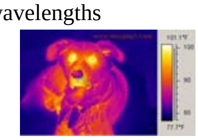
From Classical to Quantum Mechanics
Chapter 12

The need for non-classical thinking - Quantum Mechanics:

Inability of classical mechanics to explain atomic and molecular phenomena, in particular three important physical observations.

1. Blackbody Radiation
2. The Photoelectric Effect
3. The Hydrogen Atom/Spectra

Objects at a temperature above 0 K emits ‘light’ in a range of wavelengths



https://encrypted-tbn3.gstatic.com/images?q=tbn:ANd9GcSFb531SxpyIFugn__Ijfq-zxgfMxwmVDyNYJDGnbiJ9o-vbEqh

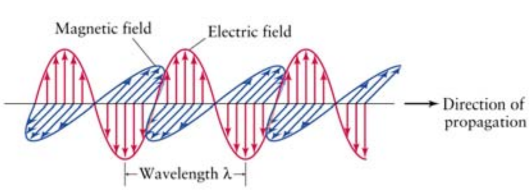
http://scottgable.com/blog/wp-content/uploads/2011/11/MG_2357-2-Edit1.jpg

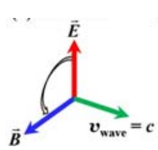
1. <u>Blackbody Radiation:</u> Objects at any temperature above 0 K emits light in a range of wavelengths.

If the object is perfectly ‘black’ (so it doesn't reflect any light to outside), it’s emissions are termed; <u>*blackbody radiation*</u>.

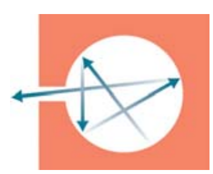
Background - <u>electromagnetic theory</u> (EMT) is highly successful in unifying the disciplines of magnetism, electricity and waves.

<u>Light</u> (EMT) - <u>a wave</u> of oscillating electrical and magnetic fields in orthogonal planes.





Right Hand Rule



<u>Black body</u>: Ideally it is a heated closed container (of temperature, T), a pinhole can be made from which light is leaked/emitted. A perfect emitter of radiation.

All of the emitted radiation has been thermally equilibrated inside the container by many reflections.

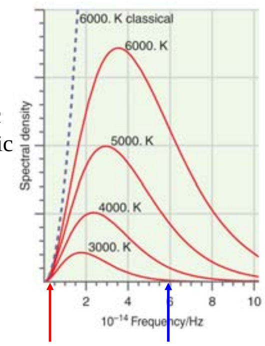
<u>Blackbody radiation</u>.

<u>Classical view.</u>

Radiation is an electromagnetic wave, produced when an electric charge vibrates.

At larger temperatures the vibrations are more energetic – more light is emanated – brighter at ***all*** frequencies.

Blackbody spectrum



cut off

Classical theory assumes that each frequency of vibration should have the same energy. The electrons in a hot object can vibrate with a range of frequencies and there is *no limit to how high such frequencies can be*.

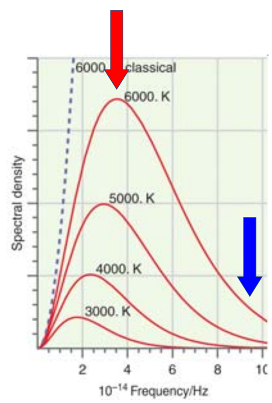
Implication: there should be no limit to the frequency of the light produced by the electrons vibrating at high and low frequencies.

Classical theory would predict that even relatively cool objects should radiate in the UV and visible regions !?

Classical physics predicts that there would be no darkness.

Fact: The intensity of blackbody spectrum always becomes low at the high frequency end.

Classically the shape, The observed intensity distribution (i.e. presence of the maximum) of the spectrum cannot be explained.



