QUANTIZATION OF ENERGY

- Quantization is a familiar concept and encounter frequently, albeit, unconsciously.
  - The naira is an integral multiples of kobo.
  - Musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp.
    - these instruments cannot produce a continuous range of frequencies, their frequencies are quantized.
  - The electrical charge is also quantized: an ion may have a charge of −1 or −2 but *not* −1.33 electron charges.

- Origin of energy quantization

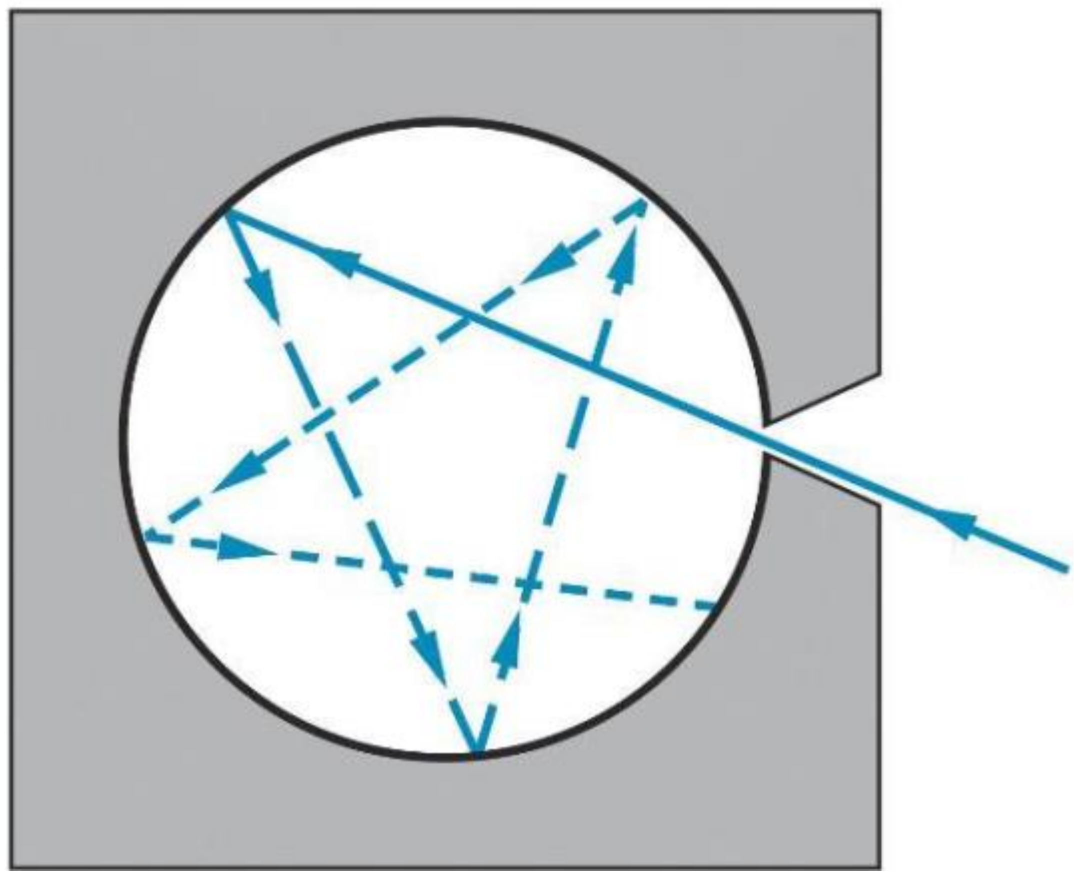
- Up to the end of the 19th century, Physics was complete except for a few decimal places !
- Newtonian mechanics explained macroscopic behavior of matter -- planetary motion, fluid flow, elasticity, etc.
- Thermodynamics had its first two laws and most of their consequences
- Basic statistical mechanics had been applied to chemical systems
- Light was explained as an electromagnetic wave

