

atomic absorption and emission of light

1889 Rydberg generalized to other H emission lines:

$$\therefore \frac{mv^2}{r} = \frac{ke^2Z}{r^2} \quad \mathbf{L = mvr = n \hbar} \quad E = \frac{1}{2}mv^2 - \frac{ke^2Z}{r}$$

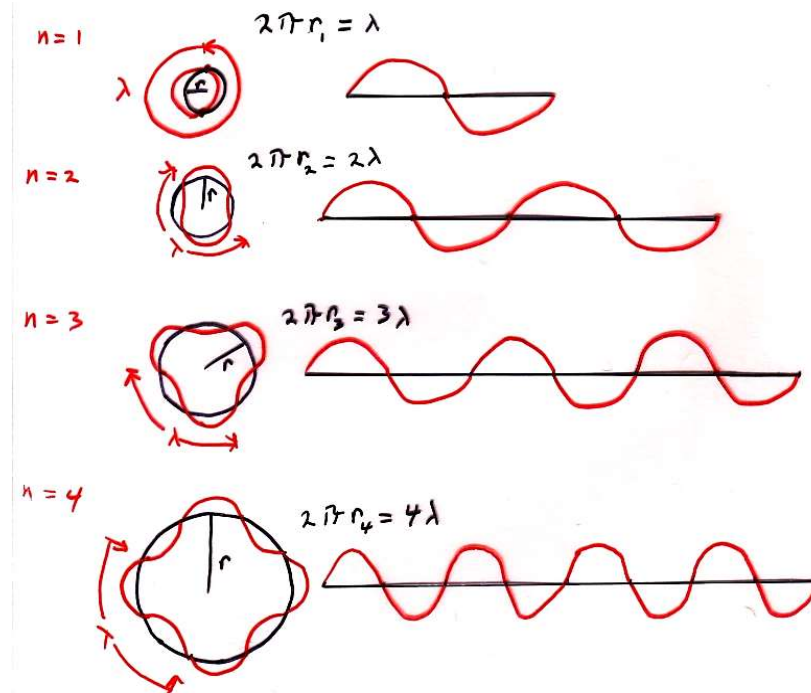
$$r = .53 \frac{n^2}{Z} (\text{\AA})$$

$$E_n = -13.6 \frac{(Z^*)^2}{n^2} (\text{eV})$$

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

Mosley's Law

$$E_f = E_{n=2} - E_{n=1} \quad *$$



Experimental backdrop to atomic quantum theory development

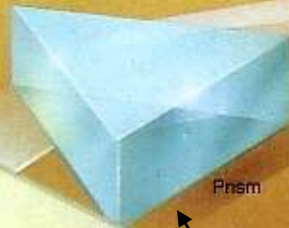
Spectroscopy (emission)

