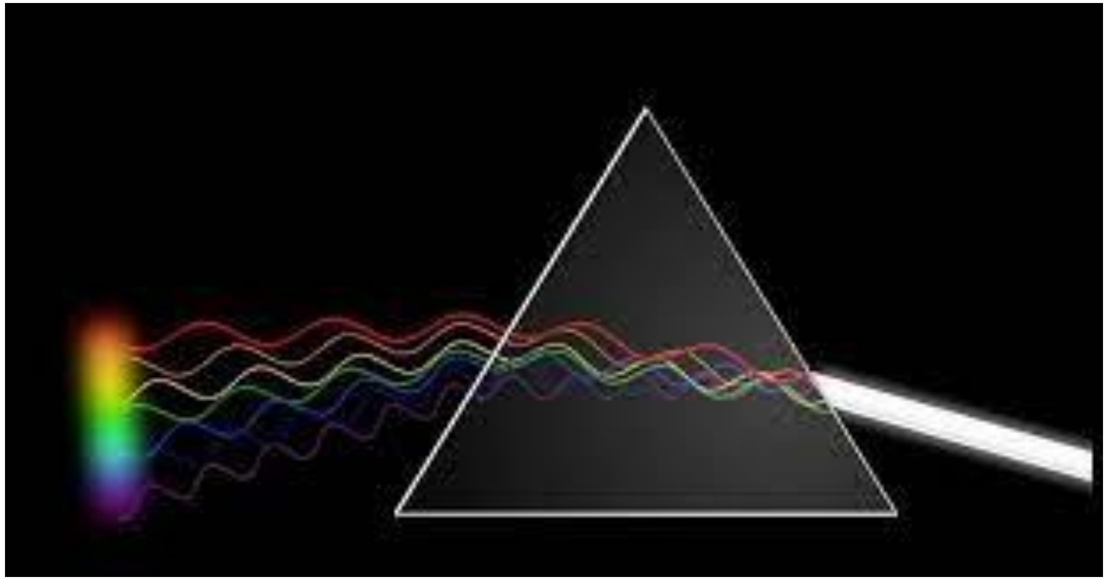
The Optical Spectroscopy

Chapter One
Basics of spectroscopy science



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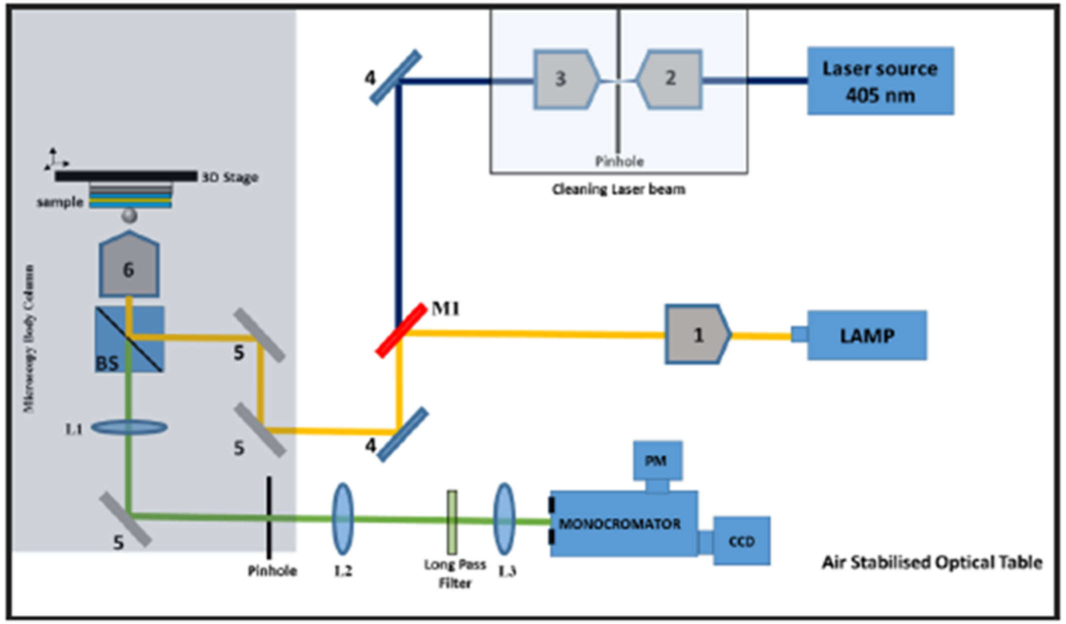
Where does the word spectroscopy come from?

It started with light. The word spectroscopy is **derived from two words: spectrum, which means image in Latin, and skopia, which means observation in Greek**.

Is spectroscopy an optic?

All optical spectroscopy instruments are optical devices in that they use light sources, manipulate the light and measure the light.



Home made spectroscopic set-up/Physics Department-Hull University

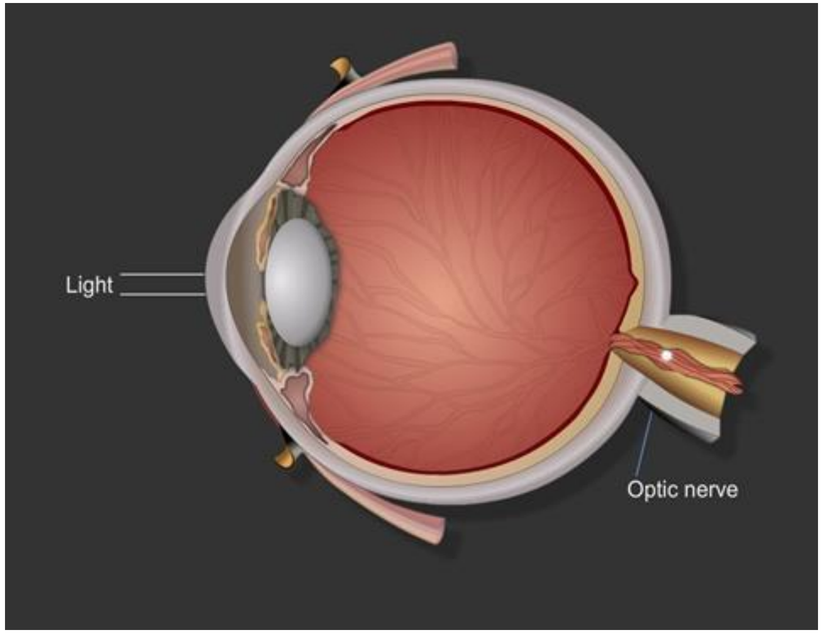
So Optics is the branch of physics that studies the behavior and properties of light, There are two major branches of optics, physical and geometrical. Physical optics deals primarily with the nature and properties of light itself (**like reflection, refraction, interference, diffraction, polarization etc.**) .

Geometrical optics has to do with the principles that govern the image-forming properties of lenses, mirrors, and other devices that make use of light.

While

Spectroscopy is used as a tool for studying the structures of atoms and molecules. The large number of wavelengths emitted by these systems makes it possible to investigate their structures in detail, including the electron configurations of ground and various excited states.