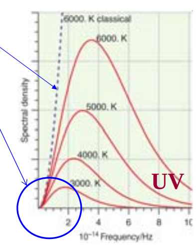
Classical approach leads to: $\rho(\nu,T)\,d\nu = \frac{8\pi\nu^2}{c^3}\bar{E}_{osc}\,d\nu$

Heat is the kinetic energy of random motion, therefore; $\bar{E}_{osc}\ \alpha\ KE \qquad \bar{E}_{osc} = k_B T$

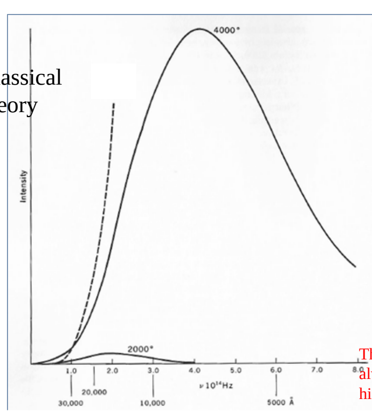
$$\rho(\nu,T)\,d\nu = \frac{8\pi k_B T\nu^2}{c^3}\,d\nu$$

The Rayleigh-Jeans Law was successful at predicting the energy density at low frequencies, but failed at high frequencies - UV.

This inadequacy is known as the ***"UV catastrophe."***



Classical theory



The blackbody spectrum always less at the high ν side.

Peter O'D. Offenhartz, Atomic and Molecular Orbital heory, Mc-Graw Hill Book Company, New York 1970

Planck's insight: Matter is made of molecules/atoms that oscillate. Black body radiation arises from the vibrations of electrical dipoles (oscillators). Rate of vibration of an oscillator - ν. Dipoles vibrate in a range of ν values.

$$E\ \alpha\ \nu \qquad \Rightarrow E = h\nu$$

Oscillators are '*excited*' (or activated) only if they can acquire/absorb an energy of at least $h\nu$ amount of energy.

Energy of an oscillator = a definite quantity of energy, termed as a ***quantum of energy,*** *of the oscillator***.**

For the oscillators of higher frequencies to '*come about into action*' requires high temperatures; because there is a minimum of energy for given oscillator.

Plank proposed that radiation is emitted or absorbed in packets of energy of definite size (quanta); i.e. light by way of energy is not continuous but made of 'packets/particle'.

The energy of a quantum is proportional to the frequency of the oscillator.

Energy packet from a vibration of frequency ν is proportional to ν, equal to hν (photon - a single quantum); *h* a proportionality constant.

Of the photon energy expression hν, h is a proportionality constant!

$$h = 6.63\times10^{-34}\ \text{J s}$$

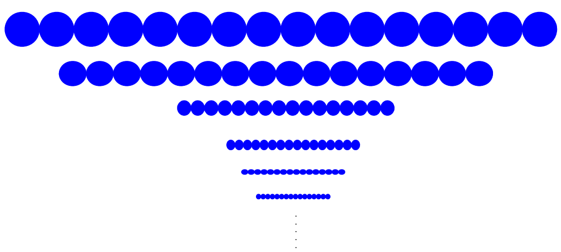
For the higher frequencies, the energy is too great for the walls of the black body to supply the required energy and so they will not be excited/activated at low T.

Also with increasing temperature, the energy of an oscillation of frequency ν can increase as $n \times h\nu$ where n is an integer, n increasing with T.

$$E = nh\nu$$

$$h = 6.63\times10^{-34}\ \text{J s}$$

The *very small value* of h, the Planck's constant, is the reason, that the 'character' of *energy packets* of radiation was noticed before.



$$\bar{E}_{osc} = \cancel{k_B T} \qquad \bar{E}_{osc} = \frac{h\nu}{e^{h\nu/k_BT} - 1} \qquad \text{(Planck)}$$

$$\rho(\nu,T)\,d\nu = \frac{8\pi \cancel{k_B T}\nu^2}{c^3}\,d\nu$$

$$\boxed{\rho(\nu,T)d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT} - 1}d\nu}$$

Valid @ all frequencies and T.

In the region $kT >> h\nu$: $\bar{E}_{osc} \rightarrow k_B T$

$$\bar{E}_{osc} = \frac{h\nu}{e^{h\nu/k_BT} - 1} = \frac{h\nu}{(\cancel{1} + h\nu/k_BT + \cancel{\ldots}) - \cancel{1}} \approx k_BT$$

Correspondence Principle *(a detour)*.

