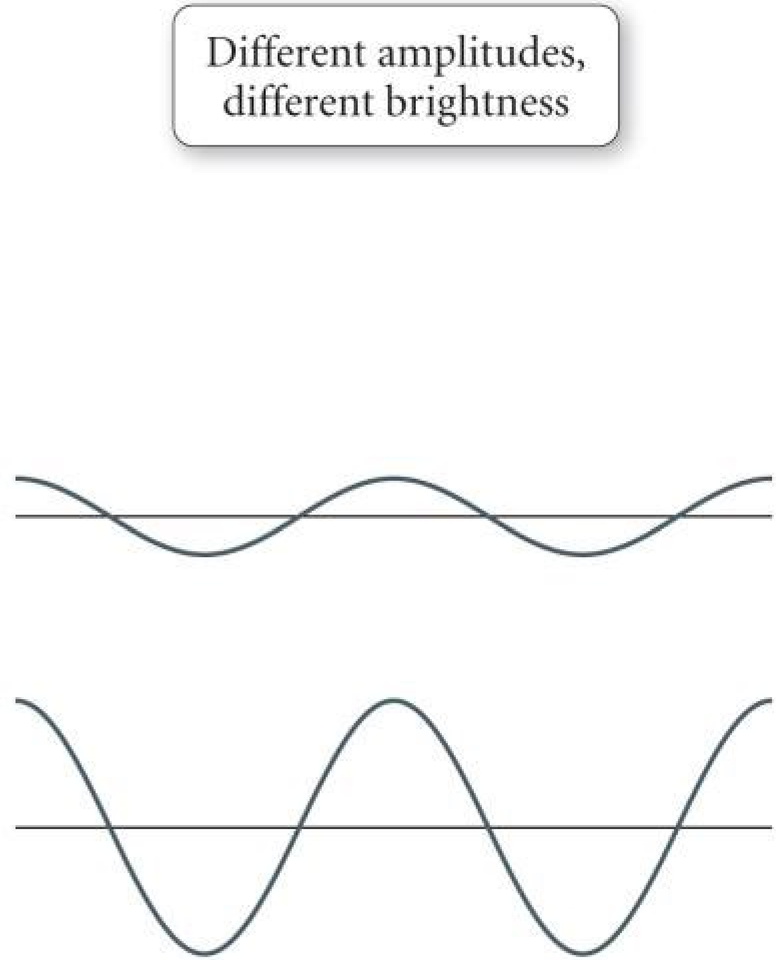


- All electromagnetic radiation travels at the same velocity: The speed of light (c) is 3.00×10^8 m/s.

$$c = \lambda \nu$$

Amplitude & Wavelength





Electromagnetic Radiation

Table 6.1 Common Wavelength Units for Electromagnetic Radiation

Unit	**Symbol**	**Length (m)**	**Type of Radiation**
Angstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Television, radio
Kilometer	km	1000	Radio

- There are many types of electromagnetic radiation.
- They have different wavelengths and energies from each other.
- The typical wavelength unit used vary based on the lengths.

RADIATION SOURCE	TYPE OF INTERACTION WITH MATTER
X - RAY	energy transfer results in an inner shell electron being ejected causing other electrons to cascade (emit) down to lower levels. High energy & short wavelength.
UV/Vis	energy is transferred to outershell electron resulting in the excitation of that electron which eventually cascades back down to lower(ground) energy state.
Ir	energy is transferred to molecule causing the molecule to vibrate; sometimes even lower energy is emitted back out or the energy is lost as heat.
Microwave	energy is transferred to molecule causing the molecule to vibrate and rotate; the higher initial energy is lost as vibrational and rotational energy and as heat. Low energy and long wavelength.

LIGHT

VISIBLE LIGHT IS ORDERED AS:

R	O	Y	G	B	I	V
red	orange	yellow	green	blue	indigo	violet

700nm ... 380nm

low energy ... high energy

long wavelength ... short wavelength

Example:

a) What frequency is associated with a wavelength of 634.9 nm?

b) Identify this radiation.

a) $\nu = c/\lambda$

$\nu = (3\text{x}10^{8}\ \text{m/s})/(6.349\text{x}10^{-7}\ \text{m}) = 4.725\text{x}10^{14}\ \text{s}^{-1}$

b) red-orange light (visible) –it is the cusp.

LIGHT

VISIBLE LIGHT IS ORDERED AS:

R	O	Y	G	B	I	V
red	orange	yellow	green	blue	indigo	violet
700nm						380nm
low energy						high energy
long wavelength						short wavelength

Example:

a) What frequency is associated with a wavelength of 488.6 nm?

b) Identify this radiation.

a) $\nu = c/\lambda$

$\nu = (3 \times 10^{8}\ m/s)/(4.886 \times 10^{-7}\ m) = 6.140 \times 10^{14}\ s^{-1}$

b) Blue-Green light (visible)

LIGHT
ELECTROMAGNETIC RADIATION

Example:

A radiation source has a frequency of 2.35 x 10^{14} hertz,

a) what is the wavelength & energy associated with this light

b) identify the type of radiation.

$\lambda = c/\nu$

$\lambda = (3x10^{8}\ m/s)/(2.35x10^{14}\ s^{-1}) = 1.28x10^{-6}m\ (1x10^{9}\ nm/1m)$

$\lambda = 1276\ nm.$

$E=hv = (6.63x10^{-34}Js)(2.35x10^{14}\ s^{-1})=1.56x10^{-19}J$

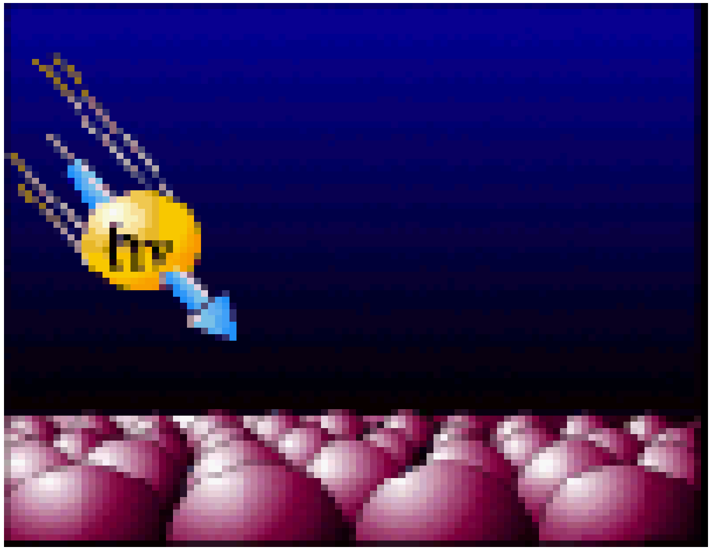
Infrared light

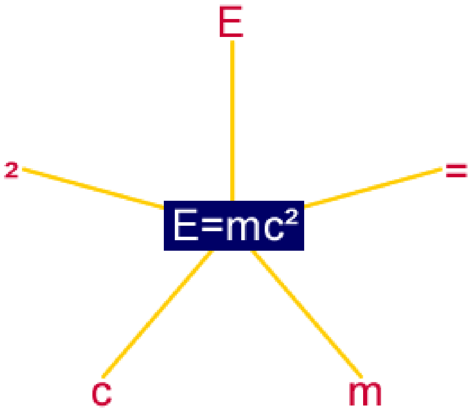
Electronic Properties Not Explained by Waves

- Three observed properties associated with how atoms interact with electromagnetic radiation can **Not** be explained by waves:
  1) the emission of light from hot objects (**blackbody radiation**)
  2) the emission of electrons from metal surfaces on which light is shone (the **photoelectric effect**)
  3) emission of light from electronically excited gas atoms (**emission spectra**)

Einstein's Photoelectrical Effect

If you use just the right wavelength on just the right material, the energy can be transferred to the matter. In some cases ejecting an electron. This is how your remote control, TV, microwave and many other devices work.