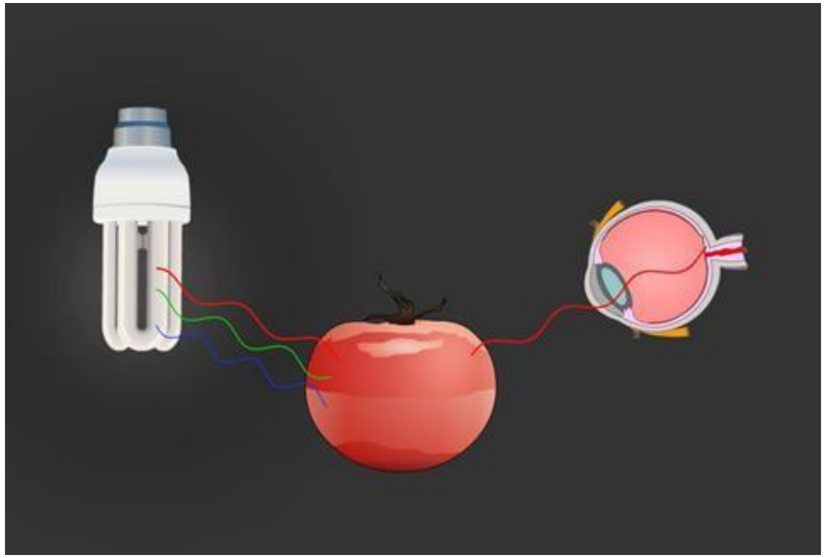
The human eye and brain together translate light into colour. Light receptors within the eye transmit messages to the brain, which produces the familiar sensations of colour.

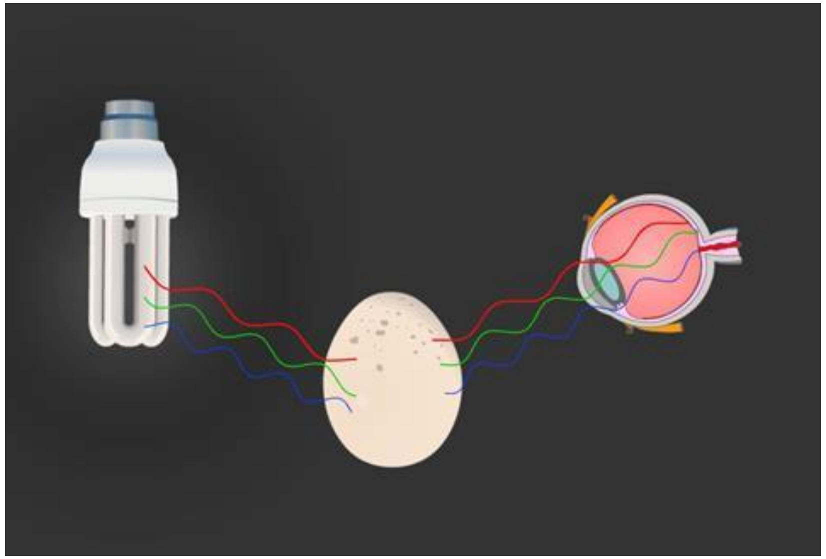


Newton stated that the surface of an object reflects some colours and absorbs all the others. We perceive only the reflected colours.

The surface of the red apple is reflecting the wavelengths we see as red and absorbing all the rest

object appears white when it reflects all wavelengths, and it appears black when it absorbs all wavelengths.





1- BASIC CONCEPTS

Meaning of Spectroscopy

The science of spectroscopy grew out of studies of the interaction of electromagnetic radiation (energy) with **matter**. When light **shines** on an object, for example, we know that part of the energy (light) is **scattered** (reflected) and part is **absorbed**. Of the initial part that is absorbed, some is later **emitted** by matter as light of a different color or wavelength. (energy is absorbed or emitted by matter in discrete quantities (quanta).

- **It is valuable to know information on the nature and constitution of matter for example Measuring the Wavelength of the absorbed or emitted radiation by the matter.**

- **Spectroscopy** is that science which attempts to determine what specific energies and amounts of **incident light are absorbed by specific substances**, and what **specific energies and amounts are later re-emitted.**

- In **practice,** Optical instruments called ***spectrometers*** reveal in photographic or printed records as a series of specific **wavelengths or frequencies** of the light energies absorbed and emitted. These records, in turn referred to as **spectra** **give us an important information and diagnosis the material type and to understand the atomic and molecular structures which the electromagnetic energy is focused.**

- Figure 1 shows the emission line spectra for the elements hydrogen, helium, and mercury vapor.

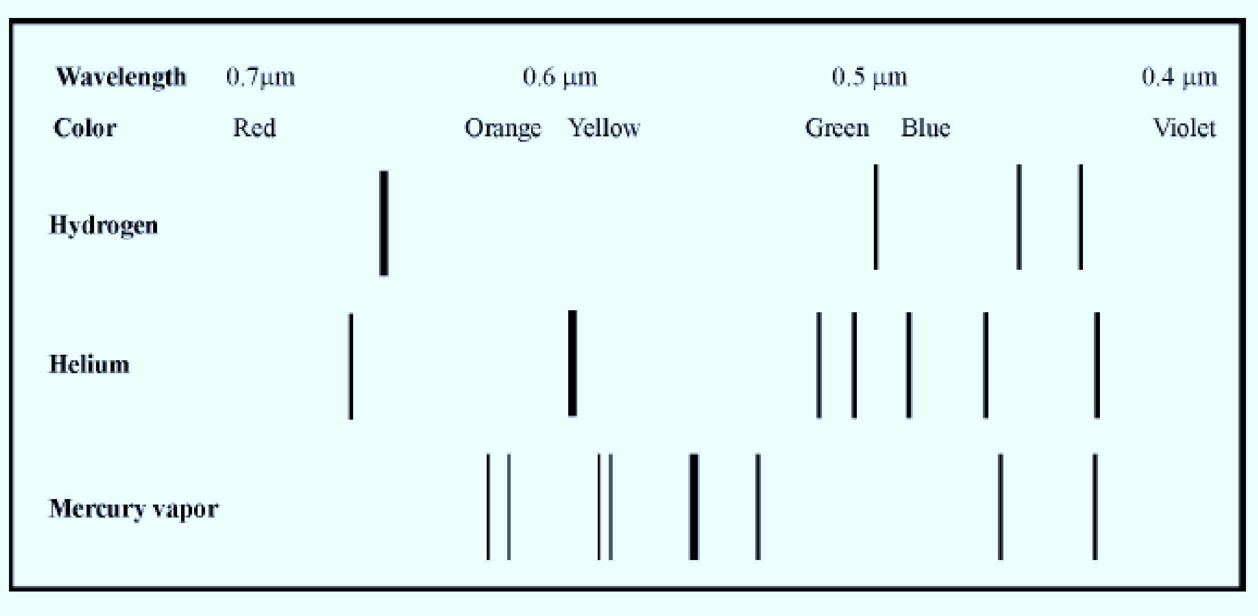


Figure 1 Line spectra for three distinct elements (Adapted from Adventures in Physics, Highsmith and Howard, 1972)

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It can be seen that the array of narrow spectral lines (the spectrum) is different for each element and thus provides one with a unique, **characteristic record or trace**. The vertical lines in the various spectra shown in Figure 1 are actually the images of a narrow slit located in the optical instrument (spectrometer) shown in Figure 2. As can be seen, light from a source enters a narrow slit, is collimated by a lens, and falls on a prism. There it is separated (dispersed) into its constituent colors (wavelengths) and focused by a second lens onto a film plate to form the spectrum.

