Chemical Principles

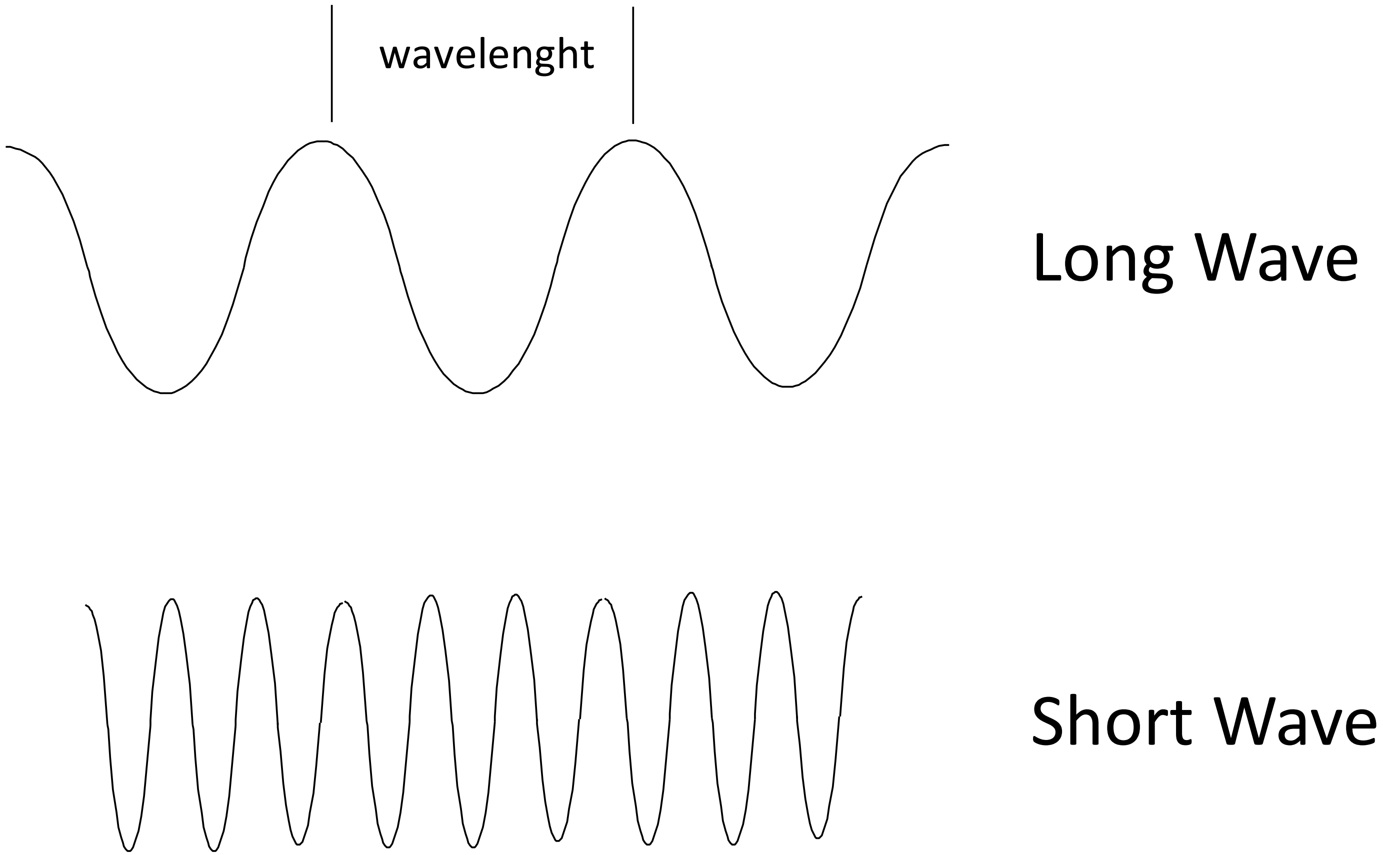
# 2. Elementary Quantum Mechanics

# Atomic Theory Overview

The **goal** of this chapter is to help you understand the reason why we need a theory for the "small-world"

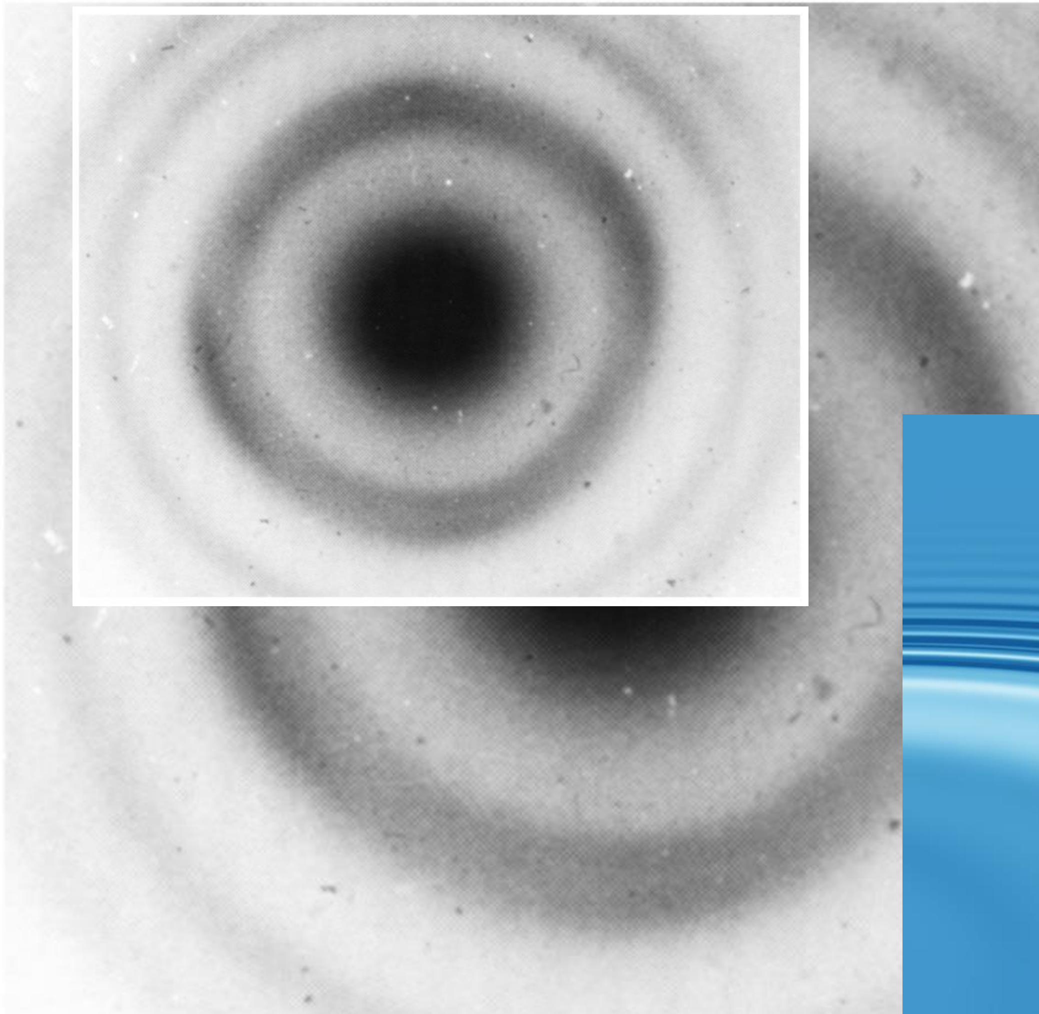
- We will see how Classical Newtonian Mechanics failed.
- We will see experiments showing how photons and electrons can behave as both waves and particles.
- Quantum Mechanics explains the wave-particle nature of matter.

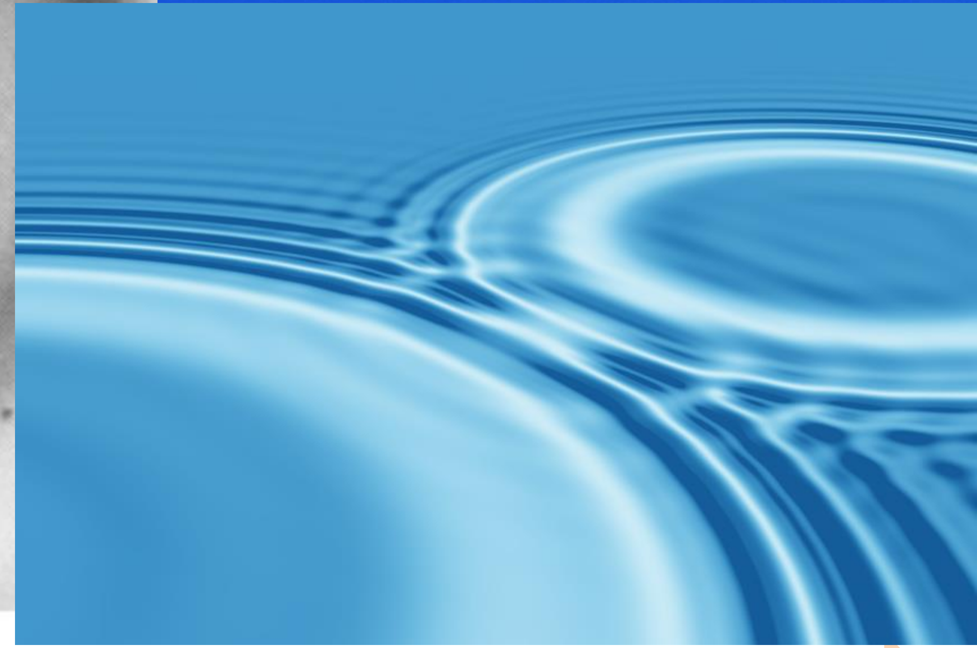
One property of a photon, is it acts like a **wave** (proven by both Faraday and Maxwell, 1850's, each gave us new sets of equations unrelated to Newtonian Physics).




freqency or Hertz = cycles per second

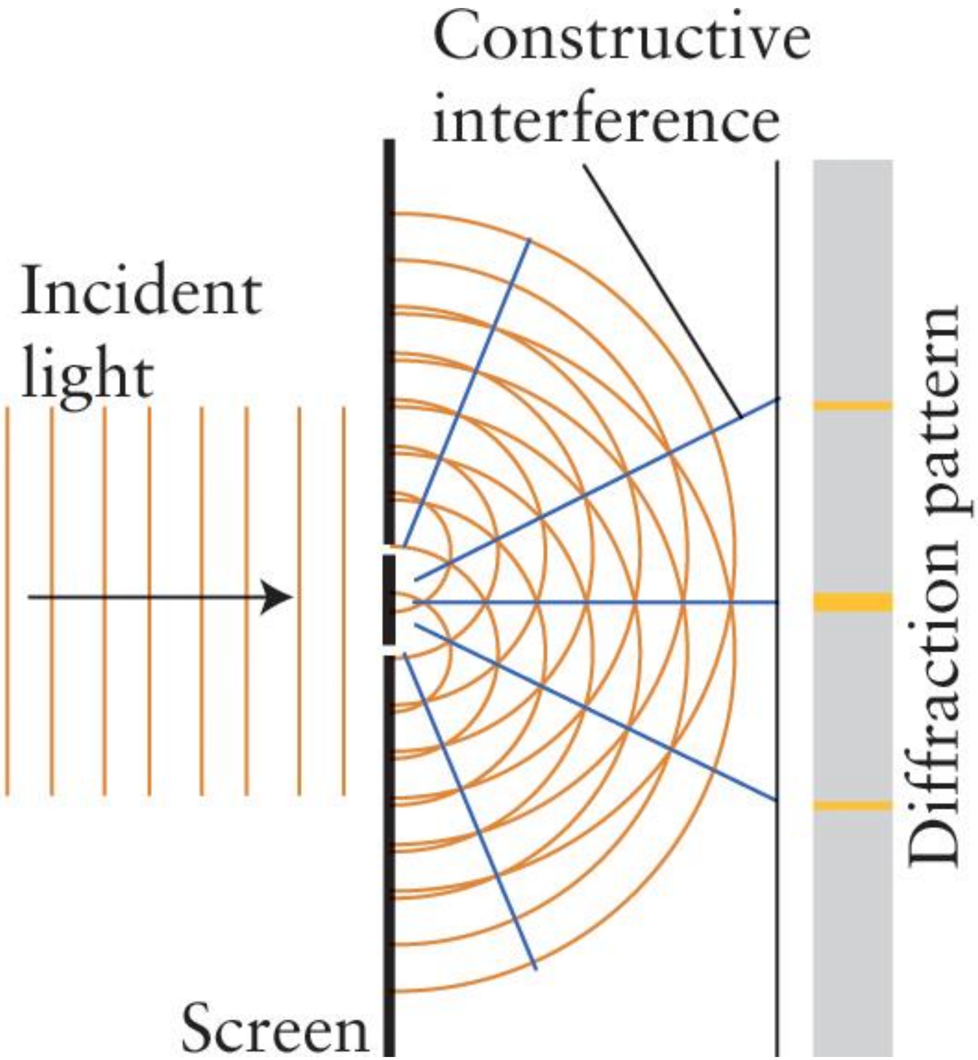
Evidence of the **Wave**-nature of light, diffraction patterns showing interference patterns from a **single-slit** experiment.





