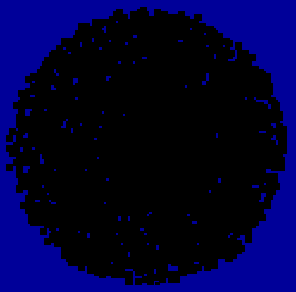
Electronic Structure of Atoms



Chemical properties of atoms (and molecules) are given by their electronic structure.

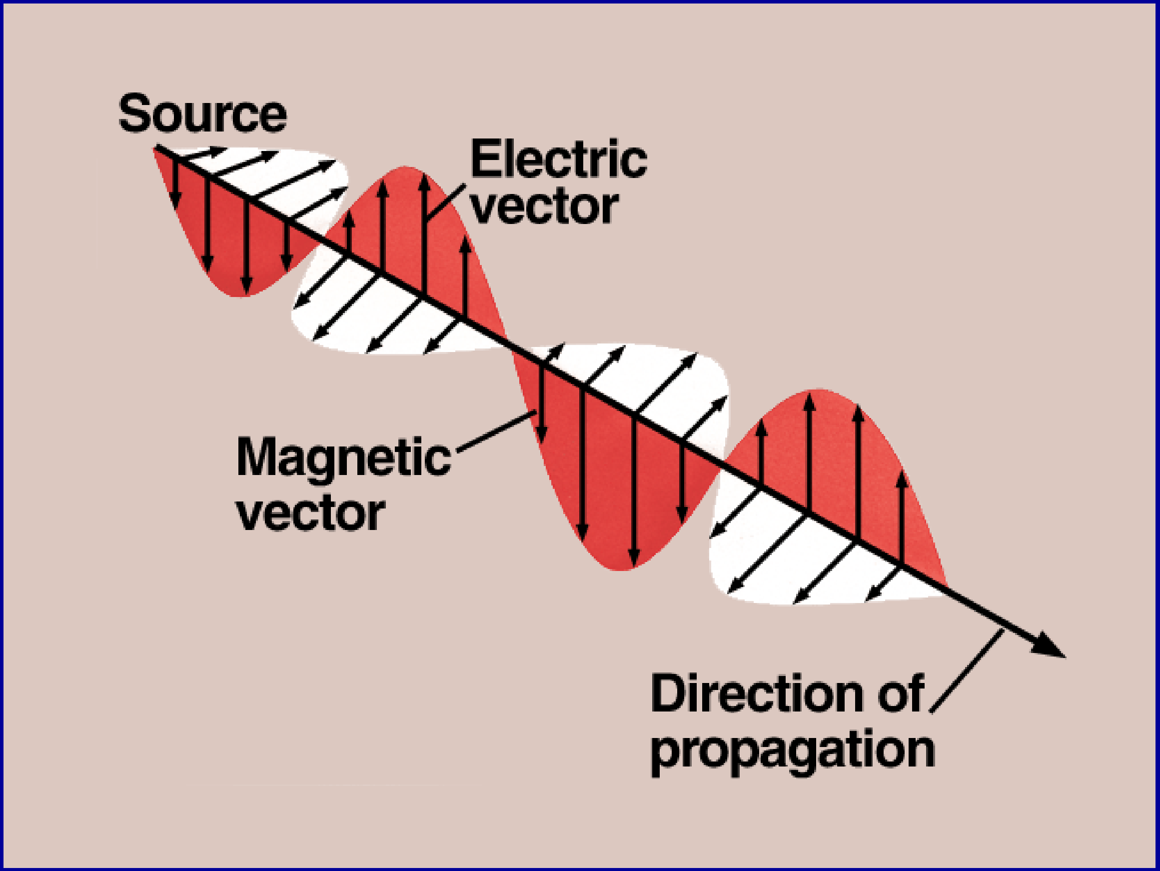
We need to know:

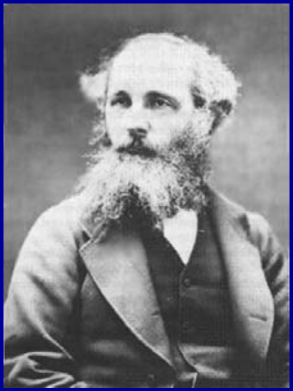
- electron **energy**
- spatial **distribution** of electrons

Knowledge about **electronic structure of atoms** was obtained by studies of radiation emitted by excited atoms (from ground state to excited state by adding energy – thermal, electrical - spark, arc)

Electromagnetic Radiation

$c = 2.998\ 10^{8}\ \mathrm{m\ s^{-1}}$ speed of light





James C. Maxwell
(1831-1879)

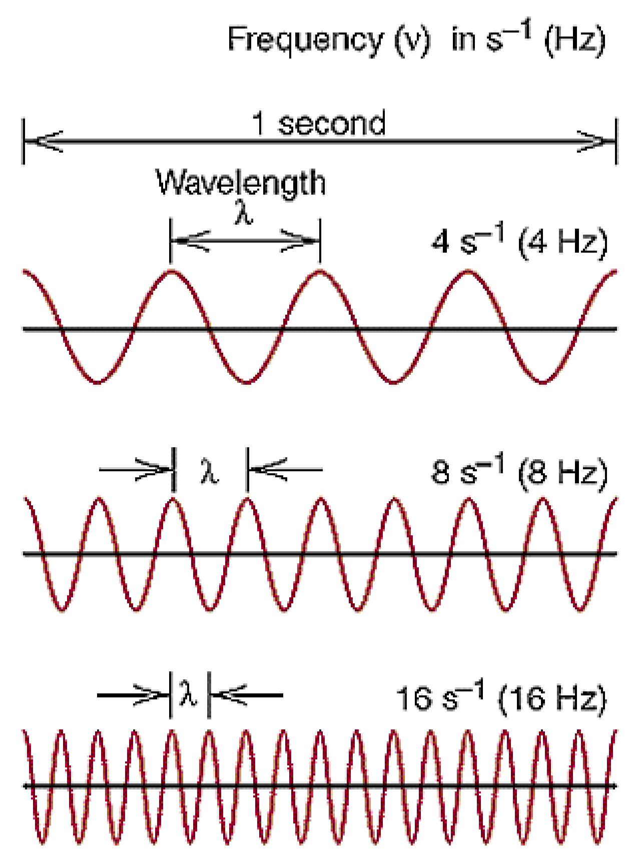
Heinrich Hertz
(1857 - 1894)

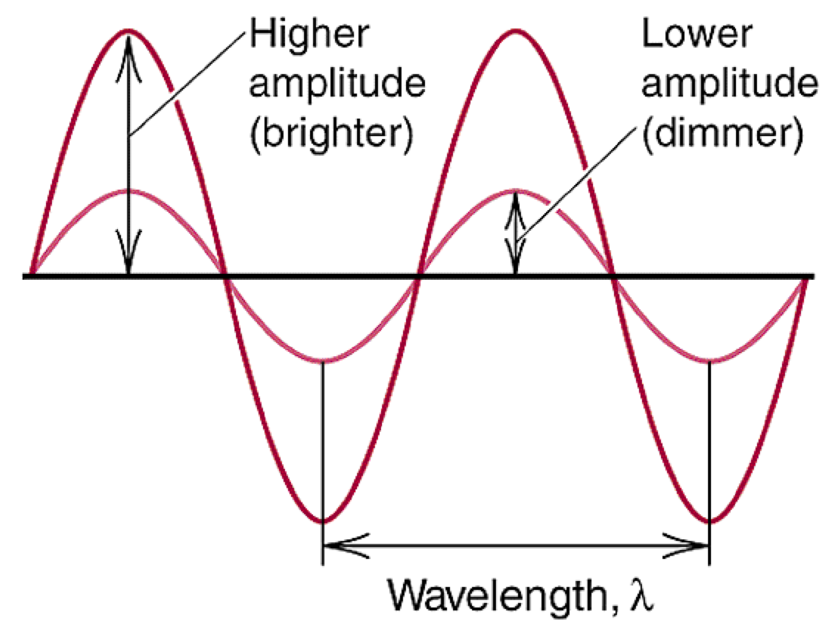
Wavelength, frequency, wavenumber, amplitude

$\nu\ \lambda = c$

$c = 2.998\ 10^8\ \mathrm{m\ s^{-1}}$

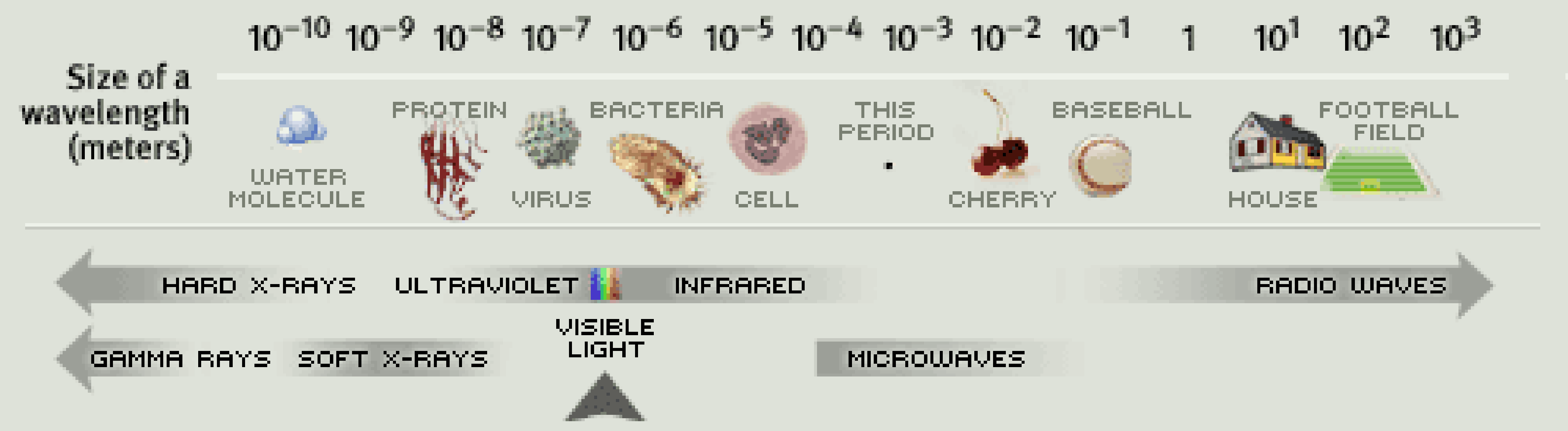
$\tilde{\nu} = 1/\lambda\ [\mathrm{cm^{-1}}]$

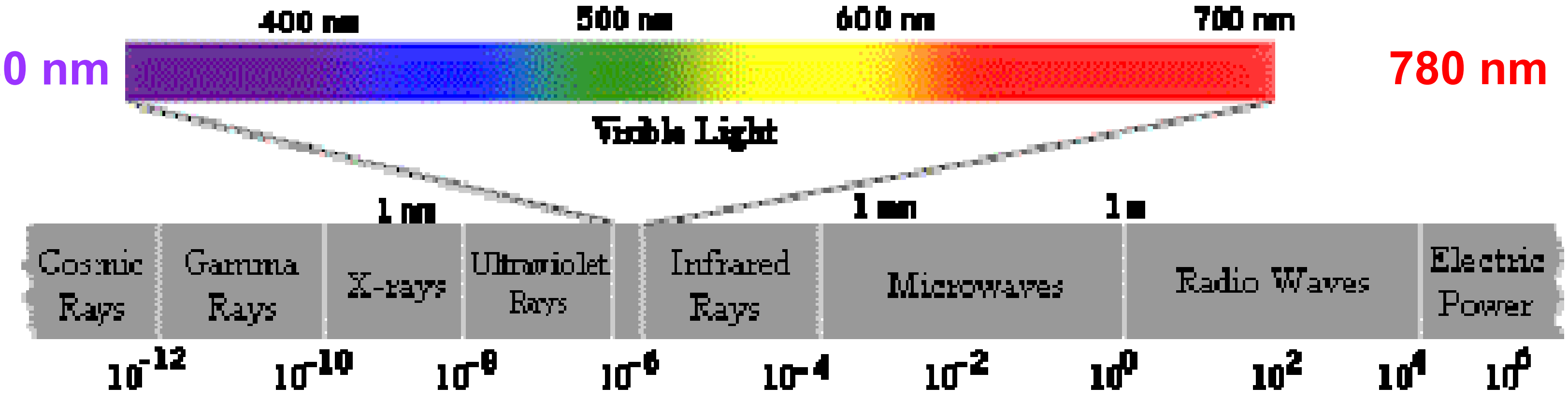




Electromagnetic Radiation

Wavelength, λ [m]