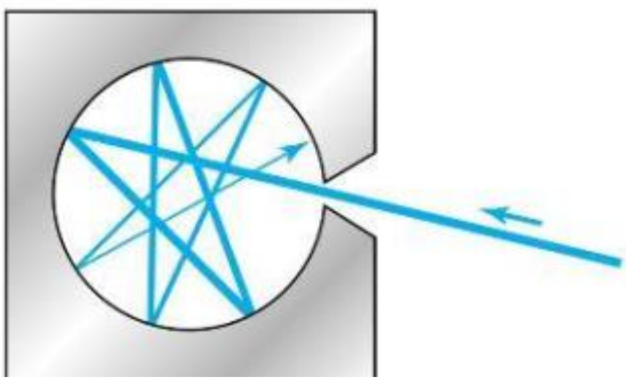
- However there were several experiments that could not be explained by classical physics and the accepted dogma !
    - Blackbody radiation
    - Photoelectric effect
    - Discrete atomic spectra
    - The electron as a subatomic particle
- Inescapable conclusions would result from these problems
    - Atoms are not the most microscopic objects
    - Newton's laws do not apply to the microscopic world of the electron

$\boxed{\text{OUTCOME}}$ $\Rightarrow$ New Rules!!!

- Quantization of Energy!!!
- Describes rules that apply to electrons in atoms and molecules
  – Explains unsolved problems of late 19th century physics
  – Explains bonding, structure, and reactivity in chemistry