As temperature increases quantum system morphs into the classical system, because for $kT >> h\nu$: $\bar{E}_{osc} \rightarrow k_B T$

$$\bar{E}_{osc} = \frac{h\nu}{e^{h\nu/k_BT} - 1} = \frac{h\nu}{(1 + h\nu/k_BT + \ldots) - 1} \approx k_BT$$

$$\rho(\nu,T)\,d\nu = \frac{8\pi\nu^2}{c^3}\bar{E}_{osc}\,d\nu$$

$$\downarrow \quad \bar{E}_{osc} = k_B T$$

High temp. limit classical

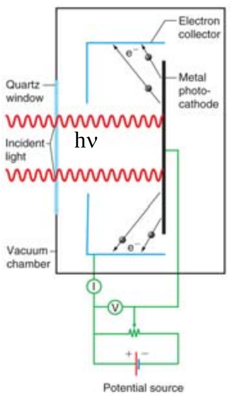
$$\rho(\nu,T)\,d\nu = \frac{8\pi k_B T\nu^2}{c^3}\,d\nu$$

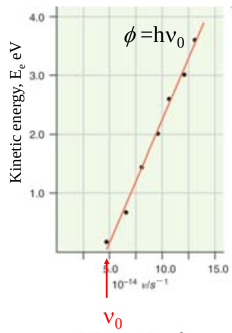
2. The Photoelectric Effect:

Phenomenon: Shining light on the surface of a metallic substance results in the metal absorbing the light energy and electrons escaping from the metal surface.

Classically, light carries energy and when using low light intensities there would be a time delay for sufficient light energy to build up and be used to eject an electron.
KE of ejected electron increases with light intensity.

Experimentally, if light of a certain frequency can eject electrons from a metal, the intensity of *light intensity makes no difference just to eject electrons. Also, no time delay* for electron generation as the classical theory predicts.





$E = \beta\nu$

$E = \beta\nu$ **

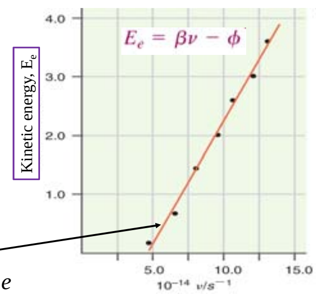
β = proportionality constant

Applying the law of conservation of energy for *e*;

$E_e = \beta\nu - \phi$

ϕ = energy to remove *e* from the metal surface, work function.

$\phi = h\nu_0$



$\beta = h$

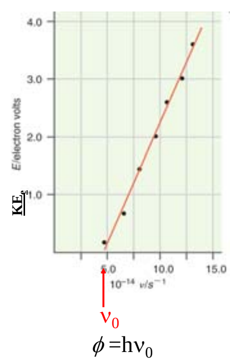
Einstein inferred - light energy proportional to ν !!!.

Einstein employing Planck's idea proposed that light energy comes as packets (quanta). Each packet is called a *photon* has an energy equal to βν (β = h = Planck's constant).

Therefore the energy of **light** is 'packed' in the photons **(particle).**

$$E_{photon} = h\nu$$

A *low intensity* light has fewer photons but that *does not alter the energy of an individual photon*. For a specific frequency light, if a single photon has enough energy to eject an electron from a metallic surface, then electrons will be ejected when the photons hit the metal.



e is proportional to intensity of light but KE_e is independent of intensity of light .

No electrons emitted below ν_0; *threshold frequency*.

Above ν_0, KE_e proportional to ν.

$$E_e = \beta\nu - \phi$$

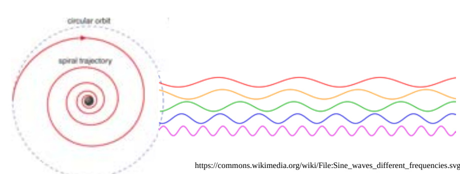
3. The Hydrogen Atom/Spectra:

Hydrogen atom consists of a positively charged proton at the center, with a negatively charged electron cloud around it (Rutherford) – The nuclear atom.