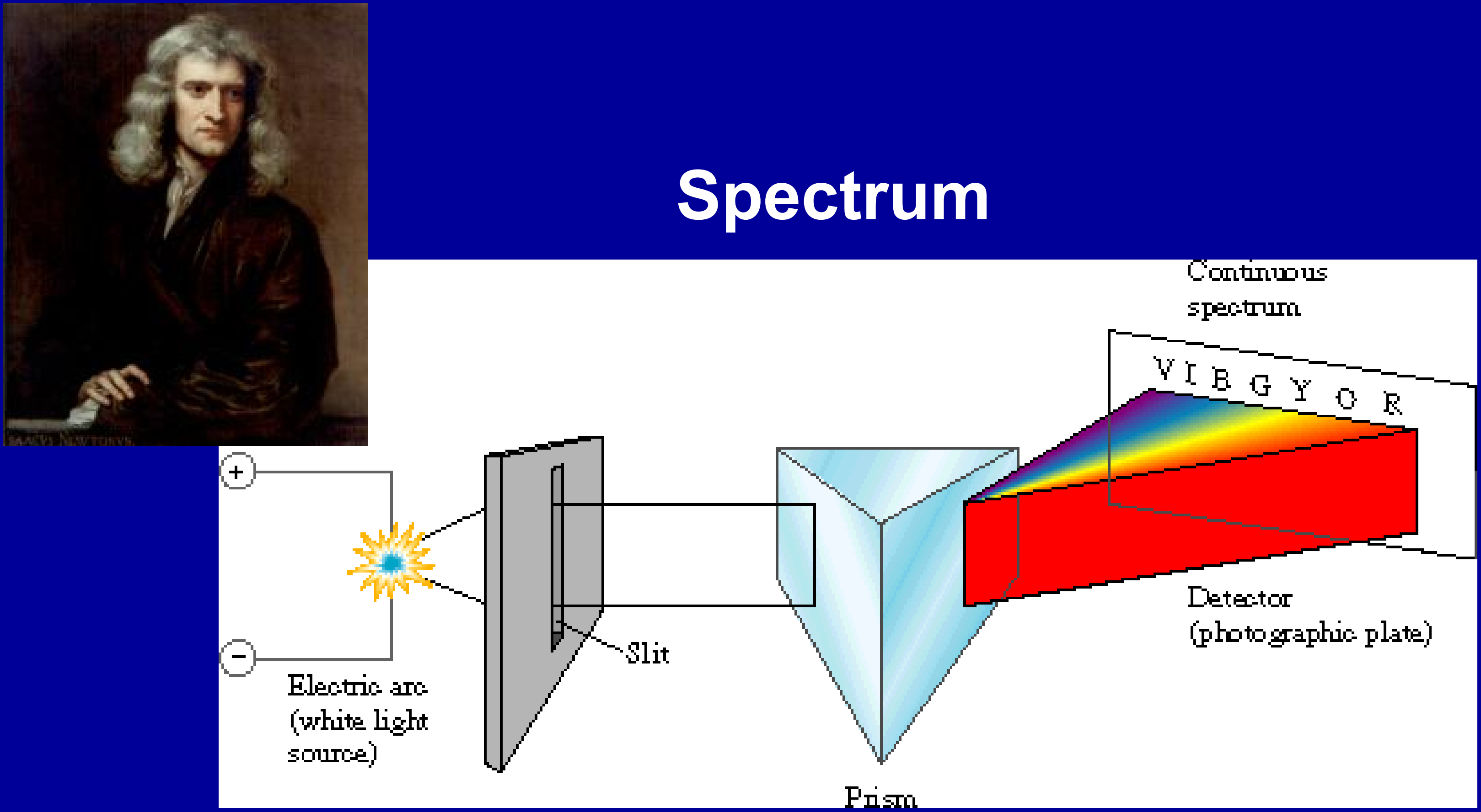




380 nm

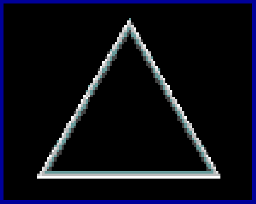
780 nm

Spectrum



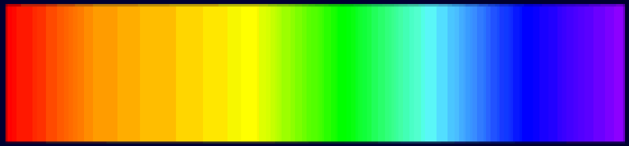
Character of light:

- Wave (interference) Huygens, Young
- Corpuscular (linear rays, reflection) Newton

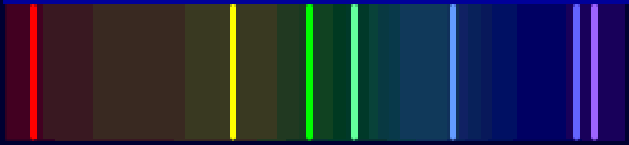


Spectrum

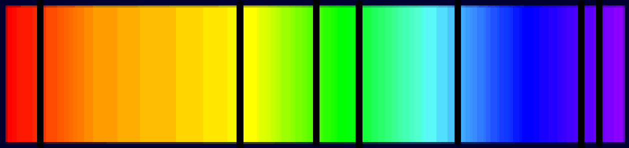
Continuous spectrum



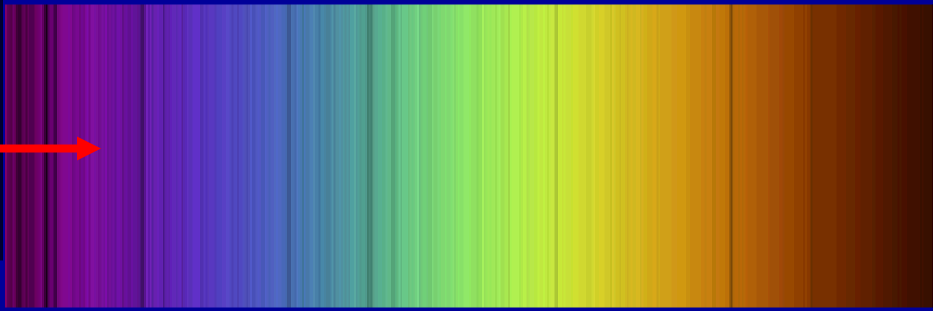
Emission spectrum



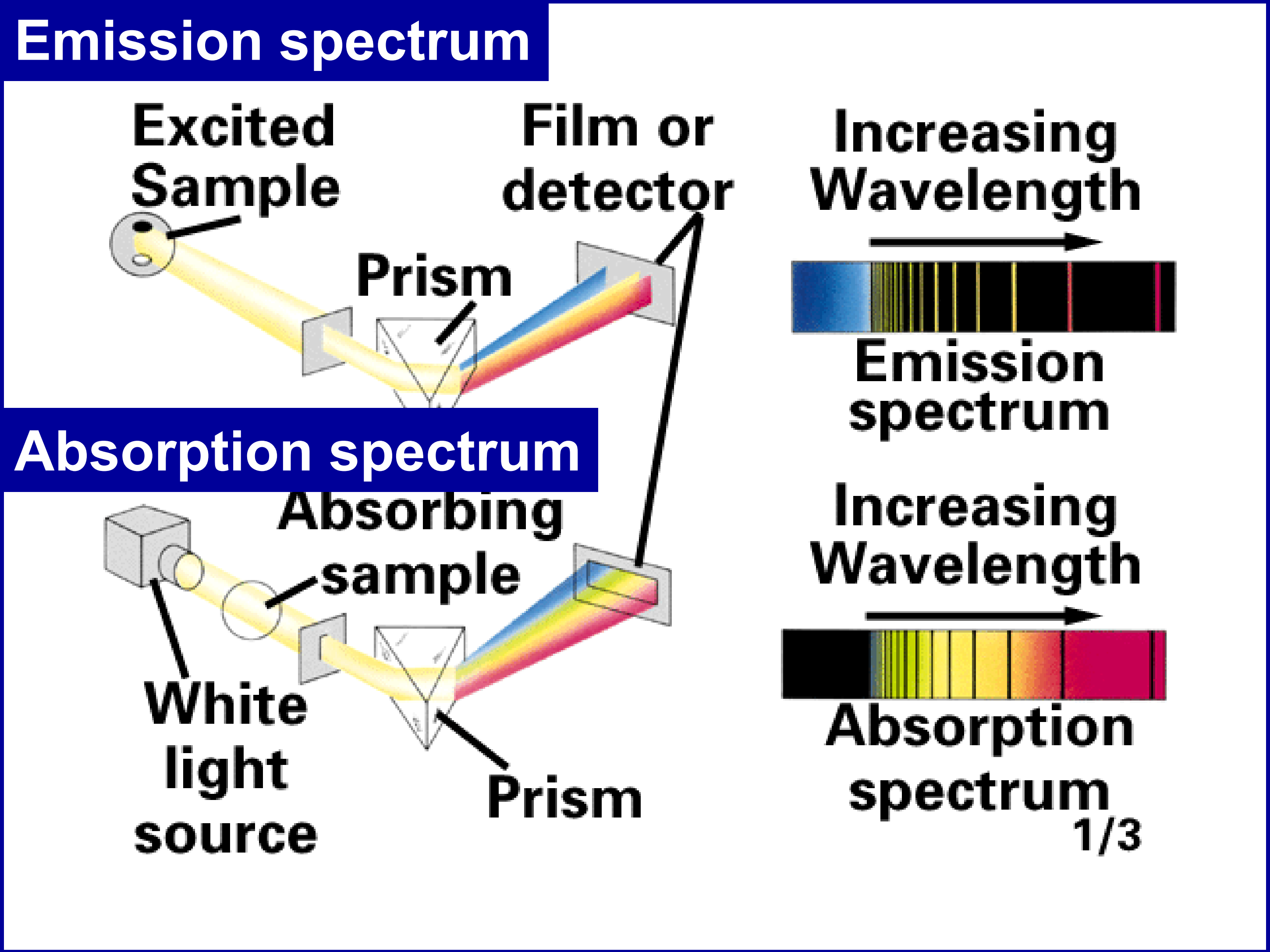
Absorption spectrum



Sun spectrum: He, Fe, Mg,...