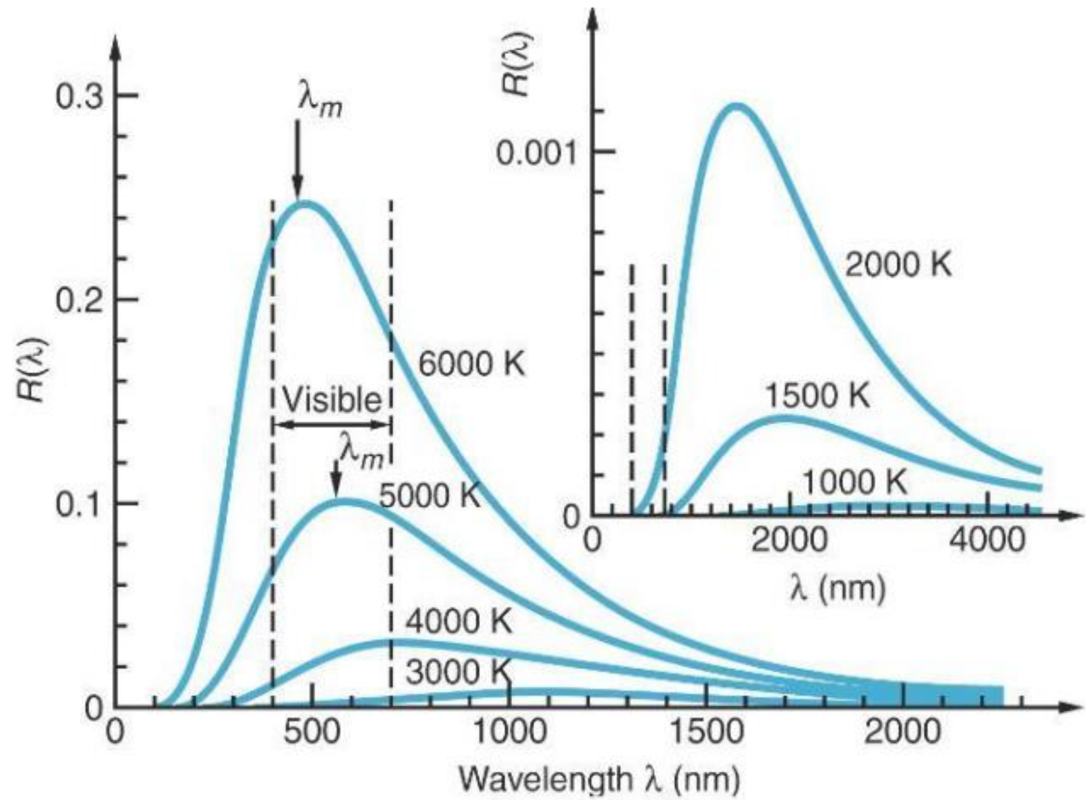
BLACK BODY/CAVITY RADIATION





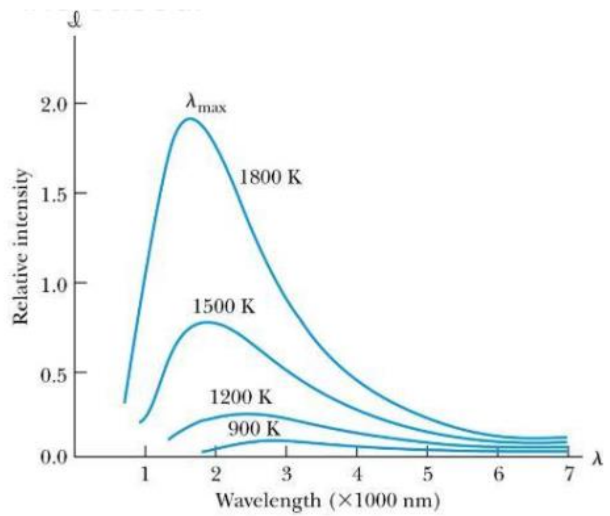
- A small hole in the wall of the cavity approximating an ideal blackbody. Electromagnetic radiation (for example, light) entering the hole has little chance of leaving before it is completely adsorbed within the cavity.
- As the walls of the cavity absorb this incoming
radiation , their temperature rises and the body begin to irradiate.
- A blackbody is a cavity within a material that only emits thermal radiation. Incoming radiation is absorbed in the cavity.
- Blackbody radiation is theoretically interesting because the radiation properties of the blackbody **are independent of the particular material**.
- The properties of irradiated intensity can be studied as a function of wavelength at fixed temperatures.

Spectral distribution function **$R(\lambda)$** measured at different temperatures. The **$R(\lambda)$** axis is in arbitrary units for comparison only. Notice the range in **λ** of the visible spectrum. The Sun emits radiation very close to that of a blackbody at **5800 K**. **λ_m** is indicated for the **5000-K** and **6000-K** curves.



WIEN'S DISPLACEMENT LAW

- The spectral intensity ***R(λ, T)*** is the total power irradiated per unit area per unit wavelength at a given temperature.
- ***Wien's displacement law***: The maximum of the spectrum shifts to smaller wavelengths as the temperature is increased.



$$\lambda_{max} T = 2.898 \times 10^{-3}\ \mathrm{m \cdot K}$$

- The total radiated power R, the spectral distribution of the radiation emitted by a blackbody is found empirically to depend only on the absolute temperature T. The dependence of maximum wavelength as a function is given as:

$$\lambda_m \propto \frac{1}{T}$$

- Such that

$$\lambda_m T = \text{constant} = 2.898 \times 10^{-3}\, mK$$

- The above is known as the Wien's displacement law
- For illustration:

➢ The wavelength at the peak of the spectral distribution for a blackbody at ***4300 K*** is ***674 nm*** (red). What would be the temperature of the blackbody that have the peak in intensity at ***420 nm*** (violet)?

➢ SOLUTION:

From Wien's law

$$\lambda_m(1)T(1) = \lambda_m(2)T(2)$$

$$\therefore T(2) = \frac{\lambda_m(1)T(1)}{\lambda_m(2)}$$

$$= \frac{674nm \times 4300K}{420nm}$$

$$= 6900K$$

WIEN'S DISPLACEMENT LAW CONT'D

This law is used to determine:

- the surface temperatures of stars by analyzing their radiation.
- It can also be used to map out the variation in temperature over different regions of the surface of an object. Such a map is called *thermograph*.
  - ✓ For example *thermograph* can be used to detect cancer because cancerous tissue results in increased circulation which produce a slight increase in skin temperature.