Created by nickel atoms spaced 250 pm apart.

Evidence of the **Wave**-nature of light, diffraction patterns showing interference patterns from a **double-slit** experiment



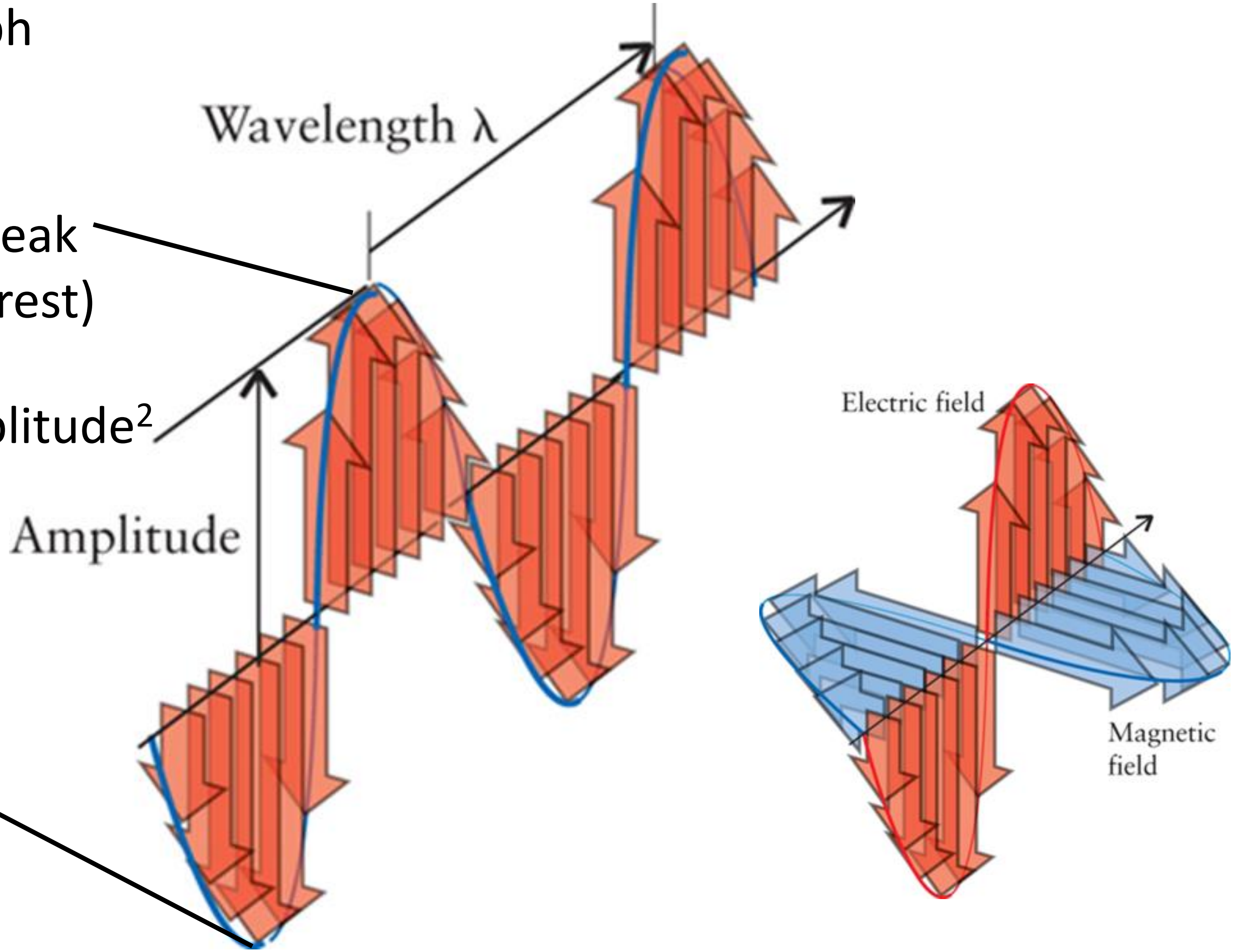

It shows that photons are at "certain," predictable locations.

Snapshot of an Electromagnetic Wave traveling $3.00\times10^{8}$ $ms^{-1}$ or 670 million mph

Peak (crest)

Intensity = amplitude$^2$

Trough




The Electric component of photons is the portion that pushes electrons.

**wavelength** × **frequency** = speed of light ($\lambda\nu = c$)

**TABLE 1.1** Color, Frequency, and Wavelength of Electromagnetic Radiation

| Radiation type | Frequency ($10^{14}$ Hz) | Wavelength (nm, 2 sf)* | Energy per photon ($10^{-19}$ J) |
|---|---|---|---|
| x-rays and γ-rays | $\geq 10^3$ | $\leq 3$ | $\geq 10^3$ |
| ultraviolet | 8.6 | 350 | 5.7 |
| visible light | | | |
| violet | 7.1 | 420 | 4.7 |
| blue | 6.4 | 470 | 4.2 |
| green | 5.7 | 530 | 3.8 |
| yellow | 5.2 | 580 | 3.4 |
| orange | 4.8 | 620 | 3.2 |
| red | 4.3 | 700 | 2.8 |

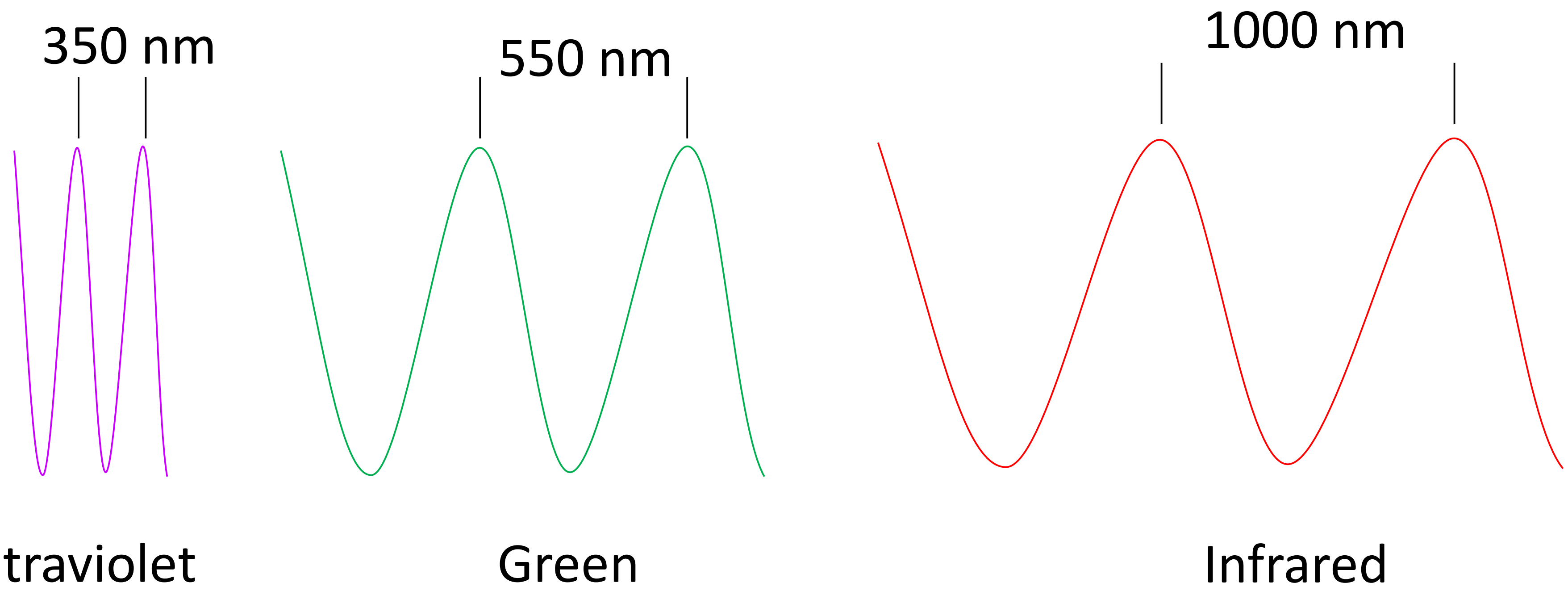
1 Hz = 1$s^{-1}$

*The abbreviation sf denotes the number of significant figures in the data. The frequencies, wavelengths, and energies are typical values; they should not be regarded as precise.

In one second, which of these photons would have the highest frequency, $\nu$?

$$\lambda\nu = c$$

A. Ultraviolet (shortest wavelength)
B. Green light (medium wavelength)
C. Infrared (longest wavelength)
D. They are all the same.




Clicker Question: 1 of 10

In one second, which of these photons would have the highest frequency, $\nu$?