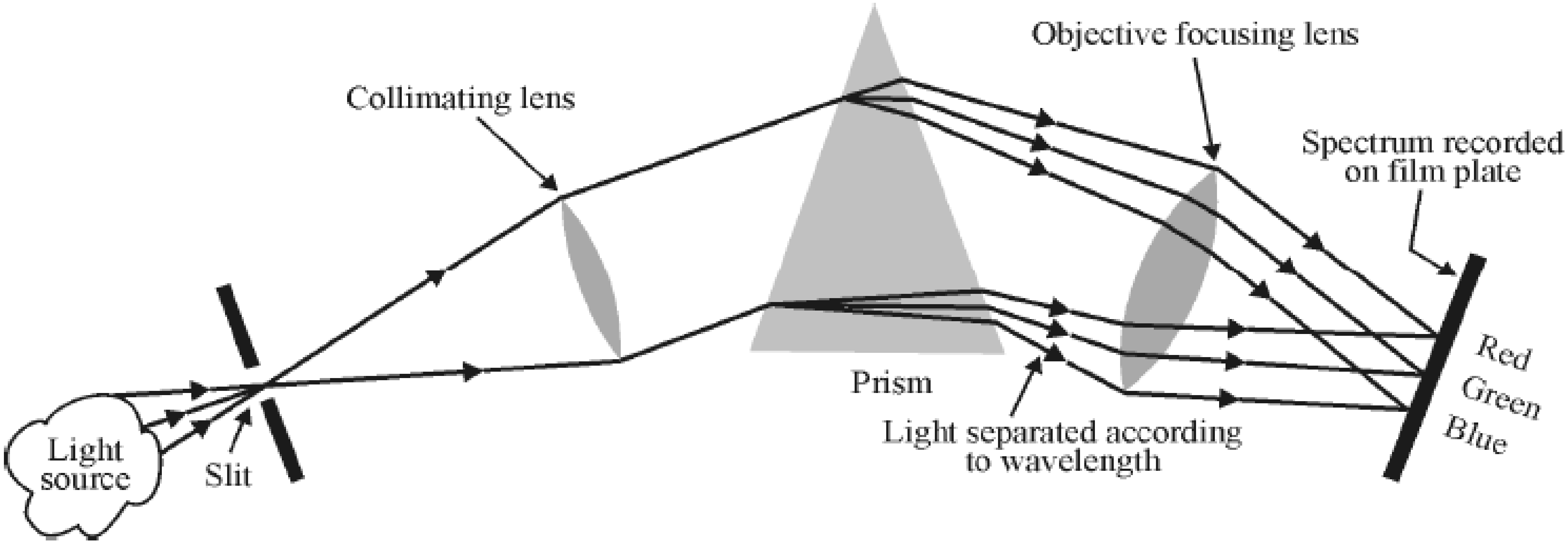

Figure 1-2 *The basic operation of a simple prism spectrometer. In other optical instruments for displaying or recording spectra, the prism is replaced by a diffraction grating or interferometer.* (Adapted from *Physical Science,* Robert Dixon, 1979)

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2- A Brief History of Spectroscopy

Before we start a review of electromagnetic spectra, photons, and the process of light absorption and **emission** in matter, let us outline briefly the development of spectroscopy as a science of detection in modern technologies.

- In ancient times, Egyptians and Greeks thought about light and color and considered light to be mostly "something" that **emanated** from the eyes.

- Following the Middle Ages (400–1350 AD) and the Renaissance period (1350–1700 AD), ancient, **classical ways of thinking gave way to more creative, academic analyses and crude optical instruments began to appear.**

Scientists like Johann Kepler, Willebrord Snell, and Galileo Galilei used **combinations of lenses in telescopes to see distant objects.**

Sir Isaac Newton, in the latter half of the 17th century, showed how a prism "broke" white light passing through it into a rainbow of separate and distinct colors.

- All through these years, the best scientific minds puzzled over the question **"what is light?"** The corpuscular or particle theory of light was championed by Isaac Newton and seemed securely entrenched in the mid-1700s.

Later, the work of **Christiaan Huygens, Thomas Young, and Augustin Fresnel** lent considerable support to the wave theory of light. So the battle between **"light as particle" and "light as wave"** continued on into the **20th century** with intellectual giants such as **James Clerk Maxwell and Albert Einstein** providing significant evidence for one or the other model.

- In the midst of all the theoretical turbulence on the nature of light, the science of spectroscopy was **nevertheless taking shape**. In 1802 a physicist named **W. H. Wolleston used a prism, lenses, and a narrow beam of light to produce an image of a *single wavelength*** of the light. Following this work, with the help of a different light dispersing element a diffraction grating scientists produced similar ***monochromatic*** images of "split light."

- During the first half of the 1800s, The spectroscope as an instrument, like that sketched in Figure 2, became a practical laboratory instrument in the hands of German physicists such as Josef Fraunhofer, G. R. Kirchoff, and Robert Bunsen.

- With Fraunhofer's study of **solar energy** and the discovery of narrow dark lines in the solar spectrum, and with the ongoing analysis of light sources based on flames produced with Bunsen burners, there appeared **bright lines as well as dark lines, and the science of spectroscopy was launched.**

- Finally, Scientists understood then that the dark and bright lines seen in **absorption** and **emission** were uniquely characteristic of the **internal makeup of chemical elements**. They assumed, correctly, that the energy in light could somehow excite the internal motions of atoms and molecules, extracting energy from the light at certain wavelengths, thereby giving rise to the narrow absorption lines.

3- Generate the electromagnetic wave

All electromagnetic (EM) waves are created by accelerating electric charges. **Thus the *frequency, wavelength,* and *energy* of EM waves all depend on charge acceleration and just how this acceleration changes with time.**

For example, for a charge moving with simple harmonic motion, the frequency *f* of the EM wave emitted by the accelerating charge is equal to the frequency ***f* of the charge's motion**.

