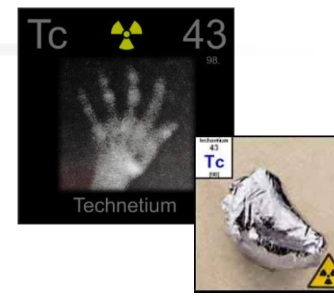
CHEMISTRY 1000

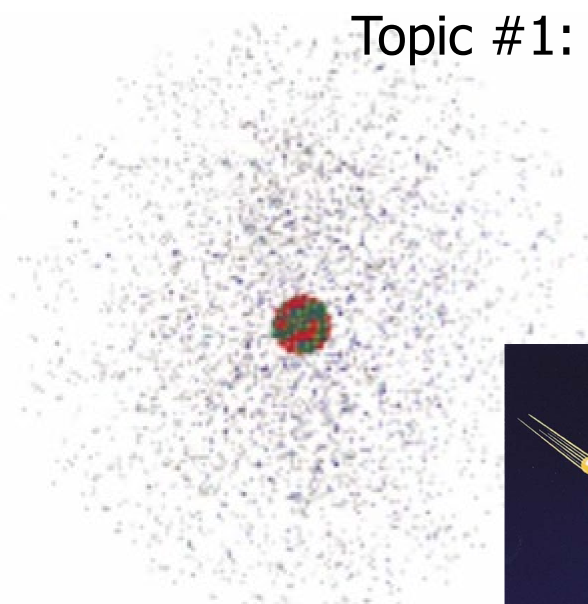


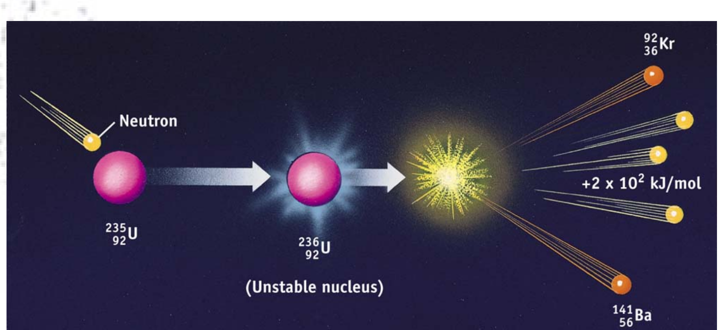
Topic #1: Atomic Structure and Nuclear Chemistry

Fall 2020

Dr. Susan Findlay

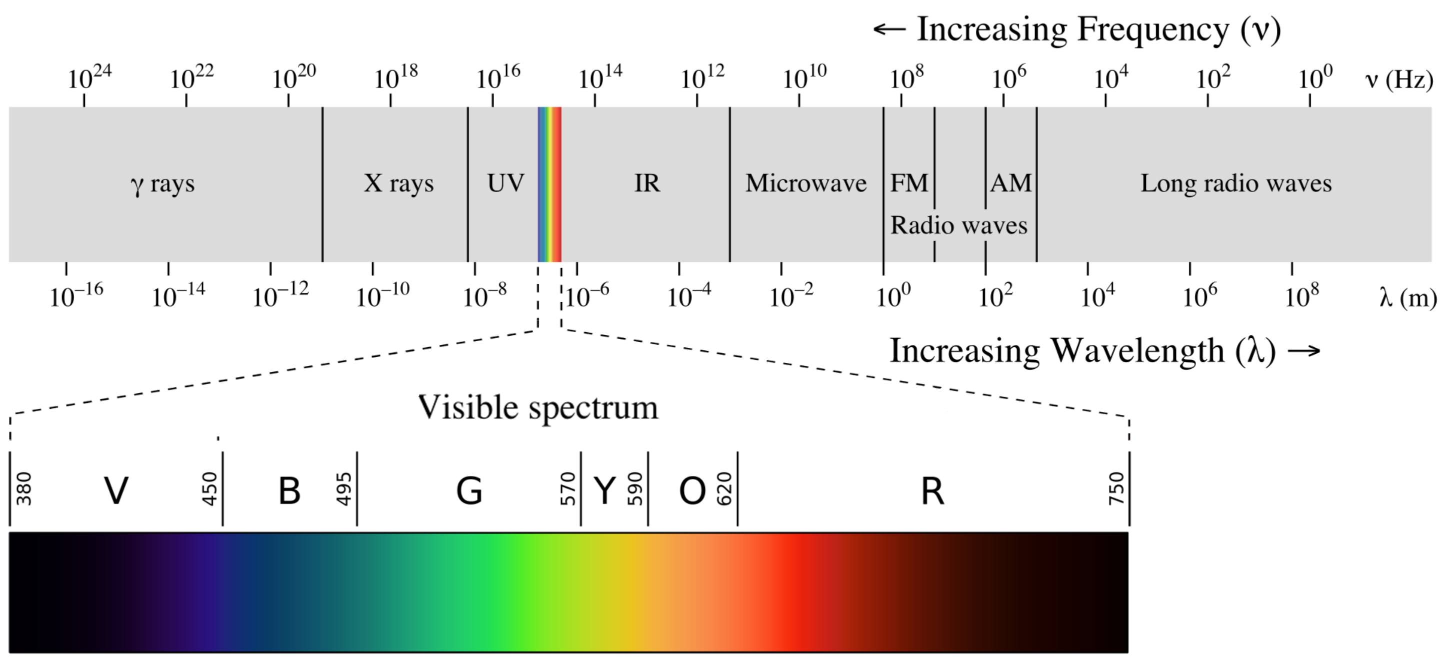
See Exercises 3.1 to 3.3





Light: Wave? Particle? Both!