Energy can be transformed into matter with enough speed.

Photoelectric Effect

Consider incident radiation which consists of a stream of photons of energy $h\nu$.

Once these particles strike the surface of a metal, the energy is absorbed by an electron.

If the energy of the photon is less than the energy required to remove an electron from the metal, then an electron will NOT be ejected.

Moreover, the energy required to remove an electron from the surface of a metal is called the *work function* (Φ) or ($h\nu_o$) of the metal.

However, if the energy of the photon is greater than the work function, then an electron is ejected with a kinetic energy equal to the difference between the energy of the incoming photon and the work function.

That is: $$KE_{electron} = \frac{1}{2}mv^2 = h\nu - h\nu_o$$

where

m = mass, v = velocity, *h* = Planck's constant, and ν = frequency.

Photoelectric Effect

These results, known as the photoelectric effect, can be summarized alongside with Einstein's theory:

1. **An electron can be driven out of the metal only if it receives at least a certain minimum energy, Φ, from the photon during the collision. Therefore, the frequency of the radiation must have a certain minimum value if electrons are to be ejected. This minimum frequency depends on the work function and hence on the identity of the metal.**

2. **Provided a photon has enough energy, a collision results in the immediate ejection of an electron.**

3. **The kinetic energy of the ejected electron from the metal increases linearly with the frequency of the incident radiation according to the equation $\frac{1}{2} mv^2 = h\nu - h\nu_o$.**

Photoelectric Effect

$$KE_{electron} = \tfrac{1}{2} mv^2 = h\nu - h\nu_o$$

where m = mass, v = velocity, *h* = Planck's constant, and ν = frequency.

Ejected Electrons

- One photon at the threshold frequency gives the electron just enough energy for it to escape the atom.
  - **Binding energy, ϕ**
- When irradiated with a shorter wavelength photon, the electron absorbs more energy than is necessary to escape.
- This excess energy becomes kinetic energy of the ejected electron.

$$\text{Kinetic Energy} = E_{\text{photon}} - E_{\text{binding}}$$

$$KE = h\nu - \phi$$

The Photoelectric Effect.

Q. Calculate the ~ionization/binding energy of an Iridium atom, given that radiation of wavelength 76.2 nm produces electrons with a speed of 2980 km/s.

If the photon energy is less than the work function, no electrons are emitted!

Conditions: $\nu < \nu_o$ means NOT enough energy to remove an electron! Ionization is positive – it is the amount of energy added to the system to eject an electron. Must have $\nu > \nu_o$ for enough excess energy to remove electron. 76.2 nm is in the extreme UV range, Calculate the minimum wavelength that can be used to eject an electron under these conditions?

To calculate the minimum we must have $h\nu >$ KE or $4.045\text{x}10^{-18}$ J since KE is the . so….

$4.045\text{x}10^{-18} = 6.63\text{x}10\text{-}34\ \nu$ so $\nu = 6.10\text{x}10^{15}$ /s

$\lambda = c / \nu$ so $\lambda = 3\text{x}10^{8} / 6.10\text{x}10^{15} = 4.91 \text{ x } 10^{-8}$ m or less than 49 nm.

The Photoelectric Effect.

Q. Calculate the ~ ionization (binding) energy of an Iridium atom, given that radiation of wavelength 45 nm produces electrons with a speed of 2980 km/s.

$KE_{e-} = \frac{1}{2} mv^2 = h\nu - h\nu_o$ *Which represents ionization energy?*

"the energy required to remove an electron from the surface of a metal is called the work function (Φ) or ($h\nu_o$) of the metal."

Next get all units the same:

45 nm is 45×10^{-9} m; 2980km/s is 2980×10^{3}m/s

Then convert 76.2 nm to frequency

$$\nu = c/\lambda = 3 \times 10^{8} \text{ m/s} / 45 \times 10^{-9}\text{m} = 6.67 \times 10^{15} \text{ hz}$$

$$h\nu_o = h\nu - \frac{1}{2} mv^2$$

$$= (6.63x10^{-34} Js)(6.67 \times 10^{15}/s) - 0.5(9.109 \times 10^{-31}kg)(2.980 \times 10^{6} m/s)^2$$

$$h\nu_o = 375 \times 10^{-19} \text{ J}$$

de Broglie Relation and the Wave-Particle Duality of Matter

$\lambda = h/\mathrm{mv}$

Which measurement needs to be converted first?

$$\lambda = \frac{6.63\text{x}10^{-34}\,\text{Js}}{(9.109\text{x}10^{-31}\,\text{kg})\,(1\text{x}10^{7}\,\text{m/s})}$$

$\lambda = 7.279\text{x}10^{-11}$ **m** for units: $\dfrac{\text{kgm}^2\ (\text{s})\ (\text{s})}{\text{kg m s}^2}$

0.07279 nm

or better

0.7279 Å X-ray

Example: If an electron travels at a velocity of 1.000 x 10^7 m/s and has a mass of 9.109 x 10^{-28} g, what is its wavelength?

Heisenberg Uncertainty Principle

Heisenberg determined that there is a fundamental limitation to just how precisely one can know both the position and the momentum of a particle at a given time. That is,

$$\Delta x \bullet \Delta p \geq h/4\pi$$

where x = the locati linear momentum, and h = Planck's co ionship means that the more precisely w e's motion, the less precisely we can know its momentum, and vice versa. The uncertainty principle implies that we cannot know the exact path of the electron as it moves around the nucleus. It is therefore not appropriate to assume that the electron is moving around the nucleus in a well-defined orbit.

$$\Delta mv \geq h/4\pi \Delta x$$

$$\Delta v \geq h/4\pi m \Delta x$$

$$\Delta v \geq 5.8x10^{7} m/s$$

Example: An electron with a mass of 9.109×10^{-31} kg is known to have an uncertainty of 1 pm in its position. Determine the uncertainty in its speed.

NIELS BOHR (1885-1962)
A MODEL for THE HYDROGEN ATOM

Bohr built upon Planck's & Einstein's ideas about quantized energy.