hot dense
body



Bulb

prism



Prism



Screen

Black body
spectrum

or diffraction grating



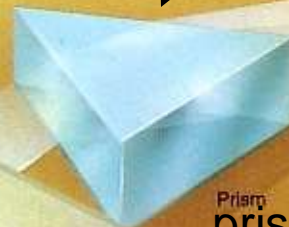
Developed in 1800's

hot (dilute)
gas



Heated hydrogen
gas

prism
prism



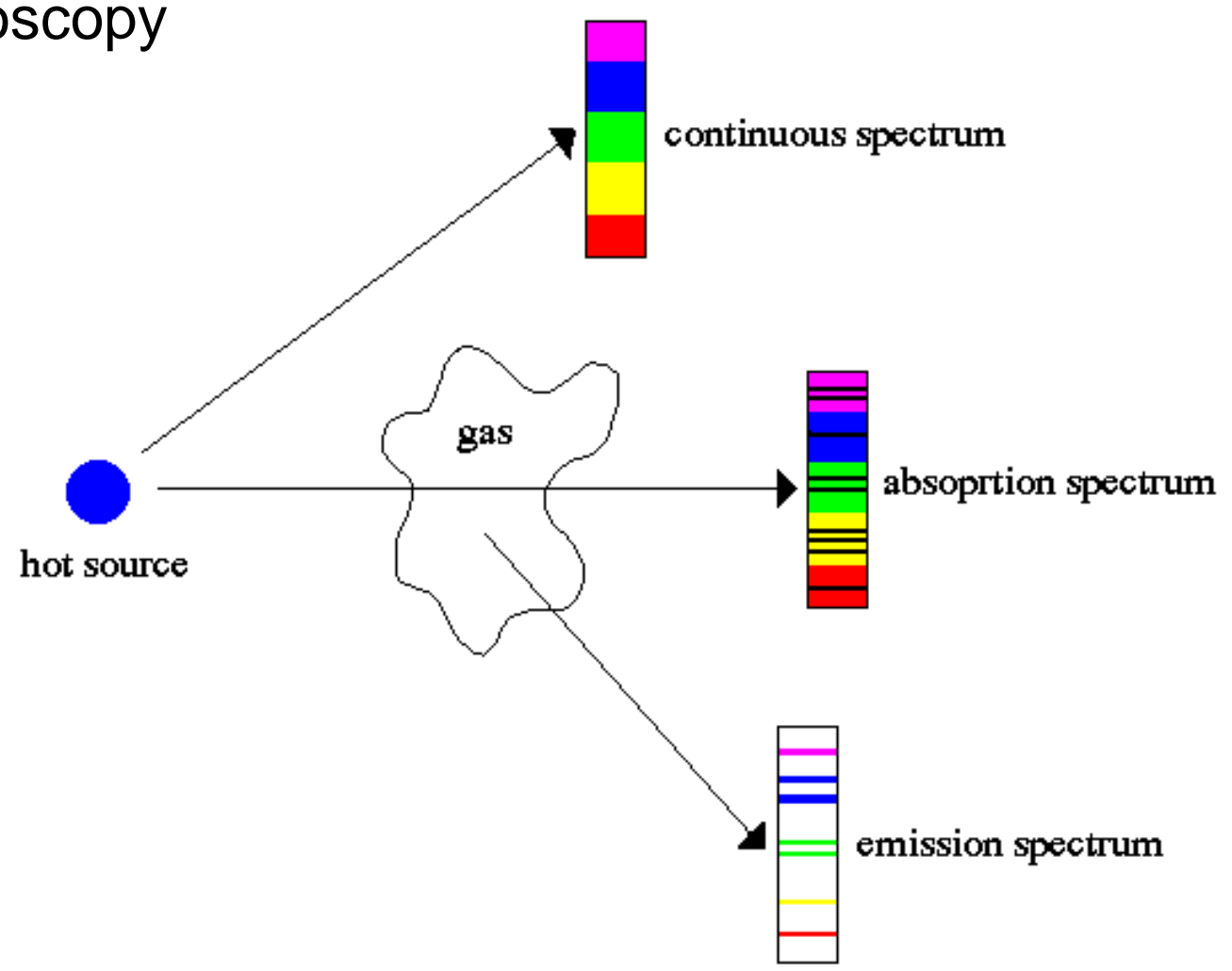
Prism



Screen

emission
or
"bright line"
spectrum

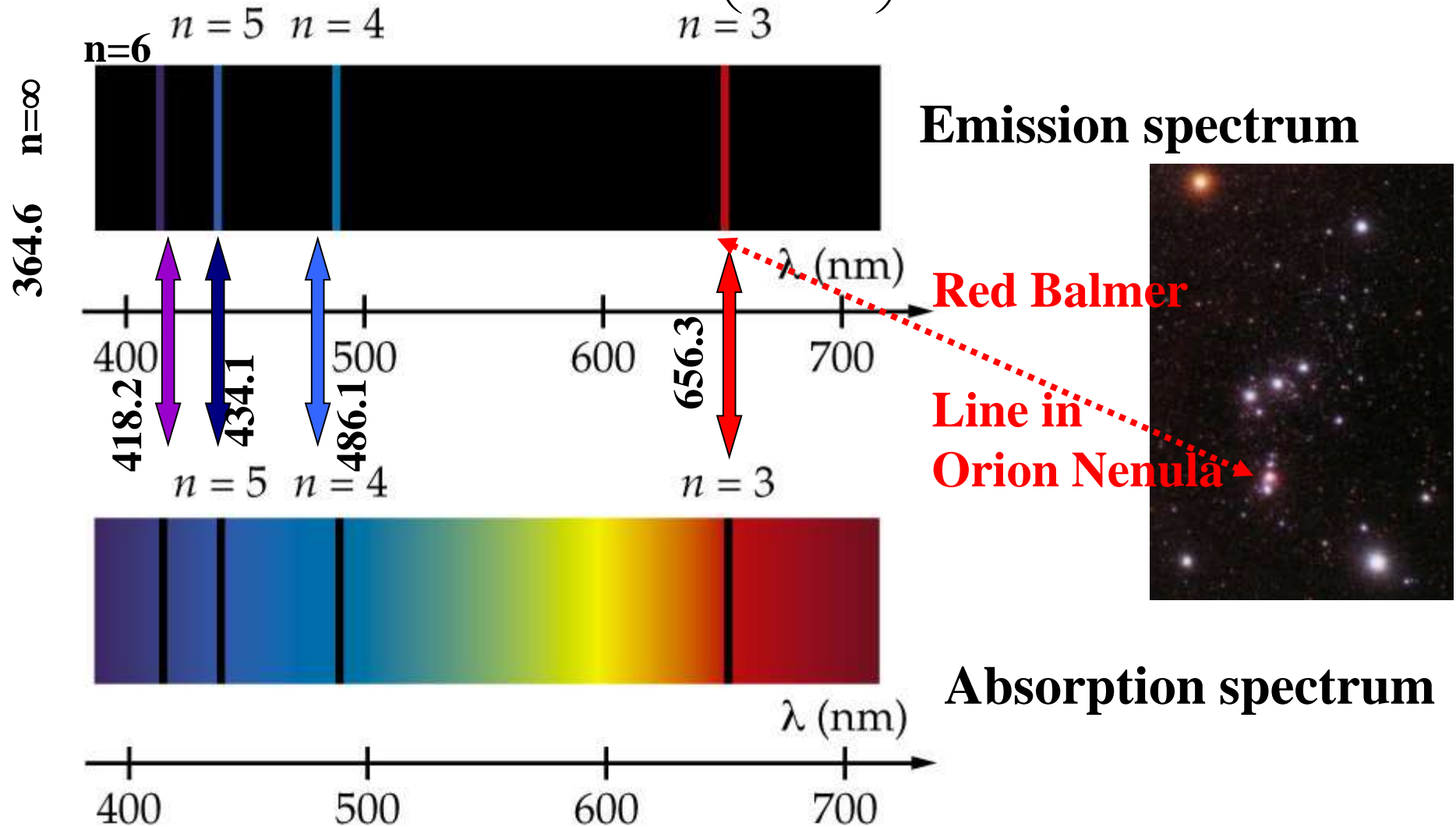
Spectroscopy



H atom absorbs and emits specific wavelengths (energies) of light

1885 Balmer: visible light