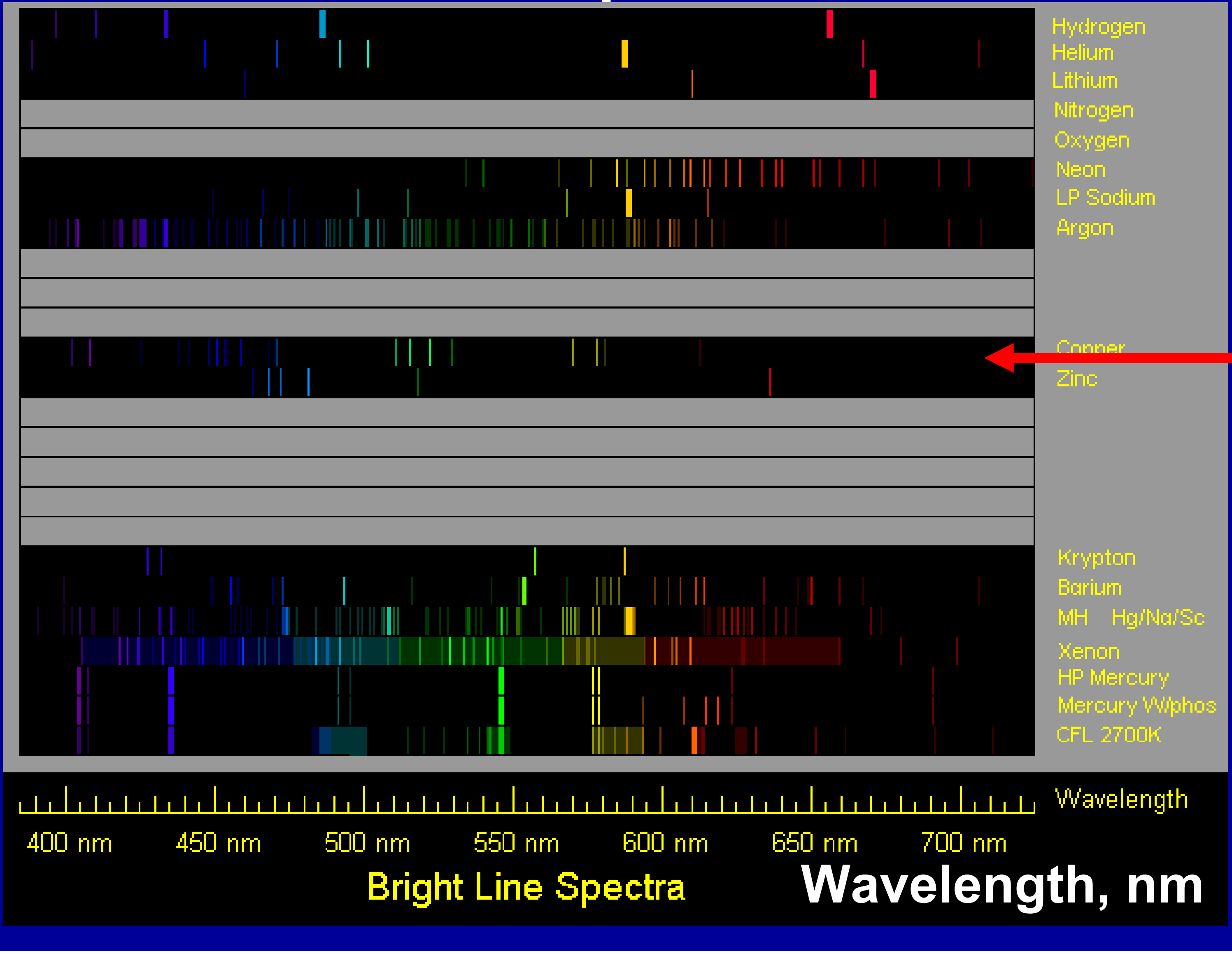
Line Spectra of Elements



Emission spectrum

Absorption spectrum

Emission Line Spectra of Elements



Wavelength, nm

H

He

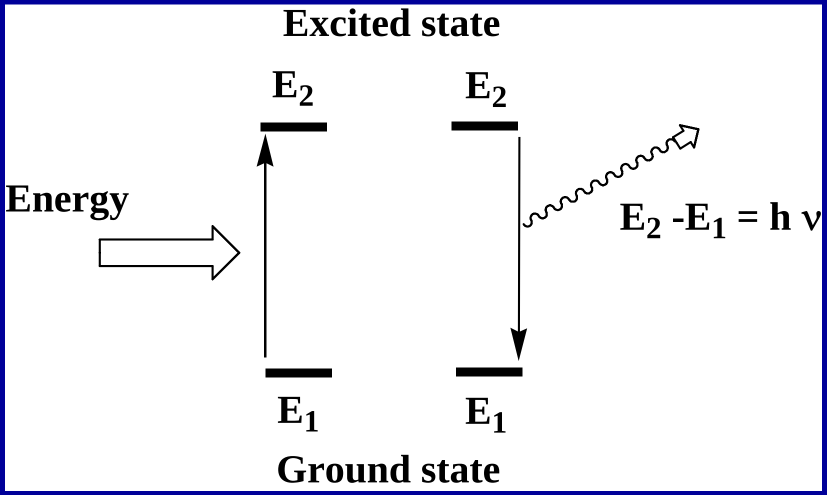
Li

Cu

Zn

Quantized Energy

1900 Energy of radiation with wavelength λ could be absorbed or emitted only in discrete amount = **quantum**



Quantum of light = **photon**

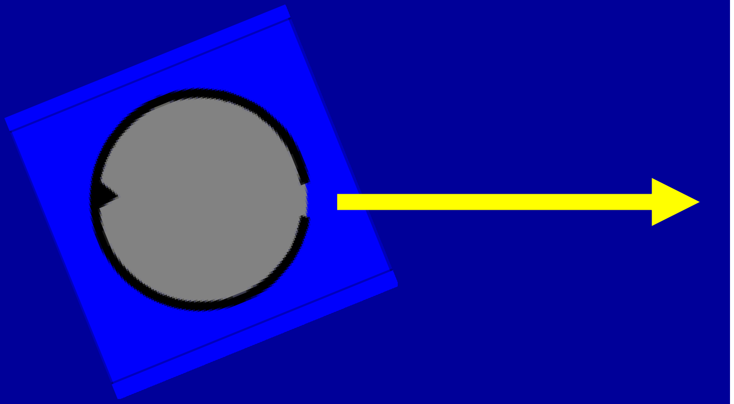
$$\Delta E = n h \nu = n h c / \lambda$$

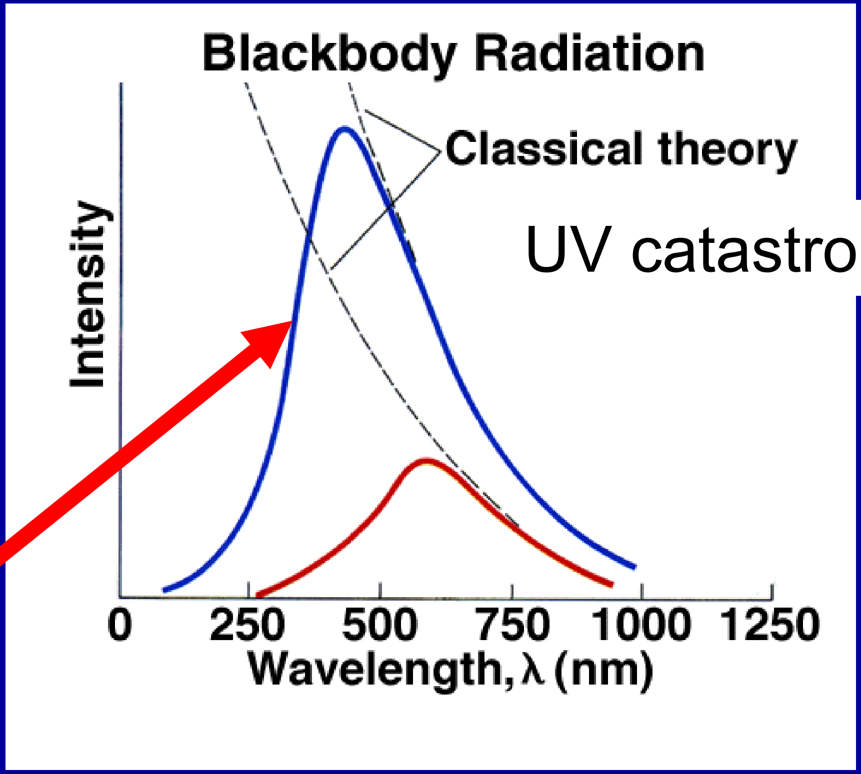
Planck constant $h = 6.626\ 10^{-34}$ J s

Max Planck
(1858 - 1947)
NP in Physics 1918

Black Body Radiation

Black Body = perfectly absorbs all incoming radiation, perfectly emits all wavelengths





UV catastrophe

Atoms = oscillators

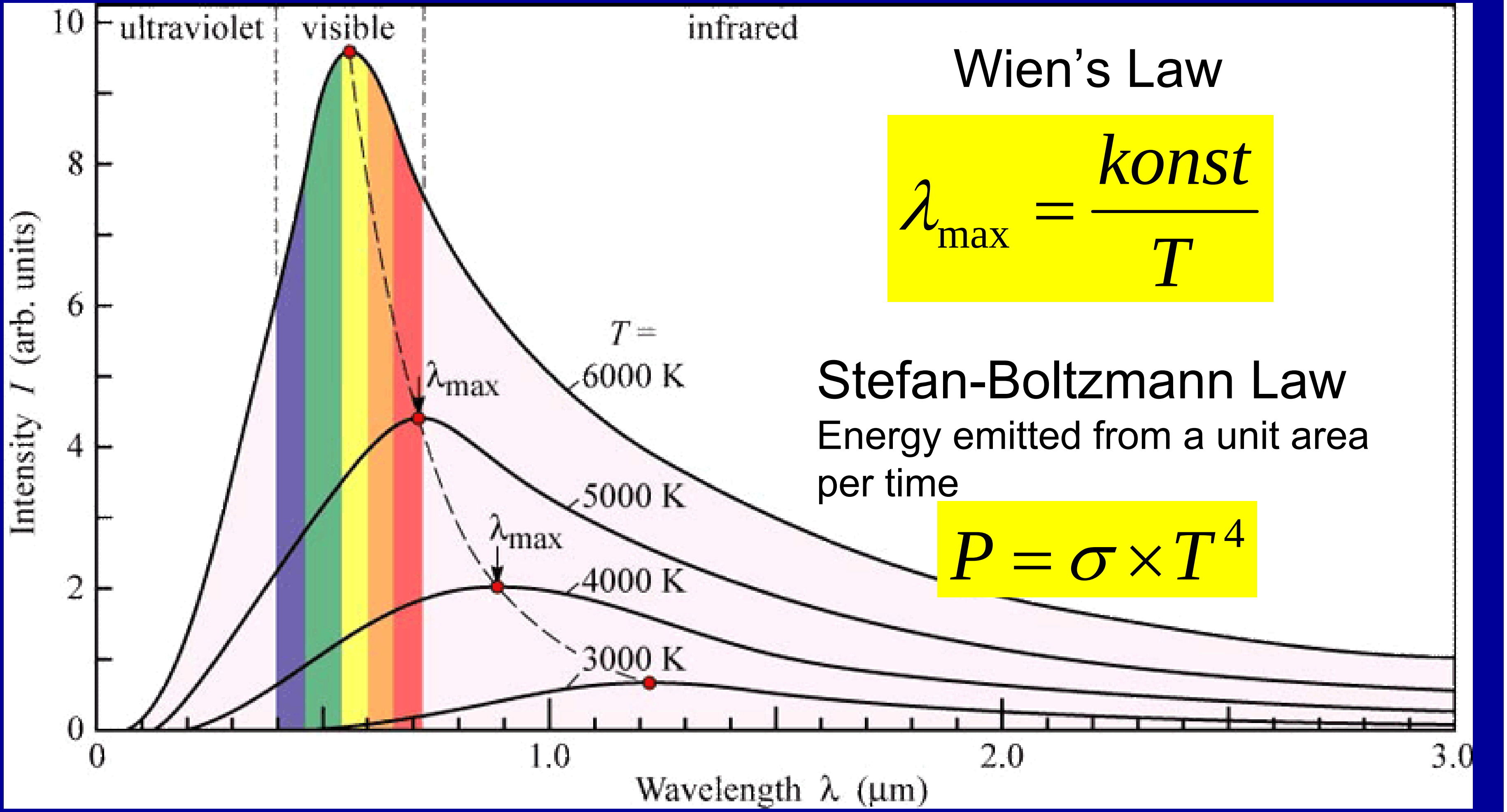
Quantized Energy E = h ν

Max Planck derived

$$P_\lambda = \frac{2\pi hc^2}{\lambda^5\left(e^{\frac{hc}{\lambda kT}} - 1\right)}$$

Energy emitted at wavelength λ is only a function of temperature

Black Body Radiation



Wien's Law

$$\lambda_{max} = \frac{konst}{T}$$

Stefan-Boltzmann Law

Energy emitted from a unit area per time

$$P = \sigma \times T^4$$

Photoelectric Effect

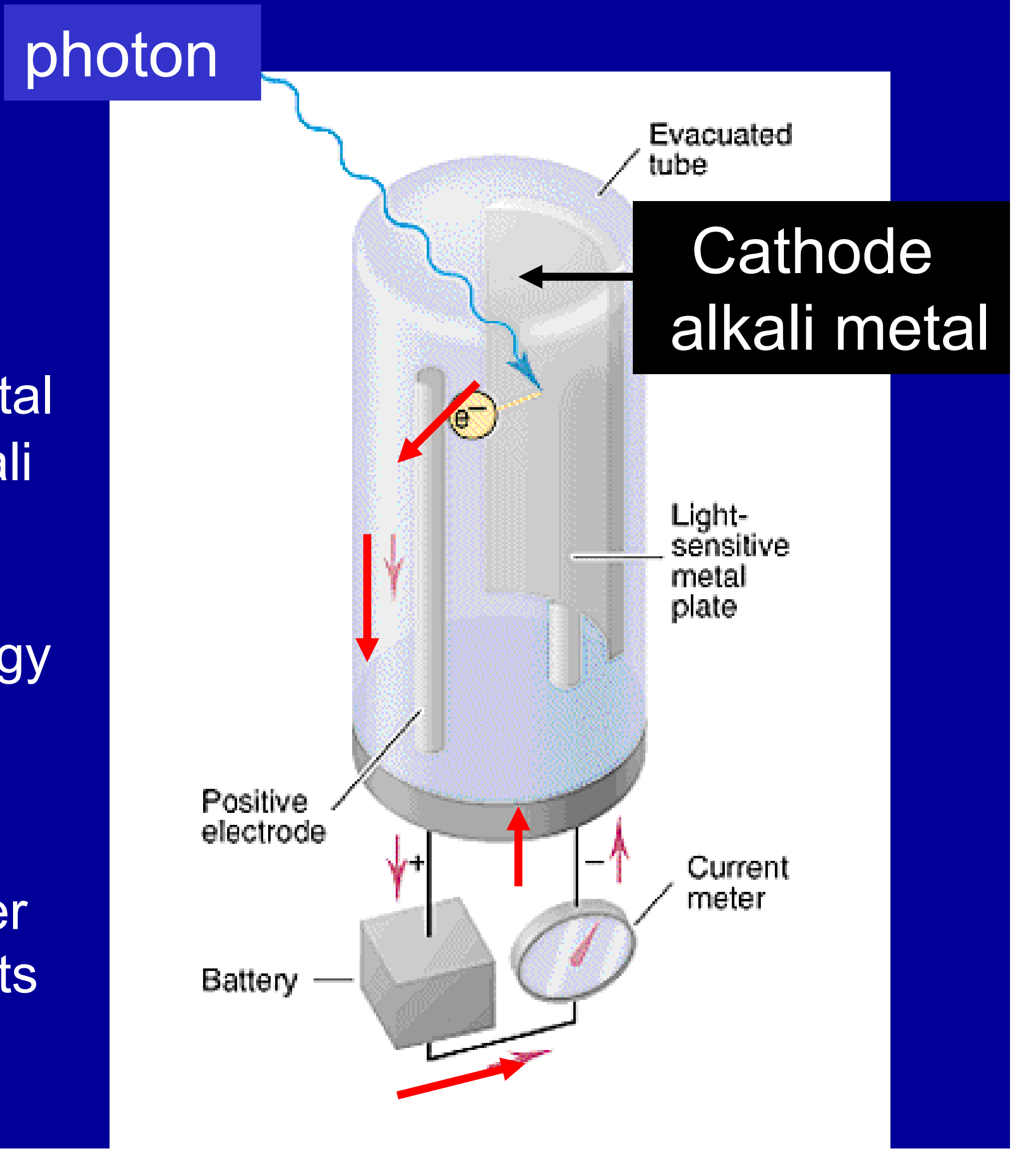
1887 Heinrich Hertz
1898 J. J. Thomson

Observations

- electrons are emitted from the metal surface upon irradiation by UV (alkali metals by visible light)