- Modern models of the atom were derived by studying the relationships between matter and light.
- Society tends to consider visible light, radio waves and x-rays as different; however, they are all forms of **electromagnetic radiation** and all belong to the **electromagnetic spectrum**

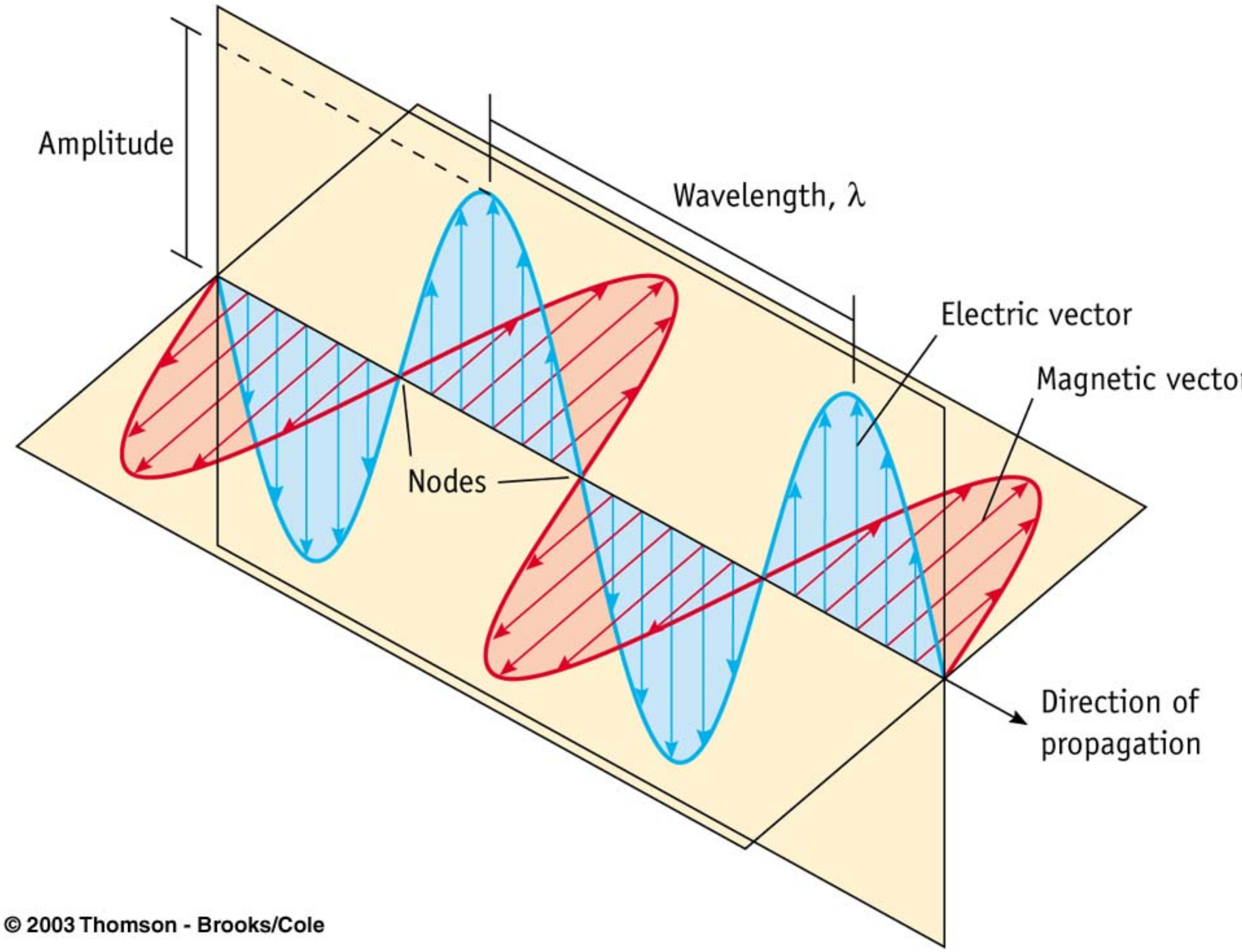


https://upload.wikimedia.org/wikipedia/commons/3/30/EM_spectrumrevised.png

Light as a Wave

- In 1865, James Clerk Maxwell proposed that electromagnetic radiation could be treated as a wave. He knew that:
  - An electric field varying with time generates a magnetic field.
  - A magnetic field varying with time generates an electric field.
  - In the early 1800s, two separate units were used for electric charge: one for electrostatics and one for magnetic fields involving currents. The ratio between the two units was the speed of light!
- While on a quest to explain this “incredible coincidence”, Maxwell mathematically proved that an electromagnetic disturbance should travel as a wave at the speed of light. He therefore concluded that light waves were electromagnetic.
- Maxwell also noted that:
  - Electromagnetic waves do not need matter to propagate.
  - The electric and magnetic fields oscillate in phase – perpendicular both to each other and to the direction of propagation.

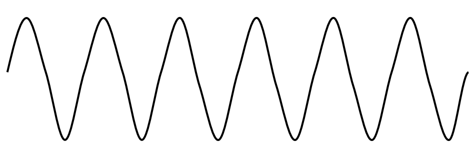
Light as a Wave



Light as a Wave

- Waves are characterized by several interrelated properties:
  - **wavelength** (λ): the distance between successive crests or successive troughs
  - **frequency** (υ): the number of waves passing through a point in a given period of time
  - **amplitude** (A): the height of a wave (from the **node**)
  - **speed** (c for light; v for other waves) = wavelength × frequency

- The speed of light is constant, ($c = 2.99792458 \times 10^8$ m/s), but not all light waves have the same energy:



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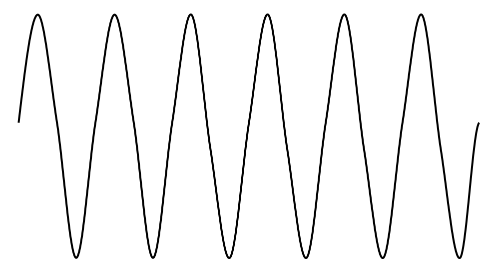
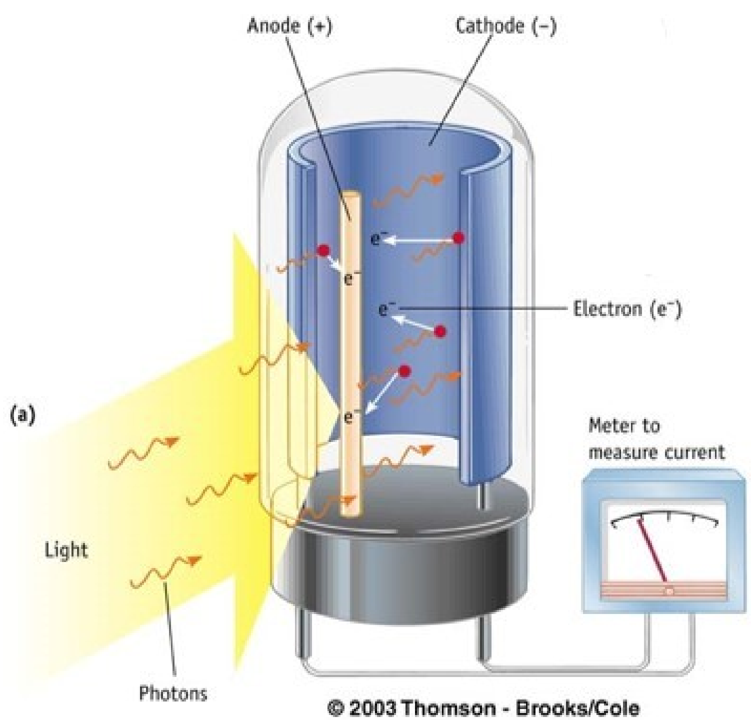
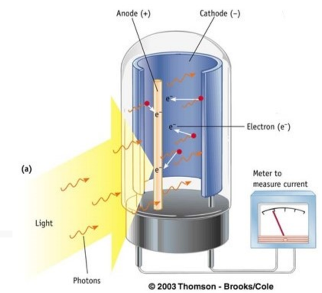


Light as a Particle

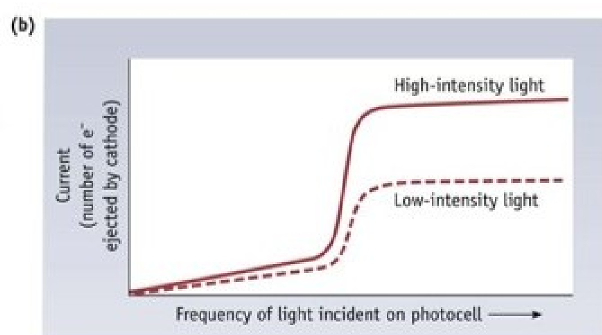
- In 1888, Heinrich Hertz discovered that electrons could be ejected from a sample by shining light on it. This is known as the **photoelectric effect**.



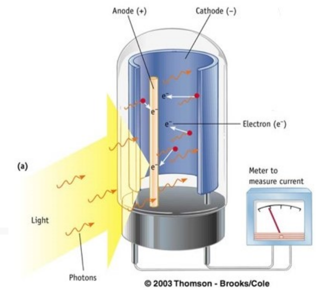
Light as a Particle



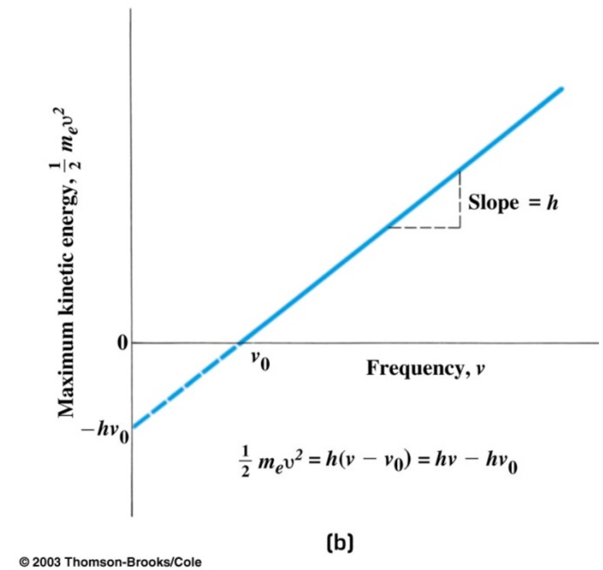
- This experiment shows that light does not only act as a wave.
  - If light only acted as a wave, what should happen to the energy of the ejected electrons as you increase the intensity of the light?
  - What actually happens to the energy of the ejected electrons as you increase the intensity of the light?
  - What does change as you increase the intensity of the light?



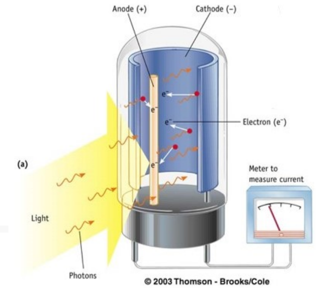
Light as a Particle



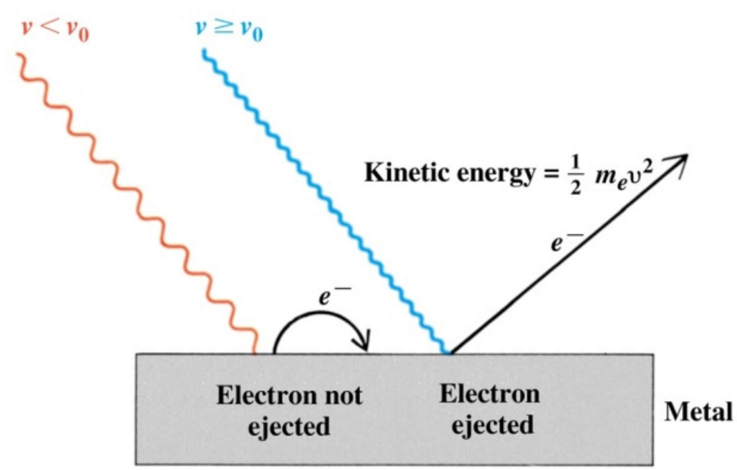
- This experiment shows that light does not only act as a wave.
  - If light only acted as a wave, what should happen to the energy of the ejected electrons as you increase the frequency of the light?
  - What actually happens to the energy of the ejected electrons as you increase the frequency of the light?



