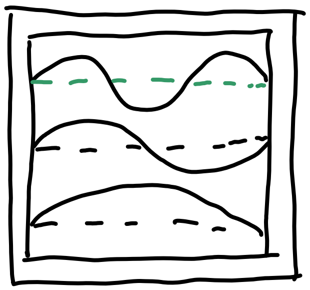
Lecture 5: 01/28/09

- Planck's Theory of Blackbody Radiation
- The quantized Atom
  - Line Spectra
  - Evidence for quantized Energy Levels

Niels Bohr (1885 – 1962): Nobel Prize 1922

Recap:

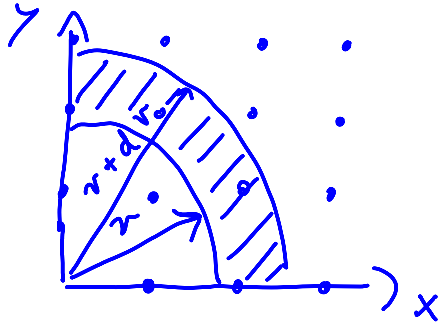
$I_{1,4}$ Blackbody Radiation



metal box

$$\rho_T(\nu) = \left(\frac{\text{energy of radiation in}[\nu,\ \nu+d\nu]}{\text{volume of cavity}}\right)$$

$$= \left(\frac{\#\text{ of standing wave modes in}[\nu,\nu+d\nu]}{\text{volume of cavity}}\right)\left(\begin{matrix}\text{average}E\\ \text{per mode}\end{matrix}\right)$$



- for 3 space dimensions:

$$\left(\frac{\#\text{ of modes between }\nu\text{ and }\nu+d\nu}{\text{volume of cavity}}\right) = 8\pi\frac{\nu^2}{c^3}d\nu$$

- average energy per standing wave at T:

Boltzmann Principle: $P(E) \propto e^{-E/kT}$

Here: P(E) gives the probability the a given standing electromagnetic wave in the cavity will have energy E, if the walls of the cavity are at temperature T.

Classical physics: energy of oscillator can have any value (continuous energy)

$$\begin{pmatrix}\text{average energy}\\ \text{per mode}\end{pmatrix} = \begin{pmatrix}\text{weighted average over the probability}\\ \text{that a given energy state is occupied}\end{pmatrix}$$

$$\langle E \rangle = \frac{\int_0^\infty E\, e^{-E/kT}\, dE}{\int_0^\infty e^{-E/kT}\, dE} = kT$$

← normalization

Note: $\langle E \rangle$: same value for all standing waves, indep. of frequency!

step ③:

$$\Rightarrow \rho_T(\nu)\,d\nu = \left(\frac{\#\text{ of modes in } [\nu, \nu+d\nu]}{\text{volume of cavity}} \right) \langle E \rangle$$

$$= \left(8\pi \frac{\nu^2}{c^3}\, d\nu \right) (kT)$$

Rayleigh Jeans formula for blackbody radiation

→ approaches experimental results for low frequencies

but:

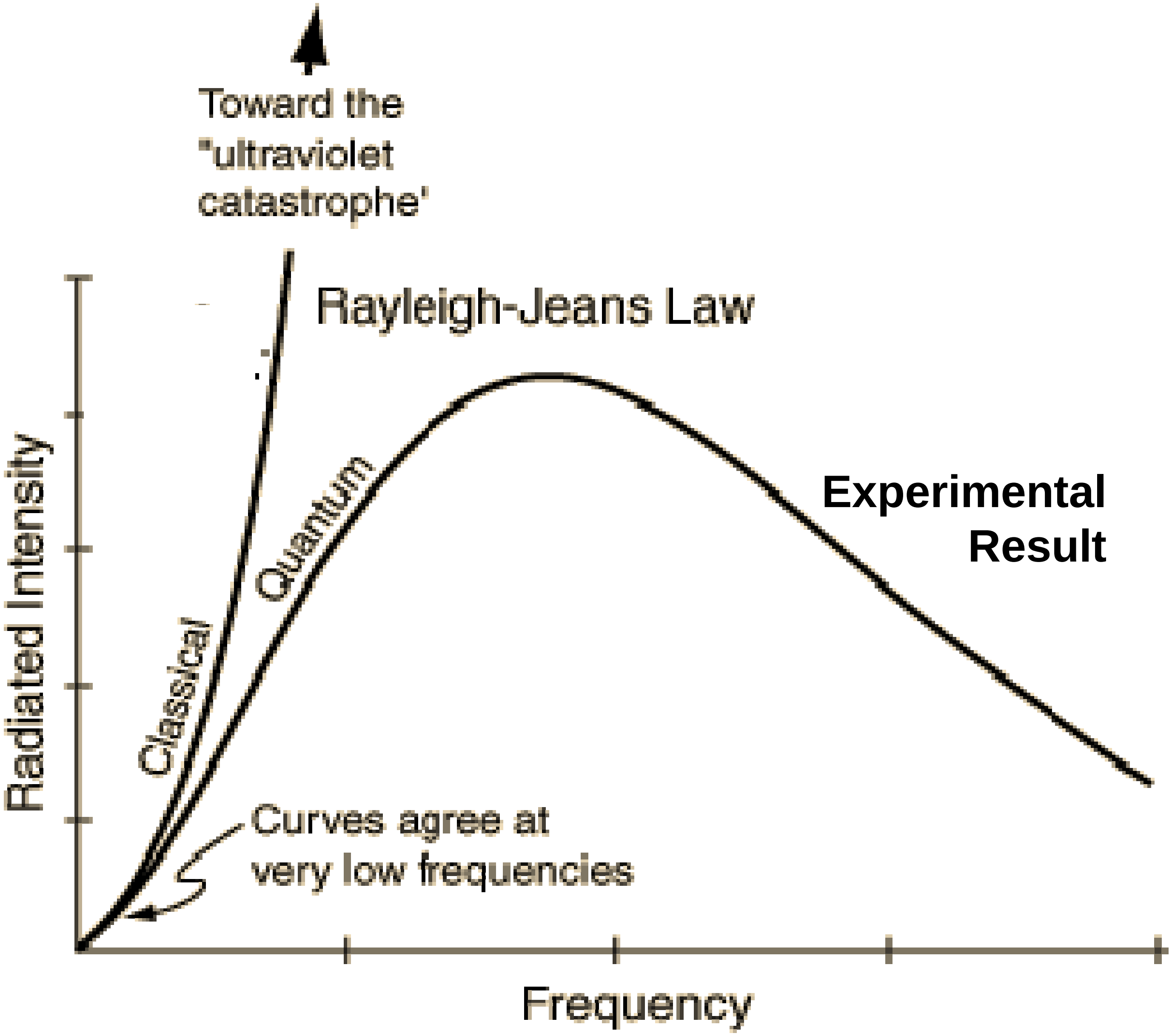
1) $\rho_T(\nu) \propto \nu^2 \rightarrow \infty$ for large frequencies

"ultraviolet catastrophe"

2) total energy in cavity $\propto \int_0^\infty \rho_T(\nu)\,d\nu = \infty$

⇒ classical result can't be correct!

Blackbody Radiation Spectrum



What is the reason for the "ultraviolet catastrophe" in the classical theory?

A. The predicted number of standing waves satisfying the boundary conditions at the metal walls of the box is infinite ← correct

B. The predicted spectral density of modes (# of modes per volume per frequency interval) is proportional to frequency^2 ← correct

[✓ C.] Each standing wave has a predicted non-zero average energy, no matter how high the frequency of the mode

classical: average energy per standing wave $= kT > 0$

– Solution (Planck 1900)

- to get finite total energy: need $\langle E \rangle \xrightarrow[\nu \to \infty]{} 0$
- Planck: get finite answer if one assumes that energy in each mode is quantized (i.e. continuous!)

$$E = 0, \Delta E, 2\Delta E, 3\Delta E \ldots$$

$$\Delta E = h\nu$$

quantum mechanics

↑ Planck's constant

⇒ allowed energy in a standing wave:

$$E_n = nh\nu \qquad n : \text{integer} \geq 0$$

- at high frequencies:

smallest non-zero energy $= E_1 = h\nu \gg kT$ ⇒ little chance that energy is non-zero!