$\lambda\nu = c$

A. Ultraviolet
B. Green light
C. Infrared
D. They are all the same.

Since 1 Hz = 1 $s^{-1}$, then $\nu = \frac{c}{\lambda}$, so for a ultraviolet photon would cycle more

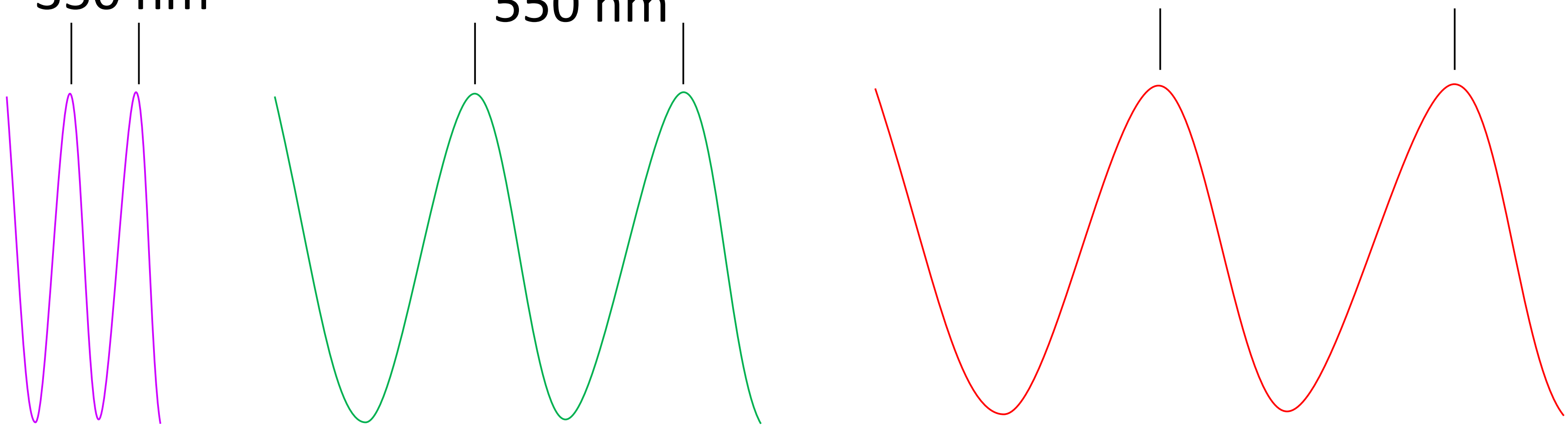
$$\nu = \frac{3.00\times10^{8}\,\mathrm{ms}^{-1}}{3.5\times10^{-7}\ \mathrm{m}} = 8.5\times10^{14}\ \mathrm{s}^{-1}$$

than an infrared $3.0\times10^{14}\ \mathrm{s}^{-1}$.

350 nm

550 nm

1000 nm



Ultraviolet

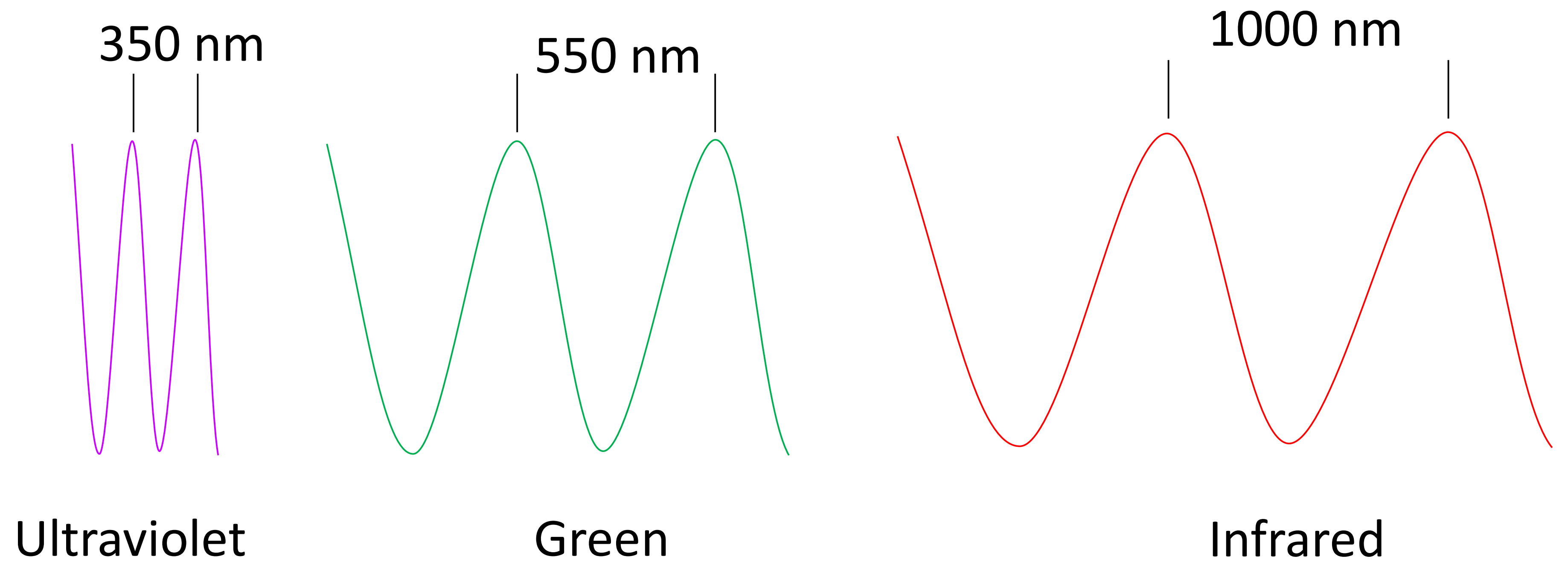
Green

Infrared

Clicker Answer: 1 of 10

Which type of photon travels the fastest in a vacuum according to $\lambda\nu = c$?

A. Ultraviolet
B. Green light
C. Infrared
D. They all travel at the same speed.

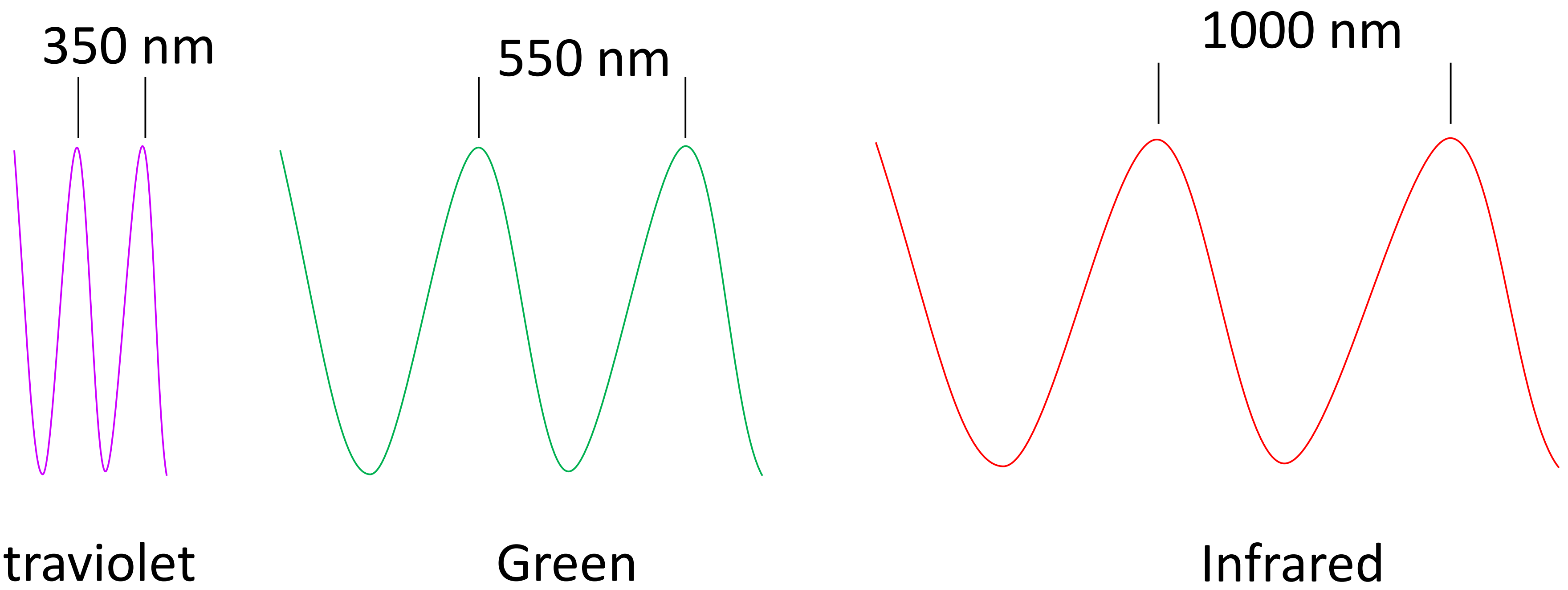



Clicker Question: 2 of 10

Which type of photon travels the fastest in a vacuum according to $\lambda\nu = c$?

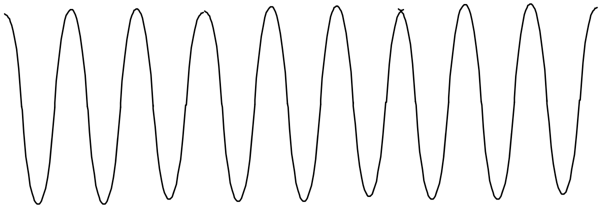
Answer: They all travel at the same speed in a vacuum, $3.00 \times 10^{8}$ $ms^{-1}$.

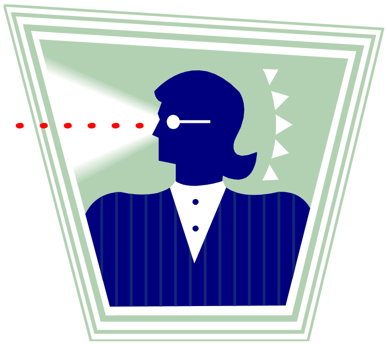
A. Ultraviolet
B. Green light
C. Infrared
D. They all travel at the same speed.