Light as a Particle

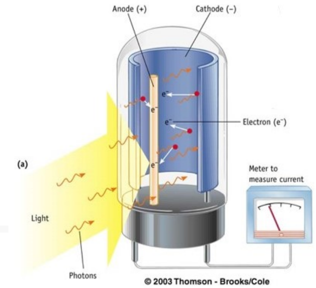


- In 1905, Albert Einstein showed that the photoelectric effect was consistent with treating light as something that came in "parcels" or "particles" – properly termed **photons**.
  - If a photon strikes a metal atom with enough energy to eject an electron, it does.
  - If the photon had more-than-enough energy to eject the electron, the electron carries the rest of the energy as kinetic energy.
  - If a photon striking a metal atom does not have enough energy to eject an electron, the electron isn't ejected and no current flows.



(a)

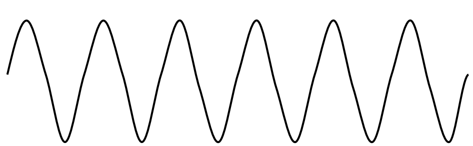
Light as a Particle



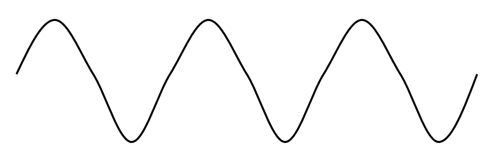
- The energy carried by a photon is directly proportional to its frequency, and can be calculated using **Planck's equation**:

  where **Planck's constant (h)** is 6.626070×10^{-34} J/Hz

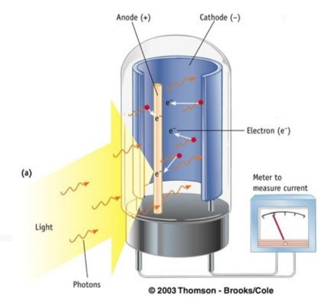
- Which of the waves below corresponds to light with higher energy photons?



vs



Light: Wave? Particle? Both!



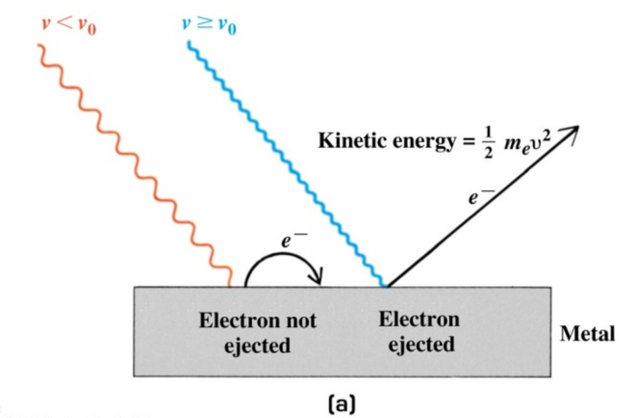
- This also means that if we measure the kinetic energy of the ejected electrons (which can be done by measuring a “stopping potential”), we can calculate the threshold energy for a metal.

$$E_{photon} = E_{threshold} + E_k(electron)$$

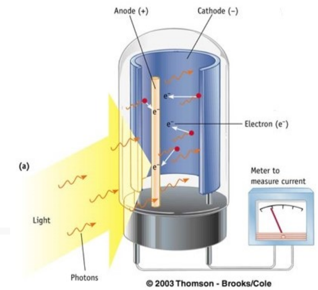
Threshold energy is sometimes referred to as work function.

- Planck’s equation relates the threshold energy to the threshold frequency:

$$E_{threshold} = h \cdot \nu_{threshold}$$

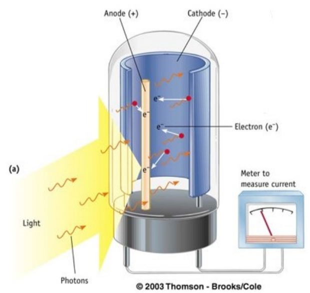


Light: Wave? Particle? Both!



- The threshold energy of zirconium (Zr) is $391\ \frac{kJ}{mol}$.
  - What is the minimum frequency of light that can induce a photoelectric effect in a sample of zirconium?
  - What is the maximum wavelength of light that can induce a photoelectric effect in a sample of zirconium?

Light: Wave? Particle? Both!



- If a sample of zirconium is struck with light with a wavelength of 225 nm, what is the maximum kinetic energy for each electron emitted?

Light: Wave? Particle? Both!

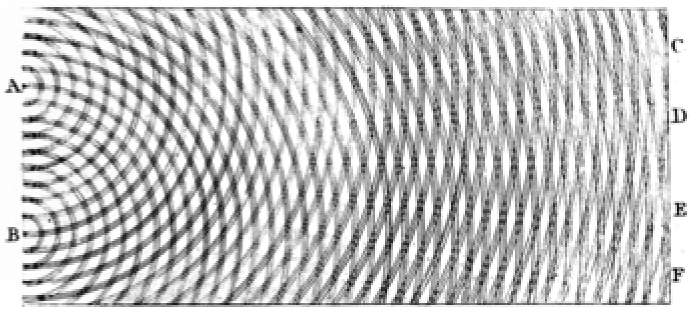
- The discovery that light can act as a particle does not mean that it should no longer be treated as a wave. It has properties of both:

Light is a wave	Light is a particle
It can be diffracted.	Typically, it reacts with matter one photon at a time.
It has wavelength and frequency.	It can transfer "packets" of energy when it strikes matter.
$c = \upsilon\lambda$	$E = h\upsilon$

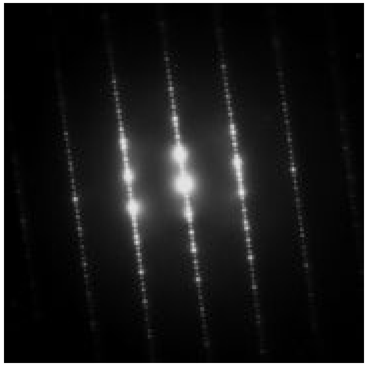
- The wave properties and particle properties of light can be related through the **de Broglie equation**:

Wave-Particle Duality

- Light is not alone in having properties of both waves and particles. In 1924, Louis de Broglie proposed that other small particles of matter can also behave as waves. Thus, his equation is not limited to electromagnetic radiation.
- In 1927, this was demonstrated by two separate experiments. Americans C.J. Davisson and L.H. Germer diffracted a beam of electrons through a nickel crystal, and Scot G.P. Thompson diffracted a beam of electrons through a thin aluminum foil.
- de Broglie called waves associated with matter (such as electrons) “matter waves”. We will revisit matter waves soon.