$$\Rightarrow \langle E \rangle = \xrightarrow[\nu \to \infty]{} 0$$

(high ν modes are "frozen out")

⇒ average energy per standing wave with quantized energies:

$$\langle E\rangle = \frac{\sum_{n=0}^{\infty} E_n \, e^{-E_n/kT}}{\sum_{n=0}^{\infty} e^{-E_n/kT}} = \frac{\sum_{n=0}^{\infty} nh\nu \, e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}}$$

sum over all allowed, quantized energies

see next page

$$\overset{\downarrow}{=} \frac{h\nu}{e^{h\nu/kT}-1}$$

Note: 1) for $h\nu \ll kT$ (low frequencies)

$$\langle E\rangle = \frac{h\nu}{(1+h\nu/kT+\dots)-1} \approx kT$$ classical result

2) for $h\nu \gg kT$ (high frequ.)

$\langle E\rangle \longrightarrow 0$ ⇒ these modes don't contribute to $\rho_T(\nu)$

Detailed calculation:

$$\langle E\rangle = \frac{\sum_{n=0}^{\infty} nh\nu\, e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu\, S_2}{S_1}$$

- $\underline{S_1} = \sum_{n=0}^{\infty} a^n = 1+a+a^2+\dots$: geometric sum, $a = e^{-h\nu/kT} < 1$

$$\Rightarrow a S_1 = a + a^2 + \dots \Rightarrow S_1 - aS_1 = 1 \Rightarrow \underline{S_1 = \frac{1}{1-a}}$$

- $\underline{S_2} = \sum_{n=0}^{\infty} n a^n = a\frac{d}{da}\sum_{n=0}^{\infty} a^n = a\frac{d}{da} S_1 = a\left\{-\frac{1}{(1-a)^2}(-1)\right\} = \underline{\frac{a}{(1-a)^2}}$

$$\Rightarrow \langle E\rangle = \frac{h\nu\, e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2} \Bigg/ \frac{1}{1-e^{-h\nu/kT}}$$

$$= \frac{h\nu\, e^{-h\nu/kT}}{1-e^{-h\nu/kT}} = \underline{\frac{h\nu}{e^{h\nu/kT}-1}}$$

$\underline{\text{q.e.d.}}$

$\Rightarrow$ Planck's Blackbody spectrum:

$$\underline{\underline{\rho_T(\nu)\,d\nu}} = \left(\frac{\#\text{ of modes in } [\nu, \nu + d\nu]}{\text{volume of cavity}} \right) \langle E \rangle$$

$$\underline{\underline{= \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \, d\nu}}$$

$\Rightarrow$ very good agreement with experiment :D

– More on Planck's Postulate:

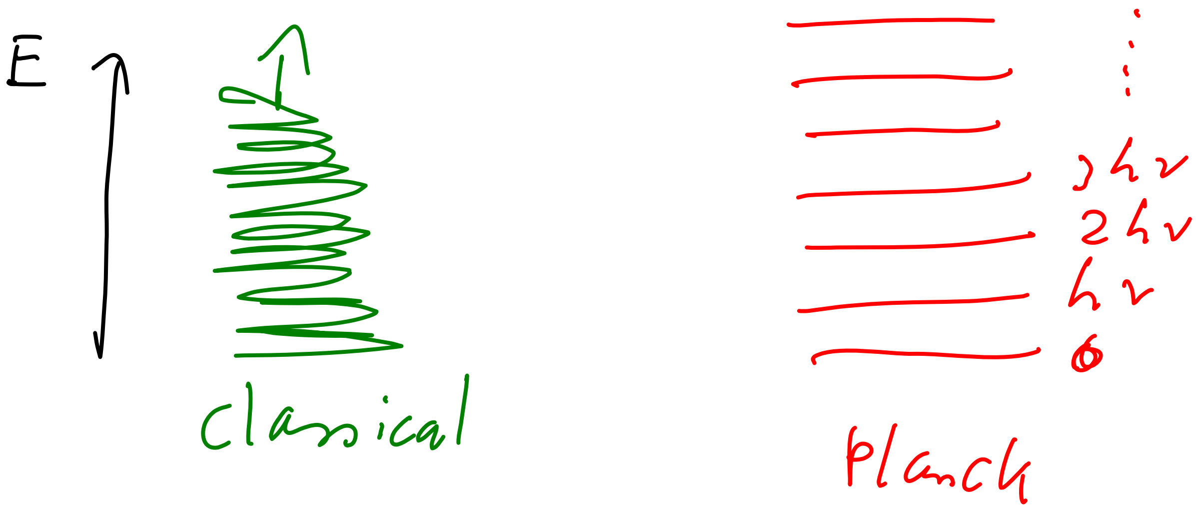
Planck: any physical entity with one degree of freedom whose "coordinate" is a sinusoidal function of time