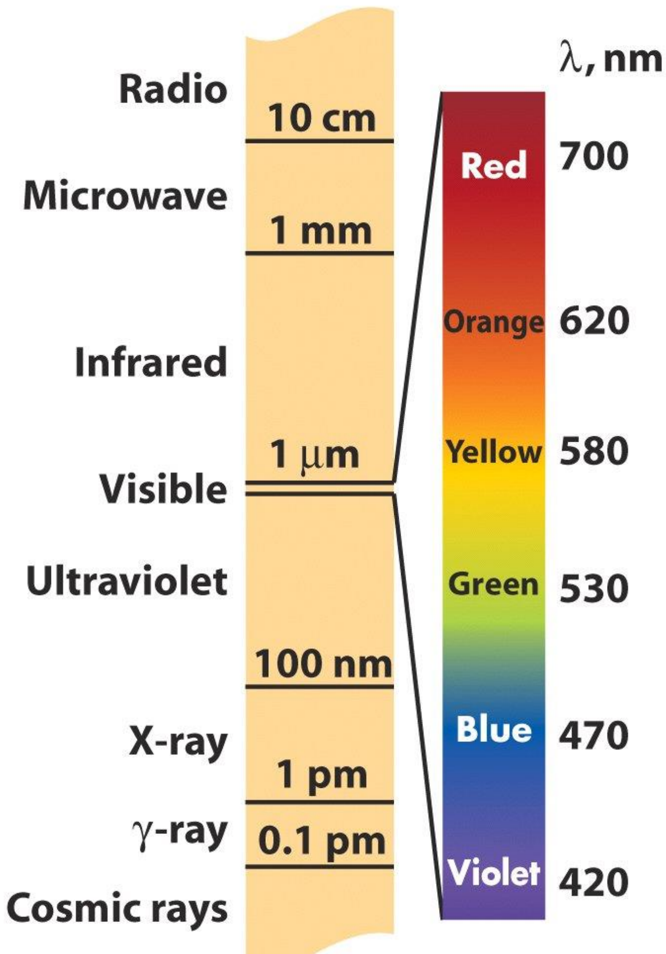


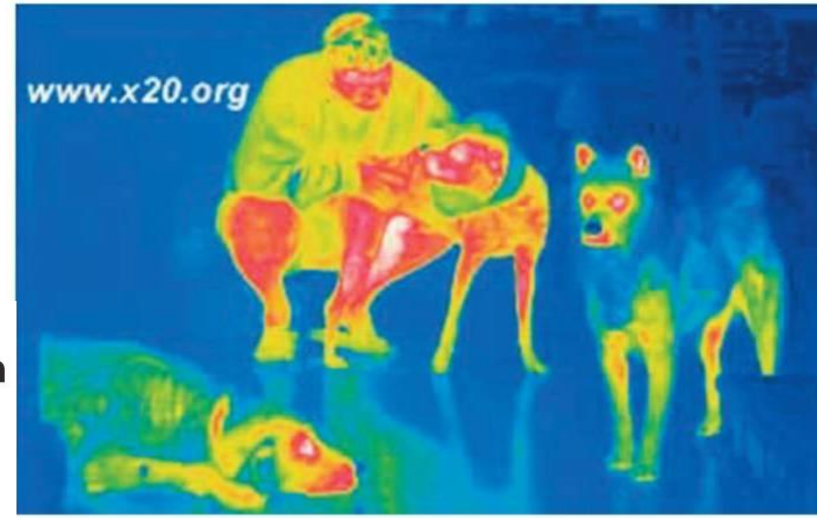

Clicker Answer: 2 of 10

# It's all about wavelength size







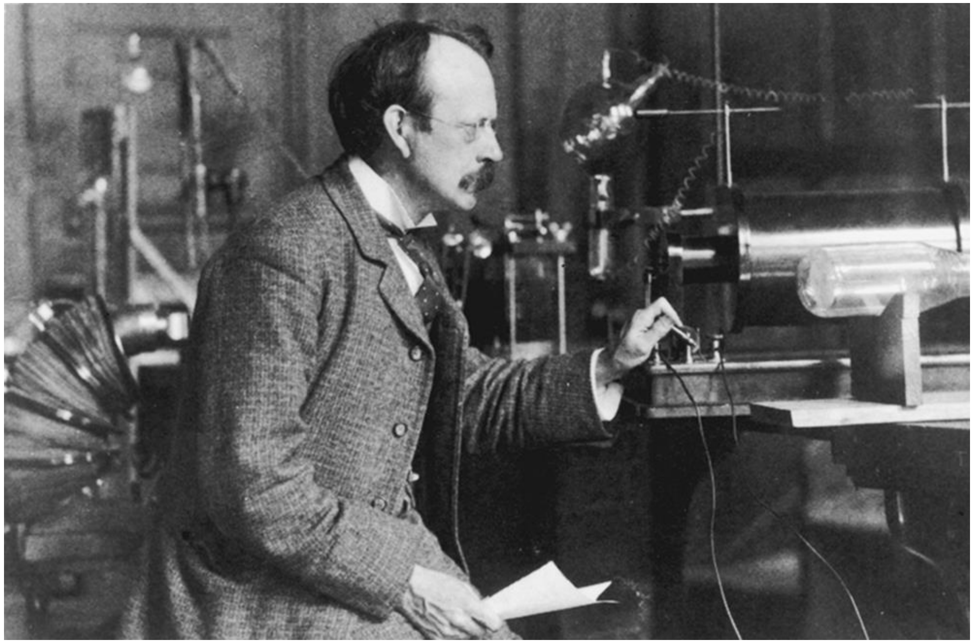




If we had infrared vision

If we had X-ray vision

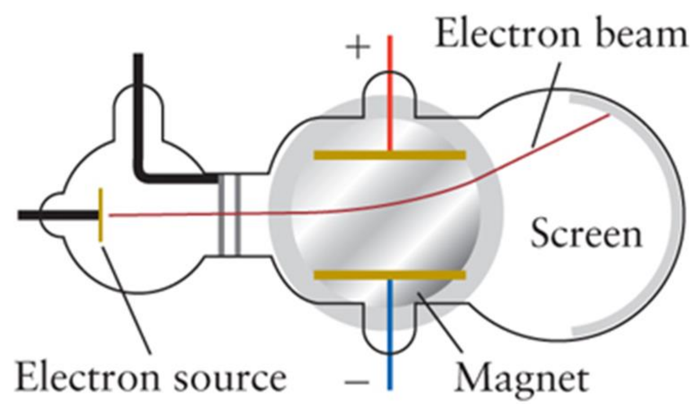
visible vision

# electron



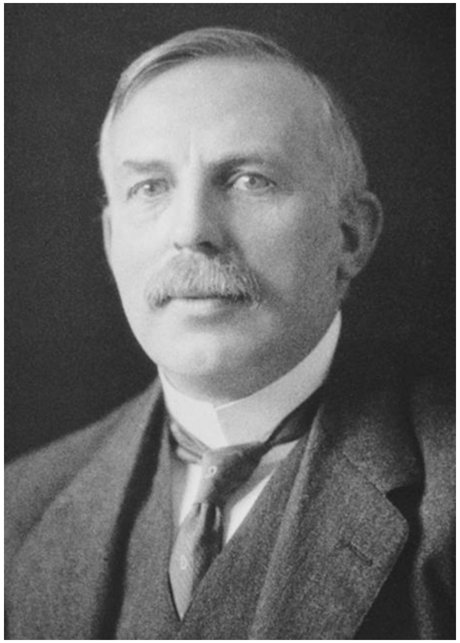
In 1897 British physicist **J. J. Thomson** provided the earliest evidence that atoms had **internal structure**.

cathode rays



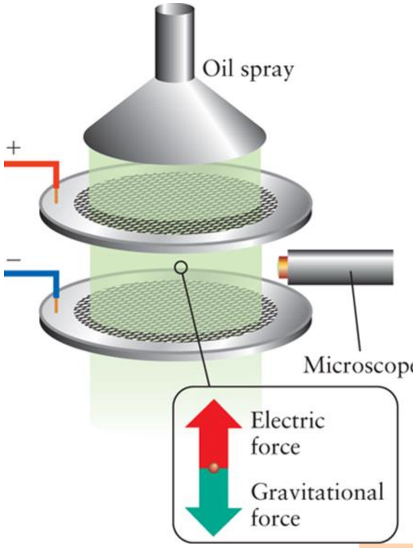

Thomson was able to measure the value of $\frac{-e}{m_e}$, the ratio of an electron's charge **$-e$** to its mass **$m_e$**

# electron charge



Later, American physicist **Robert Millikan**, carried out experiments determining the **electrical charge**.

By observing tiny electrically charged oil droplets, the strength of the electric field opposing the gravitational field, he determined the charges on the particles.

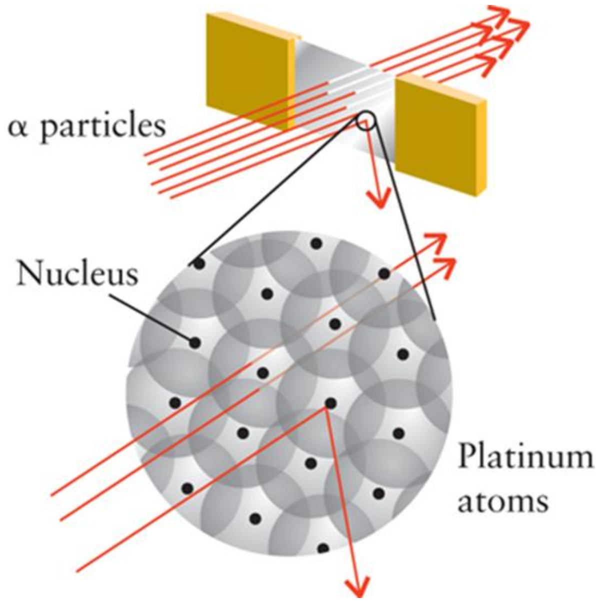



He found the charge on one electron to be $-e$, were $e = 1.602 \times 10^{-19}$C and is considered to be **“one unit“** of negative charge.

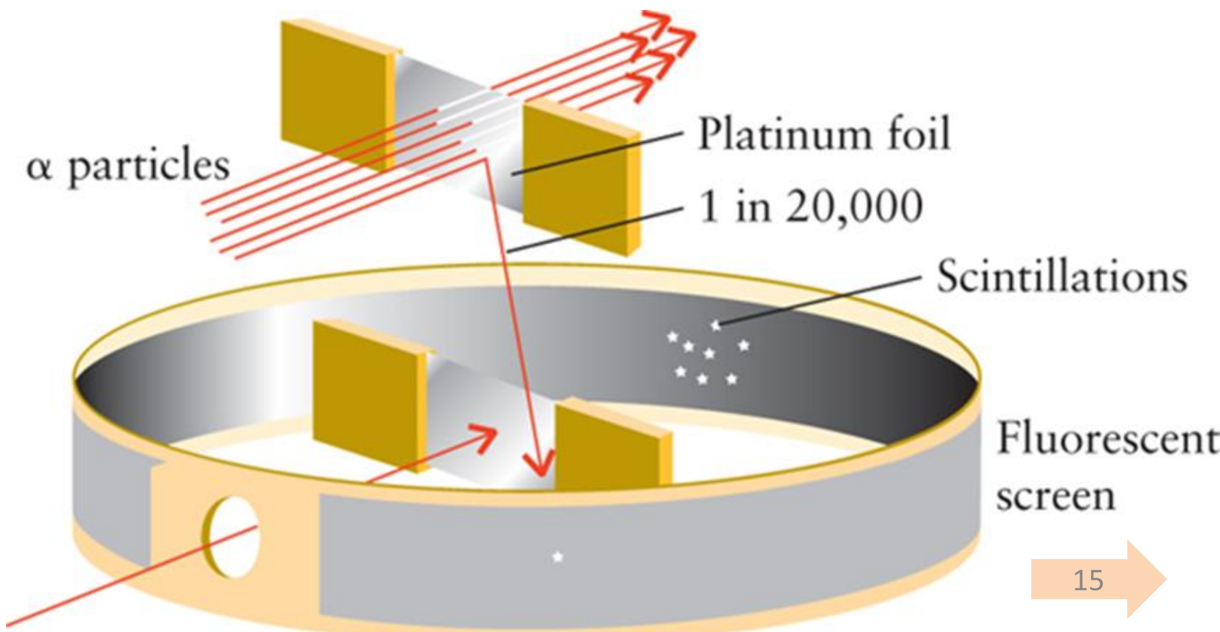
# Nuclear

Thomson's model of an atom was a ***jellylike material*** with a positively charged and electrons suspended in it like raisins in pudding.

**Rutherford** tested Thompson's hypothesis.




Very small portion of the alpha-particles ($He^{2+}$) are bounced back




Almost all the mass is concentrated in the tiny nucleus

# Nuclear Atom

The **nucleus of an atom** contains particles called **protons**, each of which has a charge of +e ("one unit of positive charge"), and **neutrons**, which are uncharged particles.

The number of protons in the nucleus is different for each element and is called the **atomic number**, **Z**

The total charge on an atomic nucleus of atomic number Z is +Ze and, for the atoms to be electrically neutral, there must be Z **electrons** around it.

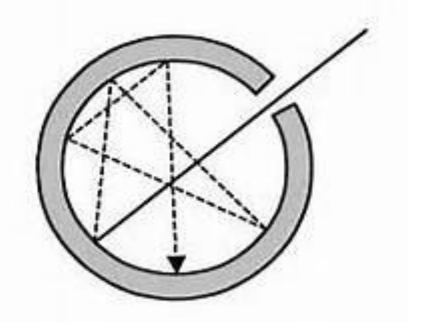
## Two basic experiments that classical Newtonian mechanics can not explain which lead to development of QM

1. **Ultraviolet catastrophe**: why don’t atoms and vibrate faster—hints at a particle nature of light.