The radiation emitted by the surface of the sun emits maximum power at wavelength of about ***500 nm***. Assuming the sun to be a blackbody emitter,
(a) what is it surface temperature?

(b) Calculate $\boldsymbol{\lambda_{max}}$ for a blackbody at room temperature, $\boldsymbol{T=300\ K}$.

STEFAN-BOLTZMAN LAW

- Total amount of radiation emitted by blackbody at all wavelengths and found it varied with absolute temperature. – Stefan's experimental findings
- Theoretical calculation of the variation of the total amount of radiation with temperature – Boltzman.
- The total power radiated as a function of absolute temperature is given as:

$$P(T) = \int_0^\infty R(\lambda, T)\, d\lambda = \sigma T^4$$

- Where

$$\sigma = 5.67 \times 10^{-8}\ Wm^{-2}K^{-4}$$

- Blackbody radiation – Absorbed all radiation incident on it and when heated, emit light of all wavelength!
- Classically –
  - Radiation from a blackbody is the result of electrons oscillating with frequency ν
  - The electrons can oscillate (& radiate) equally well at any frequency

⇒ Rayleigh-Jeans Law for spectral density $\rho(\nu)$, where intensity of emitted light in frequency range from ν to $\nu+d\nu$ is $I(\nu) \sim \rho(\nu)d\nu$

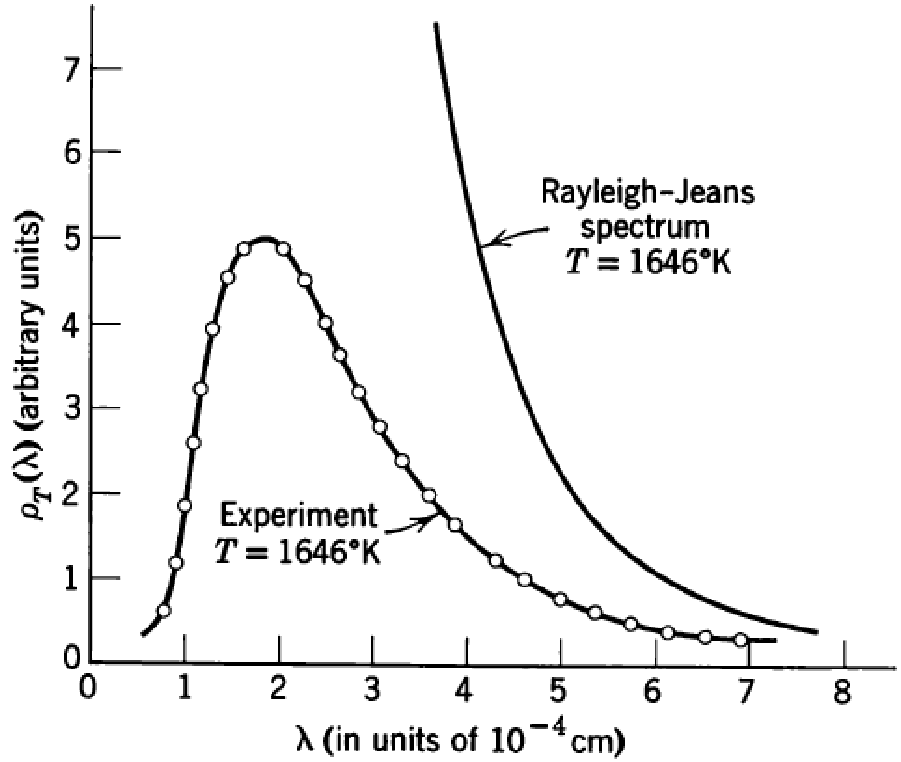
$$d\rho = \rho(\nu, T)d\nu = \frac{8\pi kT}{c^3}\nu^2 d\nu \quad \boxed{\propto \nu^2}$$

where $d\rho(\nu, T)$ = density of radiative energy in frequency range from ν to $\nu+d\nu$ at temperature T

k = Boltzmann's constant [= R/N_A (gas constant per molecule)]

c = speed of light

- A comparison of the Rayleigh-Jeans spectrum and experiment.