The electrical attraction between the proton and the electron (centrifugal force) keeps the nucleus and the electrons in the atom 'together'.

However classical physics predicts, because the moving/ orbiting electron possesses an acceleration and it should also emit electromagnetic radiation.

Classical physics predicts



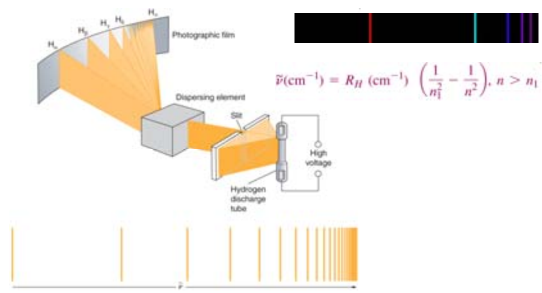
https://commons.wikimedia.org/wiki/File:Sine_waves_different_frequencies.svg

Therefore the electron should continually lose energy and eventually lose all of its kinetic energy and spiral down into the nucleus. Emission spectrum is 'continuous' with a *range of frequencies*.

This is contrary to observation.

Atoms emits light that consists of *few discrete colors.*

When sample hydrogen gas is heated it emits light that consists of *just a few colors.*



$$\tilde{\nu}(\text{cm}^{-1}) = R_H\ (\text{cm}^{-1}) \left(\frac{1}{n_1^2} - \frac{1}{n^2}\right),\ n > n_1$$

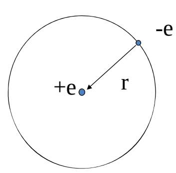
n = integers only !!

Light emanating from the energized atoms is of well defined frequencies (wavelengths) contrary to classical understanding.

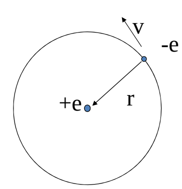
Photons emanating from the energized atoms is quantized, contrary to classical understanding.

If theory doesn't agree with nature, there are two choices: change the theory, or change nature. Unfortunately, all attempts to change nature have failed. The only choice left is - <u>change the theory</u>.

Bohr – made a bold assumption – to explain the atomic spectra; the electron revolves around the atom in well defined <u>circular orbits.</u>



Determining orbits – radii ?



Coulombic attraction = Centrifugal force

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}$$

r

Invoking wave-particle duality of e's; for a nondestructive wave to exist in the orbit, the circumference = nλ.

DBR

$$2\pi r = n\lambda = n\frac{h}{p}$$

$$m_e v r = n\hbar, \text{ where } n = 1,2,3\ldots$$

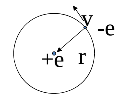
Starting with $\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r} \Rightarrow \frac{1}{2}m_e v^2 = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r}$

multiply by m_e; $\frac{m_e e^2}{4\pi\varepsilon_0 r} = \frac{m_e^2 v^2}{1} \Rightarrow m_e^2 v^2 = \frac{m_e e^2}{4\pi\varepsilon_0 r}$

Also; $m_e vr = n\hbar \Rightarrow m_e^2 v^2 = \frac{n^2\hbar^2}{r^2}$

Equating; $\frac{n^2\hbar^2}{r^2} = \frac{m_e e^2}{4\pi\varepsilon_0 r} \Rightarrow \frac{1}{r} = \frac{m_e e^2}{4\pi\varepsilon_0 n^2\hbar^2}$

Radius: $r = \frac{\varepsilon_0 h^2 n^2}{\pi m_e e^2} = \frac{4\pi\varepsilon_0\hbar^2 n^2}{m_e e^2}$



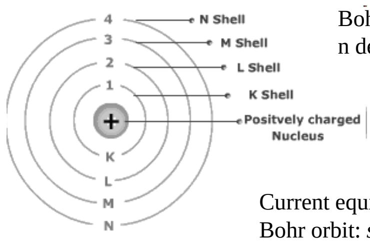
Total energy of atom:

$$E_{total} = E_{kinetic} + E_{potential} = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$E_{total} = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0 r}\right) - \left(\frac{e^2}{4\pi\varepsilon_0 r}\right) = -\frac{e^2}{8\pi\varepsilon_0 r}$$