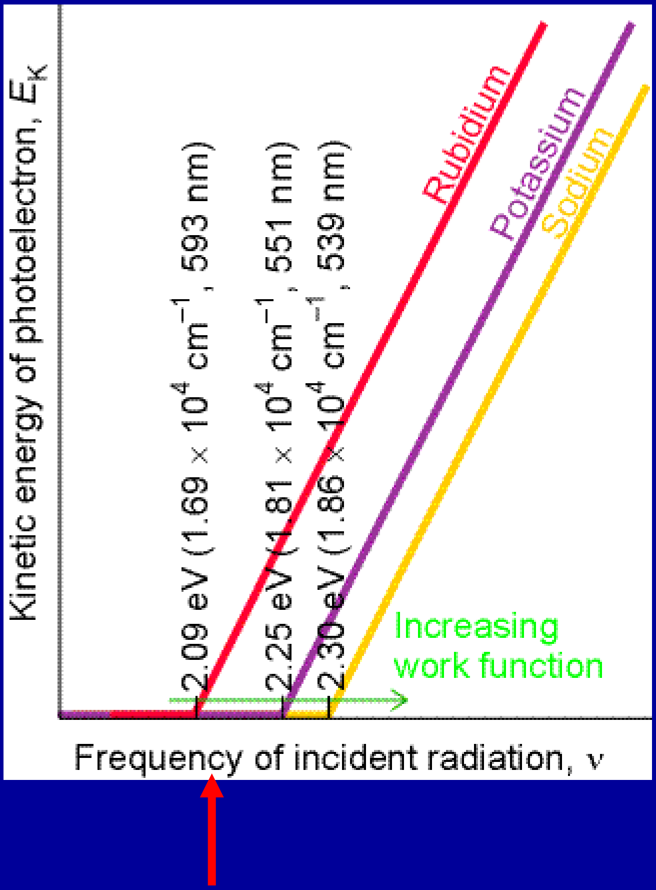
- minimum ν, photons of lower energy cannot eject electrons

- kinetic energy of photoelectrons depends on ν, increases with higher light energy, but not dependent on its intensity



Photoelectric Effect

Kinetic energy of photoelectrons



kinetic energy of photoelectrons depends on ν, increases with higher light energy, but not dependent on its intensity

$h\nu_0$ = work function

Below ν_0 no emission
No matter how intense the light is!

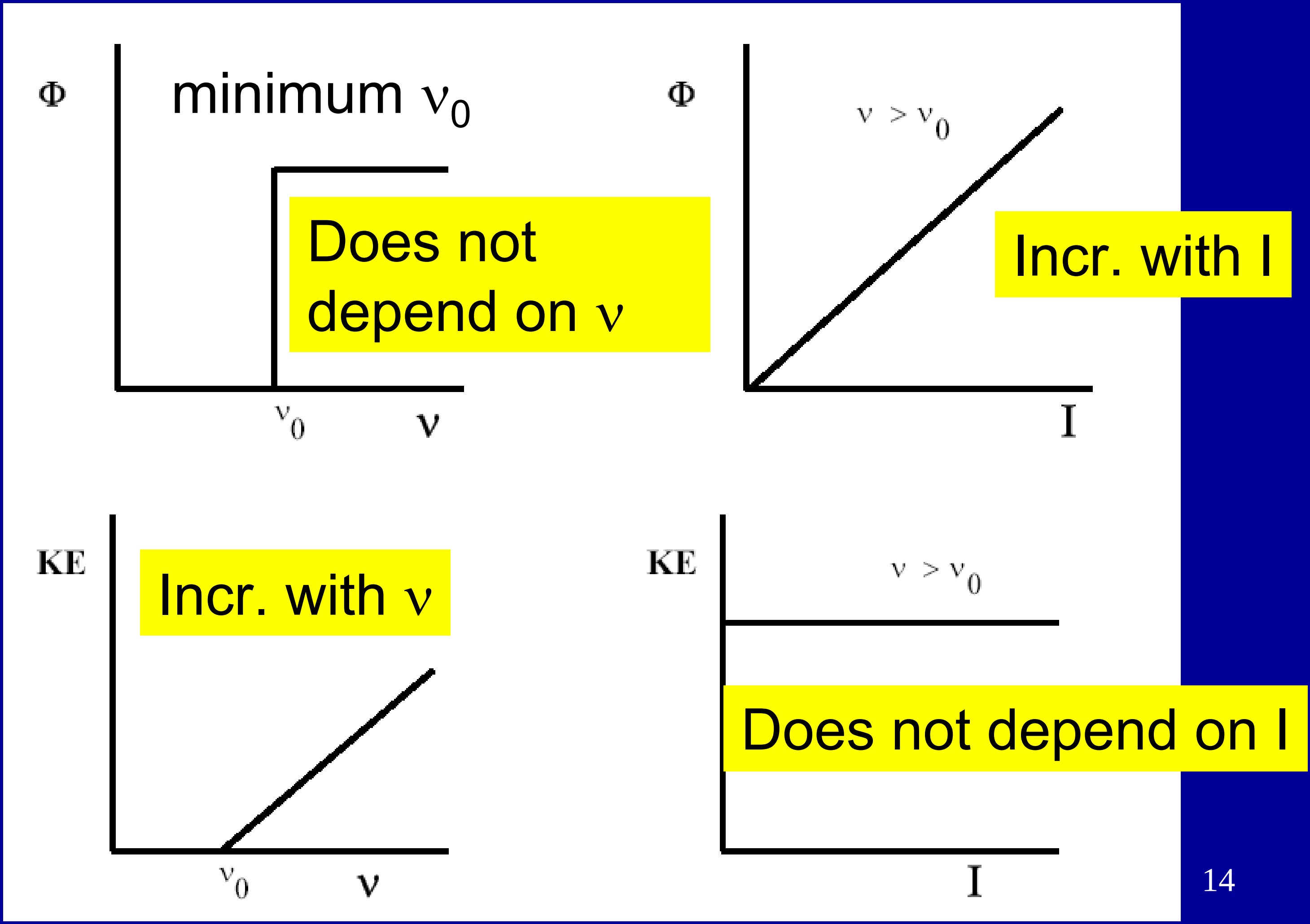
Photoelectric Effect

Φ = photoelectron flux

$h\nu_0$ = work function

I = UV light Intensity

KE = Kinetic energy



minimum ν_0

Does not depend on ν

Incr. with I

Incr. with ν

Does not depend on I

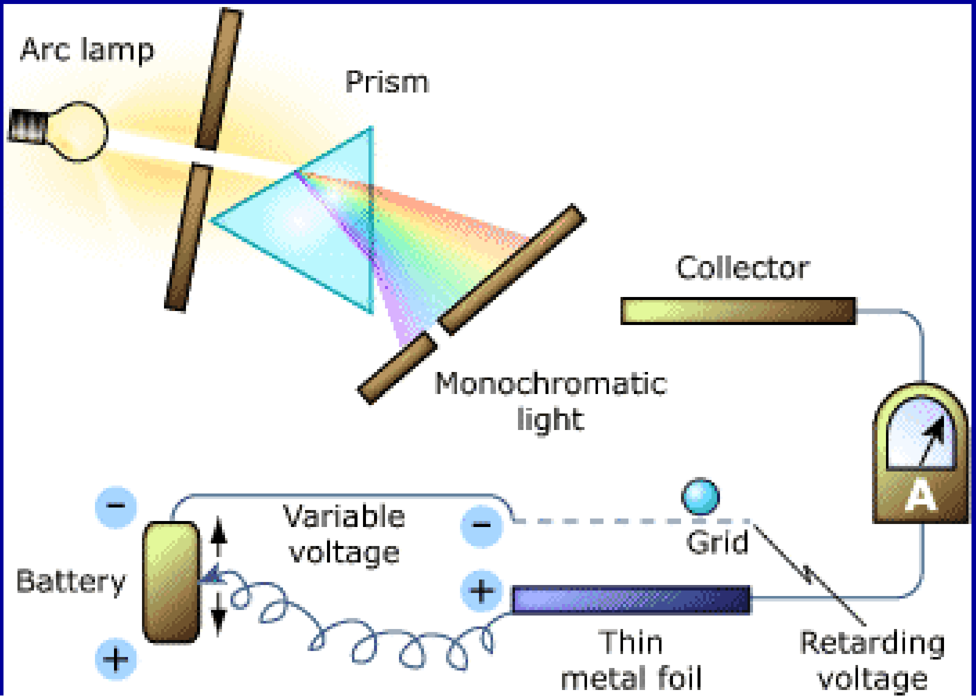
1905

Photoelectric Effect

Particle character of electromagnetic radiation
Light = photons
Photon energy $E = h\nu$
Ejected electron energy $E_{kin} = ½ mv^2$