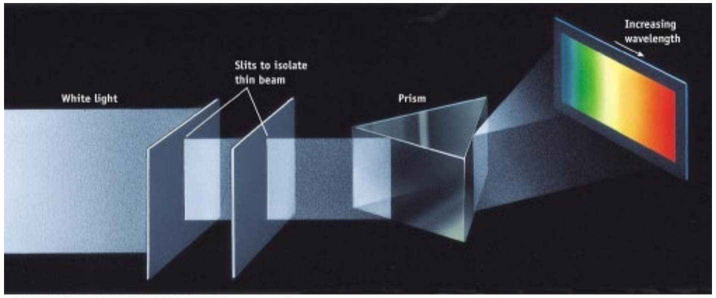
A general picture of diffraction


A diffraction pattern

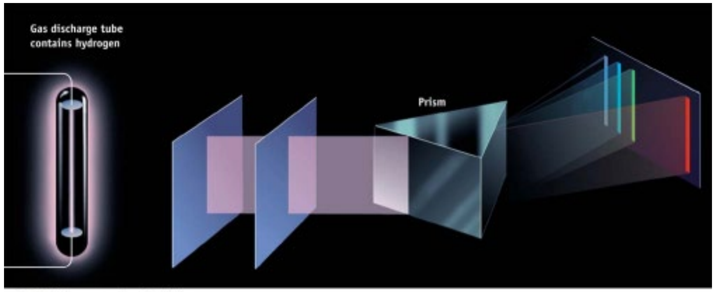
What's Light Got To Do With It?

- Consider the models of the atom you learned in high school…
  - If an atom were simply a nucleus and a random cloud of electrons (Rutherford model), it would absorb light of all wavelengths and later emit that same continuous spectrum of light. This is not observed:

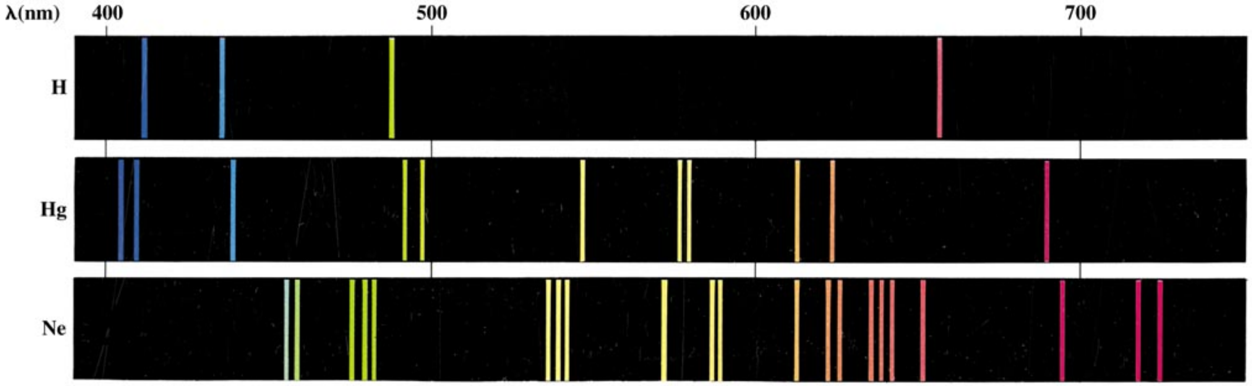
NOT:



BUT:

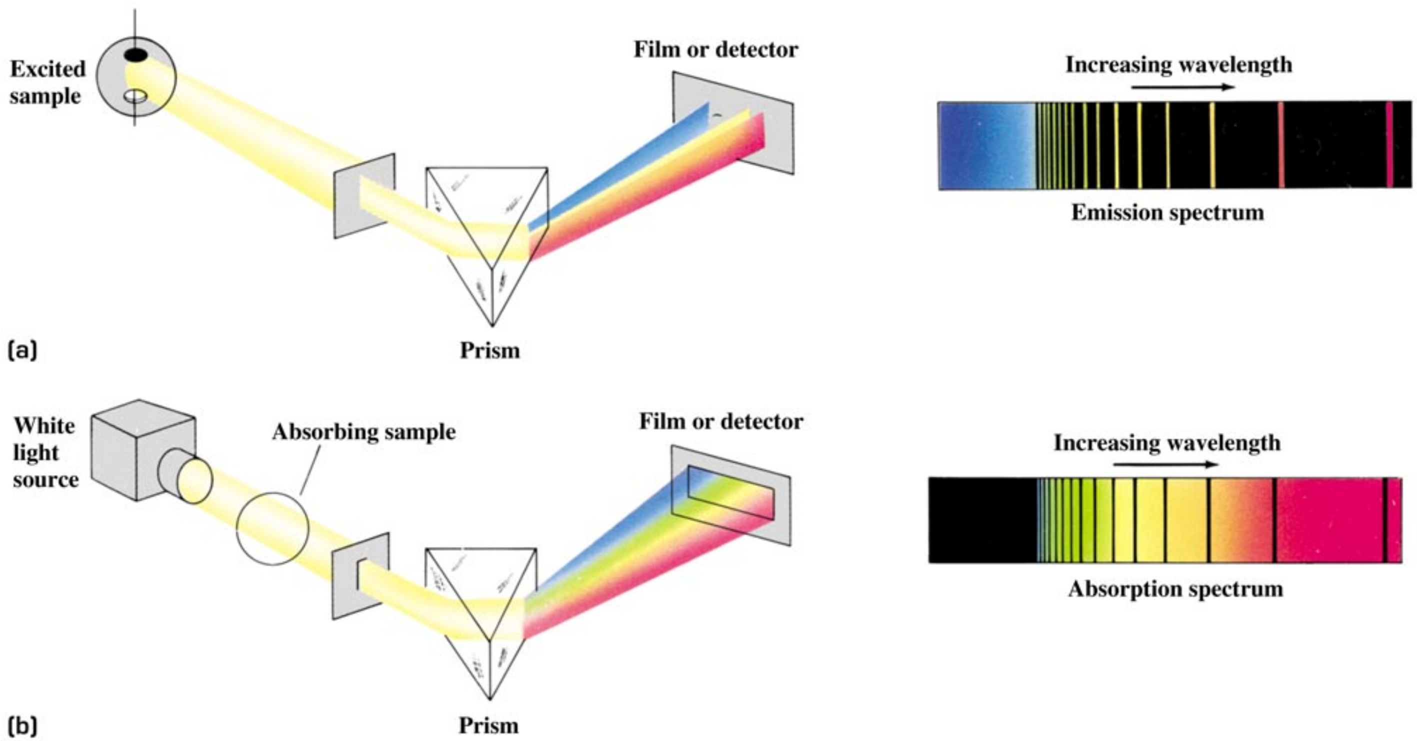


  - Instead, each element absorbs (and emits) only certain wavelengths. As such, each element has its own characteristic **line spectrum**:



What's Light Got To Do With It?

- A popular application of this property is spectroscopy, both emission (top image) and absorption (bottom image). Note that compounds also absorb and emit characteristic wavelengths of light; however, we shall limit our discussion here to pure elements.



What's Light Got To Do With It?

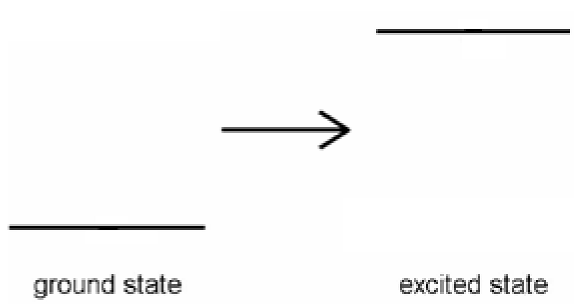
- Light is not the only type of energy that can be absorbed by elements. Atoms can be excited by heating in a hot flame (e.g. Bunsen burner). When they relax back to their ground state, they emit only the wavelengths of light in their line spectra. Thus, each element imparts a characteristic colour to the flame:

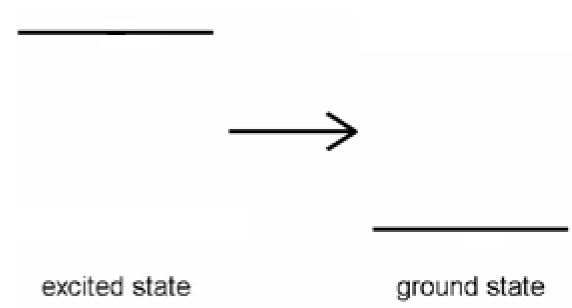
Three white solids: NaCl, $SrCl_2$, $B(OH)_3$

The same three white solids in burning alcohol

What's Light Got To Do With It?

- If an atom is struck by a photon that has enough energy, it will absorb the photon. This puts the atom into an **excited state**. (An atom that has absorbed no energy from external sources is said to be in its **ground state**.)





- Qualitatively, what does the existence of a line spectrum for hydrogen (or any other element) tell us about its excited states?

What's Light Got To Do With It?

- The line spectrum for hydrogen was first reported by Anders Ångström in 1853. Over approximately the next 50 years, line spectra for the remaining known elements were obtained.
- It wasn't until 1885 that the mathematical relationship between the visible lines of the hydrogen line spectrum was demonstrated (by Swiss mathematics teacher Johann Balmer):

$$\frac{1}{\lambda} = 1.0974 \times 10^{7}\ \mathrm{m}^{-1}\ \left|\frac{1}{4} - \frac{1}{n^2}\right|$$

- Later, Johannes Rydberg generalized this equation so that it described all the spectral lines emitted by hydrogen:

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

  where n_1 and n_2 are any integers and R = 1.0974×10^{7} m^{-1}. The series of wavelengths with $n_1 = 2$ is the **Balmer series**.
- This equation allows prediction of all wavelengths of light emitted by an excited hydrogen atom (not just visible light).

Bohr's Hydrogen Atom

- Thus, Rutherford's 1911 model of the hydrogen atom is flawed:
  - It is inconsistent with experimental evidence (line spectra).
  - The model implies that a hydrogen atom consists of an electron circling a proton. As such, the electron would be undergoing constant acceleration due to its constant change in direction. According to classical physics, acceleration of a charged particle results in the continuous release of energy as electromagnetic radiation. What would be the natural consequences of this behaviour?