  - Note that the Rayleigh-Jeans law reproduces the experimental data at low frequencies.
  - At high frequencies, however, the Rayleigh-Jeans law predicts that the radiant energy density diverges as ν^2.
  - Because the frequency increases as the radiation enters the ultraviolet region, this divergence was termed the ultraviolet catastrophe, a phenomenon that classical physics could not reconcile theoretically.

Planck’s Theory

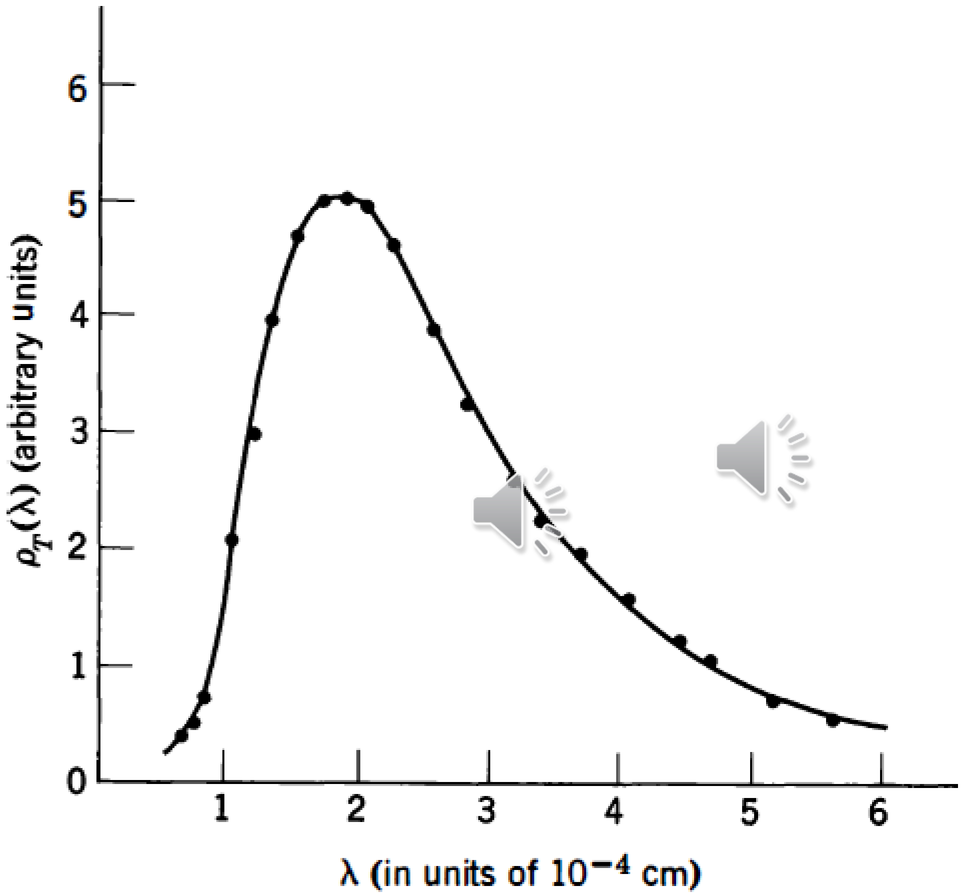
- Resolved the discrepancy between experiment and theory
- introduction of a postulate which was not only new, but also drastically at variance with certain concepts of classical physics
- Any physical entity whose single "coordinate" executes simple harmonic oscillations (i.e., is a sinusoidal function of time t) can possess only total energies ε which satisfy the relation

$$\varepsilon = nh\nu, \qquad n = 0, 1, 2, 3, \ldots$$

- where ν is the frequency of the oscillation and h is a universal constant.
- Planck used statistical mechanics to derive the expression for black body radiation as:

$$d\rho(\lambda, T) = \rho_\lambda(T)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda k_B T} - 1}$$