$h\nu = E_i + ½ mv^2$

Albert Einstein
(1879-1955)
NP in Physics 1921



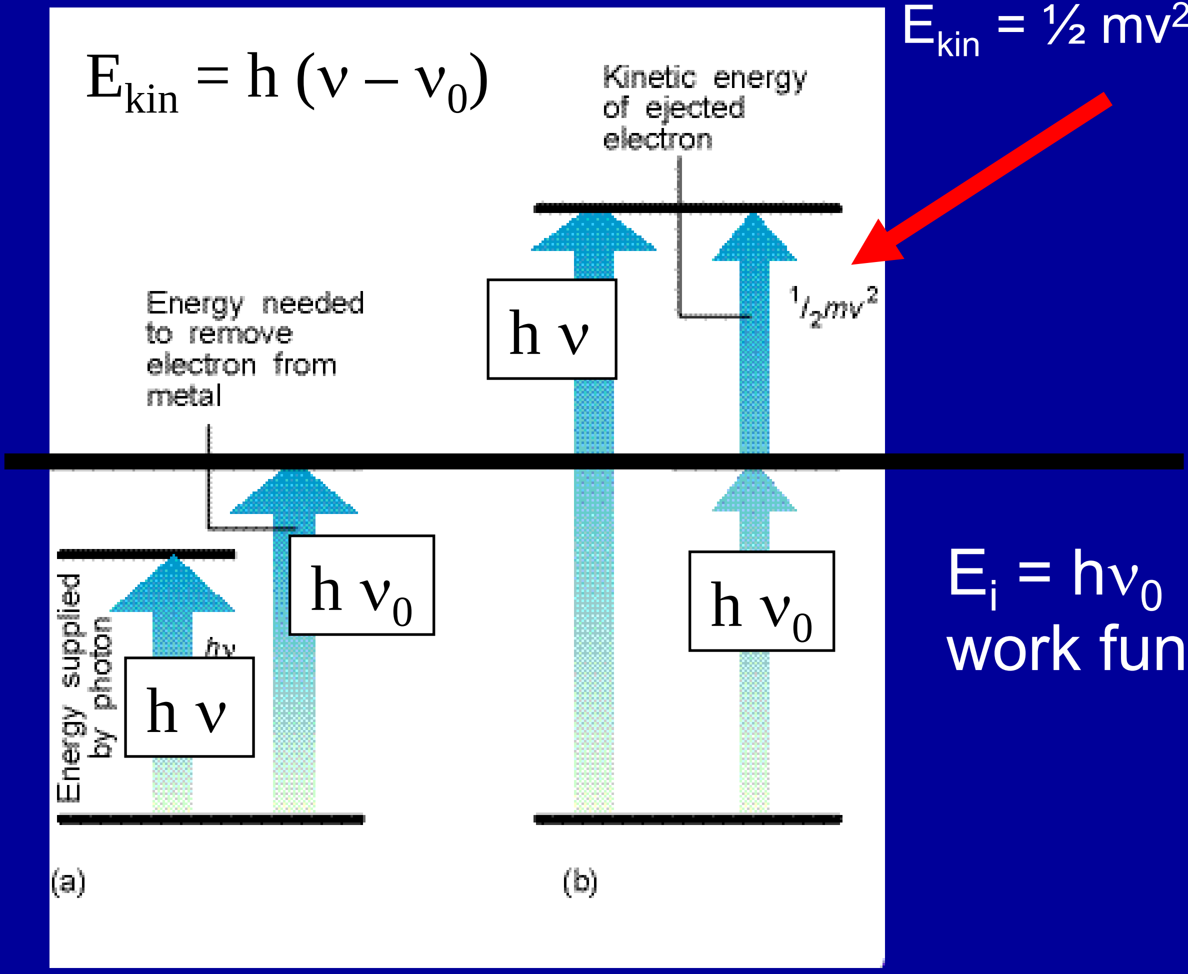
$E_{kin} = h(\nu - \nu_0)$

ν_0 = metal characteristic
h = Planck constant
$E_i = h\nu_0$ = work function

$h\,\nu = E_i + \frac{1}{2}\,mv^2$

Photoelectric Effect

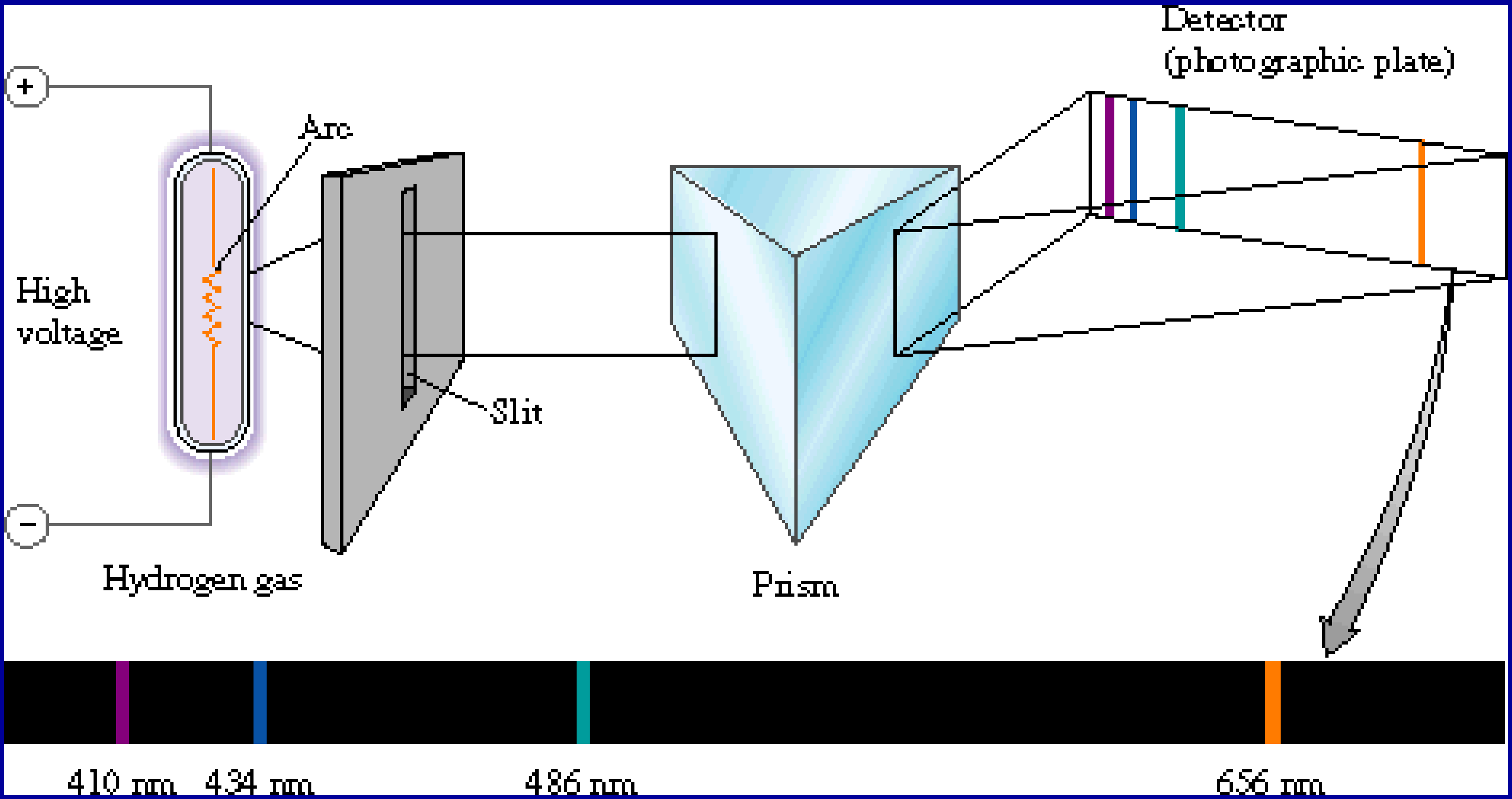
Ejected electron energy
$E_{kin} = \frac{1}{2}\,mv^2$



Photon energy
$E = h\,\nu$

$E_i = h\nu_0$
work function

Hydrogen Emission Spectrum



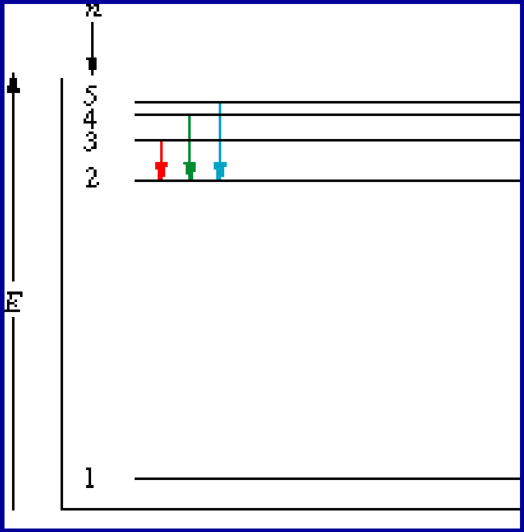
Line spectrum of light emitted by H atoms
Lines have constant wavelengths

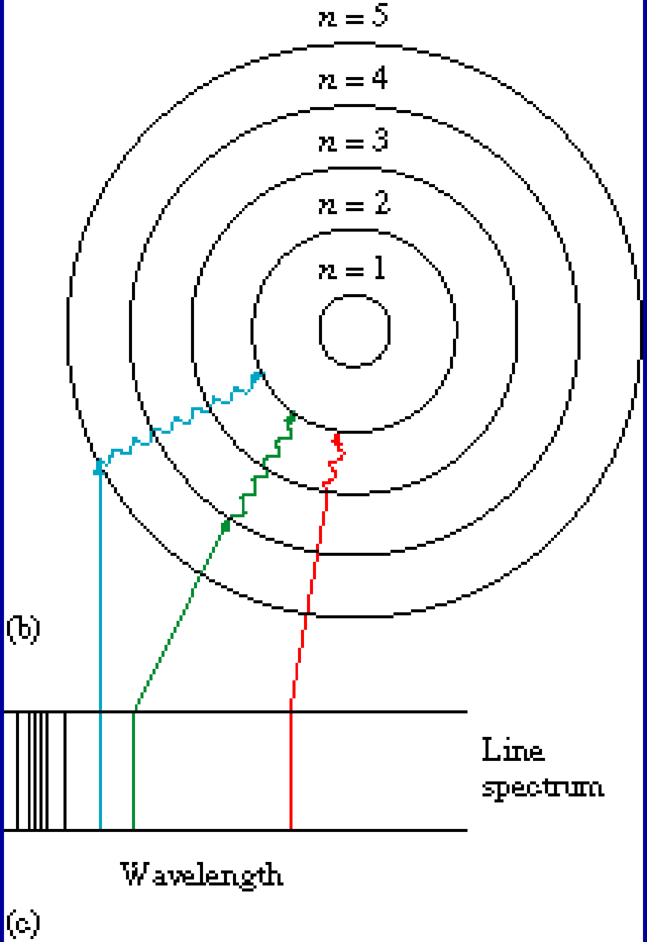
Hydrogen Emission Spectrum

Balmer series in visible range (1855)

$$\frac{1}{\lambda} = R_{\infty}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

m → n





Rydberg Equation

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

Experimental result from spectral mearurements
(visible, infrared, ultraviolet regions)

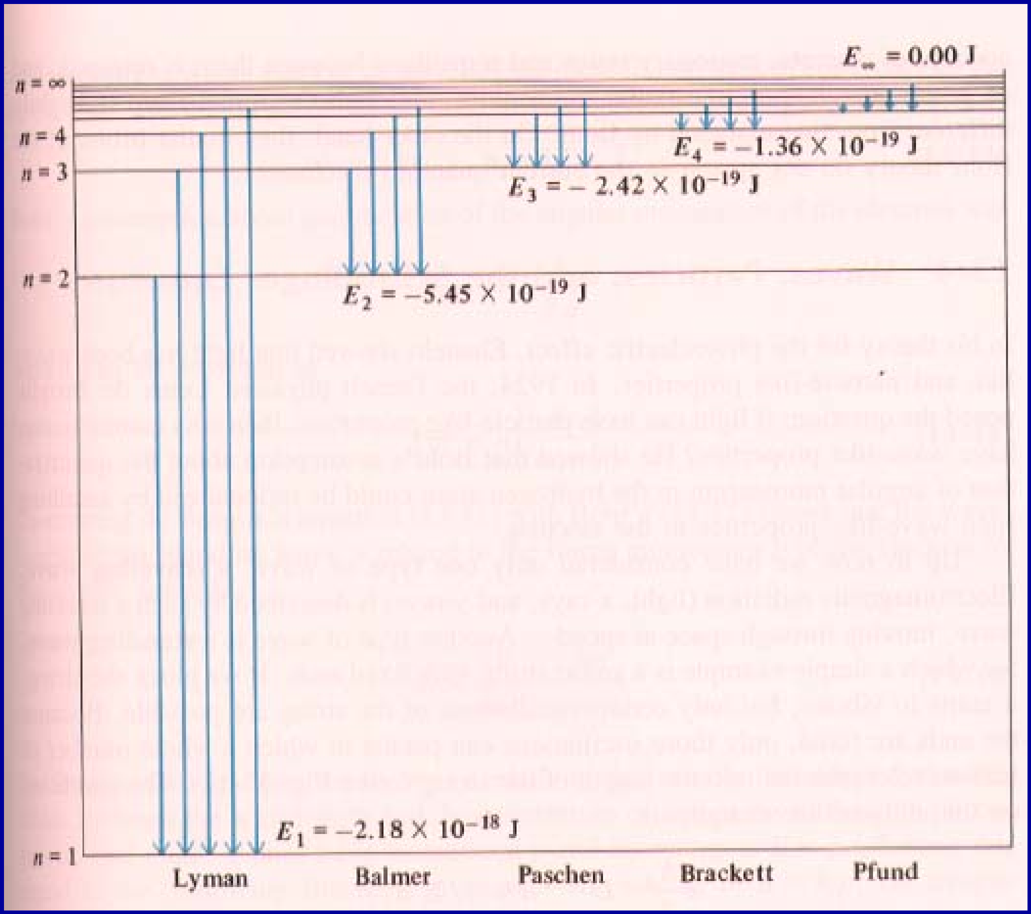
Rydberg constant, $R_\infty = 109678\ \text{cm}^{-1}$
n, m = integers,
n = 2, m = 3, 4, 5, 6,.... Balmer series in visible range (1st in 1855)

Rydberg equation holds only for H spectrum

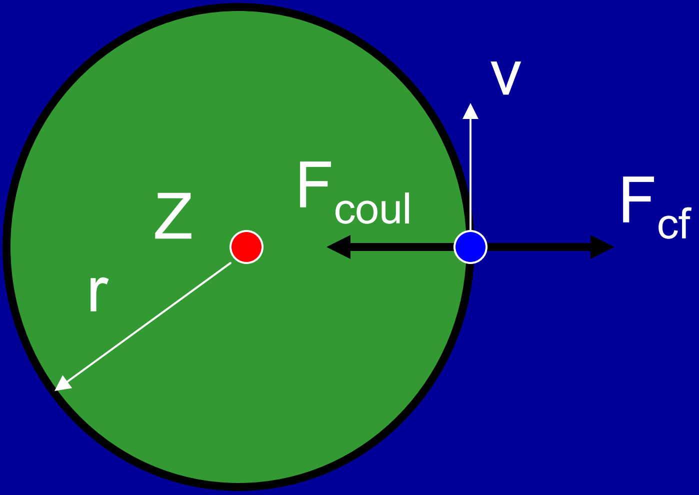
Spectral Series

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

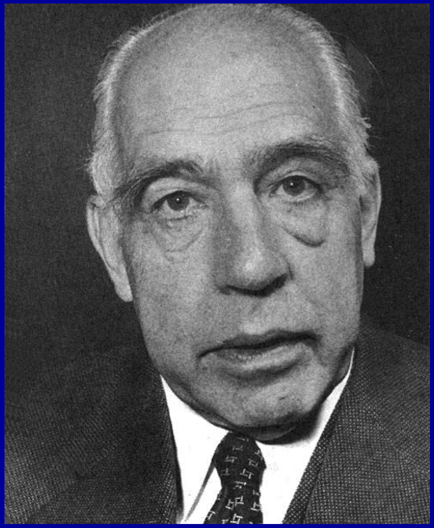
n = 1, m = 2, 3,.... Lyman
n = 2, m = 3, 4,.... Balmer
n = 3, m = 4, 5,.... Paschen
n = 4, m = 5, 6,.... Bracket
n = 5, m = 6, 7,.... Pfund