$$\lambda = (364.56) \left(\frac{n^2}{n^2 - 2^2} \right) \quad : \quad n=3,4,5,6,\dots,\infty$$



1889 Rydberg generalized to other H emission lines:

Energy (discrete set) levels of H (all atoms) are unique
⇒ photons absorbed /emitted unique finger print of atom

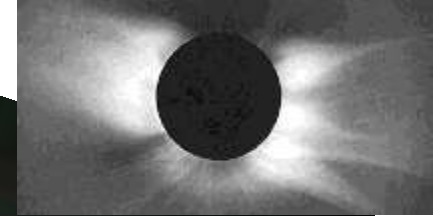
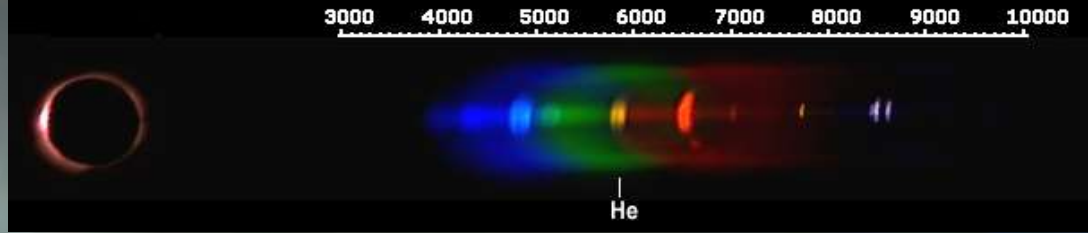
$$\frac{1}{\lambda} = \mathfrak{R}_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) : n_1 < n_2$$