If the charge oscillates back and forth with a frequency of three times per second, **it will emit a wave with a frequency of 3 cycles/sec, or 3 hertz.**

To **create light** waves in the ***visible*** part of the electromagnetic spectrum—a wavelength range of 400 nm to 0.700 nm , an electric charge must accelerate at a rate high enough to generate waves of lengths around 0.5×10^{-6} meters. Now we know that for any wave,

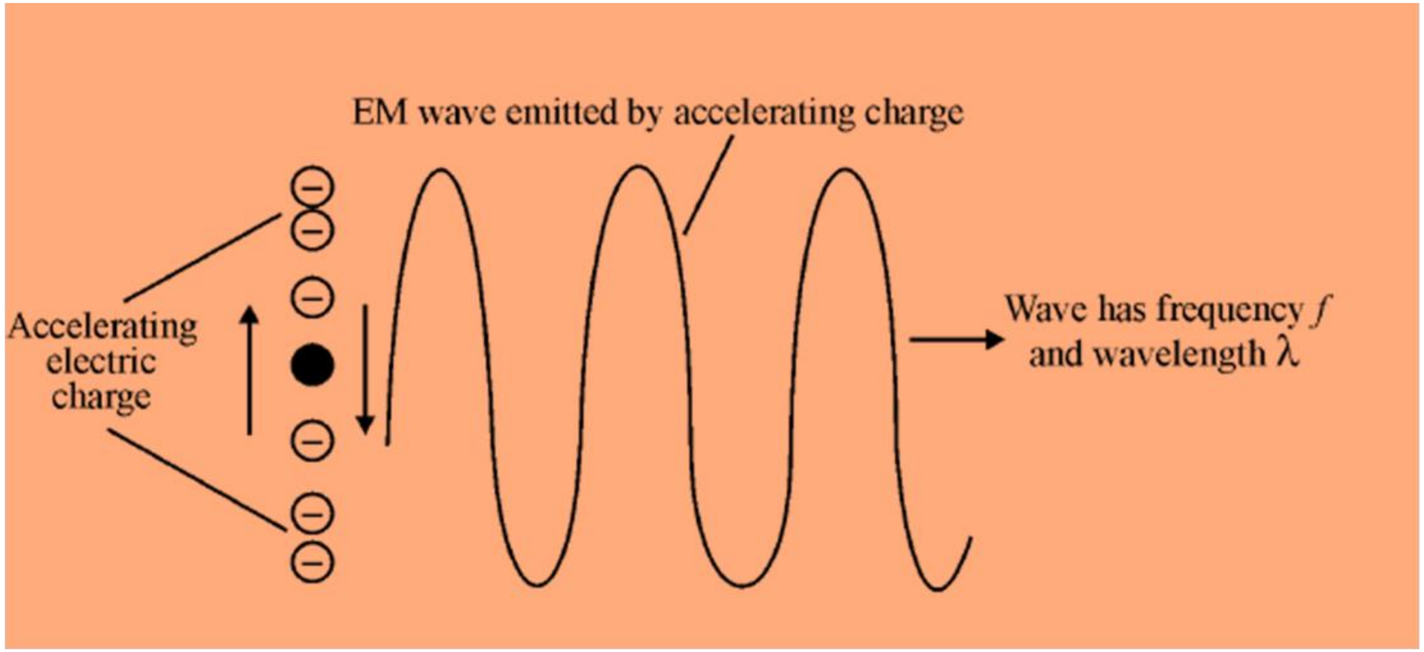
$$v = f\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ 1$$

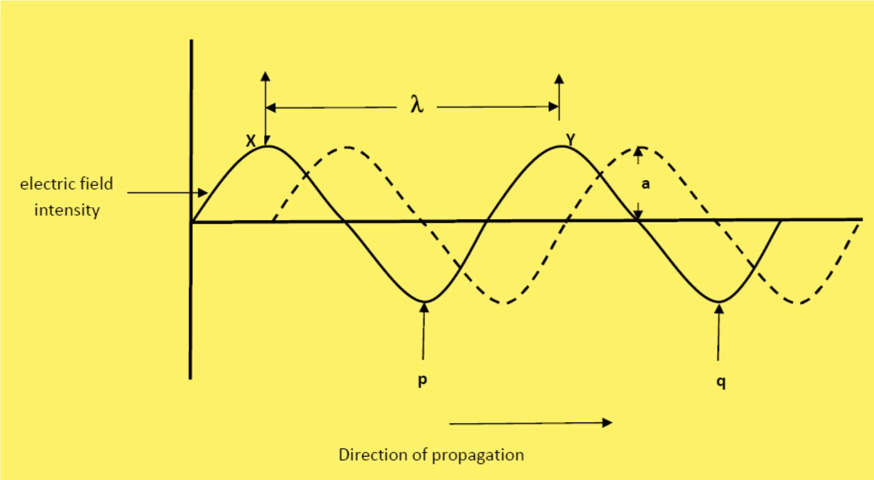
Where
v = wave speed in meters per second (m/s)
f = frequency in cycles per second or hertz (Hz)
λ = wavelength in meters (m)

Thus, for light in free space, where $v = 3 \times 10^{8}$ m/s, and for the mid-visible region of light around 0.5×10^{-6} m, the frequency from Equation 1 would be

$$f = \frac{v}{\lambda} = \frac{3 \times 10^{8}\,\text{ms}}{0.5 \times 10^{-6}\,\text{m}} = 6 \times 10^{14}\ \text{Hz}$$

A tremendously high value! Clearly, there are no ordinary "mechanical motions" of charged substances at our disposal that can attain such high frequencies. **Only in regions inside atoms and molecules—where the electrons move very rapidly around the nucleus and where atoms vibrate and oscillate very rapidly in molecules, can such high frequencies of moving electric charges be realized.** Figure below shows the creation of a single wave by an oscillating charge.





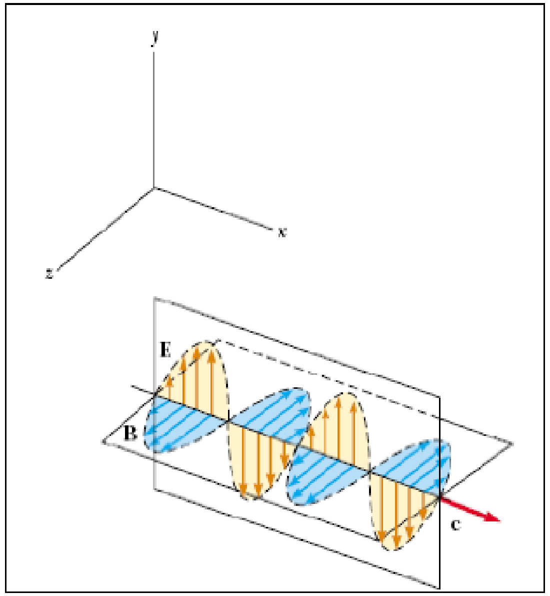
Accelerating charge e– creates an EM wave of wavelength λ and frequency f

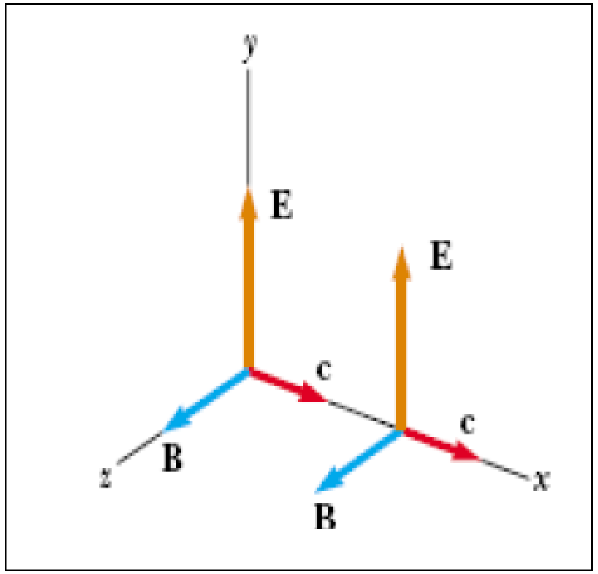
Figure 1

(unlike mechanical waves) can propagate through **empty space**. So, To understand the prediction of electromagnetic waves more fully, let us focus our attention on an electromagnetic wave that travels in the:*x* direction (the *direction of propagation*). In this wave, **the electric field E** is in the *y* direction, and the **magnetic field B is in the *z* direction**, as shown in the Figure.