Bohr’s Model of Atom



1913



Niels Bohr
(1885 - 1962)
NP in Physics 1922

Electrons move around nucleus in circular orbits, equilibrium of centrifugal and Coulombic forces

$F_O = F_C$

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

Bohr’s Model of Atom

$$\boxed{\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}} \longrightarrow \boxed{r = \frac{Ze^2}{4\pi\varepsilon_0 m v^2}}$$

$E = E_{kin} + E_{pot} = {}^1/_2\ m\, v^2 – Z\, e^2 / 4\, \pi\, e_0\, r = – Z\, e^2 / 8\, \pi\, e_0\, r$

Electrons moves on allowed orbits with certain definite E and r

On allowed orbits do not emit energy = stacionary states

Lowest energy state = the most stable = ground state
Higher states = excited states

Quantized change of energy state $E_2 – E_1 = h\nu$

Spectrum line

Bohr's Model of Atom

Bohr's postulates: electron angular momentum is an integer multiple of Planck quantum ($h/2\pi$)

n = quantum number

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

Orbit radius

$$r = n^2\frac{a_0}{Z}$$

plug in from $m v^2 = Z e^2 / 4 \pi e_0 r$

for n = 1 and Z = 1

$a_0 = e_0 h^2 / \pi m e^2$

$a_0 = 0.529$ Å Bohr radius of H atom

Speed of electron

$$v = \frac{Ze^2}{2\varepsilon_0 nh}$$

Bohr’s Model of Atom

$E = E_{kin} + E_{pot} = {}^1/_2\, m\, v^2 - Z\, e^2 / 4\, \pi\, e_0\, r$

Energy of
an electron at
level n

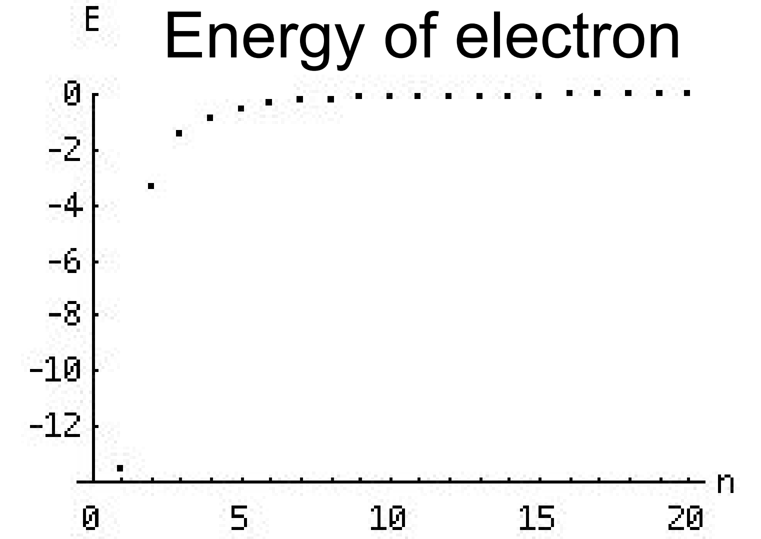
$$E_n = -E_0 \frac{Z^2}{n^2}$$

Quantized energy

E_0 $(= m\, e^4 / 8\, e_0^2\, h^2) = 2.18\ 10^{-18}$ J

(1 eV = 1.6 10 $^{-19}$ J)

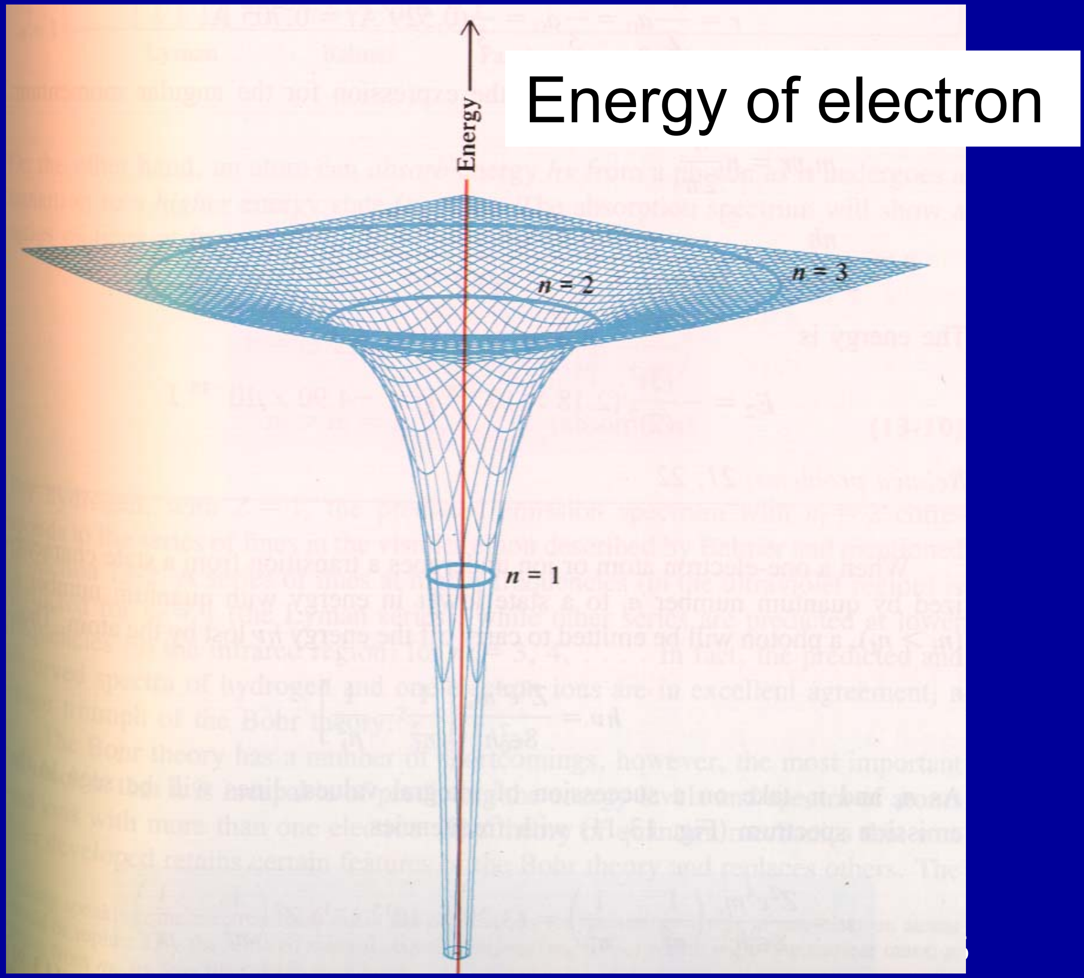
E_0 = 13.6 eV
Ionisation potential
of H atom


Energy of electron

Bohr's Model of Atom

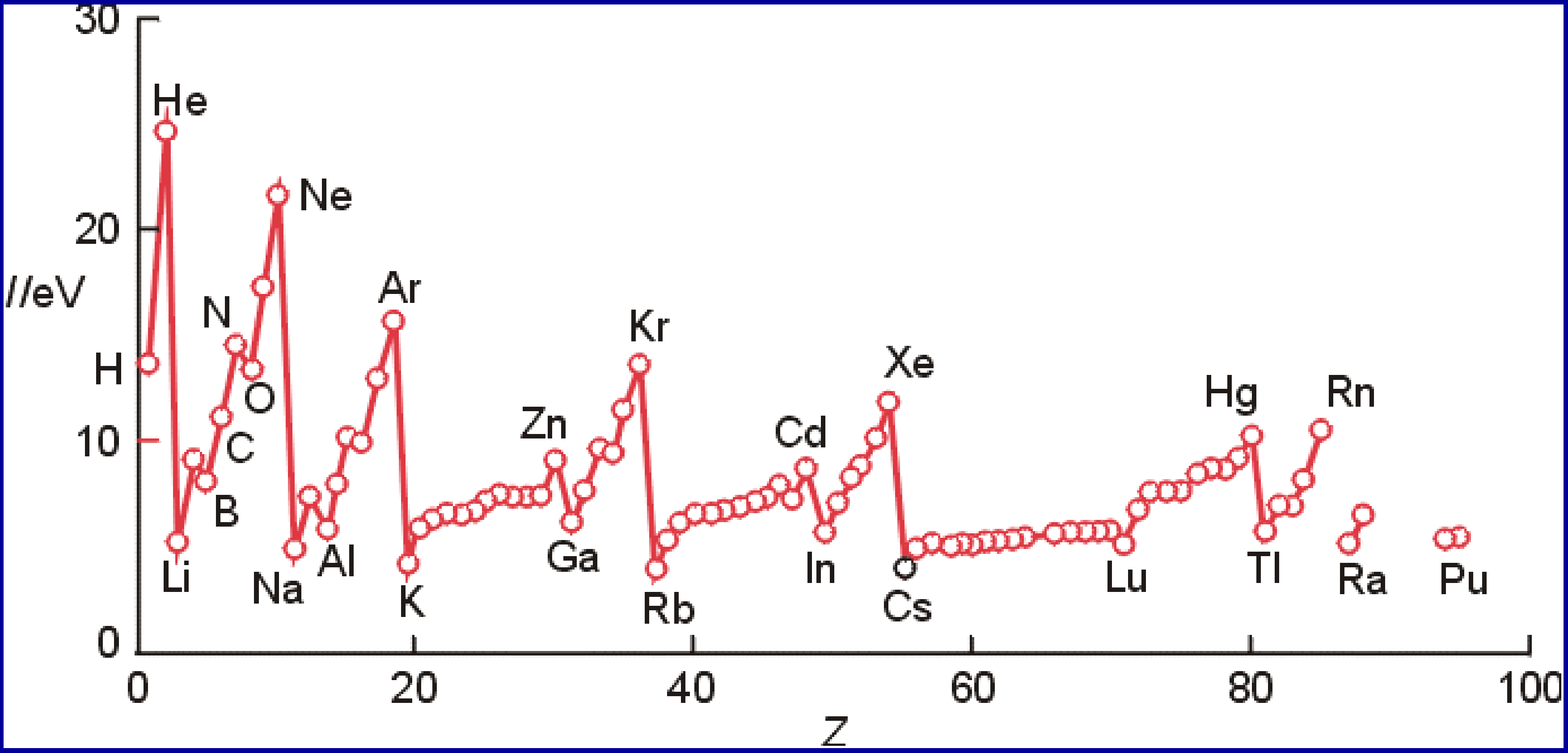
E = 0 →

The stronger is an electron bound to nucleus, the lower is its energy
(more negative)



Ionisation Energy

Energy for removing a bound electron



Atomic number, Z

Bohr's Model of Atom

Energy of
an electron at
level n

$$E_n = -E_0 \frac{Z^2}{n^2} = -\frac{me^4}{8\varepsilon_0^2 h^2} \frac{Z^2}{n^2}$$

Energy difference between two levels

$E_2 - E_1 = (-E_0 Z^2 / n_2^2) - (-E_0 Z^2 / n_1^2)$

$\Delta E = h \nu = h c / \lambda$

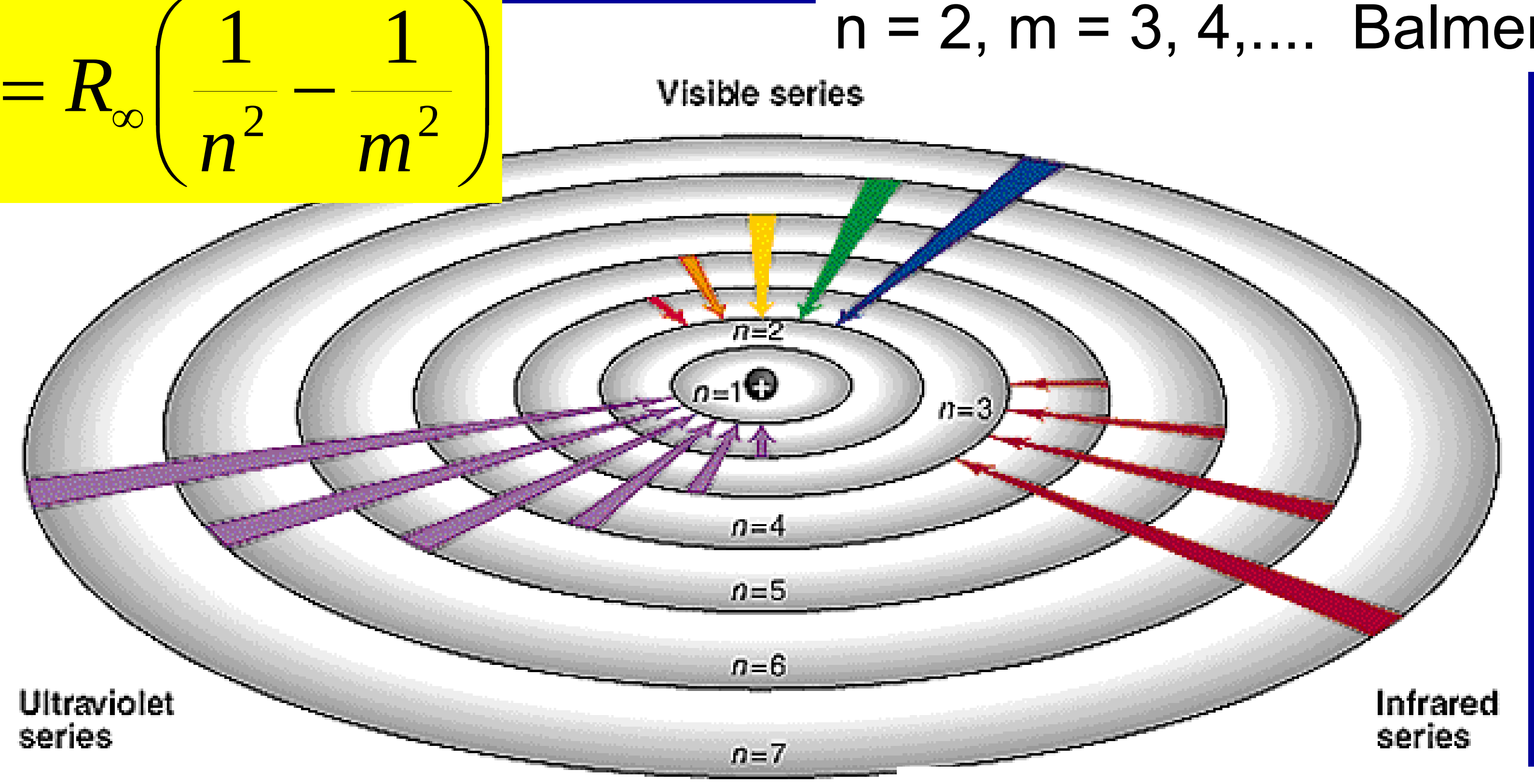
$$\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

Equation is identical to Rydberg's !!!