specifically $n_2 = n_1+1, n_1+2, \dots$

\mathfrak{R}_H is the ***Rydberg constant***

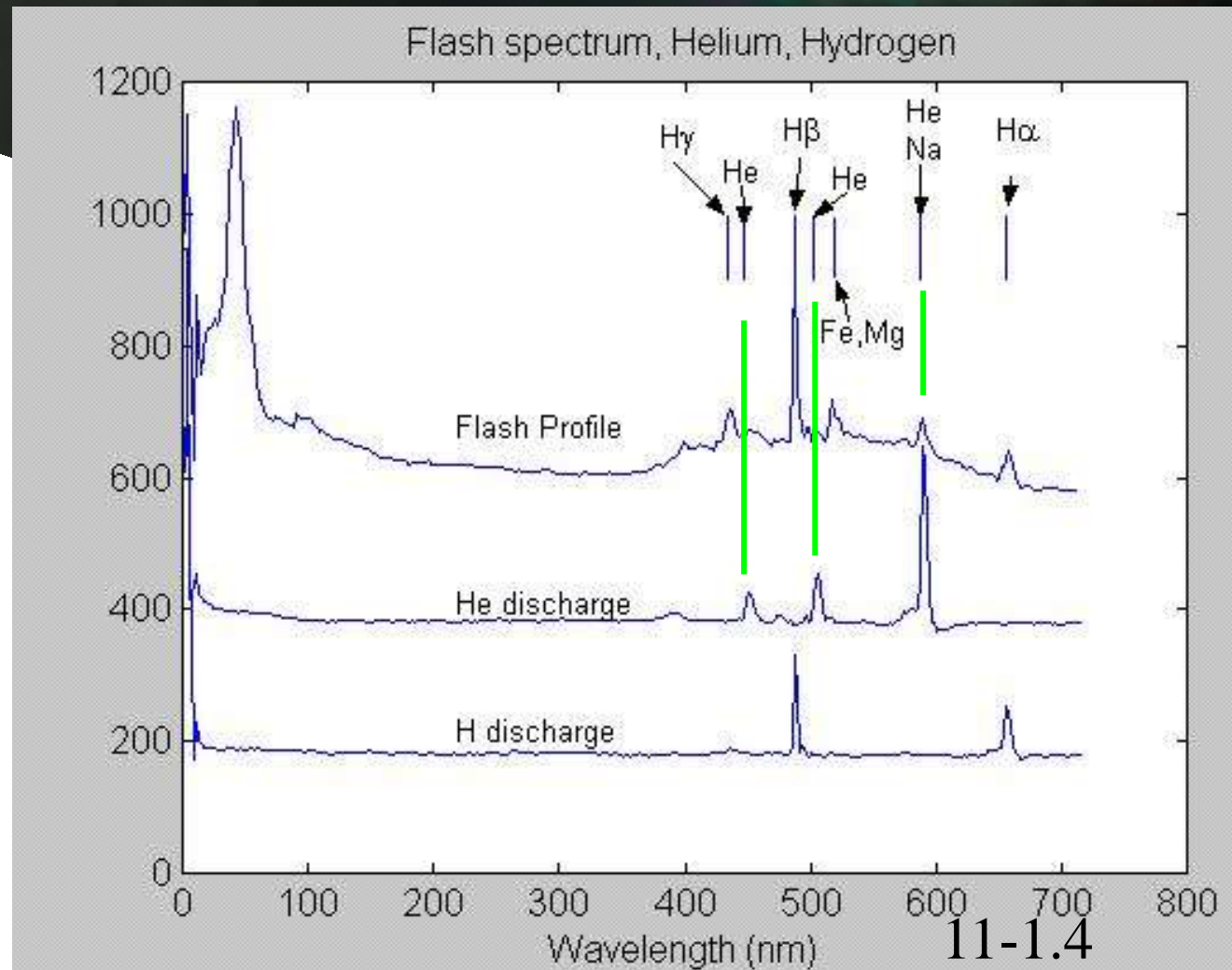
$$(\mathfrak{R}_H = 10,973,731.534 \text{ m}^{-1}).$$

Energy discrete set of H emission lines are unique (and incredibly precise) finger print of H- atom



He discovered
in solar flash
spectrum at
solar eclipse
~ 1850
long before
identified
on Earth