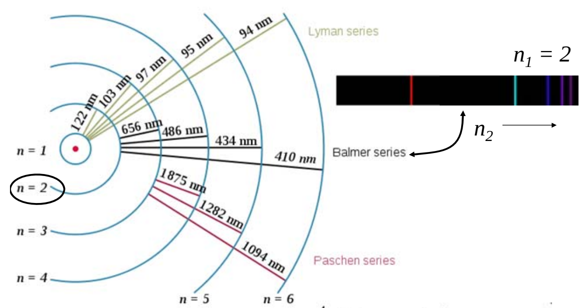
$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \quad n = 1,2,3,\ldots$$

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \quad n = 1,2,3,\ldots$$



Bohr orbits,
n defines the *orbit*.

Current equivalence of Bohr orbit: *stationary states* - spaces where electrons can exist



$$\nu_{n_2\to n_1} = \frac{m_e e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad n_2 > n_1$$

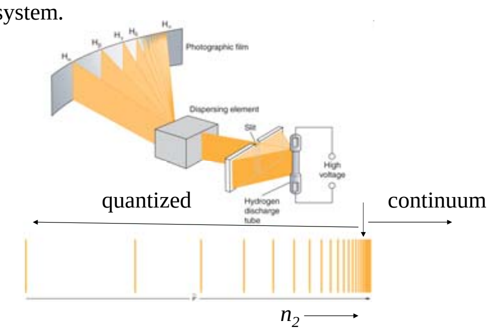
http://en.wikipedia.org/wiki/File:Hydrogen_transitions.svg

Bohr's derivation for the energy of the H-atom amounts to the tinkering of a classical mechanics model with a condition on the angular momentum.

Angular momentum condition lead to the discrete energy levels.

Correspondence Principle.

As n increases quantum system morphs into a classical system.

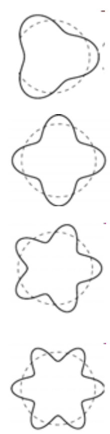


De Broglie Relationship

The particle character of photons would associate a momentum, $p = mv$, for the photon.

For *free moving particles*, the relationship between the wave character (described by a wave length, λ) and the particle character of the described by its momentum, p; was shown to be related by De Broglie as,

$$\lambda = \frac{h}{p}$$



$$2\pi r = n\lambda = n\frac{h}{p} \quad n = 1, 2, 3,...$$

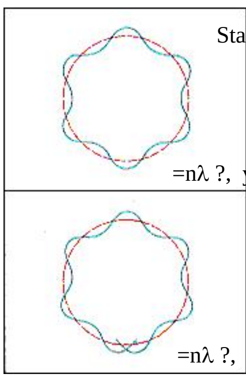
$$2\pi r = n\frac{h}{p} = n\frac{h}{mv}$$

$$2\pi mvr = nh$$

$$mvr = \frac{nh}{2\pi} = n\hbar$$

$$\mathbf{mvr} = n\hbar$$

Angular momentum is restricted to an integer multiple of a fixed unit – $nh/2\pi$ - Quantization.

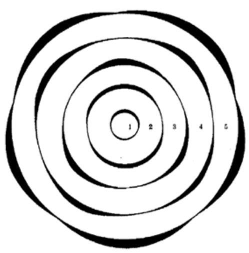


Stationary state, n = 6

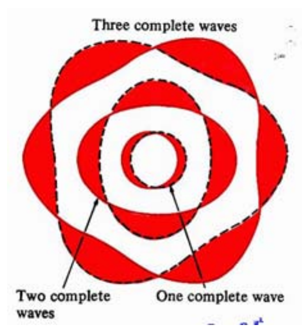
=nλ ?, yes

=nλ ?, no

http://www.geo.arizona.edu/xtal/nats101/s04-17.html



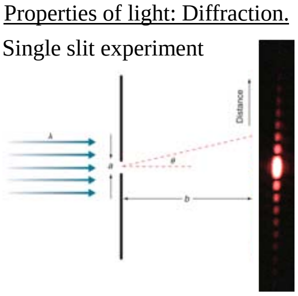
http://www.nanoworld.org.ru/data/20061011/20070102/1963.htm



http://astro1.panet.utoledo.edu/~ljc/world2b.html

Properties of light: Diffraction.