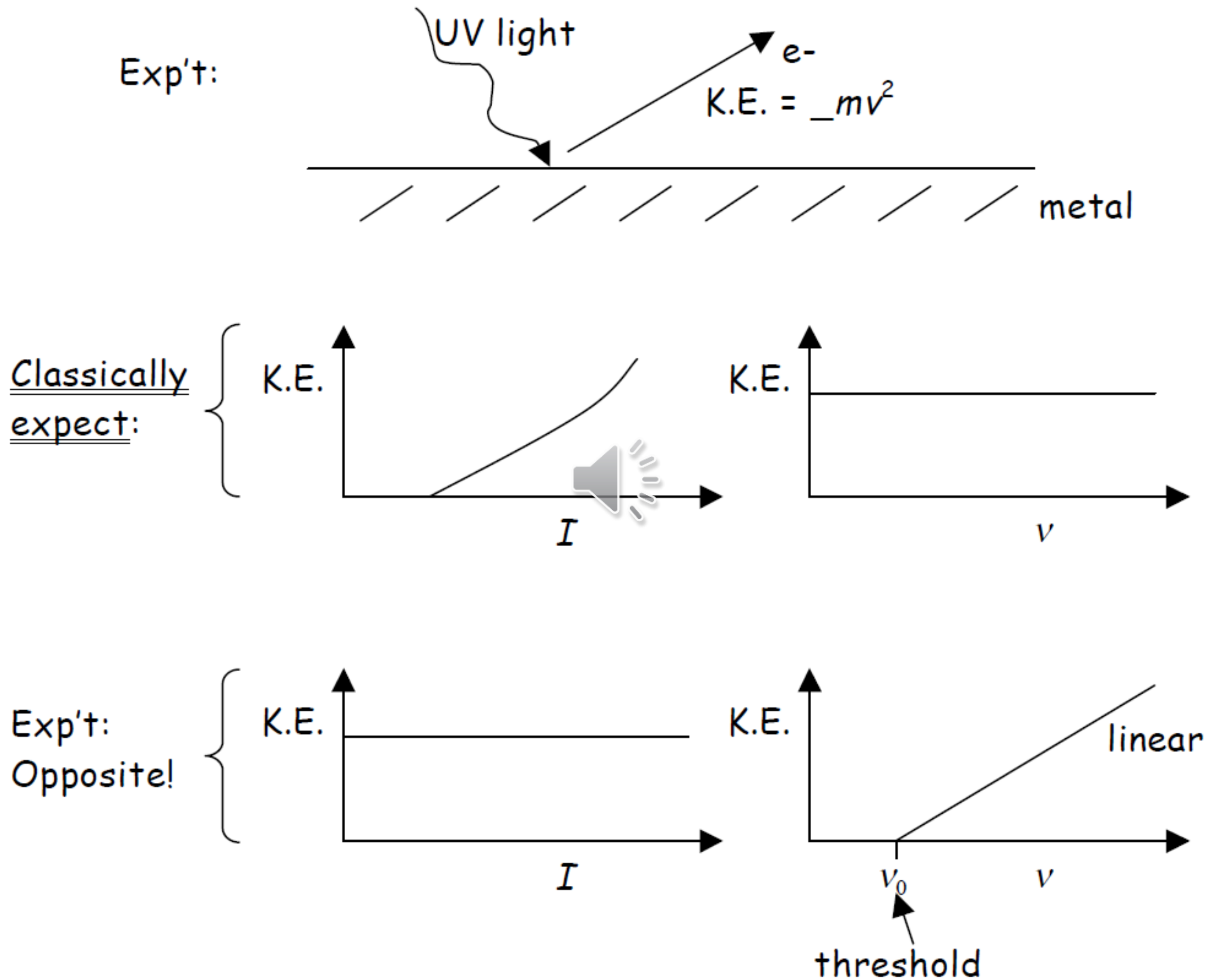
- A comparison of Planck's spectrum and experiment. The dots are experimental and the curve is theoretical. T = 1646° K.