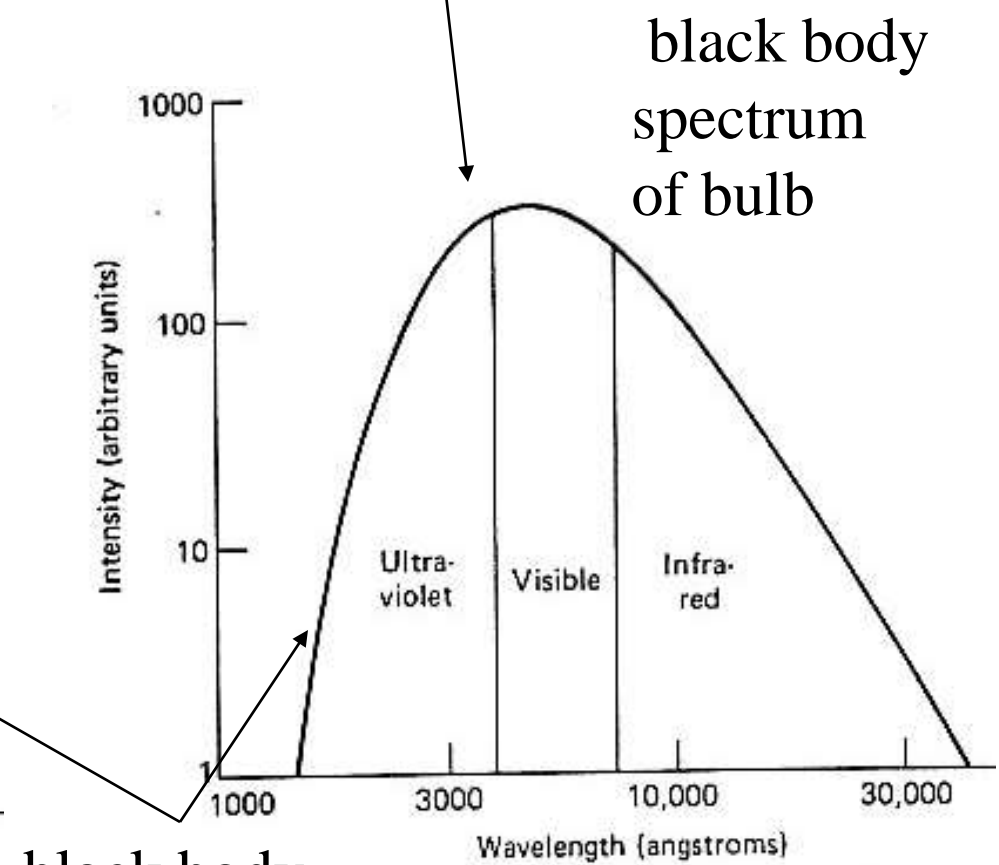
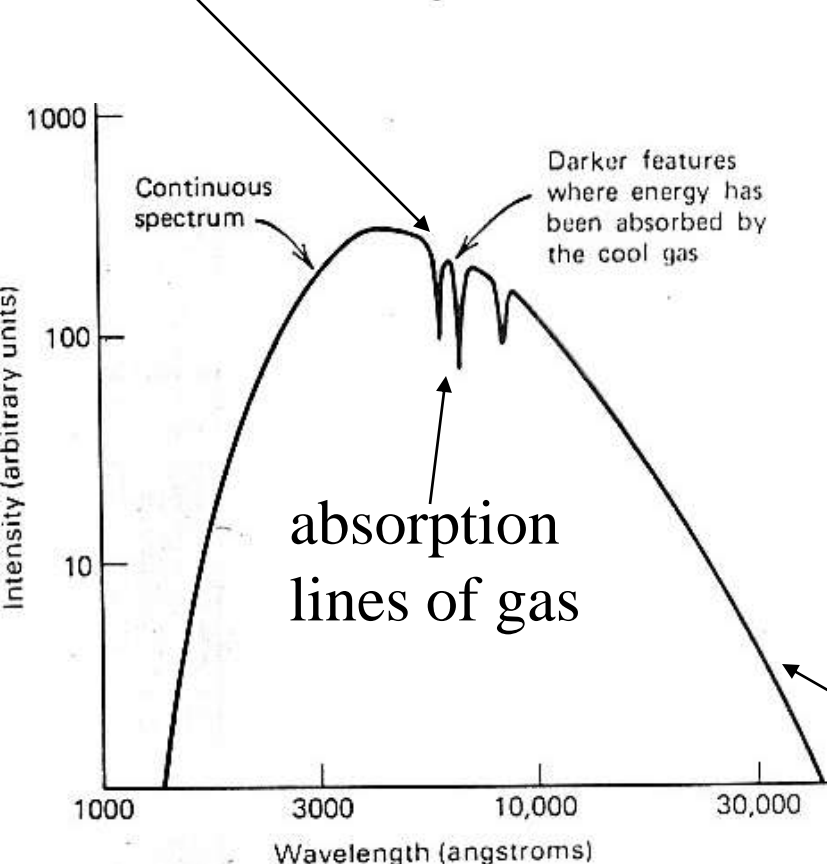
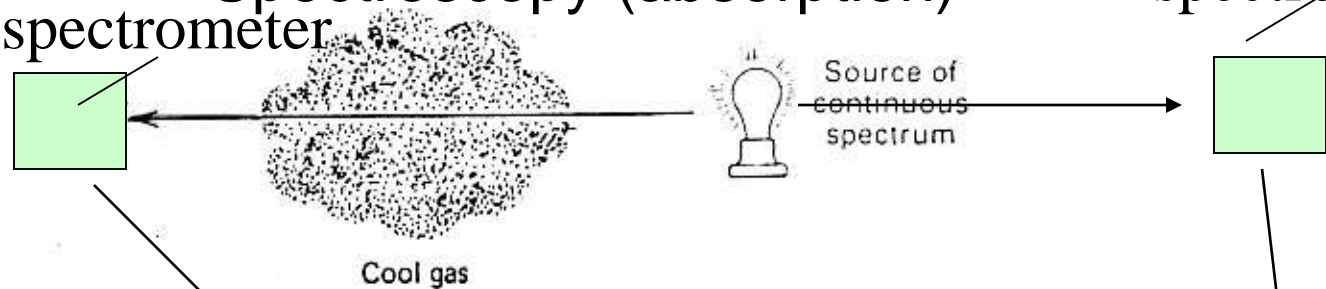
Other unique
atomic
spectra
fingerprints