States:

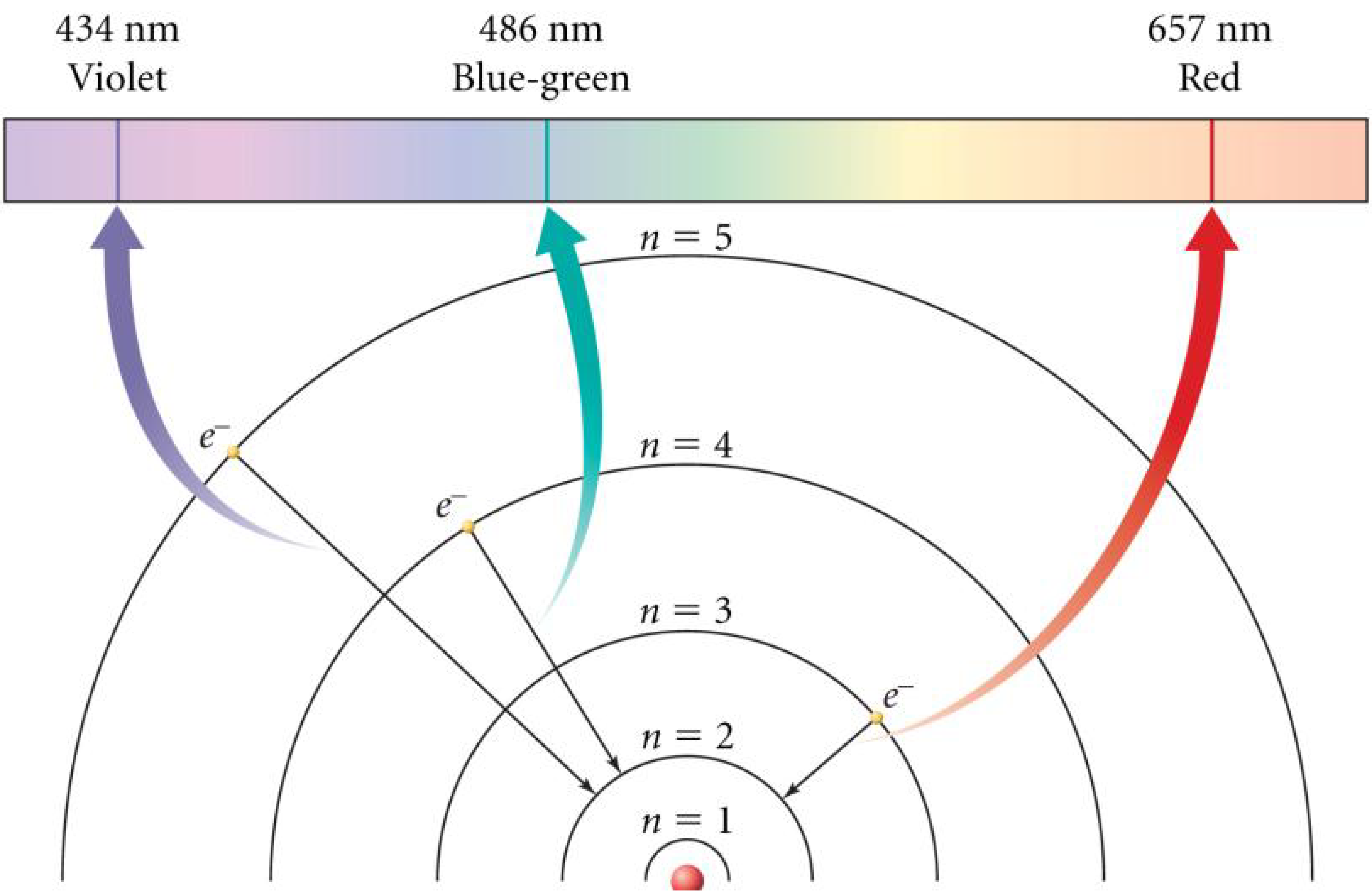
1. **The hydrogen atom has only specific allowable energy levels (quantized).**
2. **The atom does not radiate energy while within an energy level.**
3. **Electrons transition to different energy levels only by absorbing or emitting a photon whose energy equals the difference in energy between the levels.**

$$E_{photon} = E_{final} - E_{initial} = h\nu$$

Limitations:

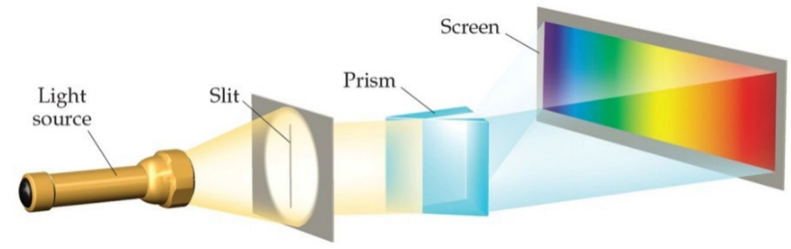
1. **Failed to predict the spectrum for other atoms.** **(does not take into account additional nucleus-electron attractions and electron-electron repulsion)**
2. **Electrons do not move in "orbits"**

The Bohr Model and Emission Spectra

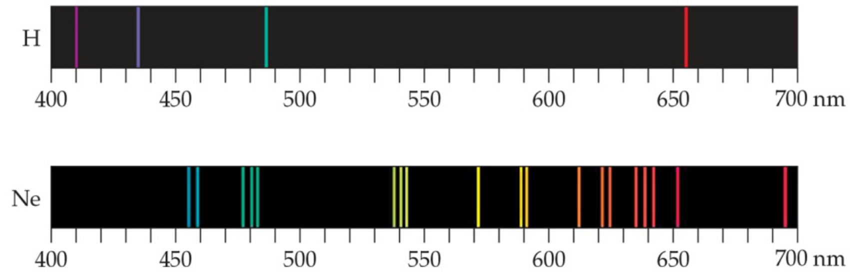


Continuous vs. Line Spectra

- For atoms and molecules, one does not observe a **continuous spectrum** (the "rainbow"), as one gets from a white light source.



- Only a **line spectrum** of discrete wavelengths is observed. Each element has a unique line spectrum.



LINE SPECTRUM

Bohr's model was an attempt to explain how light was emitted when an element was vaporized and then thermally or electrically excited (the flame test or neon sign). Through experimentation it was discovered that each element has a unique line spectrum with specific wavelengths that can be used to identify it.

RYDBERG EQUATION:

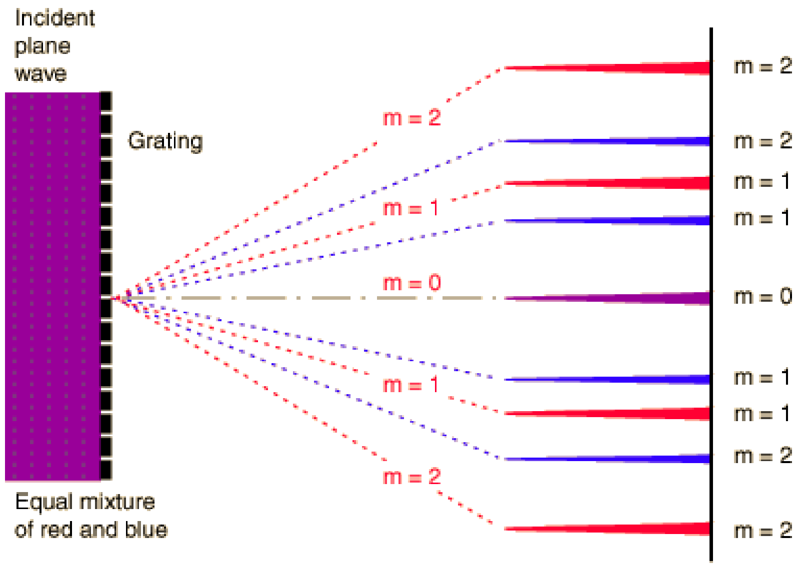
An empirical equation used to predict the position and wavelength of the lines in a given series in a specific region of the EM spectrum.