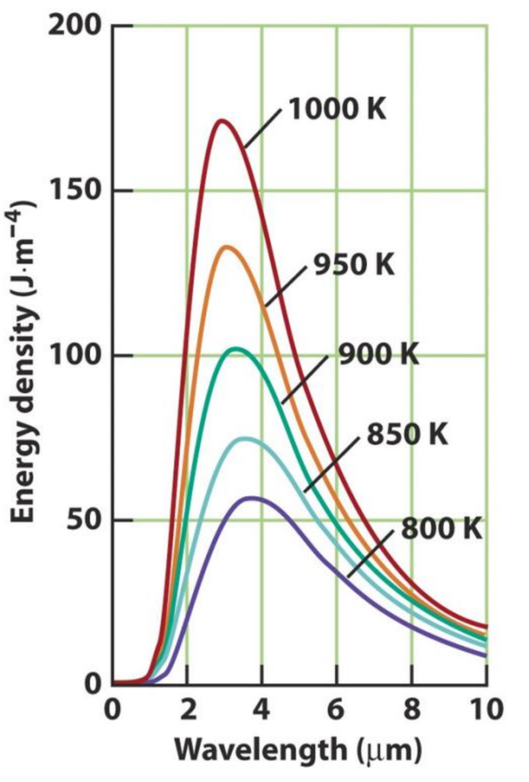
2. **Light emission spectrum**: why don’t electrons vibrate faster and make all the colors of the rainbow.

# Electromagnetic radiation emitted by a heated Black Body

The "hot object" is known as a black body (even though it might be glowing white hot!).



At high temperatures an object begins to glow—the phenomenon of **incandescence**. As the object is heated to higher temperatures it glows more brightly, and the color of light it gives off changes from red through orange and yellow toward white.



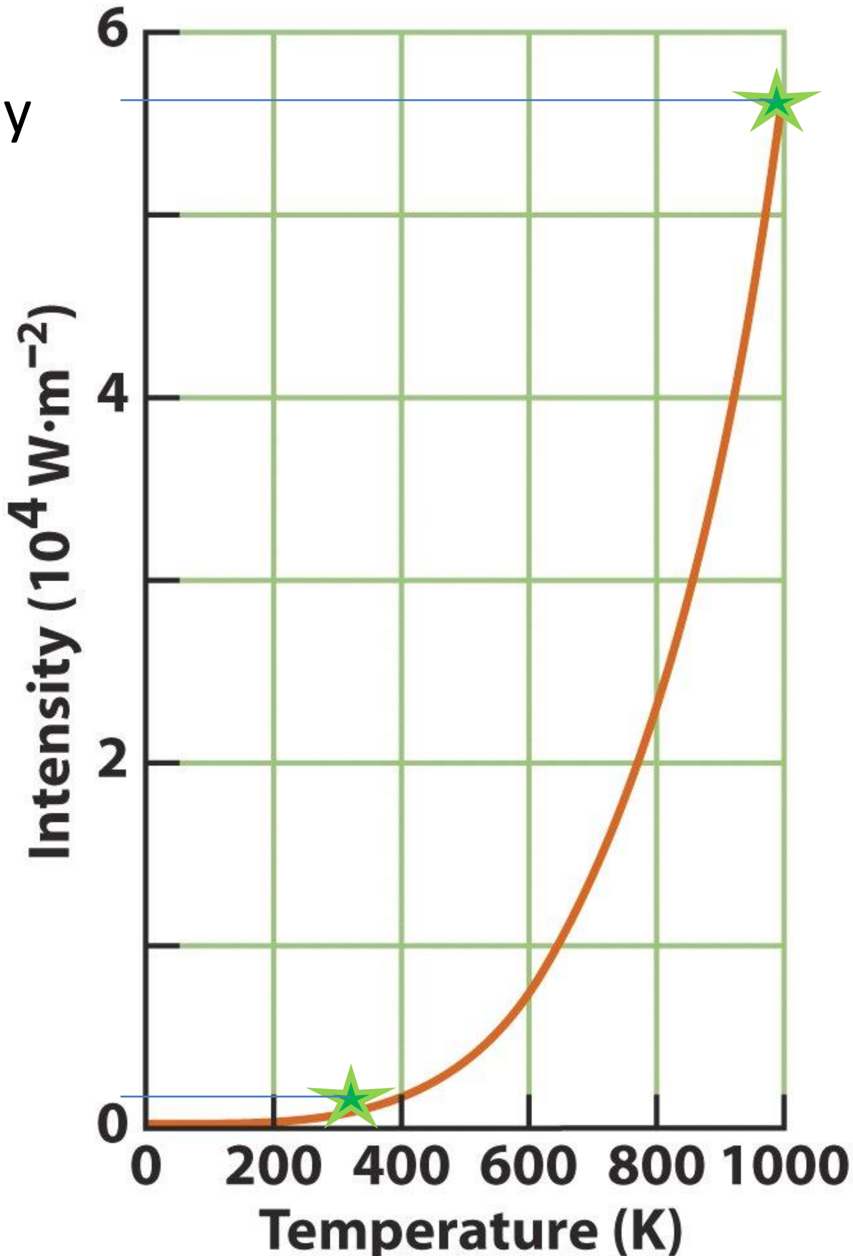
# Stefan-Boltzmann Law

Describes the **behavior** of Blackbody Radiation-intensity/temp

**Total intensity** = constant × $T^4$

The **total intensity** of radiation emitted increases as the fourth power of the temperature.

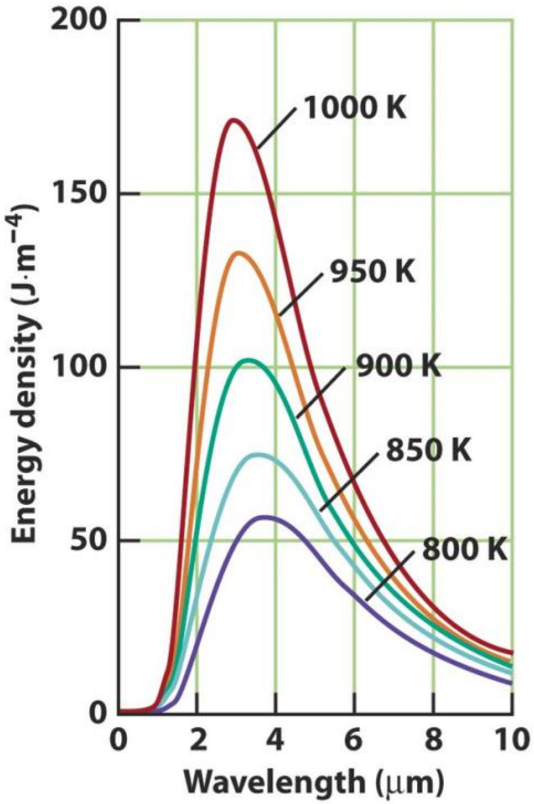
A body at 1000 K emits 120 times more energy as is emitted at 300 K.

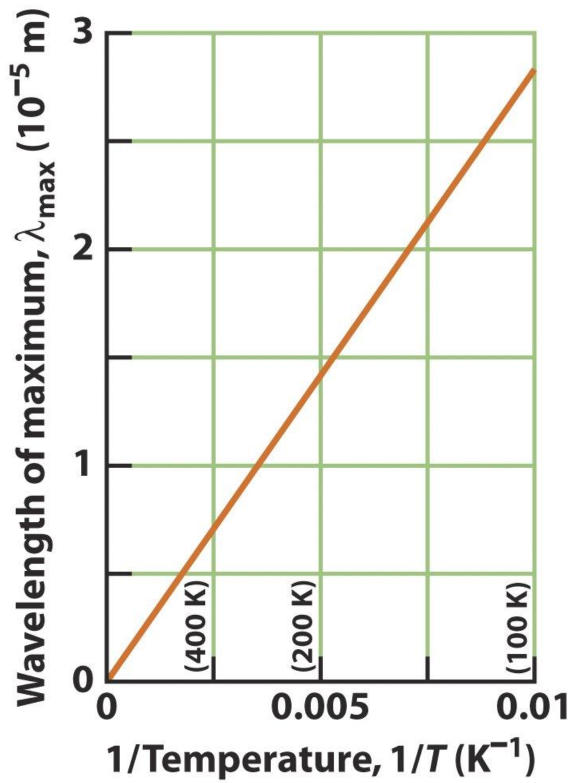


# Wien's Law

Shows that there is a **maximum wavelength** at which the intensity the highest. The maximum wavelength reversely related to temperature $T$↑, $\lambda_{max}$↓

$$\boxed{T\lambda_{max} = \text{constant}}$$

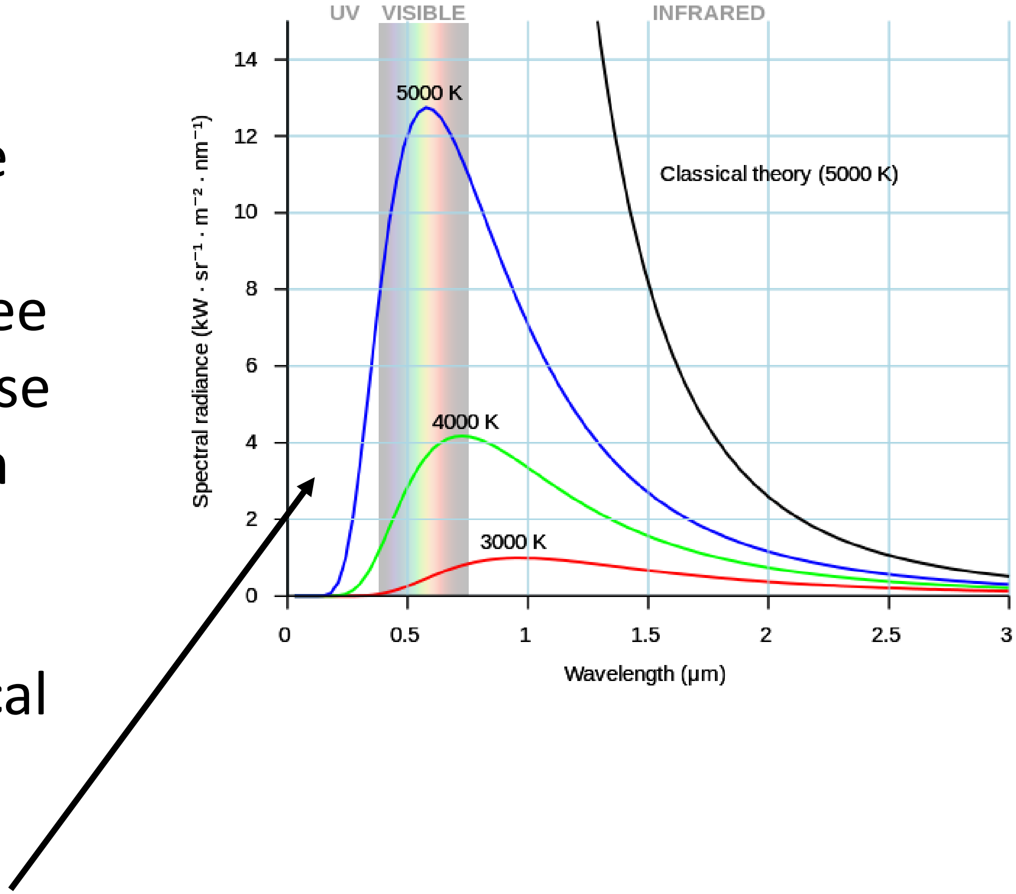



Often used by astronomers to measure a stars surface temperature.