Spectral Series of H Atom

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

n = 2, m = 3, 4,.... Balmer



n = 1, m = 2, 3,.... Lyman

n = 3, m = 4, 5,.... Paschen

Limitations of Bohr's Model

- Simple and easy to understand
- Explained lines in the H spectrum
- Explained quantization of energy in atoms
- Cannot be used for multielectron atom spectra
- Only for atoms of "hydrogen-type" (nucleus = Z^{n+}, only one electron)

Fundamentally flawed model

Overcome by quantum-mechanic model

Wave-like Character of Light

diffraction, interference, refraction, polarisation

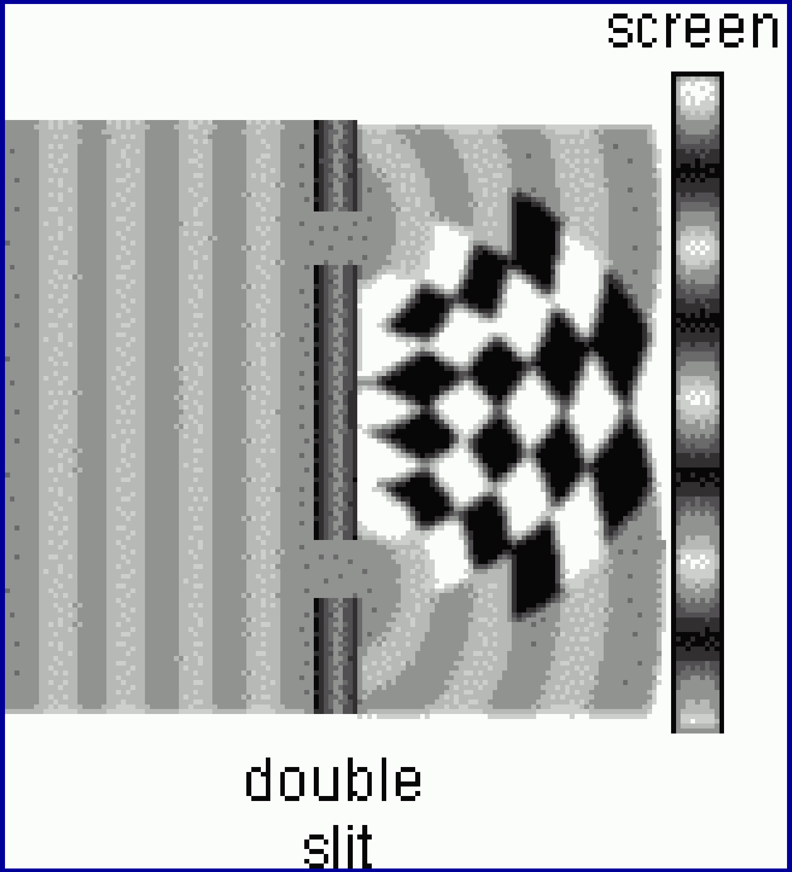
Christian Huygens

Augustin J. Fresnel

Thomas Young

James C. Maxwell

Heinrich Hertz



Particle-like Character of Light

Black body radiation, photoelectric effect, line spectra, maximum wavelength of X-rays, Compton scattering

Albert Einstein

Max Planck

Wilhelm K. Roentgen

Henry Moseley

Niels Bohr

Arthur Compton

Particle-like Character of Light

Electromagnetic radiation = **wave**

$E = h\nu$

Electromagnetic radiation = **particles** – photons

Compton scattering 1922

Photon's mass m_f

$E = h\nu = hc/\lambda$

$E = m_f c^2$

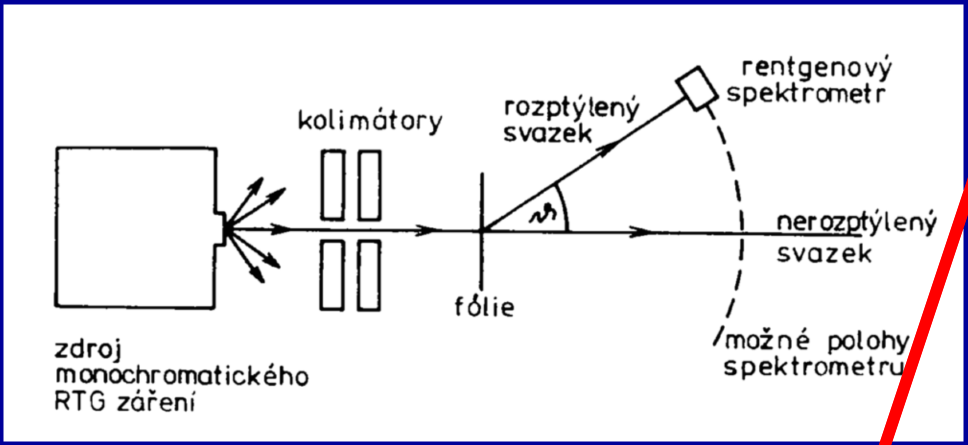
$$\boxed{m_f = \frac{h}{\lambda c}}$$

Arthur H. Compton
(1892 - 1962)
NP in Physics 1927

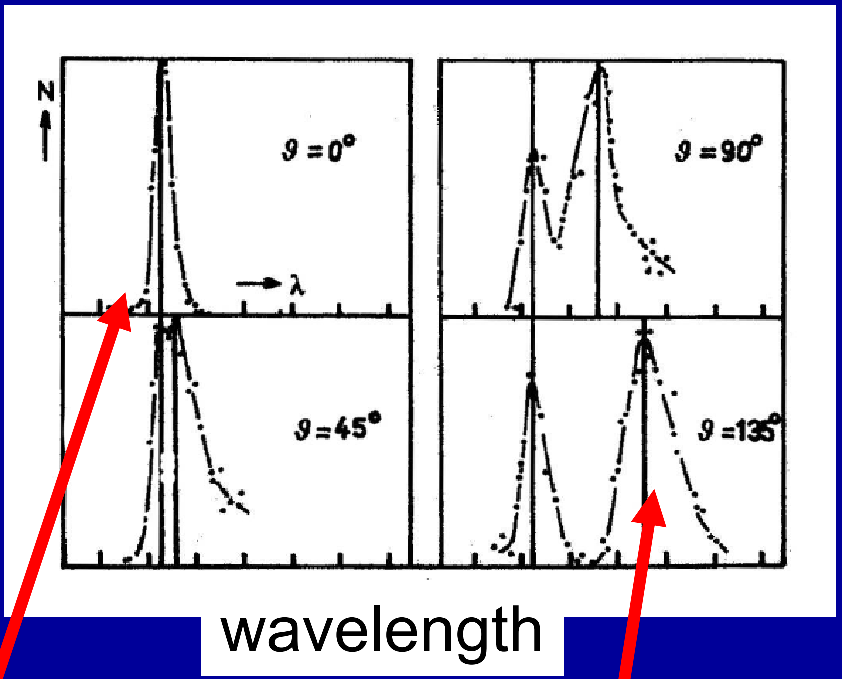
Compton Scattering

the scattering of monochromatic X-rays from electrons in a carbon target, scattered x-rays with a longer wavelength than those incident upon the target, the shift of the wavelength increases scattering angle

N = number of photons



Photons scattered on core electrons, no change in energy



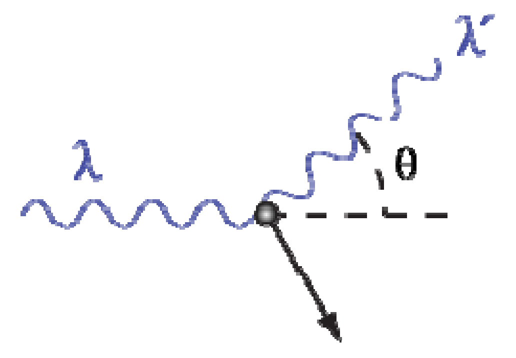
Photons scattered on outer electrons, energy transferred, wavelength increases