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

R = Rydberg constant $1.096776 \times 10^{7}\ m^{-1}$

Monochromators: Defraction Gratings

- Diffraction gratings are a surface with closely spaced parallel lines



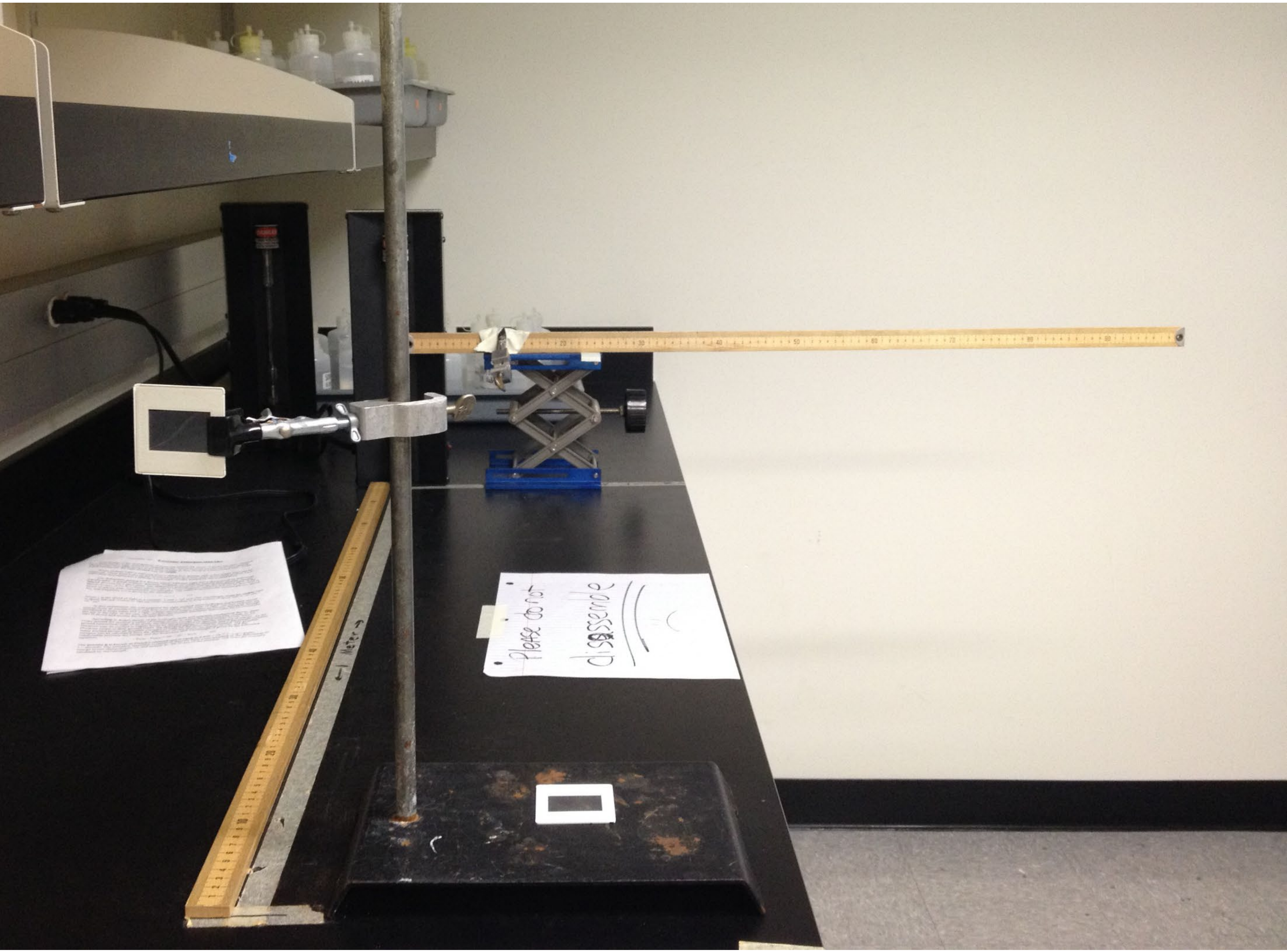
distance between slits

diffraction order

wavelength!

$$a\sin(\theta) = n\lambda$$

- These can be semi-transparent gratings or ridged mirrors
- After passing though a slit (or bouncing off a ridge) the angle at which the light leaves is given by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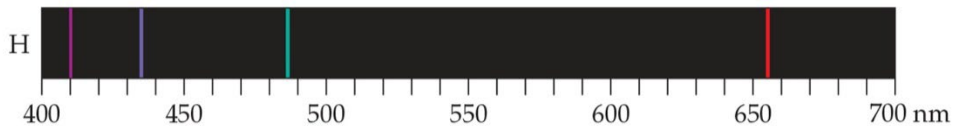
The Hydrogen Spectrum