Waves such as this one, in which the electric and magnetic fields are restricted to being parallel to a pair of perpendicular axes, are said to be **linearly polarized waves.**

Furthermore, we assume that at any point in space, **the magnitudes *E* and *B* of the fields depend upon *x* and *t*** only, and not upon the *y* or *z* coordinate.





The speed of (EM)

$$c = \frac{1}{\sqrt{\mu_0 \epsilon_0}}$$

- μ_0 is the free space magnetic permeability: $\mu_0 = 4\pi \times 10^{-7}\ \mathrm{T \cdot m/A}$
- ε_0 is the free space electric permeability: $\epsilon_0 = 8.854\,19 \times 10^{-12}\ \mathrm{C^2/N \cdot m^2}$
- c is the speed of light in vacuum: $c = 2.997\,92 \times 10^{8}\ \mathrm{m/s}$

The speed of (EM) value in free space leads us to believe that the light is electromagnetic wave

The simplest solution of the wave equation in EM waves is a sinusoidal wave, so the equations of the electric and magnetic fields can be written as follows:

$$E = E_{max} \cos(kx - \omega t)$$

$$B = B_{max} \cos(kx - \omega t)$$

Where E_{max} and B_{max} are the maximum values of the fields.

The angular wave number **($K = 2\pi/\lambda$)** is represent the number of wave per unit length.

The angular frequency **($\omega = 2\pi f$) where f is the wave frequency**. The ratio ***ω/K equals the speed of light c***

Using this solution, we can derive that

$$\frac{E_{max}}{B_{max}} = \frac{E}{B} = c$$

That is, **at every instant the ratio of the magnitude of the electric field to the magnitude of the magnetic field in an electromagnetic wave equals the speed of light.**

In an empty space the speed of light for any E.M radiation is equal to : $c = 3*10^8$ m.s^{-1}

In a transparent medium the velocity (c') is less than (c). This reduction is related to the refractive index of medium by:

Refractive index of the medium(n)

=(velocity in vacuum / velocity in medium) = c/c'

so : $c' = c/n$

As the radiation enters a region of higher ref. index, the wavelength is reduced, the frequency remains constant.

Ref. index of air is ~ 1.0028 for visible light, the effect on λ due to air maybe *ignored* except for high accuracy work.

Example **An Electromagnetic Wave**

A sinusoidal electromagnetic wave of frequency 40.0 MHz travels in free space in the x direction, as in Figure 34.4.

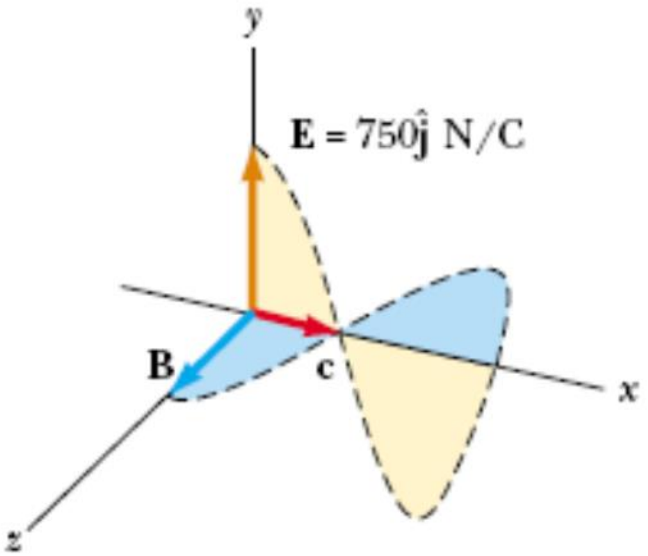
(A) Determine the wavelength and period of the wave.

Solution Using Equation for light waves and given that $f = 40.0 \text{ MHz} = 4.00 \times 10^7 \text{ s}^{-1}$, we have

$$\lambda = \frac{c}{f} = \frac{3.00 \times 10^8 \text{ m/s}}{4.00 \times 10^7 \text{ s}^{-1}} = 7.50 \text{ m}$$

The period T of the wave is the inverse of the frequency:

$$T = \frac{1}{f} = \frac{1}{4.00 \times 10^7 \text{ s}^{-1}} = 2.50 \times 10^{-8} \text{ s}$$



(B) At some point and at some instant, the electric field has its maximum value of 750 N/C and is along the y axis. Calculate the magnitude and direction of the magnetic field at this position and time.

Solution From Equation we see that

$$B_{max} = \frac{E_{max}}{c} = \frac{750 \text{ N/C}}{3.00 \times 10^8 \text{ m/s}} = 2.50 \times 10^{-6} \text{ T}$$

Because **E** and **B** must be perpendicular to each other and perpendicular to the direction of wave propagation (x in this case), we conclude that **B** is in the z direction.

(C) Write expressions for the space–time variation of the components of the electric and magnetic fields for this wave.

Solution We can apply Equation:

$$E = E_{max} \cos(kx - \omega t) = (750 \text{ N/C}) \cos(kx - \omega t)$$

$$B = B_{max} \cos(kx - \omega t) = (2.50 \times 10^{-6} \text{ T}) \cos(kx - \omega t)$$

where

$$\omega = 2\pi f = 2\pi(4.00 \times 10^7 \text{ s}^{-1}) = 2.51 \times 10^8 \text{ rad/s}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{7.50 \text{ m}} = 0.838 \text{ rad/m}$$

4-The Electromagnetic wave Spectrum

As we have mentioned in the previous section, accelerating charges produce electromagnetic waves. There are many levels in the structure of matter where moving (accelerating) charges exist. Some of the more obvious are **electrons in an atom**, **freely-moving electrons in conducting metals**, **vibrating atoms in molecules**, and **charged particles in a nucleus**.

Thus, two factors result in the many different types of electromagnetic waves we observe
1- The source of the charge motions and
2- The accelerations inherent in the motions.