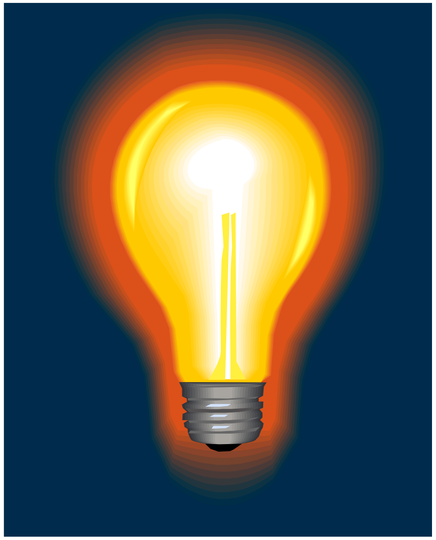
# Ultraviolet Catastrophe

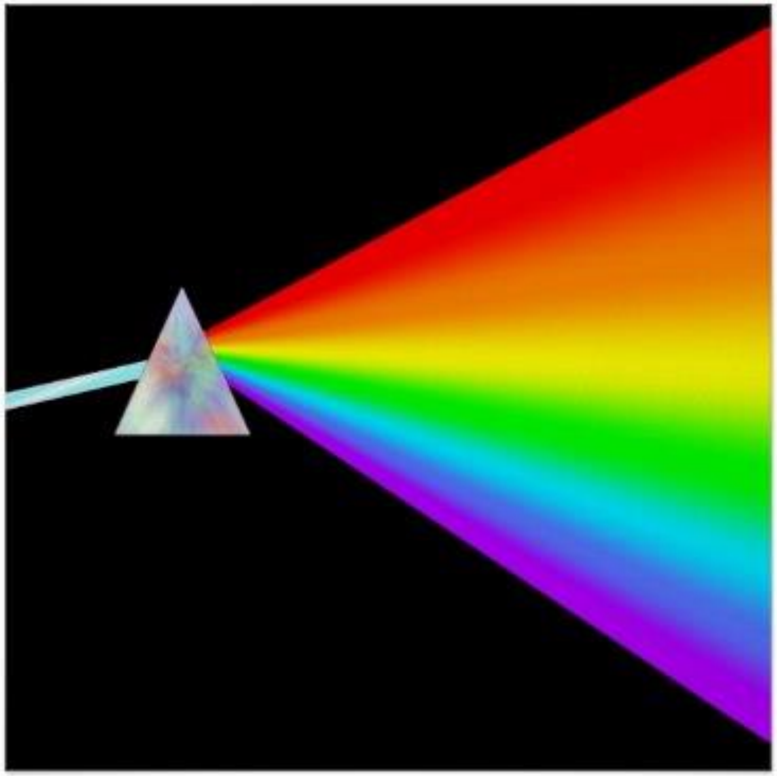
- Atoms give off light as they get hotter because atoms oscillate.
- Classical mechanics predict the more energy put in, the high frequency it emits
- However, this does not agree with the experiment because there is no radiation at high frequency (UV band) end.
- This is a "Catastrophe" for physics, because the classical mechanics cannot explain.



# Light emission spectrum

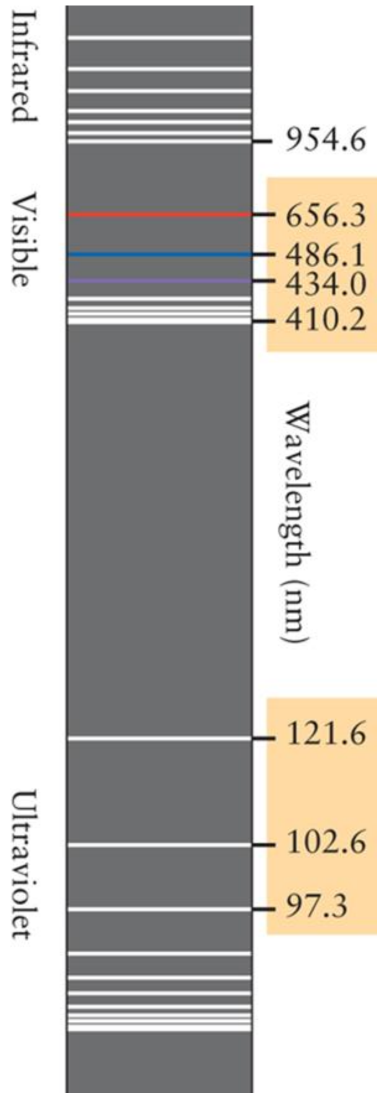
Our everyday experiences led us to think that light, either form the sun or light bulb, contains all the colors we’re familiar with.





# Light emission spectrum of hydrogen

The simplest atom: hydrogen does not show continue spectrum

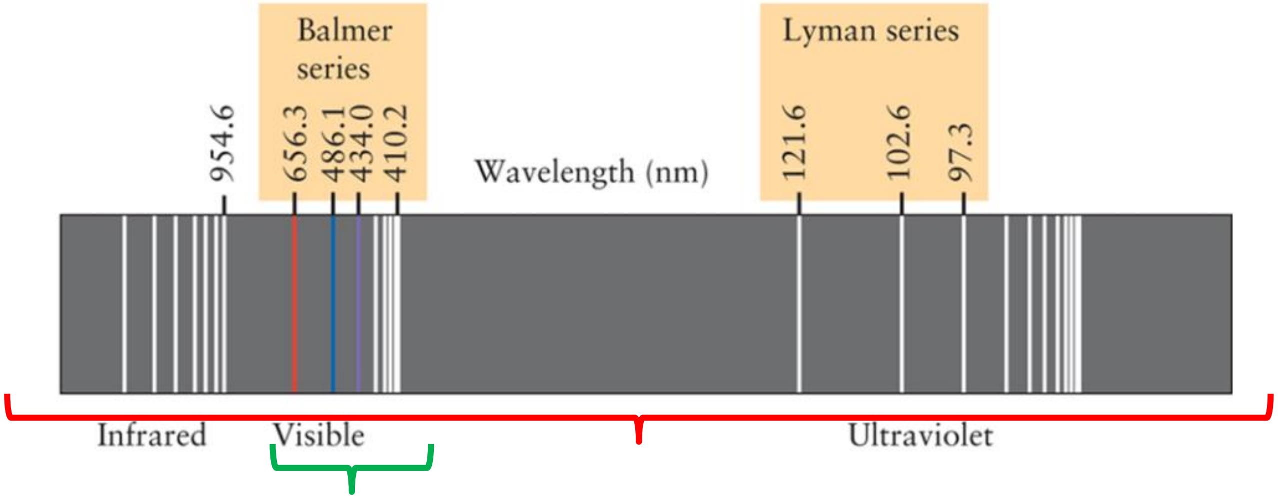



When an electric current passes through a sample of "PURE" hydrogen gas, the electric current acts like a storm of electrons, exciting the electrons in the atom to higher and higher energies.

The excited electrons quickly discard excess energy by emitting light.

However, the emitting light is **not continuous**

# Light emission spectrum of hydrogen




Joseph **Balmer**, a Swiss schoolteacher 1885, identified a pattern in the lines of the visible region of the spectrum. The frequencies of all the lines could be generated by:

$$\nu \propto \frac{1}{2^2} - \frac{1}{n^2} \quad n = integer$$

Later, Swedish spectroscopist Johann **Rydberg** noticed that **all** of the **lines** could be predicted by:

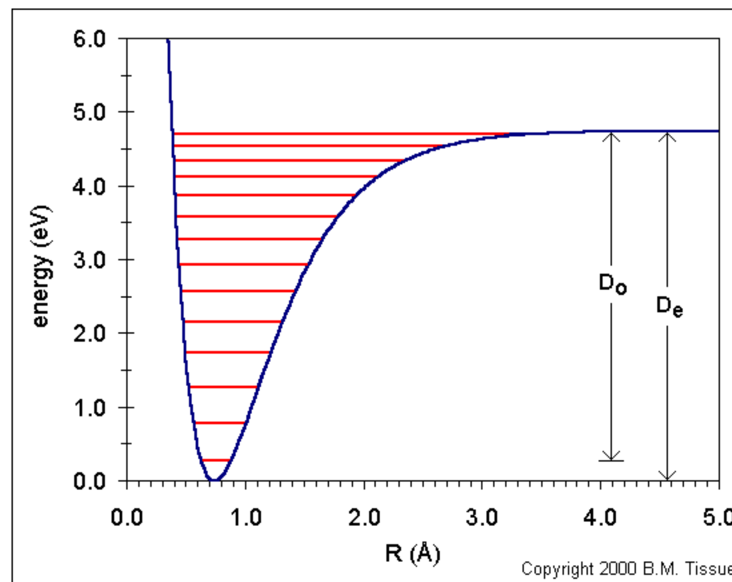
$$\nu = \mathcal{R}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \quad n_1 = 1, 2, \ldots \quad \text{Where } n_2 = n_1+1, n_1+2, \ldots$$

# Quanta

The **UV catastrophe** and **emission spectra** helped us **break away** from the continue energy world

Planck hypothesizes that oscillation frequencies are not continues, but at a particular energy levels with a minimum energy increment.

To make oscillations occur at higher energy level requires a specific or minimum amount of energy or "**Packet**" sometimes called quanta, h*v*.



# Quanta

Planck $E = h\upsilon$ Plank's constant

$\boldsymbol{h}$ **= 6.626 × 10$^{-34}$ Js**

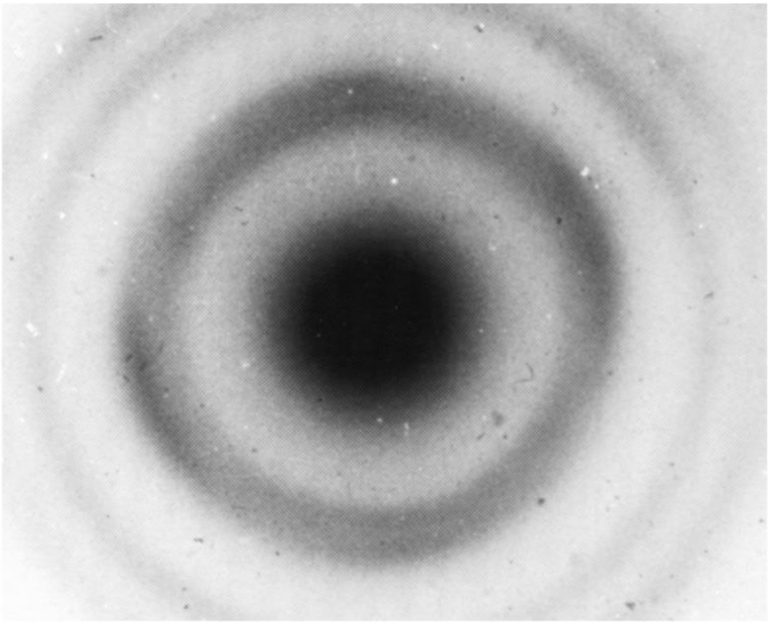
Using this model with statistical mechanics, the UV catastrophe problem can be solved.

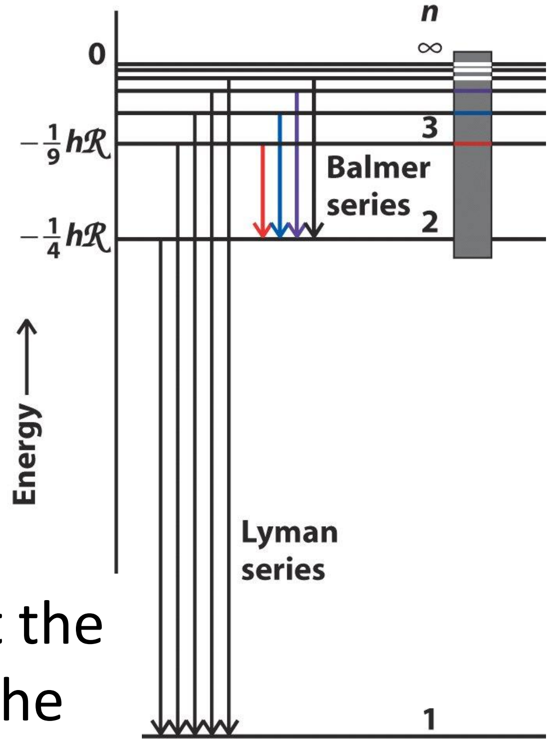
Considered one of the **greatest achievements** in physics. It **shifted** the way we look at our world. He gives us a new of looking at tiny objects.