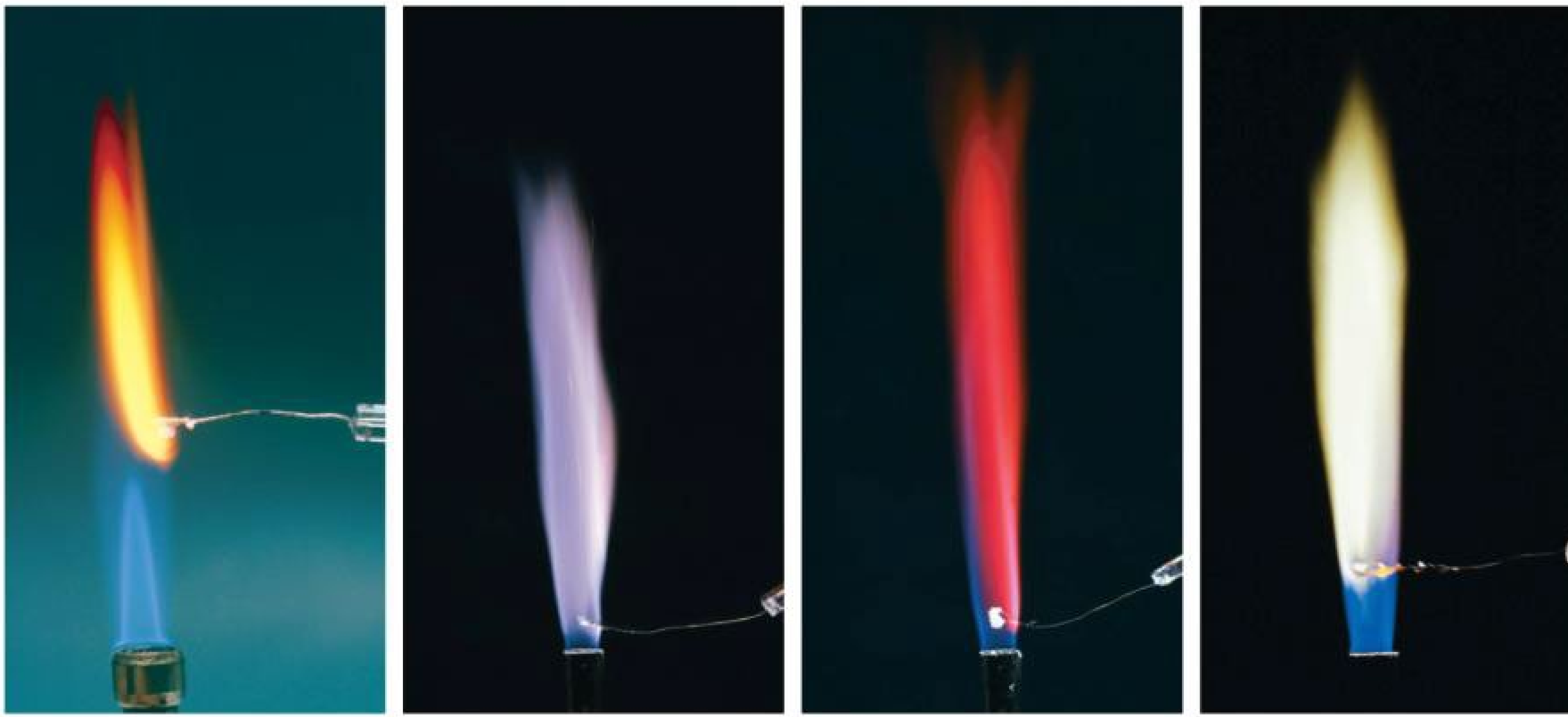


- Johann Balmer (1885) discovered a simple formula relating the four lines to integers.
- Johannes Rydberg advanced this formula. (R_H is called the Rydberg constant.)

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

- Neils Bohr explained **why** this mathematical relationship works.

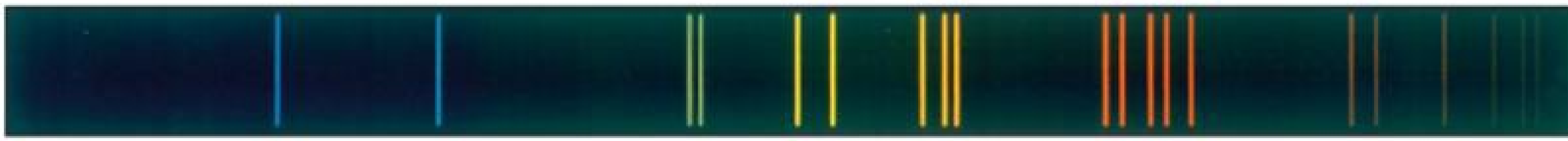
Identifying Elements with Flame Tests



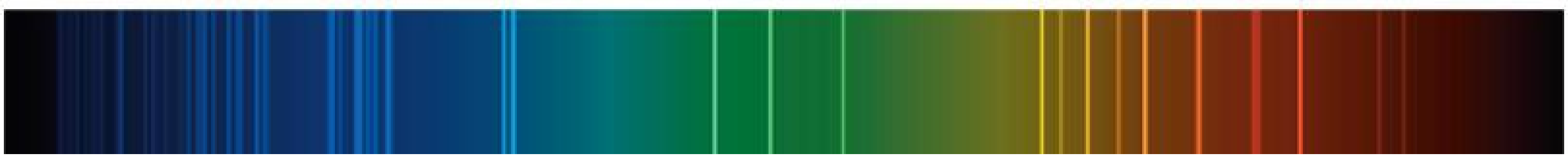
Na K Li Ba

Examples of Spectra

Helium spectrum



Barium spectrum



Oxygen spectrum

Neon spectrum

BOHR'S MODEL & RYDBERG Combined 1913

$R_H = 2.179 \times 10^{-18}$ J - Rydberg constant

The electron in the atom occupies specific energy levels (hν, 2hν, 3hν, etc.) This is called QUANTIZATION

$$E = \frac{R_H}{n^2}$$

The electron may undergo a transition from one energy level to another. Remember that the energy of emitted photon=h*v*=E_i - E_f

$$h\nu = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

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

These equations can be used to determine the λ or *v* of the hydrogen atom.

ENERGY STATES OF THE HYDROGEN ATOM

This creates a direct relationship between emission & absorption.

$$E = -2.18 \times 10^{-18}\ J\ (Z^2/n^2)$$

where $R = -2.18 \times 10^{-18}\ J/(hc)$

E : the energy of the atom (derived from classical physics)

Z : the charge of the nucleus

n : the energy level

To find the energy difference between any two levels and predict the spectral lines for the hydrogen atom:

$$\Delta E = h\nu = hc/\lambda$$

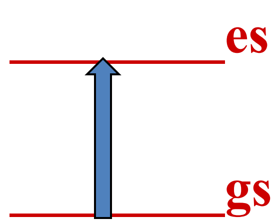
$$h\nu = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\Delta E = E_f - E_i = -2.18 \times 10^{-18}\ J\ (n_f^{-2} - n_i^{-2})$$

ENERGY STATES OF THE HYDROGEN ATOM

Absorption: **When an electron, in its ground state, absorbs energy from a photon that electron is promoted to a higher energy level (called the excited state).**