$\Rightarrow$ only discrete energies allowed

$\Rightarrow$ quantized!

$E_n = nh\nu$

n: quantum number



energy levels (energy states) (quantum state)

I_2 The Quantized Atom

<u>so far</u>:

<u>light</u> → wave properties (interference)

→ particle like properties

⇒ <u>photons</u>

- discrete chunks of energy $E = h\nu$

⇒ energy of radiation is <u>quantized</u>: $E_{rad} = n h \nu$

<u>Now</u>

small particles at small scales → wave properties

→ energy <u>quantization</u> if particle is confined to a small enough volume

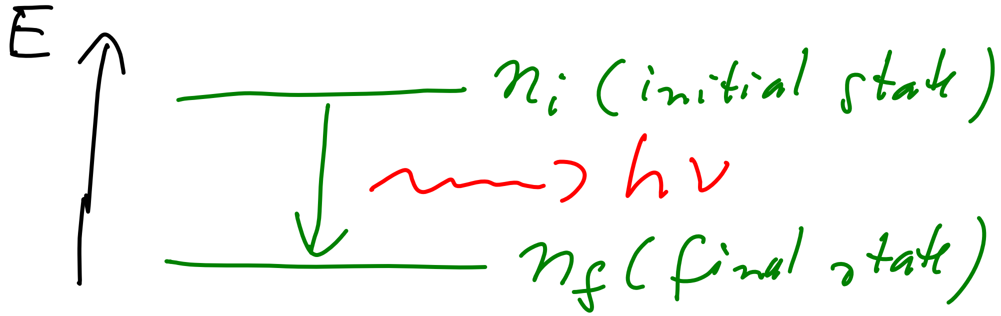
⇒ 1st example: The quantized atom

$I_{2,1}$ Evidence for quantized energy levels in atoms:

(a) Spectral Lines

- Radiation emitted by independent atoms shows sharp spectral lines (example: gas discharge at low pressure)

- key idea: associate energy of photons of a given spectral line as energy difference between two states of the atom:



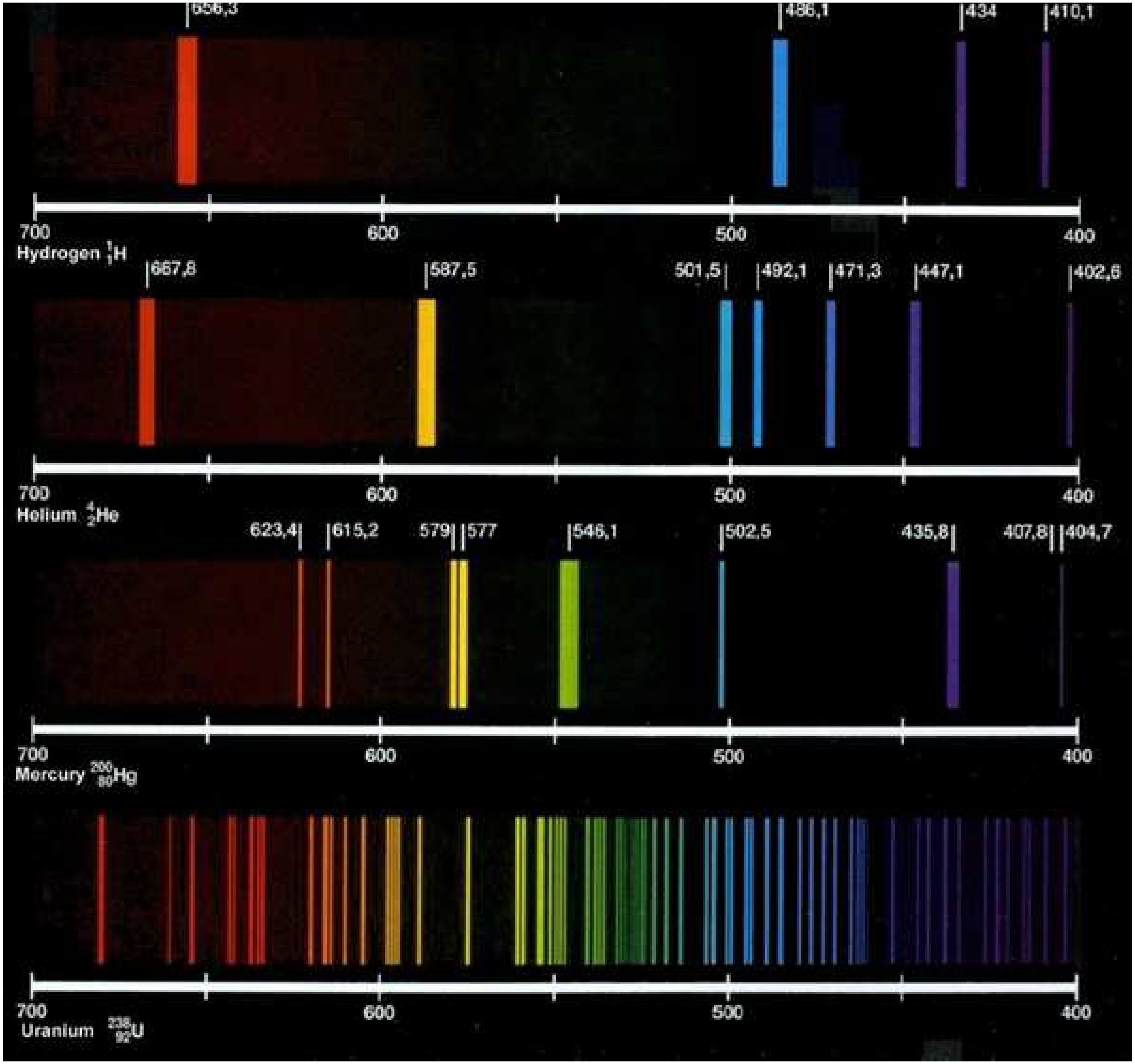
$$E_{photon} = h\nu = E_{n_i} - E_{n_f}$$