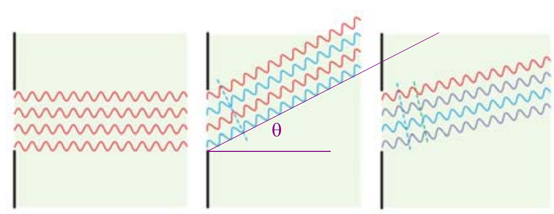
Single slit experiment



http://tsgphysics.mit.edu/front/?page=demo.php&letnum=Q%202

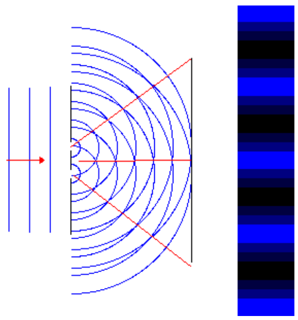
For aperture size ~ wavelength of light a diffraction pattern is generated from a parallel beam of light.

The phenomenon of diffraction is a wave character.
Light as well as *matter* (electron) beams *behave as waves*.

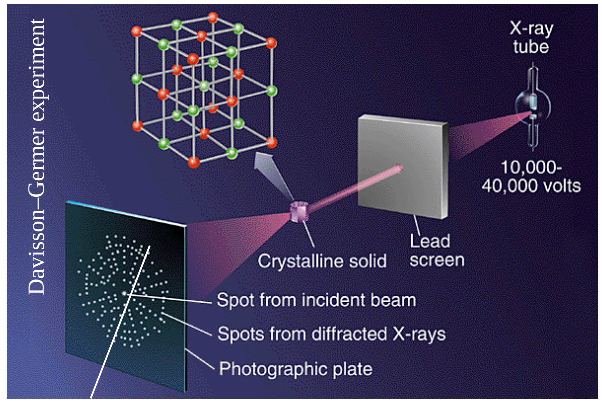


$$\sin\theta = \frac{n\lambda}{a}, \quad n = \pm 1, \pm 2, \pm 3, \pm \ldots \quad \text{maxima}$$

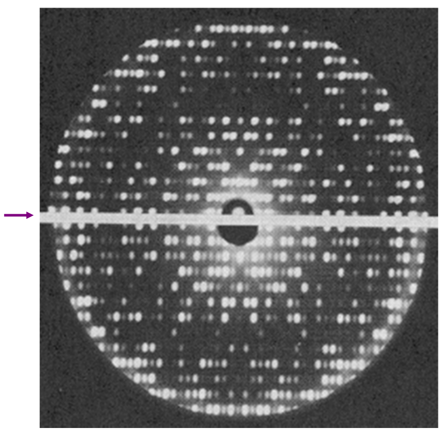
Double slit experiment

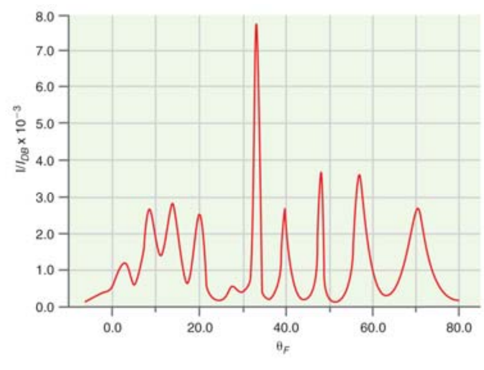


http://web.utk.edu/~cnattras/Phys250Fall2012/modules/module%201/diffraction_and_interference.htm



Davisson–Germer experimet: Diffraction of electron beams generate patterns consistent with their wave character (X rays too) .





A *characteristic feature* that distinguishes quantum mechanics from classical mechanics is the ***wave-particle duality*** of atomic systems.

The *experiment* performed on atomic and molecular systems *determines* whether the *wave or the particle behavior is operational*.

The ***quantization of energy*** *is the other characteristic feature of quantum mechanics.*