The many different types of EM waves are categorized according to their **origins** and their **frequency/wavelength** values. A typical organization of the ***electromagnetic spectrum*** is shown in table below with special emphases given to the location of the **infrared**, visible, and **ultraviolet** regions

Radiation type	Wave length (A°)	Wave number $\nu' = 1/\lambda (cm^{-1})$	Frequency (ν) $\nu = C/\lambda$ (Hz)	Energy (cal / mole)	Effects
Radio	10^{14} - 10^{12}	10^{-6} - 10^{-4}	$3x10^{4}$ - $3x10^{6}$	10^{-6} - 10^{-4}	Spin orientations
Television	10^{10}	10^{-2}	$3x10^{8}$	10^{-2}	Spin orientations
Radar	10^{8}	10^{-1}	$3x10^{10}$	2.85	Spin orientations
Microwave	10^{7}	10	$3x10^{11}$	28.5	Rotational molecular trasitions
Far IR	10^{6}	10^{2}	$3x10^{12}$	285	Rotational molecular trasitions
Near IR	10^{4}	10^{4}	$3x10^{14}$	28 k	Vibrational
Red	$8x10^{3}$	$1.2x10^{4}$	$3.7x10^{14}$	35.7 k	Inner Shell / electronic transition
Violet	$4x10^{3}$	$2.4x10^{4}$	$7.5x10^{14}$	71.4 k	Inner Shell / electronic transition
Ultraviolet	$3x10^{3}$	$3.2x10^{4}$	$1x10^{15}$	96 k	Valence Shell / electronic transition
X-rays	1	10^{8}	$3x10^{18}$	10^{8}	Valence Shell / electronic transition
γ -rays	10^{-2}	10^{10}	$3x10^{20}$	10^{10}	Nuclear transition
Cosmic rays	10^{-4}	10^{12}	$3x10^{22}$	10^{14}	Nuclear transition

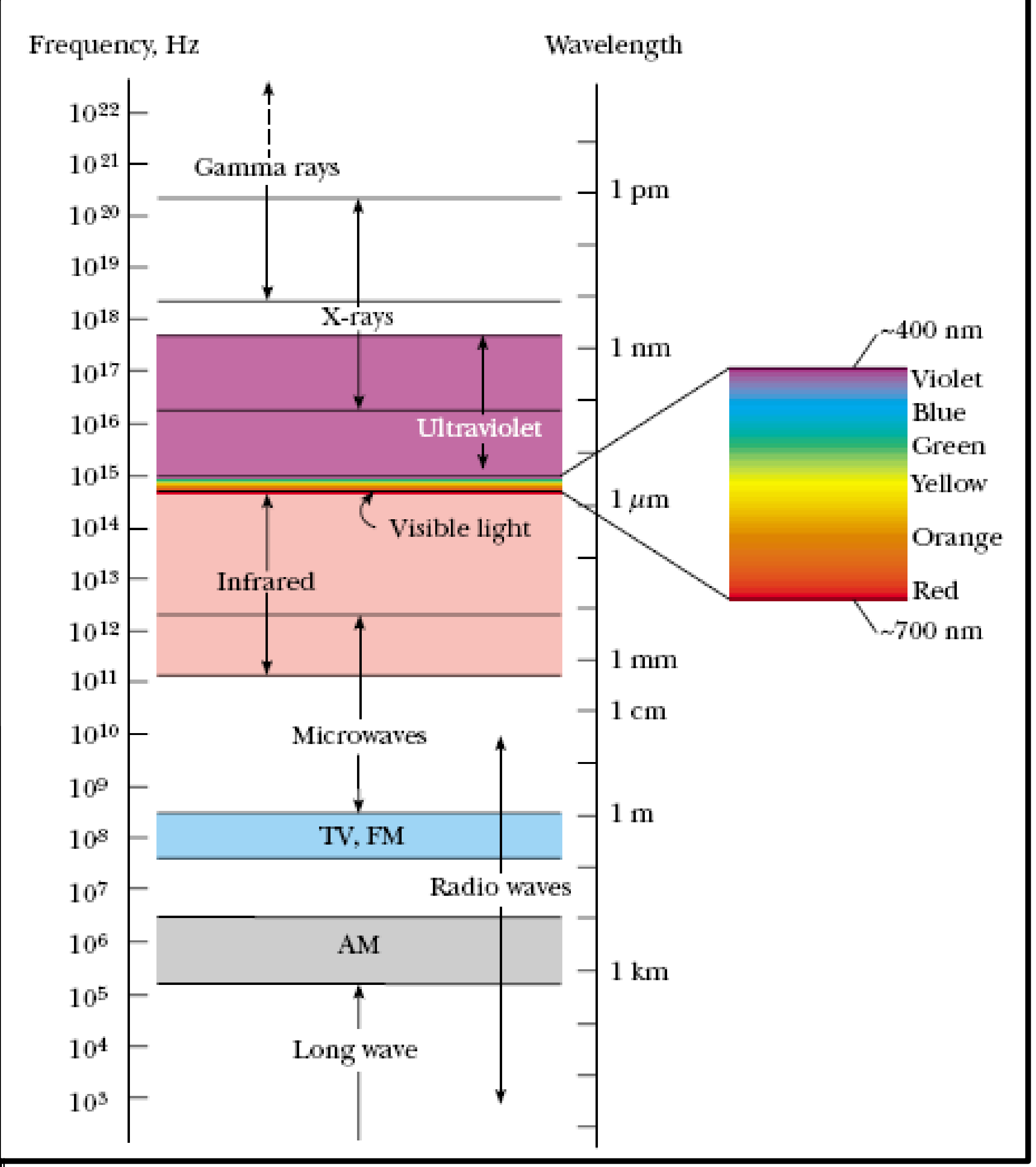


Figure (2)The electromagnetic spectrum and its principal regions

- Devices that produce or detect electromagnetic waves must be designed to operate at the frequency of the waves they **emit or receive**. For example, **radio AM and FM transmitters and similar receivers operate at frequencies in the 10^3 to 10^7 Hz range and are designed to emit or respond to these frequencies. X-ray tubes and films are designed for use in the 10^{17} to 10^{19} Hz frequency range. Lasers generally produce laser light in the frequency and wavelength range extending from the infrared to the ultraviolet.**

- The EM spectrum is generally divided into **seven** regions, **in order of decreasing wavelength and increasing energy and frequency**. The common designations are:

Radio waves, (energy transition that takes Place by Changes in nuclear spins Changes in electronic spins) whose wavelengths range from more than **10^4 m to about 0.1 m**, are the result of charges accelerating through conducting wires. They are generated by such electronic devices as *LC* oscillators and are used in **radio and television communication systems.**

Microwaves (energy transition that takes Place byRotational motions of molecules) have wavelengths ranging from approximately **0.3 m to 10^{-4} m** and are also generated by
electronic devices. Because of their short wavelengths, they are well suited for **radar systems. Microwave ovens are an interesting domestic application of these waves.**

Infrared waves (energy transition that takes Place by Vibrational motions of atoms in molecules), they have wavelengths ranging from approximately **10^{-3} m to the longest wavelength of visible light, 7 x 10^{-7}m.** These waves, produced by molecules and room-temperature objects, are readily absorbed by most materials. **The infrared (IR) energy absorbed by a substance appears as internal energy because the energy agitates. The atoms of the object, increasing their vibrational or translational motion, which results in a temperature increase.**

Infrared radiation has practical and scientific applications in many areas, **including physical therapy, IR photography, and vibrational spectroscopy.**

Visible light, **(energy transition that takes Place by Electronic rearrangements)** the most familiar form of electromagnetic waves, is the part of the electromagnetic spectrum that the **human eye can detect**. Light is produced by the Rearrangement of electrons in atoms and molecules. The various wavelengths of visible ranging from approximately from 400 nm to 700 nm. The sensitivity of the human eye is a function of wavelength.