If $n_i < n_f$ - energy is absorbed

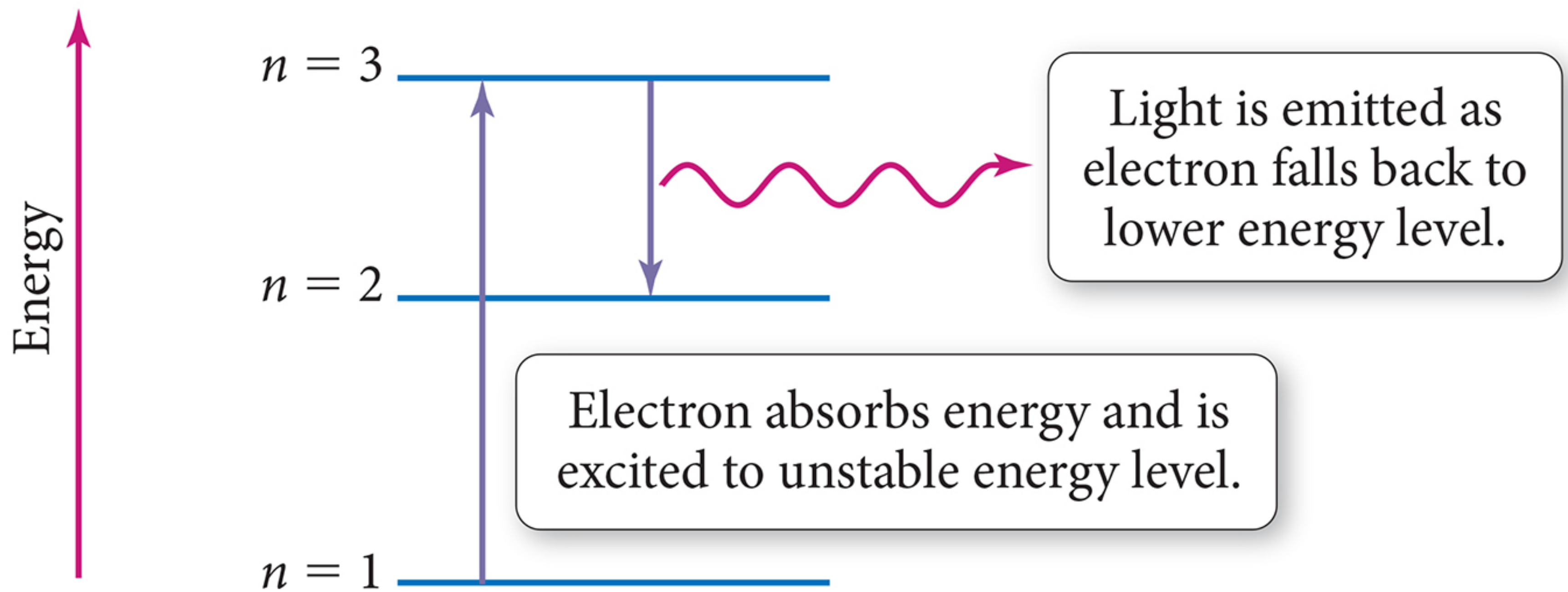


the electron jumps from a lower energy level to a higher one.

Emission **is when an electron in an excited state loses energy and returns to a lower energy level.**

Quantum Leaps

Excitation and Radiation



If $n_i > n_f$ - energy is emitted

______es
↓
______gs

the electron jumps from a higher energy level down to a lower energy level

$$\Delta E = -2.18 \times 10^{-18} \text{ J } (n_f^{-2} - n_i^{-2})$$
$$= -2.18 \times 10^{-18} \text{ J } (2^{-2} - 4^{-2})$$
$$= -4.09 \times 10^{-19} \text{ J (-emission)}$$

$\Delta E = hc/\lambda$ so $\lambda = hc/\Delta E$

$$\lambda = 6.63\text{x}10^{-34}\text{Js}(3\text{x}10^{8}\text{m/s})/\ 4.09\text{x}10^{-19}\text{J}$$

$\lambda = 489$ nm green

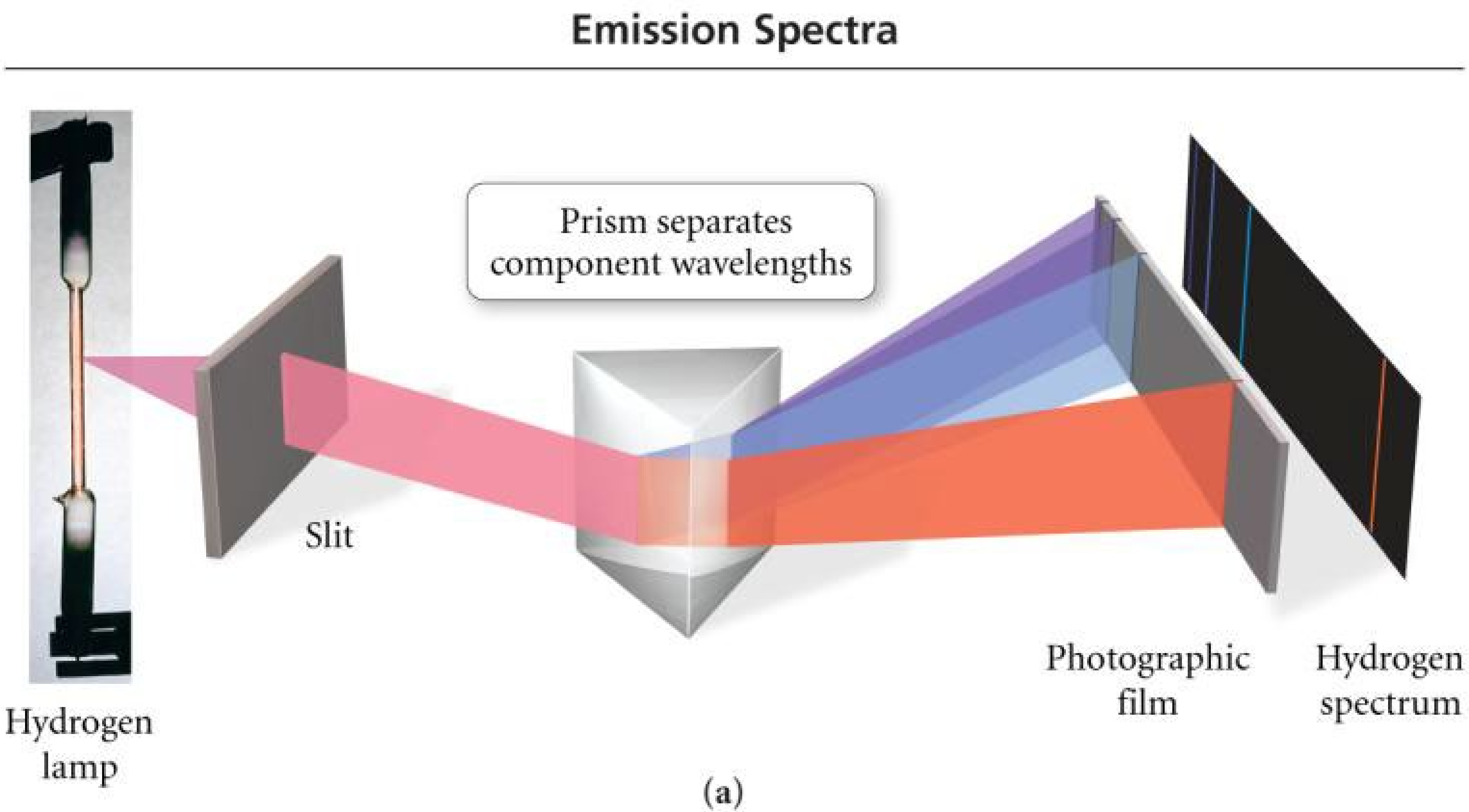
If $n_i < n_f$ - energy is absorbed

______es
↑
______gs

the electron jumps from a lower energy level to a higher one.

Example: Calculate the wavelength of light that corresponds to the transition of the electron from n = 4 to n = 2 state of the hydrogen atom. Is the light emitted or absorbed? What color is it?