Dual Character of Light

λ - incident x-ray photon wavelength

λ' - scattered x-ray photon wavelength, longer than incident one

the shift of the wavelength increases scattering angle θ



$$\lambda' - \lambda = \frac{h}{m_e c^2}\left(1 - \cos\theta\right)$$

Wave-like Character of Electrons

1923 de Broglie

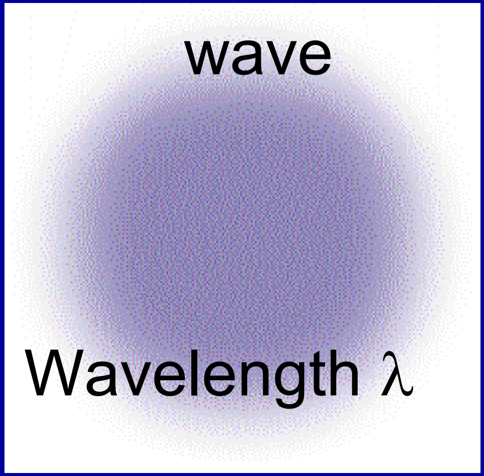
Electron has a wavelength

$$\boxed{\lambda = \frac{h}{mv}}$$

Planck + Einstein

$E = h\nu = h\ v / \lambda$

$E = m v^2$

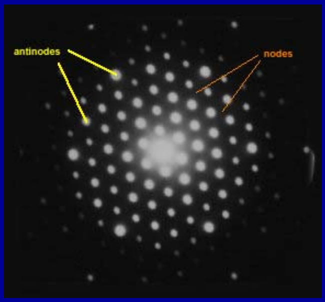


particle

Louis de Broglie
(1892 - 1987)
NP in Physics 1929

v = speed of electron
mv = p = momentum of electron

Scattering of Electrons on Ni Crystal

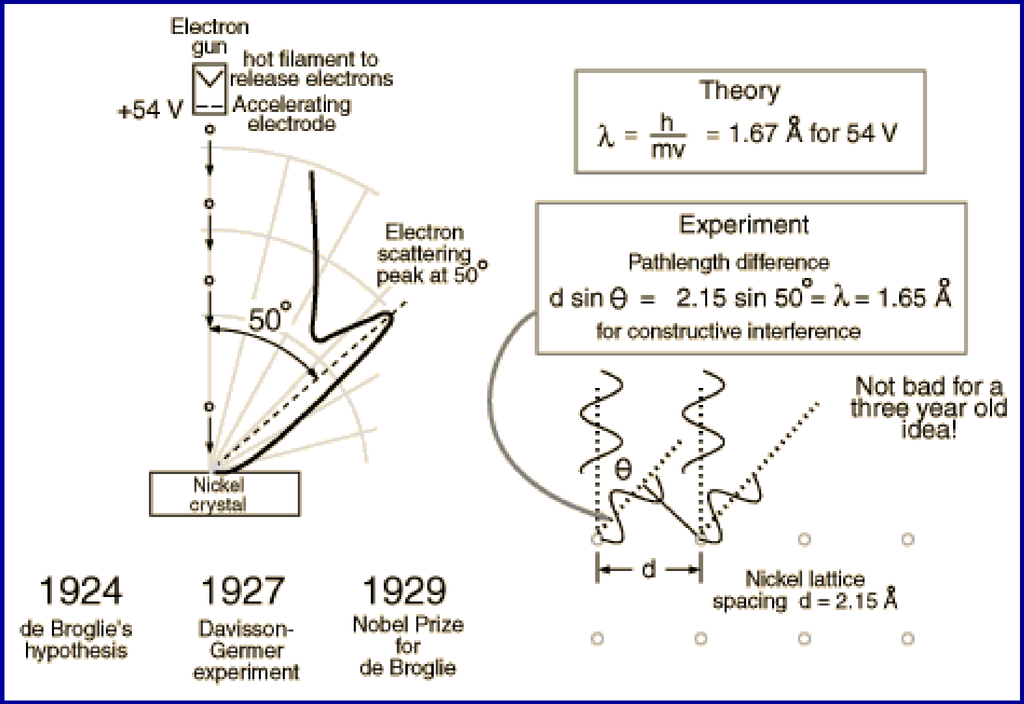


1927

C. J. Davisson
(1881-1958)
L. Germer

G. P. Thomson
(1892-1975)

NP in Physics 1937

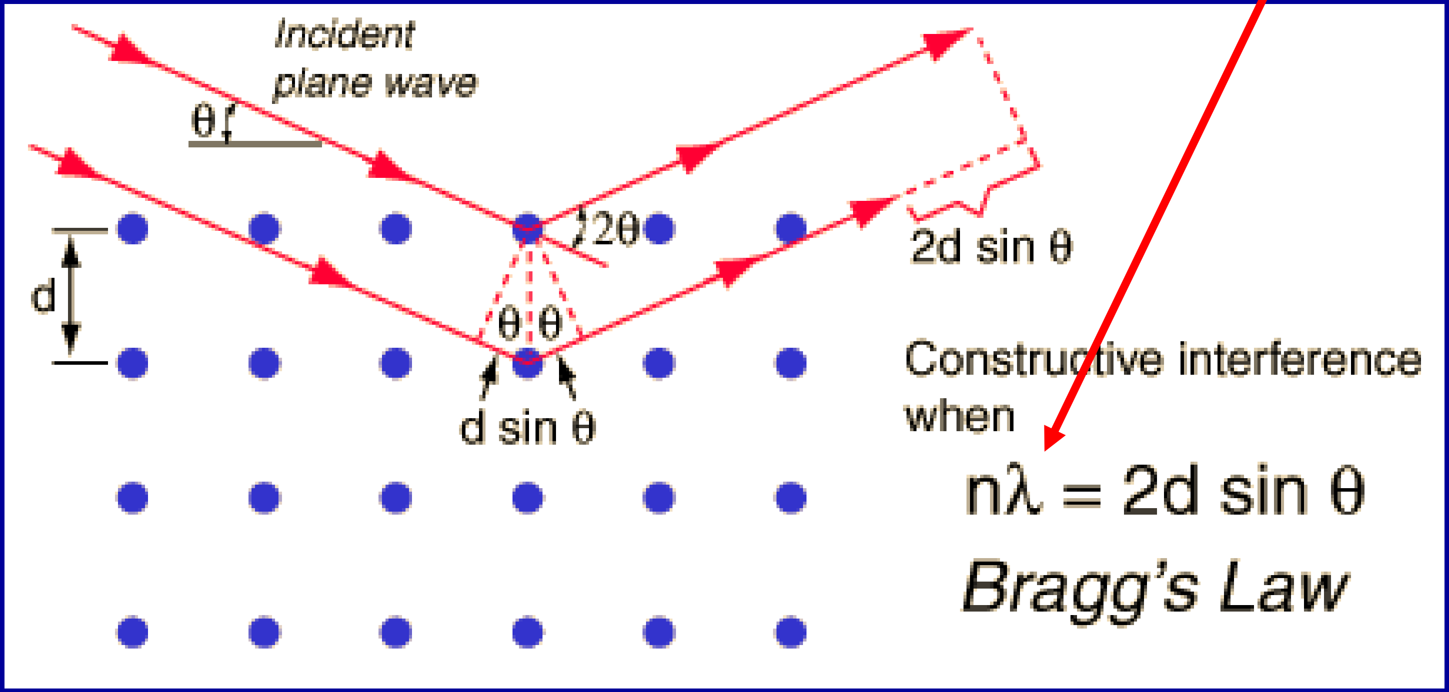


$$E = e\,V = \tfrac{1}{2}\,m\,v^2$$

Experimental evidence of wave character of electrons. Particles would scatter evenly in all directions.

Bragg Equation

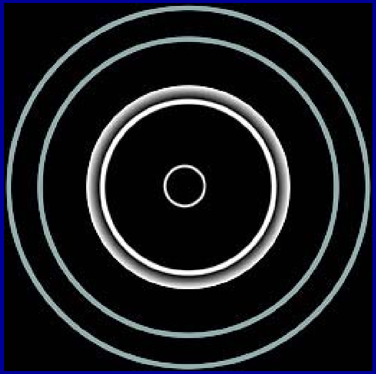
de Broglie wavelength of electron λ



Constructive interference when

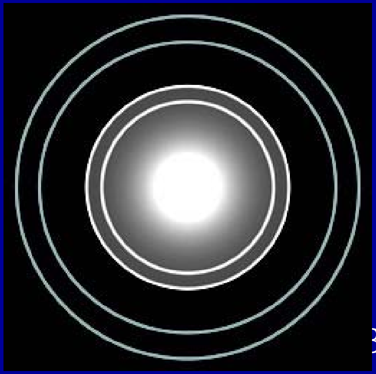
$$n\lambda = 2d \sin\theta$$

Bragg's Law



X-rays

Electrons



Electron as a Standing Wave

Electron = wave
de Broglie

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

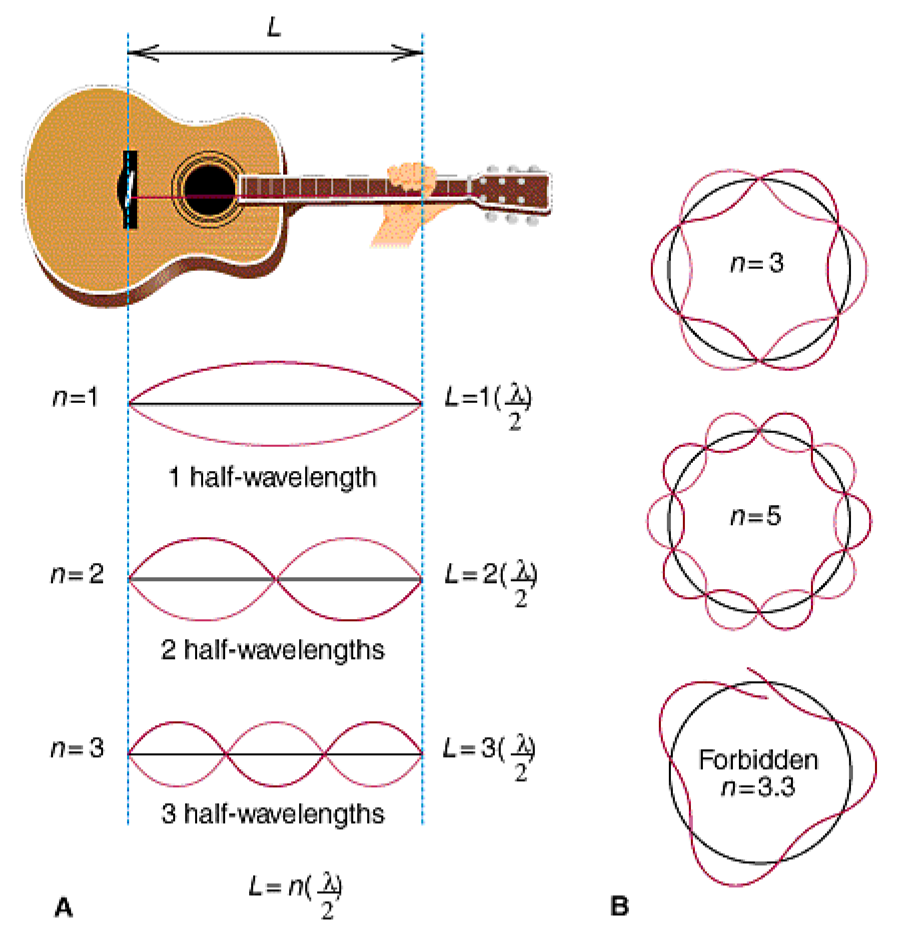
Standing wave on a circle of radius r

$n \lambda = 2 \pi r$

Combined equations

$$n\frac{h}{2\pi} = mvr$$

This is Bohr’s postulate !



Heisenberg Uncertainity Principle

1927

The more precisely the position (x) is determined, the less precisely the momentum (p = m v) is known in this instant, and vice versa.

$$\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$$

$h = 6.626\ 10^{-34}$ J s

Werner Heisenberg
(1901 - 1976)
NP in Physics 1932

Electron in H atom in ground state

$v = 2.18\ 10^{6}$ m s^{-1}

error 1%, $\Delta v = 10^{4}$ m s^{-1}

$\Delta x = 0.7\ 10^{-7}$ m = 70 nm

$a_0 = 0.053$ nm

Not possible to find precisely the position of an electron in an atom

Heisenberg Uncertainity Principle

The product of the uncertainty in an energy measurement (ΔE) and the uncertainty in the time interval of the measurement (Δt) equals h/2π or more.

$$\boxed{\Delta E \Delta t \geq \frac{\hbar}{2}}$$

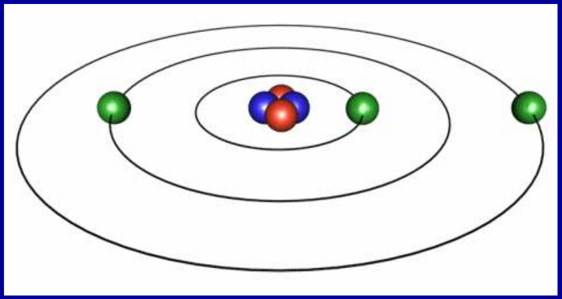
h = 6.626 10^{-34} J s

Heisenberg Uncertainity Principle

Energy of electrons is know very precisely from emission spectra

Position of an electron cannot be measured precisely

Circular orbits with defined radii = nonsense



State of an electron has to be described by quantum mechanics

a_0 = 0.053 nm – the most probable radius of electron

Schrödinger Equation

1926 Schrödinger equation = postulate

$$\hat{H}\,\Psi = E\,\Psi$$

Erwin Schrödinger
(1887 - 1961)
NP in Physics 1933

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\Psi = 0$$

$\hat{H}$ = Hamilton operator of total energy (E),
Kinetic and potential (V) energy

Schrödinger Equation

$$\hat{H}\,\Psi = E\,\Psi$$

Schrödinger Equation

$$\hat{H}\,\Psi = E\,\Psi$$

Second-order partial differential equation

Exact solution ONLY for H and one-electron systems (He^+, Li^{2+},....)

Approximate solutions for many-electron **atoms** (He,...) and **molecules**

The solution of differential equation are pairs (**E**, Ψ):

- proper **wave functions** (Eigenfunctions) Ψ

orbitals $|\Psi|^2$ – space distribution of e

- proper values of electron **energy** in orbitals (Eigenvalues) **E**

To one value of E could belong several wave functions (degenerate)

Wavefunctions

Ψ(x,y,z) – solution of a stationary Schrödinger eq.

Only certain states of electron are allowed - Ψ(x,y,z)

Ψ is a complex function of coordinates x, y, z, has no physical meaning, positive and negative values

$|\Psi|^2$ – **probability density** of electron position

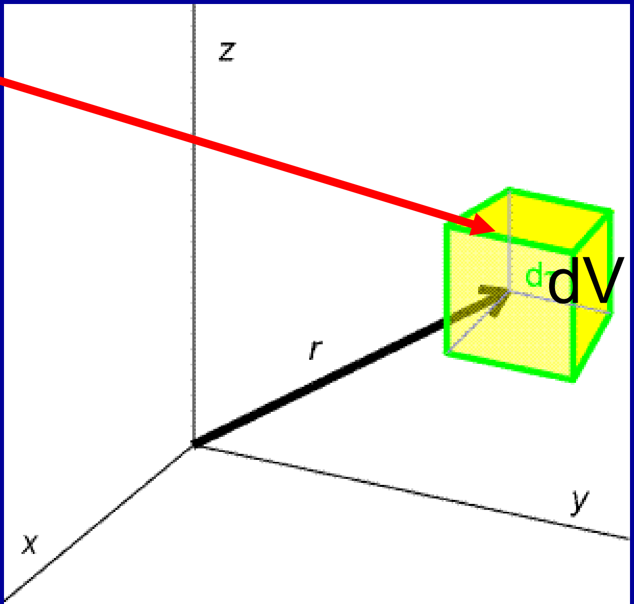
Ψ depends on integers – quantum numbers

Born Interpretation of Wavefunction

$\mathbf{\Psi(x,y,z)}$ solution of a stationary Schrödinger eq.,
(Ψ no physical meaning)

$|\Psi|^2 dV$ **probability** of finding electron in volume dV
at position **r**

(dV= dx dy dz)



Max Born
(1882 - 1970)
NP in Physics 1954

“I think I can safely say that nobody understands Quantum Mechanics”