Ultraviolet waves **(energy transition that takes Place by Electronic rearrangements)** cover wavelengths ranging from approximately **4 x 10^{-7} m to 6 x 10^{-10} m**. The Sun is an important source of ultraviolet (UV) light, which is the main cause of sunburn. **Sunscreen lotions are transparent to visible light but absorb most UV light.**

X-rays **(energy transition that takes Place by Breaking molecular bonds)** have wavelengths in the range from approximately **10^{-8} m to 10^{-12} m**. The most **common source of x-rays is the stopping of high-energy electrons upon bombarding a metal target.** X-rays are used as a diagnostic tool in medicine and as a treatment for certain forms of cancer. Because x-rays damage or destroy living tissues and organisms, care must be taken to avoid unnecessary exposure or overexposure.

Gamma rays are electromagnetic waves emitted by radioactive nuclei (such as 60Co and 137Cs) and during certain nuclear reactions. High energy gamma rays are a component of cosmic rays that enter the Earth's atmosphere from space. **They have wavelengths ranging from approximately 10^{-10} m to less than 10^{-14} m.** They are highly penetrating and produce serious damage when absorbed by living tissues.

5- Particle Properties of Electromagnetic Energy

In Figures 1&2 we have emphasized the **wave properties of light**. We treat light as a wave to describe its propagation **from one point to another** and to explain its behavior in interference, diffraction, and polarization phenomena.

To describe its behavior in the process of **reflection and refraction of light, or in the emission and absorption of light by atoms,** we find it useful to treat light as a "particle"—a **localized EM wave packet.** We refer to this wave packet as a ***photon***. A photon is the smallest division of a light beam that retains the properties of the beam. The characteristics of a photon include its frequency, its wavelength, and its energy. A photon ***should not*** be visualized merely as a particle that has physical dimension or a specific location in space. **More accurately, a photon is viewed as a "wave packet" that has a specific energy content.**

The *energy* of a photon is directly proportional to the *frequency of light* in its wave packet and is given by Equation .

$E = h*f = h * \upsilon$ h= planck's constant = $6.63*10^{-34}$ J.s

E in joules & f in $Hz = s^{-1}$

$E\ (joule) = hc/\lambda$ $= (6.63*10^{-34} *3*10^{8}) / \lambda$ (joules)

But: $1\ ev = 1.6*10^{-19}$ J

So : E in (ev) $=(6.63*10^{-34} * 3*10^{8}) /(\lambda * 1.6 *10^{-19})$ ev

$=(1.243*10^{-6})/\lambda$ ev

Examples 1, 2, and 3 illustrate the use of these two equations.

Example 1

Calculation of the energy of a photon of given frequency

Given: The frequency of a photon of HeNe laser light is 4.74×10^{14} Hz.

Find: The energy of the photon

Solution:

$$E = hf \quad \text{(Eq. 1-2)}$$

$$E = (6.625 \times 10^{-34}\ \text{J} \cdot \text{sec})(4.74 \times 10^{14}/\text{sec})$$

$$E = 3.14 \times 10^{-19}\ \text{J}$$

Example 2

Calculation of the energy of a photon of a given wavelength

Given: The wavelength of a HeNe laser light is near 633 nm.

Find: The energy of the photon of this wavelength

Solution:

$$E = \frac{hc}{\lambda} \quad \text{(Eq. 1-3)}$$

$$E = \frac{(6.625 \times 10^{-34}\ \text{J} \cdot \text{sec})(3 \times 10^{8}\ \text{m/sec})}{6.33 \times 10^{-7}\ \text{m}}$$

$E = 3.14 \times 10^{-19}$ J (Same as the photon energy calculated in Example 1 for a photon of frequency 4.74×10^{14} Hz)

Example 3

Calculation of wavelength and frequency of a photon of given energy

Given: A photon has an energy of 1.875×10^{-19} J.

Find: The frequency and the wavelength of the photon

Solution:

From Equation 1-2,

$$f = \frac{E}{h}$$

$$= \frac{(1.875 \times 10^{-19}\ \text{J})}{(6.625 \times 10^{-34}\ \text{J} \cdot \text{sec})}$$

$$f = 2.83 \times 10^{14}/\text{sec} = 283\ \text{THz}$$

Note: One terahertz (THz) equals (1×10^{12}) Hertz.

From Equation 1-3,

$$\lambda = \frac{hc}{E}$$

$$= \frac{(6.625 \times 10^{-34}\ \text{J} \cdot \text{sec})(3 \times 10^{8}\ \text{m/sec})}{(1.875 \times 10^{-19}\ \text{J})}$$

$$\lambda = 1.06 \times 10^{-6}\ \text{m} = 1.06\ \mu\text{m}$$

We conclude that

⟹ quantum theory of radiation called photons or quanta.

The wave nature was retained that this photon is still has frequency, and its energy is proportional to the frequency $E = hv$

So, Propagation of light ⟹ waves.

Interaction of light with water ⟹ corpuscles (particles).

i.e, Dual nature of E.M. radiation.

6-The interaction of light with matter

- The interaction of light with matter is best understood by treating light energy as if it were made up of photons more like localized wave packets of energy. The details of the interaction including the absorption and emission of light involve atoms, energy levels, and photons.

- Last year you have studied the Niels Bohr's model of the atom which provides you with helpful insights to these kinds of interactions.

- Here, We model the energy of an **atom according to the different positions of its electrons**. When all the electrons are in an unexcited, or ground, state, the atom is assumed to be in its lowest energy level. When the atom absorbs energy, electrons can be "excited" and moved into higher energy shells. As electrons move from one shell to another, unique amounts, or quanta, of energy are absorbed or emitted as we have noted earlier. A photon is such a quantum of energy.