Emission Spectra



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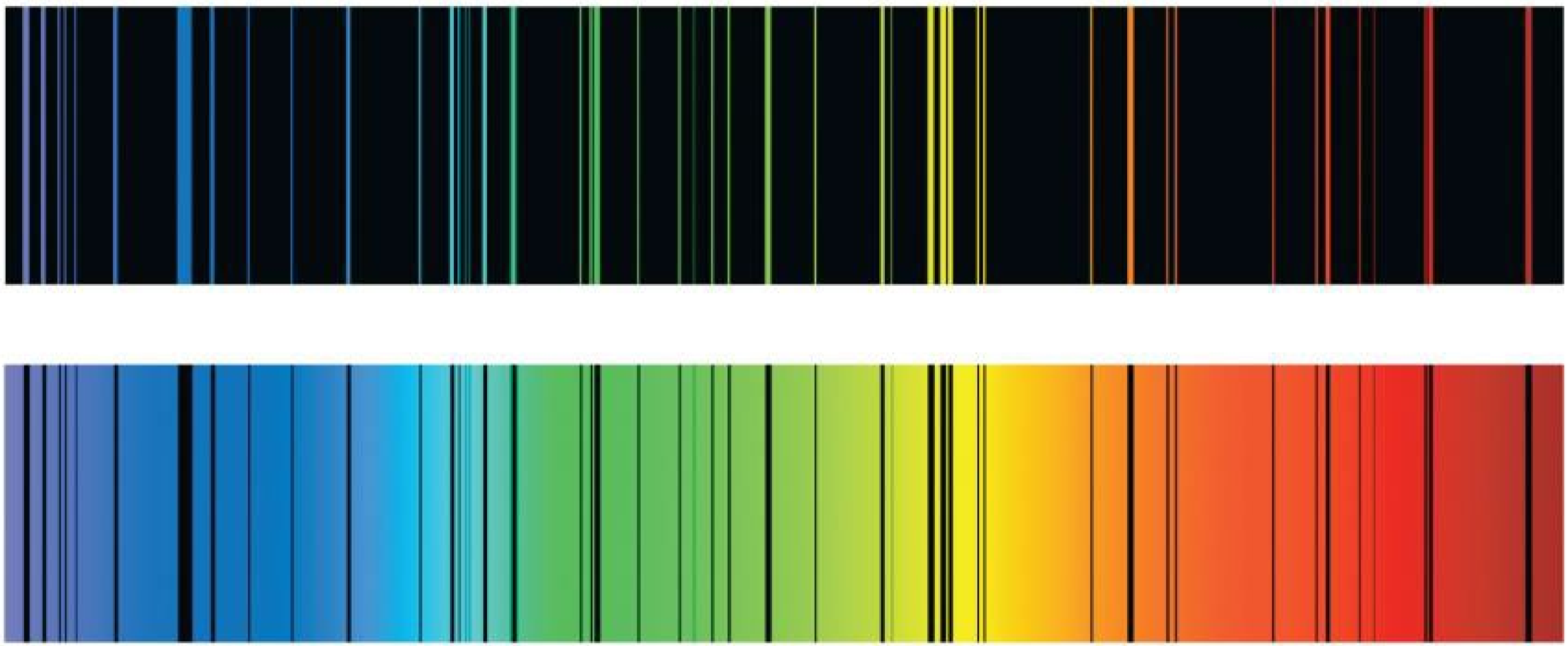
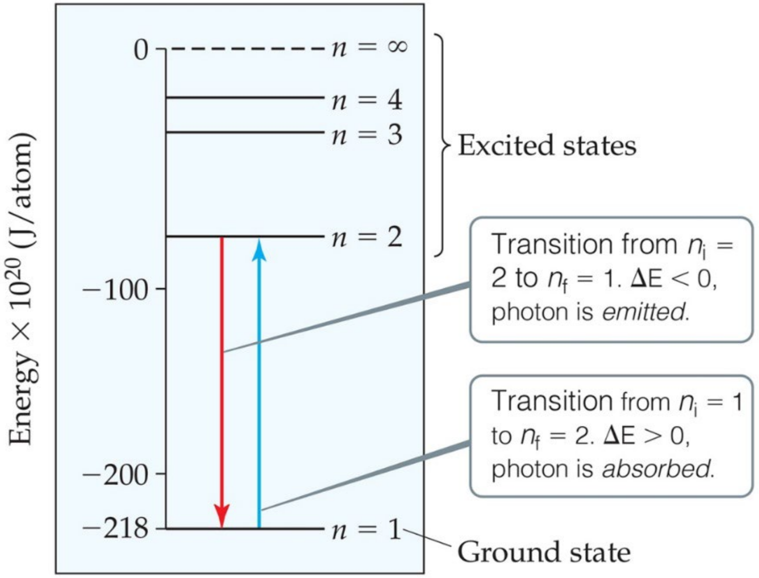
Emission vs. Absorption Spectra



Spectra of Mercury

The Bohr Model (1 of 3)

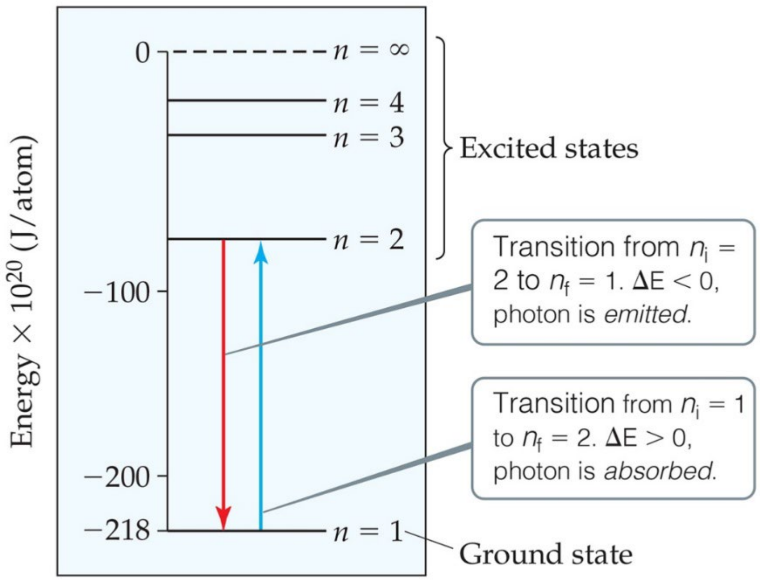
- Niels Bohr adopted Planck's assumption and explained these phenomena in this way:
    1) Only orbits of certain radii, corresponding to specific energies, are permitted for the electron in a hydrogen atom.



The Bohr Model (2 of 3)

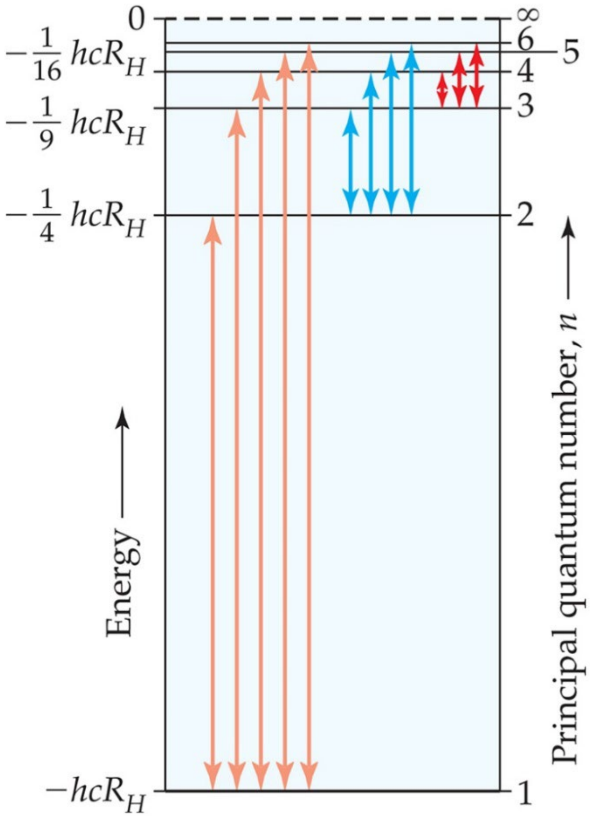
2) An electron in a permitted orbit is in an "allowed" energy state. An electron in an allowed energy state does not radiate energy, and, therefore, does not spiral into the nucleus.