Bohr's Hydrogen Atom

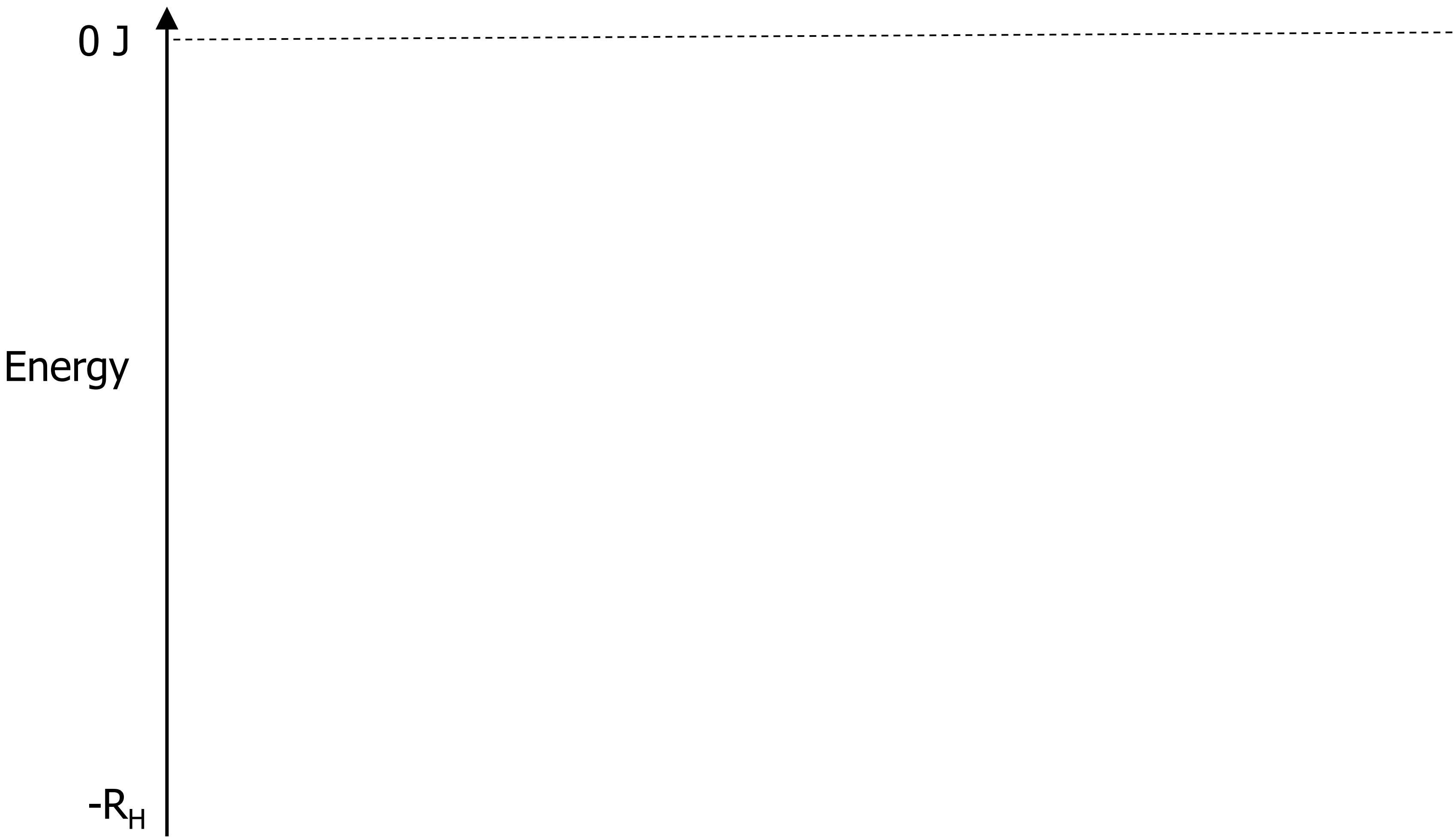
- In 1913, Neils Bohr proposed a new model of the atom to address these issues and explain the line spectrum observed for hydrogen. His solution was based on three postulates:
  - Electrons within an allowed **orbital** can move without radiating.
  - The orbital angular momentum of electrons in an atom is quantized (i.e. has a fixed set of allowed values). Only orbitals whose angular momentum is an integer multiple of $h/2\pi$ are "allowed". These orbitals are called **stationary states**.
  - The emission or absorption of light occurs when electrons 'jump' from one orbital to another.
- Using these assumptions and basic physical constants, Bohr calculated the energy of the electron in a hydrogen atom:

$$\boxed{E_n = -\frac{Rhc}{n^2} = -\frac{R_H}{n^2}}$$

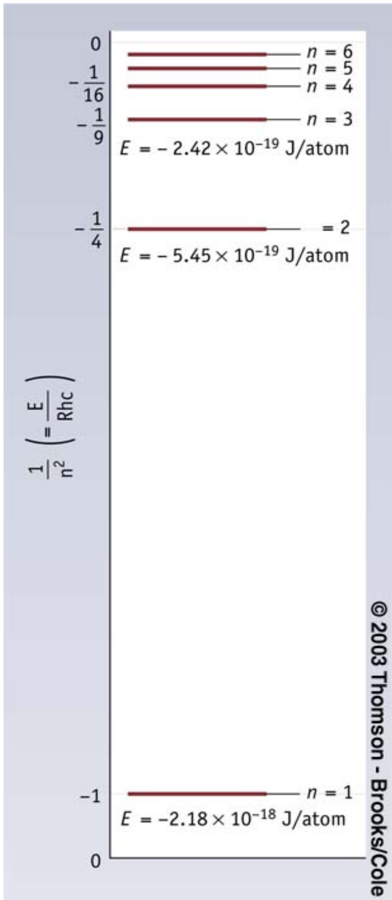
where ***n*** is the **principal quantum number** and R_H is the Rydberg constant, combining R, h and c. ($R_H = 2.179 \times 10^{-18}$ J)