Planck describes that atomic vibrations as requiring a "minimum" amount of energy to "move."

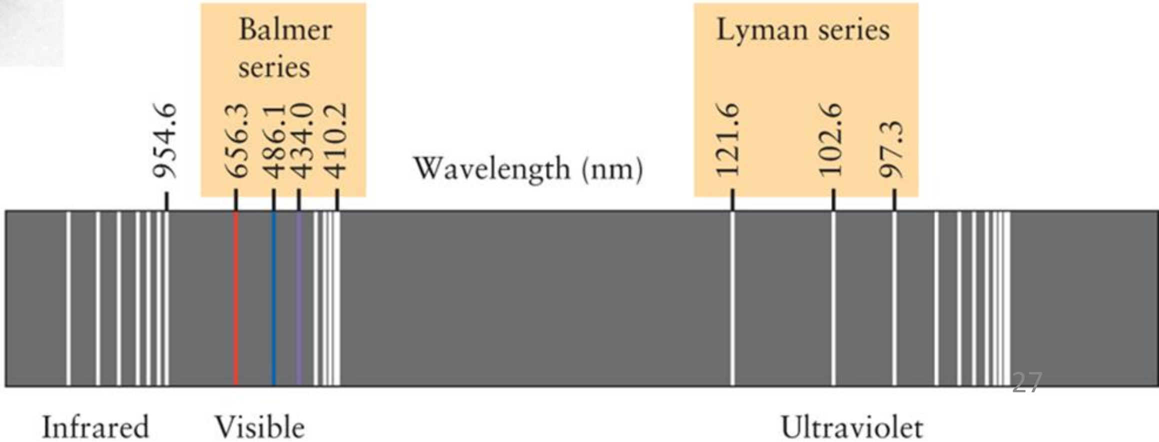
# Quanta

Bohr interpreted this picture as the atom; when electrons moved between the rings, the $h\upsilon$ corresponded to different colors.



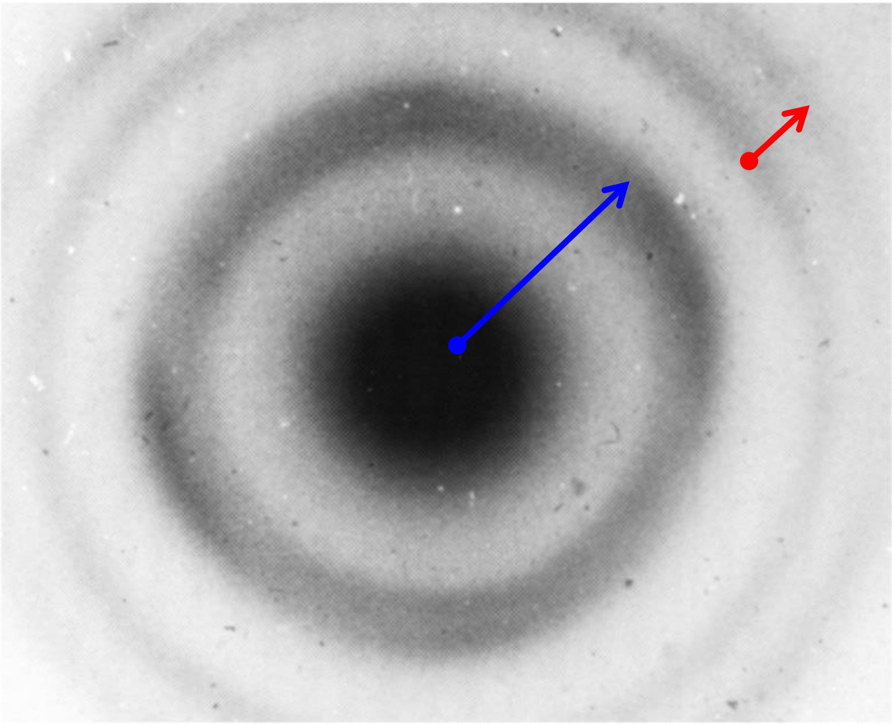



The **nucleus** is at the center, though, the size of a fly in a domed stadium.



According to the Bohr model for the hydrogen atom, the energy necessary to excite an electron from $n$ = 6 to $n$ = 7 is _________ the energy necessary to excite an electron from $n$ = 2 to $n$ = 3.

A. less than
B. greater than
C. equal to



Clicker Question: 6 of 10

According to the Bohr model for the hydrogen atom, the energy necessary to excite an electron from $n$ = 6 to $n$ = 7 is <u>less than</u> the energy necessary to excite an electron from $n$ = 2 to $n$ = 3.

A. less than
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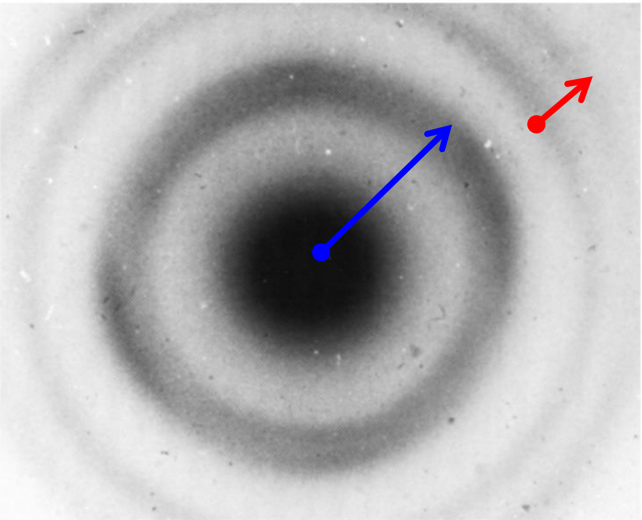
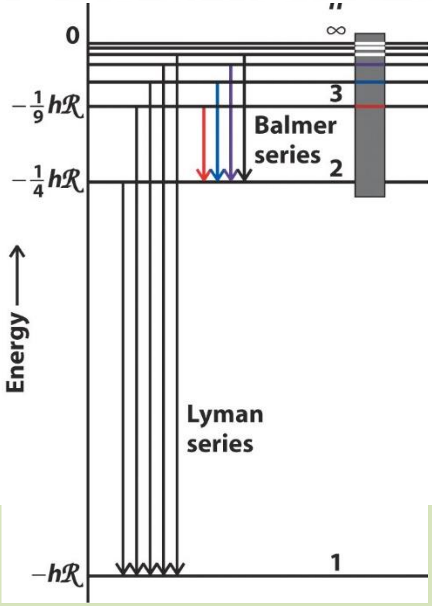


Energy levels are not evenly spaced apart. It takes more energy to excite electrons closest to the nucleus.




Clicker Answer: 6 of 10

# Wave-Particle Duality of Matter

Photoelectric Effect by Einstein: He proved that a single "strong" photon could eject one electron from an atoms.

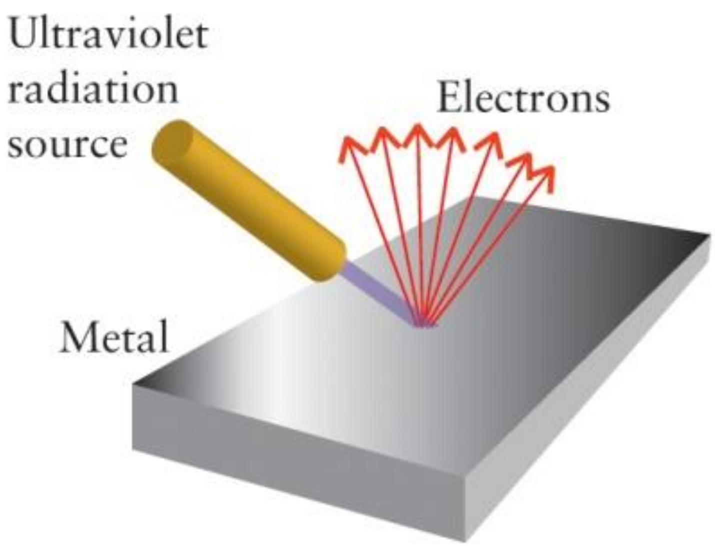



**FIGURE 1.15** When a metal is illuminated with ultraviolet radiation, electrons are ejected, provided the frequency is above a threshold frequency that is characteristic of the metal.

- The frequency matters, only above certain frequency it works
- The currency of electron depends on the intensity of light.
- Einstein proposed the electron radiation consists of particle called photon $h\upsilon$.
- Both photon and electron are particles.

# Wave-Particle Duality of Matter

Louis de Broglie used Einstein and Planck energy and quanta $E = h\nu$ and the theory of special relativity: $E = pc$ (p = momentum):

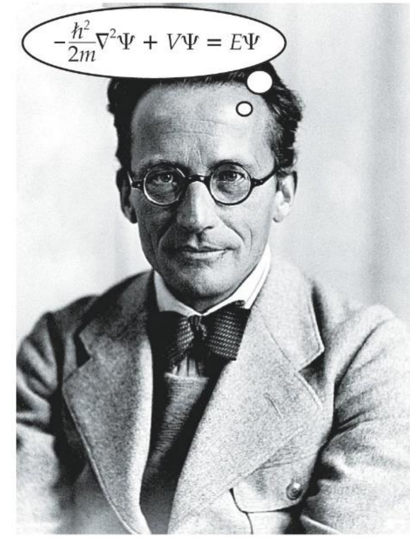
$$\boxed{\nu = \frac{E}{h}} \quad \text{or} \quad \boxed{\lambda = \frac{h}{p}}$$

Connecting the particle property (E, P) with wave property ($\lambda$, $\nu$ )

The wave-particle ($\lambda$, $p$) relationship applies to **everything in the physical world**

# Schrödinger Equation

Provides a equation describing the **energy** as a **wave-particle**.




Its time-independent equation is

$$\Bigg[\underbrace{\frac{-\hbar^2}{2\mu}\nabla^2}_{\text{KE}} + \underbrace{V(\mathbf{r})}_{\text{PE}}\Bigg]\,\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Particle Wave

$\hbar = h/2\pi$

The left side is often written as $H\Psi$. $H$ is known as the "Hamiltonian".

Solutions exist only for certain cases.