Fitting exp't to model $\Rightarrow$ $\boxed{h = 6.626 \times 10^{-34} \text{ J-sec}}$

Planck's constant

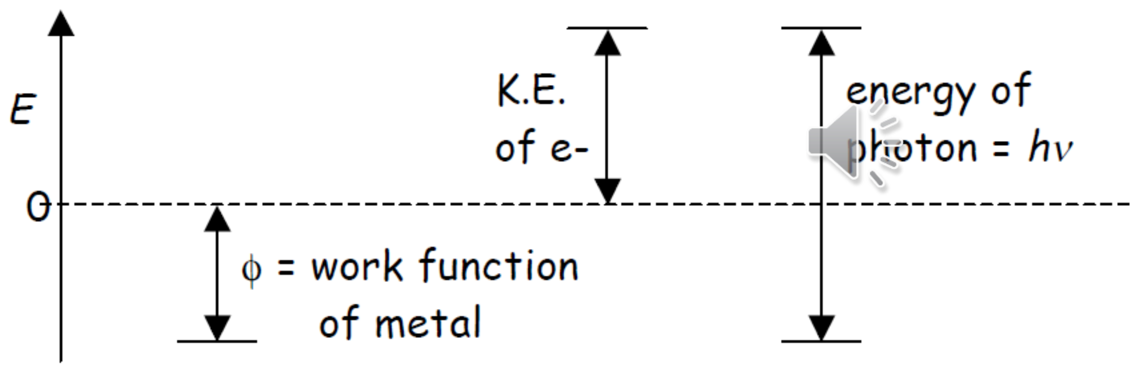
- The Photoelectric Effect



- Einstein (1905) proposed:
- Light is made up of energy "packets: "photons"
- The energy of a photon is proportional to the light frequency

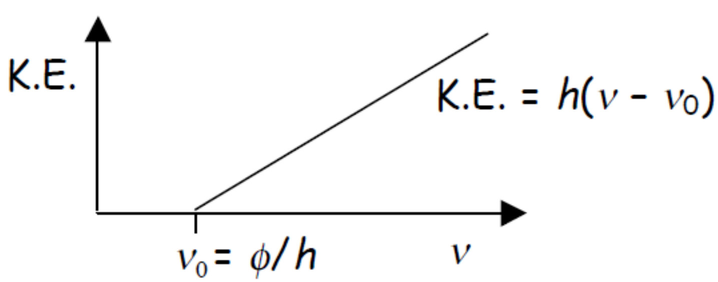
$$\boxed{E = h\nu} \qquad h \equiv \text{Planck's constant}$$

New model of photoelectric effect:



$\therefore$ K.E. = $h\nu - \phi = h\nu - h\nu_0 = h(\nu - \nu_0)$

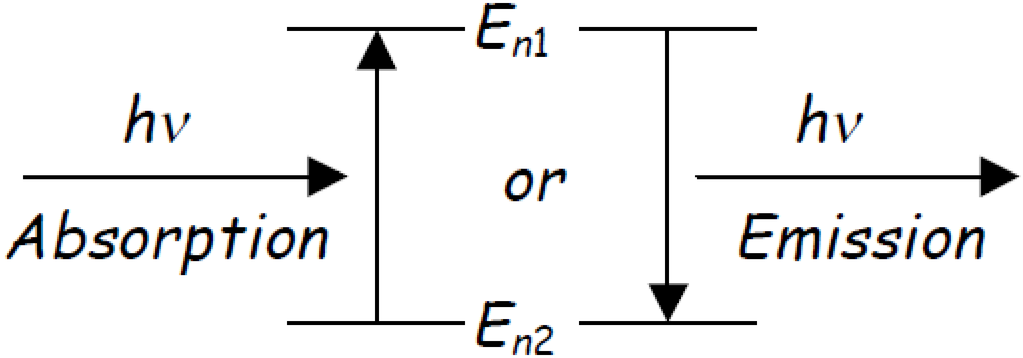
$\therefore$



Niel Bohr’s Model of the Atom

- Atoms can exist in stable “states” without radiating.
- The states have discrete energies E_n, n = 1, 2, 3,..., where n = 1 is the lowest energy state (the most negative, relative to the dissociated atom at zero energy), n = 2 is the next lowest energy state, etc.
- The number “n” is an integer, a <u>quantum number</u>, that labels the state.
- Transitions between states can be made with the absorption or ΔE emission of a photon of frequency ν given as

$$\nu = \frac{\Delta E}{h}.$$



- These two assumptions "explain" the discrete spectrum of atomic vapor emission. Each line in the spectrum corresponds to a transition between two particular levels. This is the birth of modern spectroscopy.
- Angular momentum is quantized:

$$\ell = n\hbar \quad \text{where } \hbar = \frac{h}{2\pi}$$

$$r = \frac{Ze^2}{4\pi\varepsilon_0 mv^2} \quad \Rightarrow \quad r = \frac{n^2}{Z}(4\pi\varepsilon_0)\frac{\hbar^2}{me^2}$$ The radius is quantized!!

$$(4\pi\varepsilon_0)\frac{\hbar^2}{me^2} \equiv a_0$$ the ***Bohr radius***

For H atom with $n = 1$, $r = a_0 = 5.29\times10^{-11}$ m = 0.529 Å (1 Å = 10^{-10} m)

$$E = T + V = -Ze^2/2r = -T$$

$$E = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \Rightarrow \quad \boxed{E_n = -\frac{1}{n^2}\frac{Z^2me^4}{8\varepsilon_0^2h^2}}$$ Energies are quantized!!!

For H atom, emission spectrum

$$\bar{\nu}\left(\mathrm{cm}^{-1}\right)=\frac{E_{n2}}{hc}-\frac{E_{n1}}{hc}=\frac{me^4}{8\varepsilon_0^2h^3c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

Rydberg formula ! with $R=\dfrac{me^4}{8\varepsilon_0^2h^3c}=109,737\ \mathrm{cm}^{-1}$

Measured value is 109,678 cm^{-1} (Slight difference due to model that gives nucleus no motion at all, i.e. infinite mass.)

Names, Wavelength Ranges, and Formulas for the Hydrogen Series

Lyman	Ultraviolet	$k=R_{\mathrm{H}}\left(\frac{1}{1^2}-\frac{1}{n^2}\right)$,	$n=2,3,4,\ldots$
Balmer	Near ultraviolet and visible	$k=R_{\mathrm{H}}\left(\frac{1}{2^2}-\frac{1}{n^2}\right)$,	$n=3,4,5,\ldots$
Paschen	Infrared	$k=R_{\mathrm{H}}\left(\frac{1}{3^2}-\frac{1}{n^2}\right)$,	$n=4,5,6,\ldots$
Brackett	Infrared	$k=R_{\mathrm{H}}\left(\frac{1}{4^2}-\frac{1}{n^2}\right)$,	$n=5,6,7,\ldots$
Pfund	Infrared	$k=R_{\mathrm{H}}\left(\frac{1}{5^2}-\frac{1}{n^2}\right)$,	$n=6,7,8,\ldots$

Comparing to exp't, value of "h" matches the one found by Planck!

This was an extraordinary result !

Summary:

(1) Structure of atom can't be explained classically

(2) Discrete atomic spectra and Rydberg's formula can't be explained

(3) Blackbody radiation can be "explained" by quantifying energy of oscillators $E = h\nu$

(4) Photoelectric effect can be "explained" by quantifying energy of light $E = h\nu$