3) Energy is emitted or absorbed by the electron only as the electron changes from one energy state to another. This energy is emitter of absorbed as a photon that has energy $E = h\nu$.



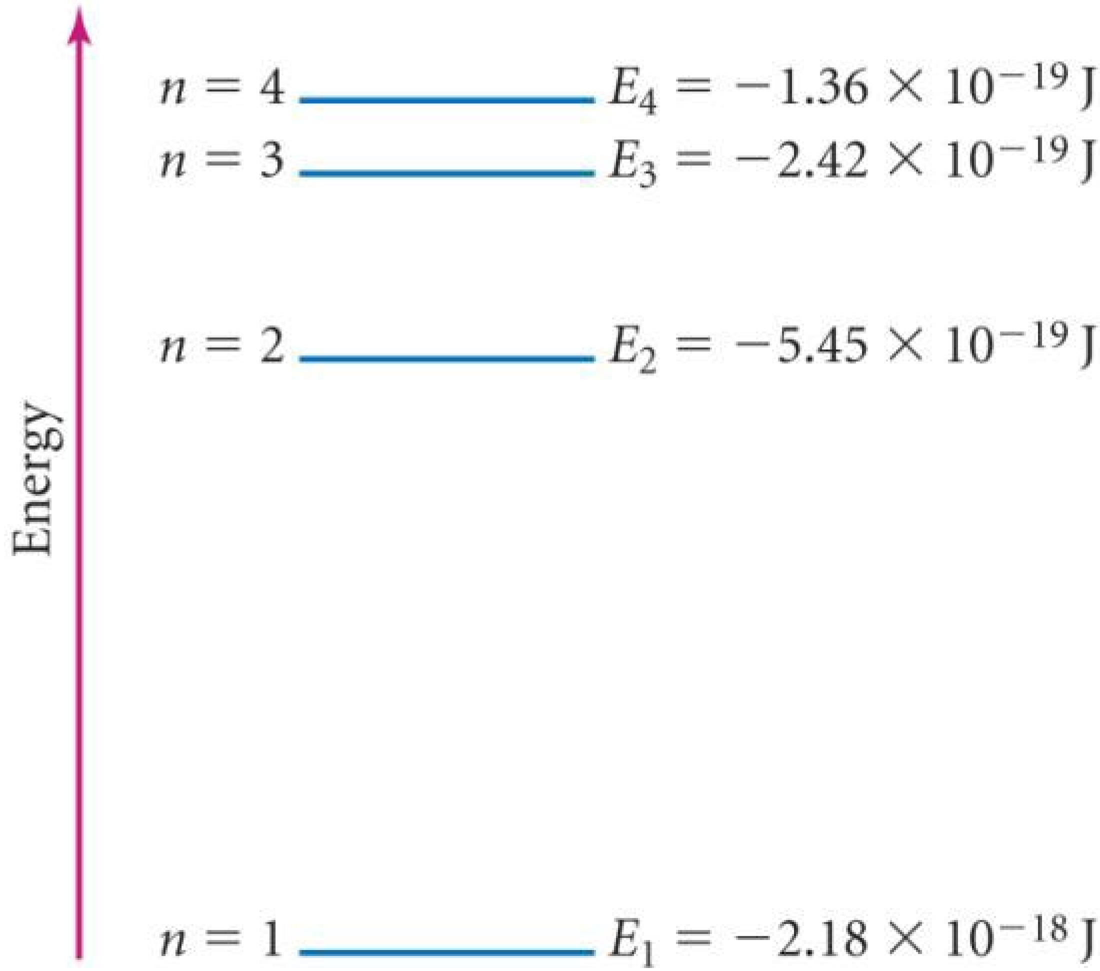
The Bohr Model (3 of 3)

- Electrons in the lowest energy state are in the **ground state**.
- Any energy higher is called an **excited state**.
- Since each orbit as a specific value compared to R_H, transitions from one energy level to another can be calculated:



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

Principal Energy Levels in Hydrogen



Energy Transitions in Hydrogen

- The energy of a photon released is equal to the difference in energy between the two levels between which the electron is jumping.
- It can be calculated by subtracting the energy of the initial state from the energy of the final state.

$$\Delta E_{\text{electron}} = E_{\text{final state}} - E_{\text{initial state}}$$

$$E_{\text{emitted photon}} = -\Delta E_{\text{electron}}$$

$$E_{\text{photon}} = -\left[\left(-2.18\times10^{-18}\ \text{J}\left(\frac{1}{n_{final}{}^2}\right)\right)-\left(-2.18\times10^{-18}\ \text{J}\left(\frac{1}{n_{initial}{}^2}\right)\right)\right]$$

$$\frac{hc}{\lambda} = E_{\text{photon}} = 2.18\times10^{-18}\ \text{J}\left[\left(\frac{1}{n_{final}{}^2}\right)-\left(\frac{1}{n_{initial}{}^2}\right)\right]$$

Bohr Model Revisited

Bohr proposed a model that included the idea that the electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits. Furthermore, Bohr concluded the following as applied to the bright-line spectrum of hydrogen:

1. Hydrogen atoms exist in only specified energy states given by the Rydberg energy equation:

$$E = -2.178 \times 10^{-18} \text{ J } (Z^2/n_{final}^2 - Z^2/n_{initial}^2)$$

where E = Energy (J), Z = atomic number, and *n* = orbital level.

2. Hydrogen atoms can absorb only certain amounts of energy, and no others.

3. When excited hydrogen atoms lose energy, they lose only certain amounts of energy, emitted as photons.

4. The different photons given off by hydrogen atoms produce the color lines seen in the bright-line spectrum of hydrogen. The greater the energy lost by the atom, the greater the energy of the photon.

NOTE:

At first, Bohr's model appeared to be very promising. The energy levels calculated by Bohr closely agreed with the values obtained from the hydrogen emission spectrum. However, when Bohr's model was applied to atoms other than hydrogen, it did not work at all. It was therefore concluded that Bohr's model is fundamentally incorrect for atoms with more than one electron.

SELF-STUDY on Light & Bohr's Model

1. An object with a mass of 5.15×10^{-28} kg is known to have an uncertainty of 2 pm in its position. Determine the uncertainty in its speed.

2. If an object travels at a velocity of 5.0×10^{8} m/s and has a mass of 5.15×10^{-28} g, what is its wavelength?

3. Determine the energy of the line in the spectrum of hydrogen that represents the movement of an electron from a Bohr orbit with $n = 6$ to $n = 4$.

4. Determine the wavelength of light that must be absorbed by a hydrogen atom in its ground state to excite it to the $n = 2$ orbit.

5. Calculate the ionization energy of a rubidium atom, given that radiation of wavelength 58.4 nm produces electrons with a speed of 2450 km/s.