# Example – a free particle

If the particle is free – without external potential

$$V(x) \equiv 0$$

Then the Schrödinger Equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} = \mathrm{E}\Psi(x)$$

The solution:

Energy: $\mathrm{E} = \frac{\hbar^2 k^2}{2m} = \frac{P^2}{2m}$ $(\lambda = \frac{h}{p}$ $or$ $P{=}\hbar\mathrm{k})$

Wavefunciton: $\Psi(x) = Asin(kx)$

# A particle confined in a box

The wave function

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, \ldots$$

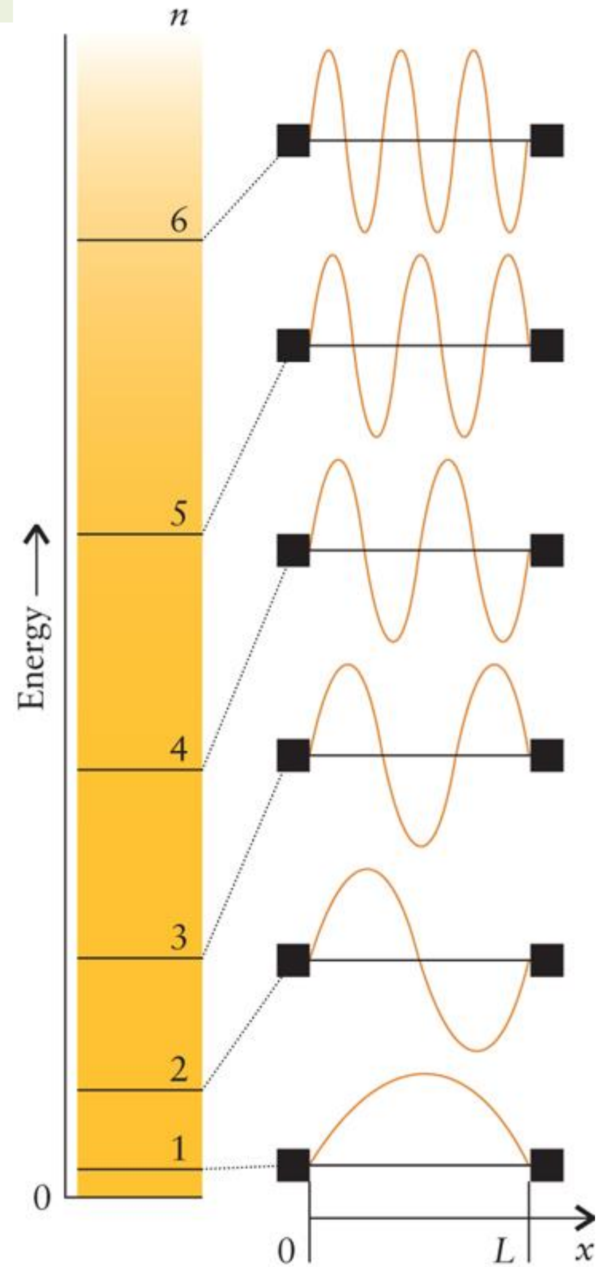
The energy is

$$E_n = \frac{n^2 h^2}{8mL^2}$$

n = 1, 2, 3, … is the quantum number

(n-1) node is the wave function

The more nodes, the higher energy.



# Quantum Effect

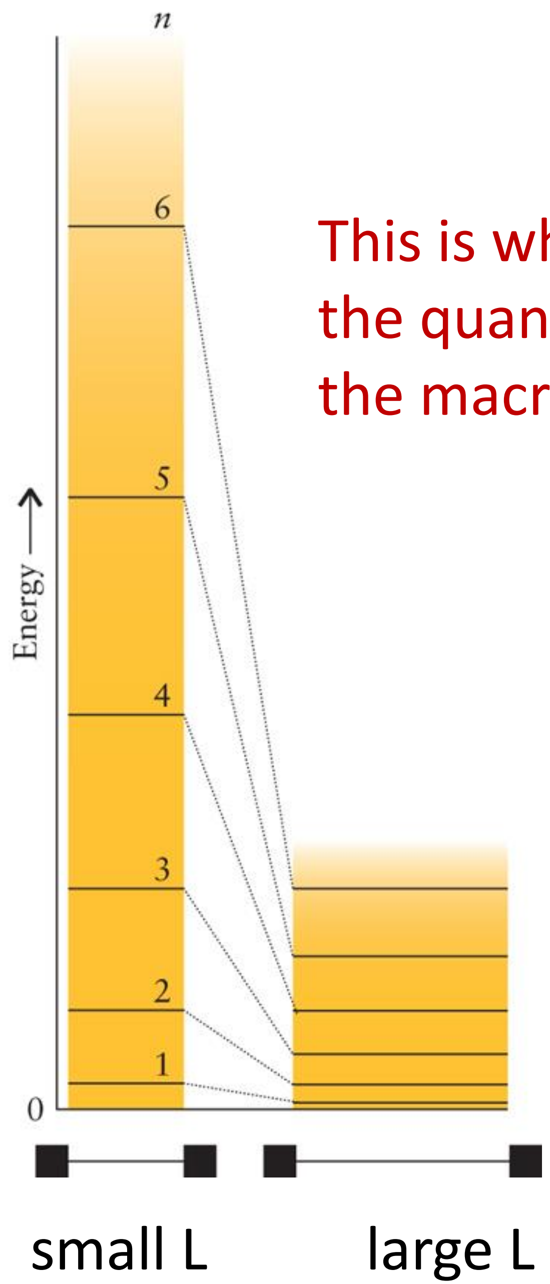
$$E_n = \frac{n^2 h^2}{8mL^2}$$

n = 1, 2, …
L is the length of the box;
m is mass; h is a constant.

As *L* increases or mass increase:

- energies of levels decrease
- separations between levels decrease

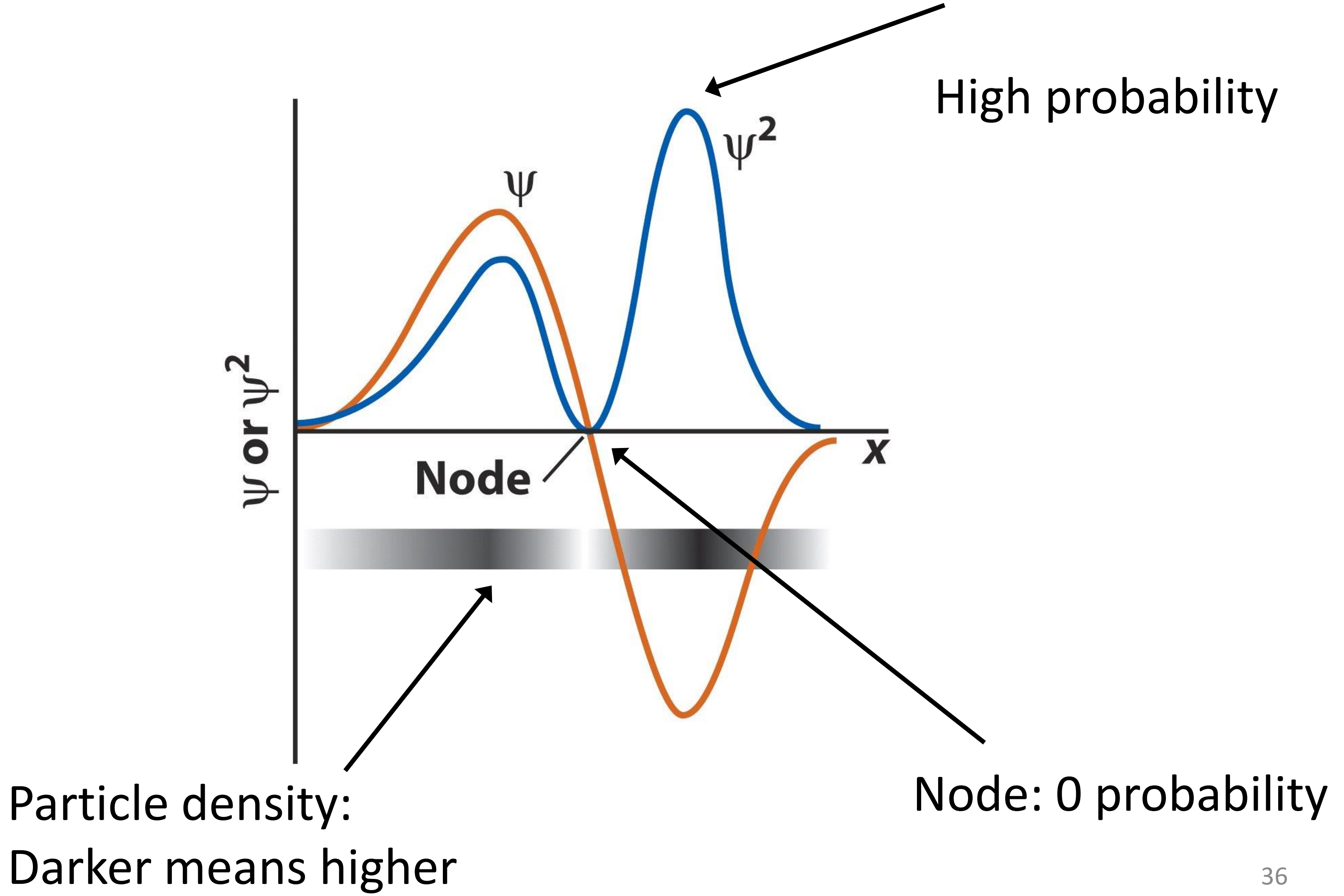
➢ The quantum effect decreases.




This is why we cannot see the quantum effect on the macro-scale

# The Born interpretation of wave-function

$\psi(x)$ describes a wave; $\psi^2(x)$ gives the probability of finding the particle.



# The Heisenberg's Uncertainty Principle

Due to wave-particle duality, position and momentum cannot be measured exactly at the same time. Mathematically expressed in terms of standard deviations

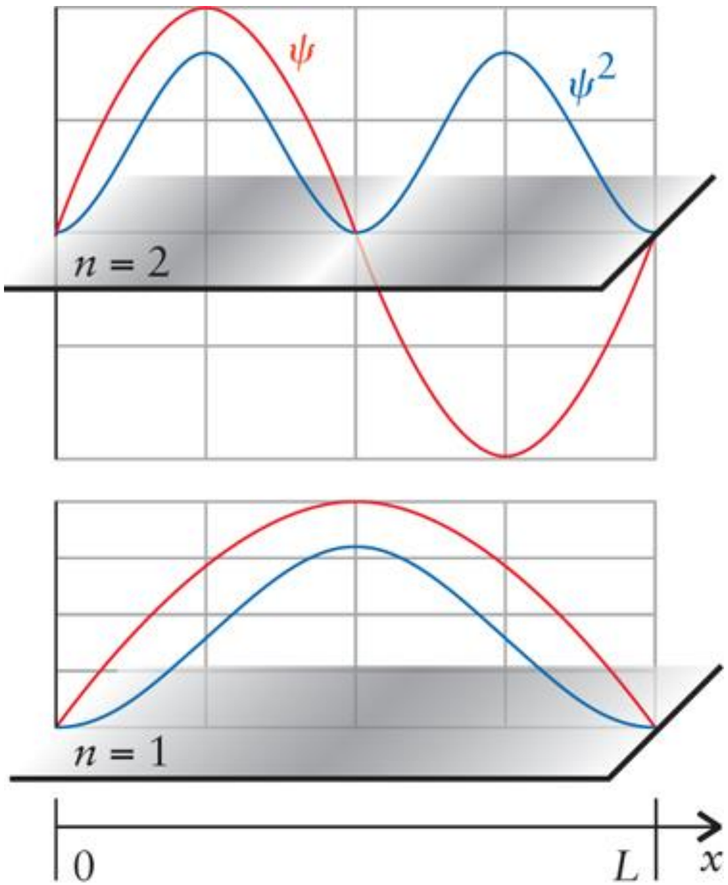
$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

This is not due to the observe effect - disturbing measurement. *It is not a statement about the observational success of current technology*.

The quantum uncertainty is inherent in the properties of all wave-like systems, arising in quantum mechanics simply due to the matter wave nature of all quantum objects.

It is a *fundamental property of quantum systems*

# Energy cannot be zero




A particle in a container cannot have **zero energy**;

The wave cannot remain perfectly still.

The **Particle in the Box** reveals the foundation behind all of the ideas that follow.