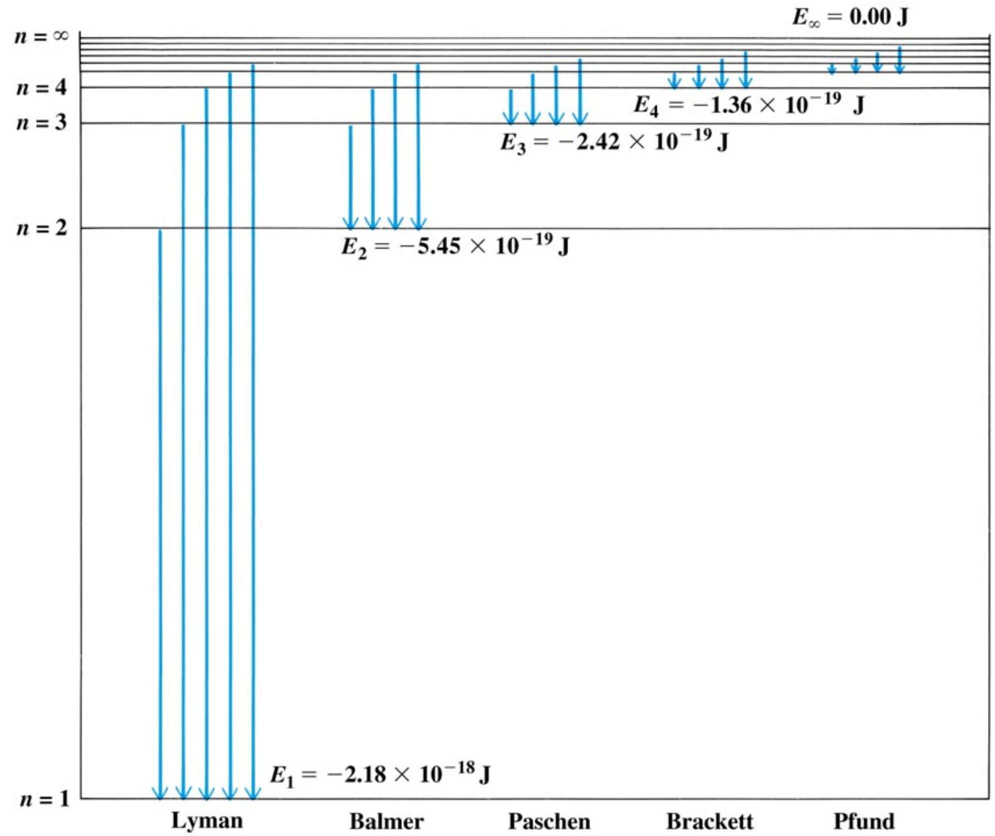
Bohr's Hydrogen Atom

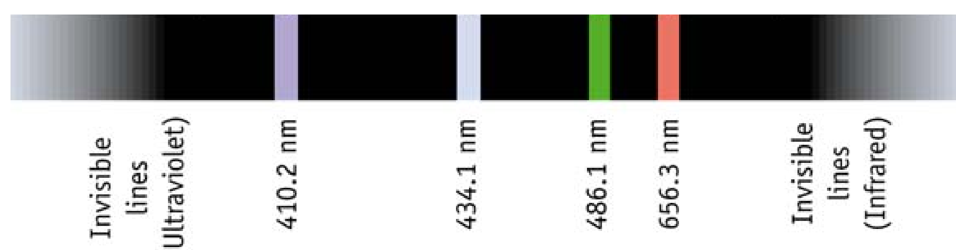
$$E_n = -\frac{R_H}{n^2}$$



Bohr’s Hydrogen Atom







Bohr's Hydrogen Atom

- This formula only describes hydrogen atoms; however, it can be extended to one-electron ions such as He^+ and Li^{2+} by introducing one more term. What is the relevant structural difference between H, He^+ and Li^{2+}?

$$\boxed{E_n = -R_H \frac{Z^2}{n^2}}$$

- *Note that E_n is always less than zero! What does this tell us?*

- Bohr also developed a formula to calculate the radius of each orbital in these one-electron atoms/ions:

$$\boxed{r_n = a_0 \frac{n^2}{Z}}$$

where a_0 is the **Bohr radius**. (a_0 = 5.29177 × 10^{-11} m)

Bohr's Hydrogen Atom

- Is more energy released when an atom relaxes from an excited state to the n = 1 state or to the n = 2 state?
- Calculate the energy and wavelength of a photon emitted when a hydrogen atom relaxes from the n = 5 state to the n = 3 state. What type of electromagnetic radiation is this?

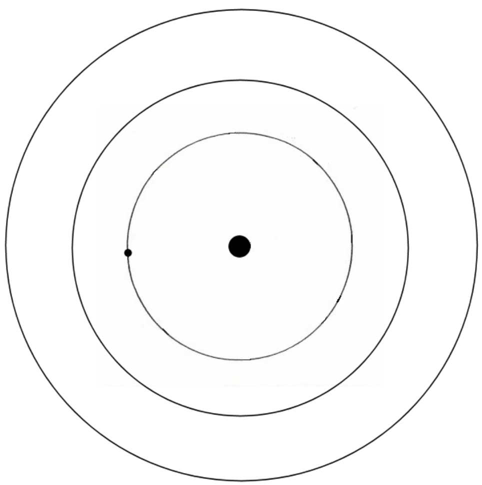
Bohr's Hydrogen Atom

- Calculate the energy required to excite an electron completely out of a ground state hydrogen atom (its **ionization energy**). What type of electromagnetic radiation is required for this reaction?

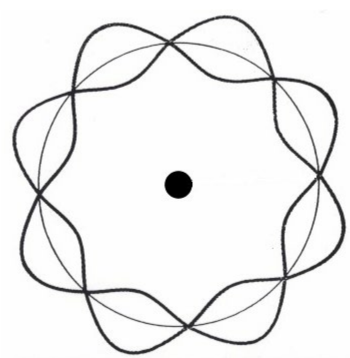
- What's left after the electron leaves? (i.e. What is H^+?)

But We Said That an Electron is a Wave…

- The original Bohr model of the atom pictured an electron as a particle circling the nucleus of an atom in a fixed orbital similar to the way that planets circle the sun (except, of course, that planets cannot 'jump' from one orbital to another!).
- We've seen, however, that electrons can also behave as waves (de Broglie). How does this affect Bohr's model of the atom?



Bohr model of the atom
(electrons as particles)



deBroglie model of an orbital
(electrons as waves)

But We Said That an Electron is a Wave…

- Considering an electron to behave as a wave supports Bohr’s model of the atom because it explains why electrons would be restricted to certain orbitals (those in which the electron could exist as a **standing wave**):

- It is important to recognize that these waves are **<u>not</u>** showing a pathway along which an electron travels and that these are two-dimensional **<u>models</u>** for a three-dimensional phenomenon.

Utility of Bohr/de Broglie Theory

- Successes of Bohr/de Broglie theory
  - The energy of each state (n = 1, 2, 3, etc.) of a hydrogen atom can be calculated.
  - The average radius of a hydrogen atom in each state (n = 1, 2, 3, etc.) can be calculated.
  - Experiments measuring these values show that the calculated values are correct.

- Failures of Bohr/de Broglie theory
  - Angular momentum is not treated correctly. *(see next section)*
  - Electrons do not appear to orbit at fixed distances from the nucleus.
  - Calculations only work for hydrogen (or one-electron cations). A more complex model is needed for atoms with more than one electron. *Why is that?*