Hydrogen

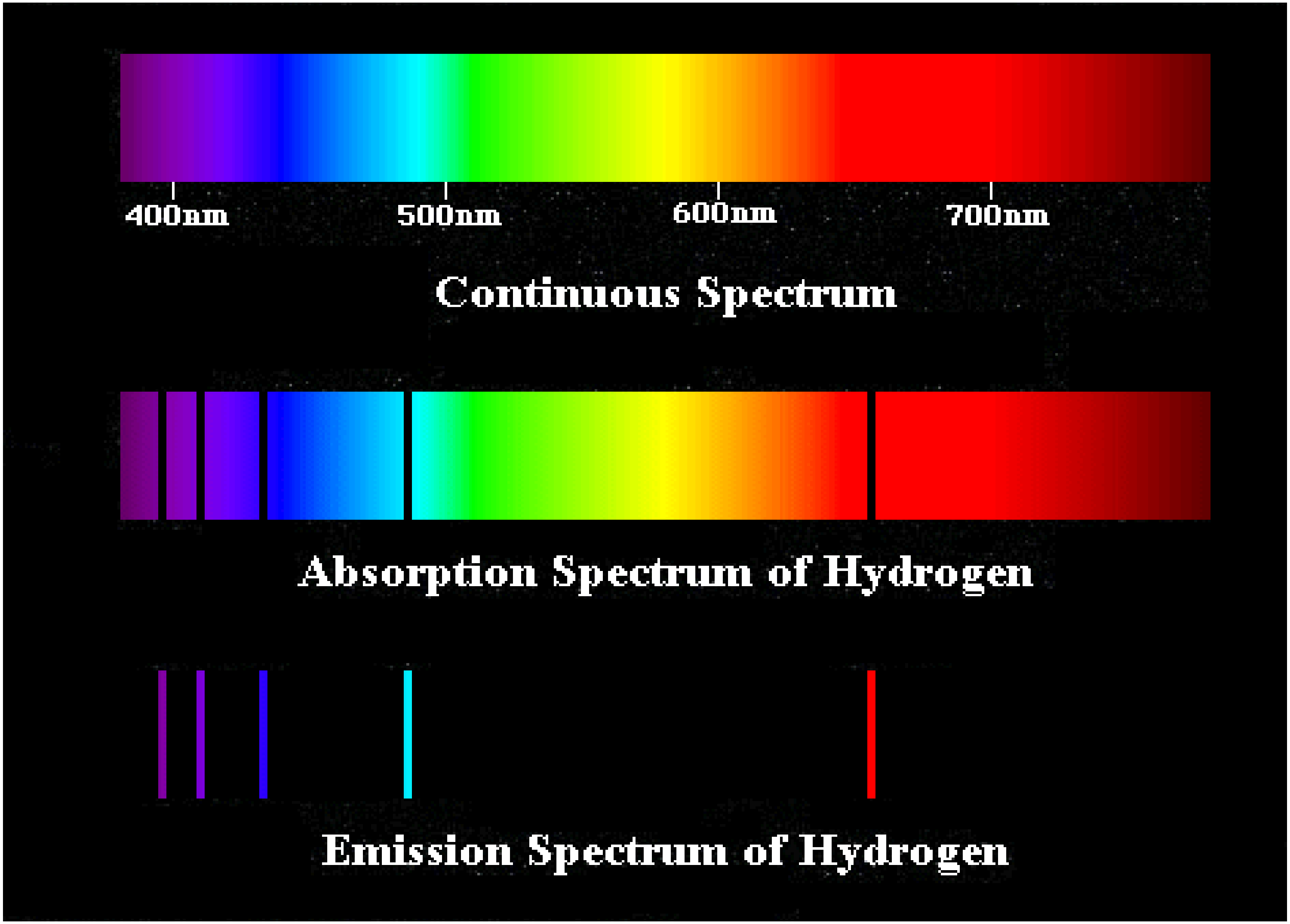
Helium

Mercury

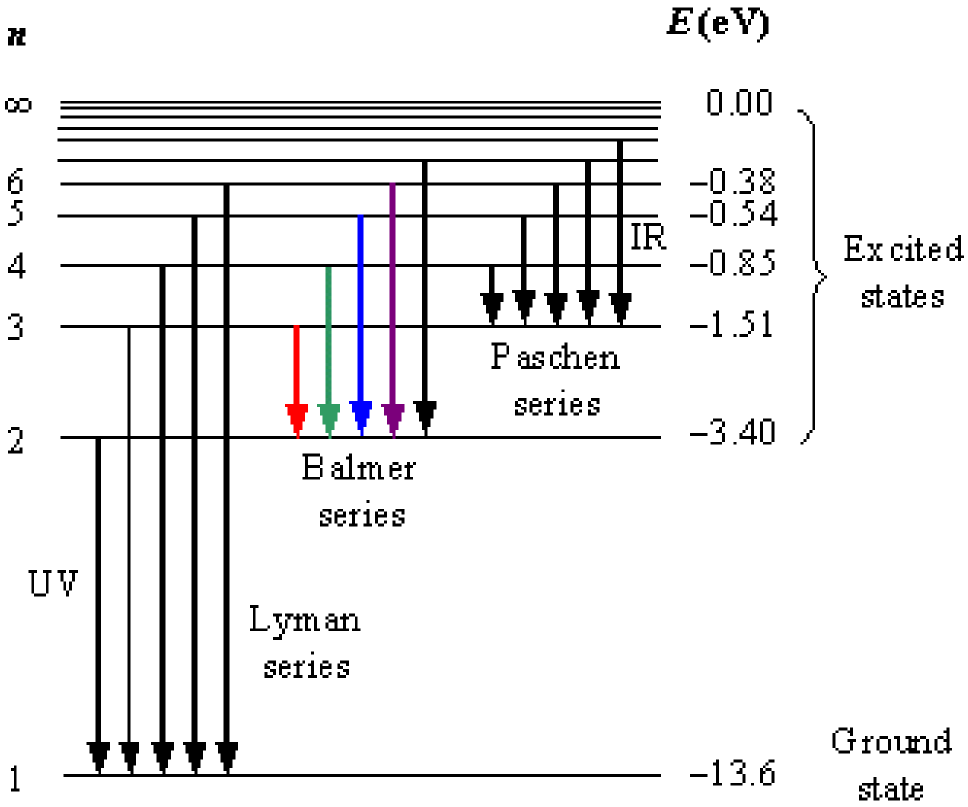
Uranium



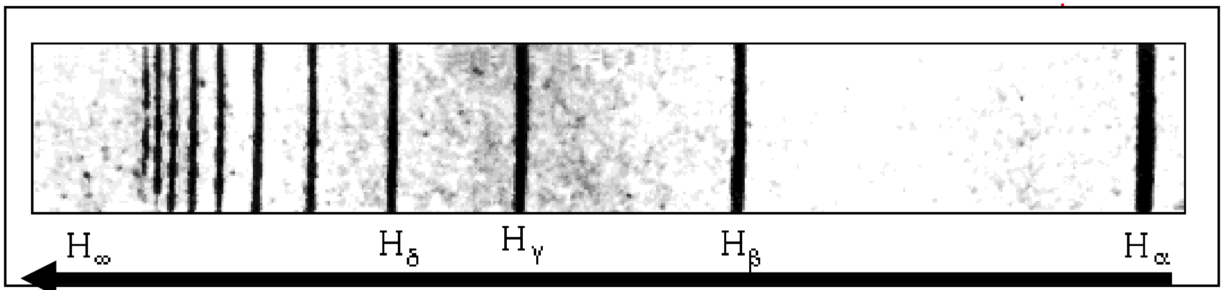
Emission and Absorption Spectrum



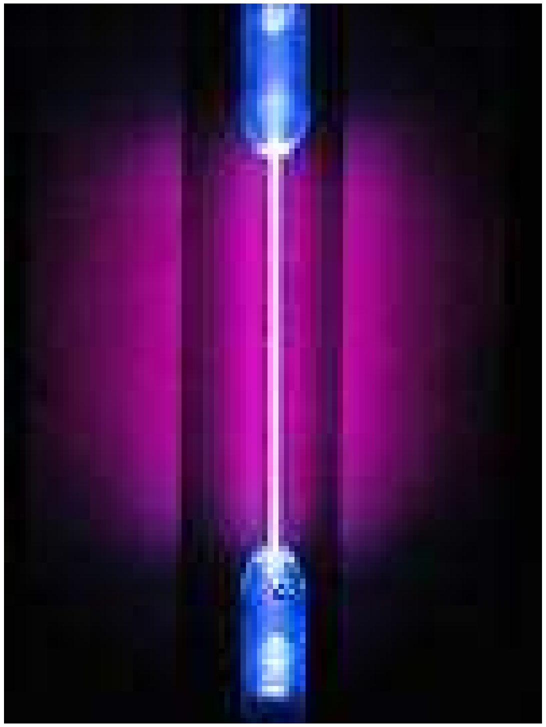
Emission Spectrum for Hydrogen



Balmer Series



Discharge Lamp



J.J. Balmer (1885):

$$\frac{1}{\lambda_n} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right) \qquad n=3,4,\ldots$$

· for hydrogen: visible lines described by

Balmer Series: $$\frac{1}{\lambda_n} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, \ldots$$

$R_H = 109700\ \text{cm}^{-1}$: Rydberg constant

$$\Rightarrow E_{photon} = h\nu = \frac{hc}{\lambda_n} = hcR_H\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right)$$

$$= hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$n_f = 2 \Rightarrow$ Balmer Series

$n_f = 1 \Rightarrow$ Layman Series (UV)

$n_f = 3 \Rightarrow$ Pashen Series (IR)