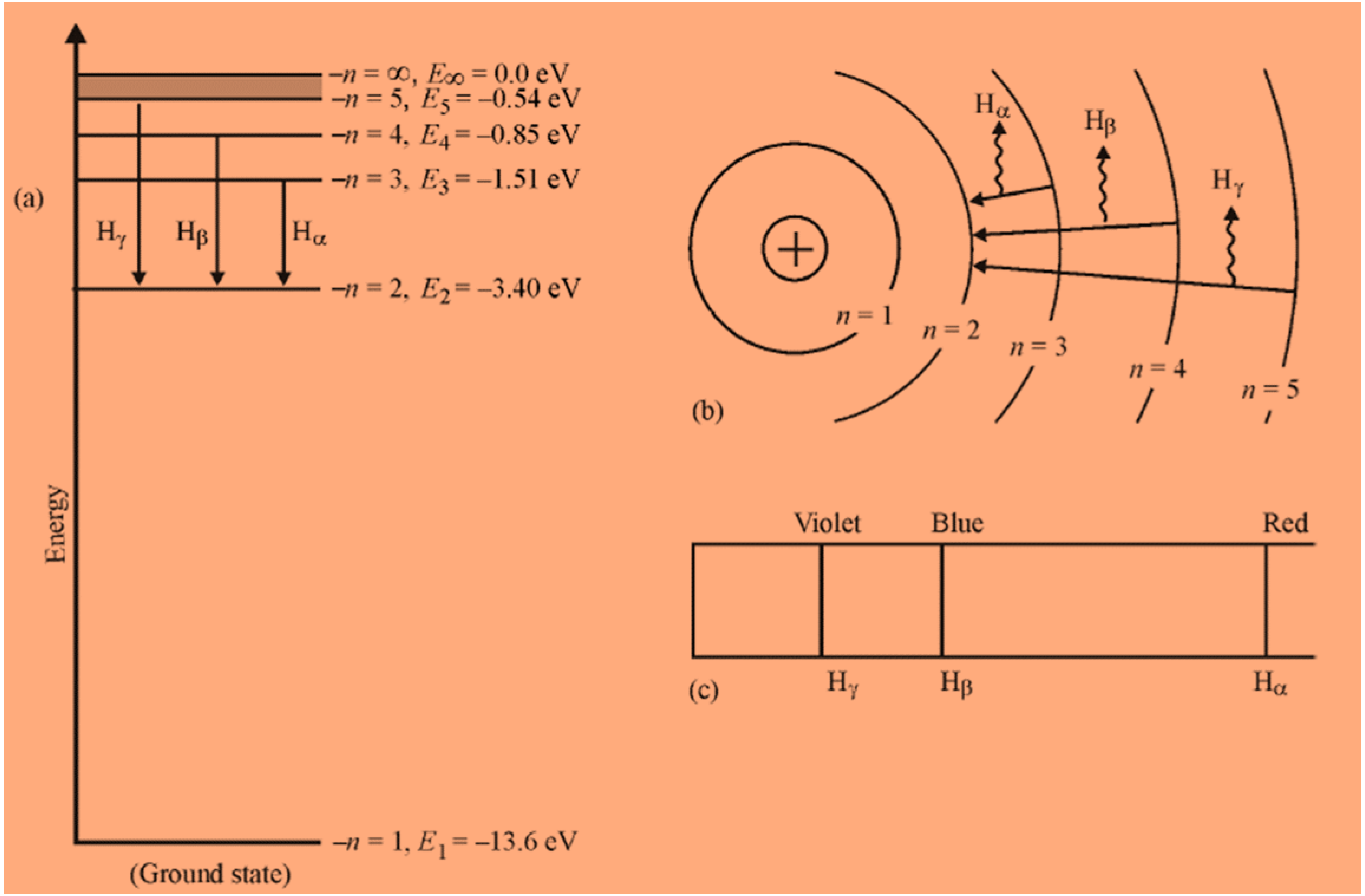
- An atomic energy-level diagram shows the unique electron energies available in a given atom.

- An energy-level diagram for **hydrogen** is shown in Figure 3a. **Hydrogen has only one electron**, and so it can exist in only one of the available energy levels shown at a time. The lowest level, E_1, is the ***ground state***. Energy must be added to the atom for the electron to move to a higher level. Note that energy levels range from a negative value of –13.6 eV (electron volts) for the lowest energy level ($n = 1$) to a value of 0.0 eV for the very highest energy level ($n = \infty$) when the electron breaks free from the atom.
- Next to the energy level diagram for hydrogen, we show (Figure 3b) the available energy shells and principal energy transition from higher energy levels down to the energy level marked $n = 2$ or E_2. There we see Hα for the 3-to-2 transition, Hβ for the 4-to-2 transition, and Hγ for the 5-to-2 transition.
- Suppose a hydrogen atom is in an excited energy state that corresponds to the $n = 3$ level. The atom can make a transition to the $n = 2$ level by ***emitting a photon***. **The energy of the emitted photon equals the decrease in energy of the atom (in going from E_3 to E_2), as illustrated below.**

$$\begin{aligned} E_{\text{photon}} &= E_3 - E_2 \\ &= -1.51\ \text{eV} - (-3.4\ \text{eV}) \\ &= 1.89\ \text{eV}^{(2)} \end{aligned}$$

(Be sure to pay close attention to negative signs for the energies.)

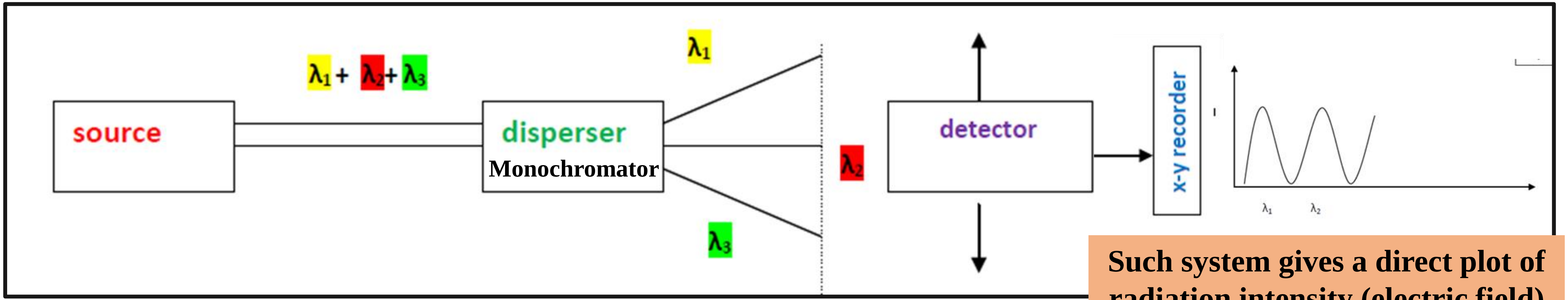
The atom can also ***absorb photons***. This happens when the energy of a photon exactly matches **the difference between two electron energy levels**. For example, a hydrogen atom in the $n = 2$ state can absorb a photon whose energy is 1.89 eV. The electron in the atom will then move from energy level *E*2 to energy level *E*3.



<u>Figure 3</u> **Energy levels, shells, and line spectra for the hydrogen atom. In (a) transitions from levels n = 5, 4, 3 to n = 2 yield the energy emissions (spectral lines) Hγ , Hβ , Hα respectively, as shown in (b), the energy shell view, and in (c), the line spectra view as seen on film—with colors shown in the visible EM region.**

7- Essential Parts of the Spectroscopic System

Any spectroscopic system consists of 3 basic elements:



Such system gives a direct plot of radiation intensity (electric field) versus wavelength.

Note: Electric component is more important for spectrometric studies over magnetic component? why

Source : Source of radiation under investigation .

Disperser : spreads or separates the light out spatially into its constituent wavelengths (or spectrum)

Detector : records the incident intensity of the separated monochromatic radiation as a function of position (ie wavelengths).