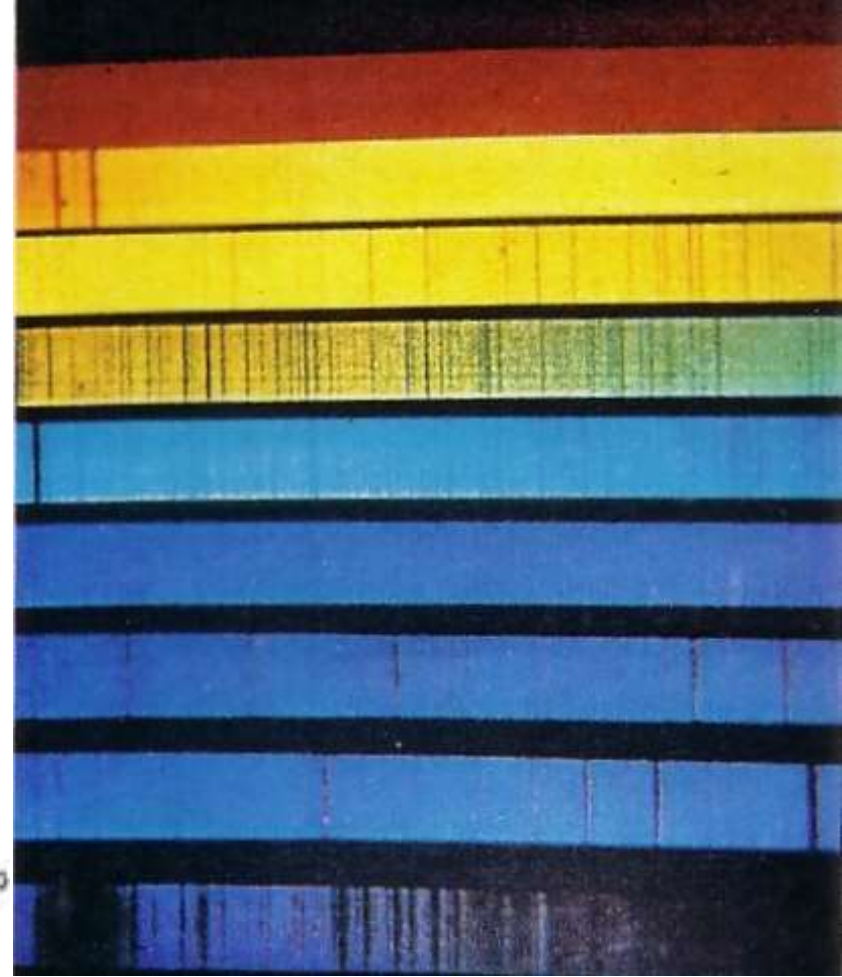
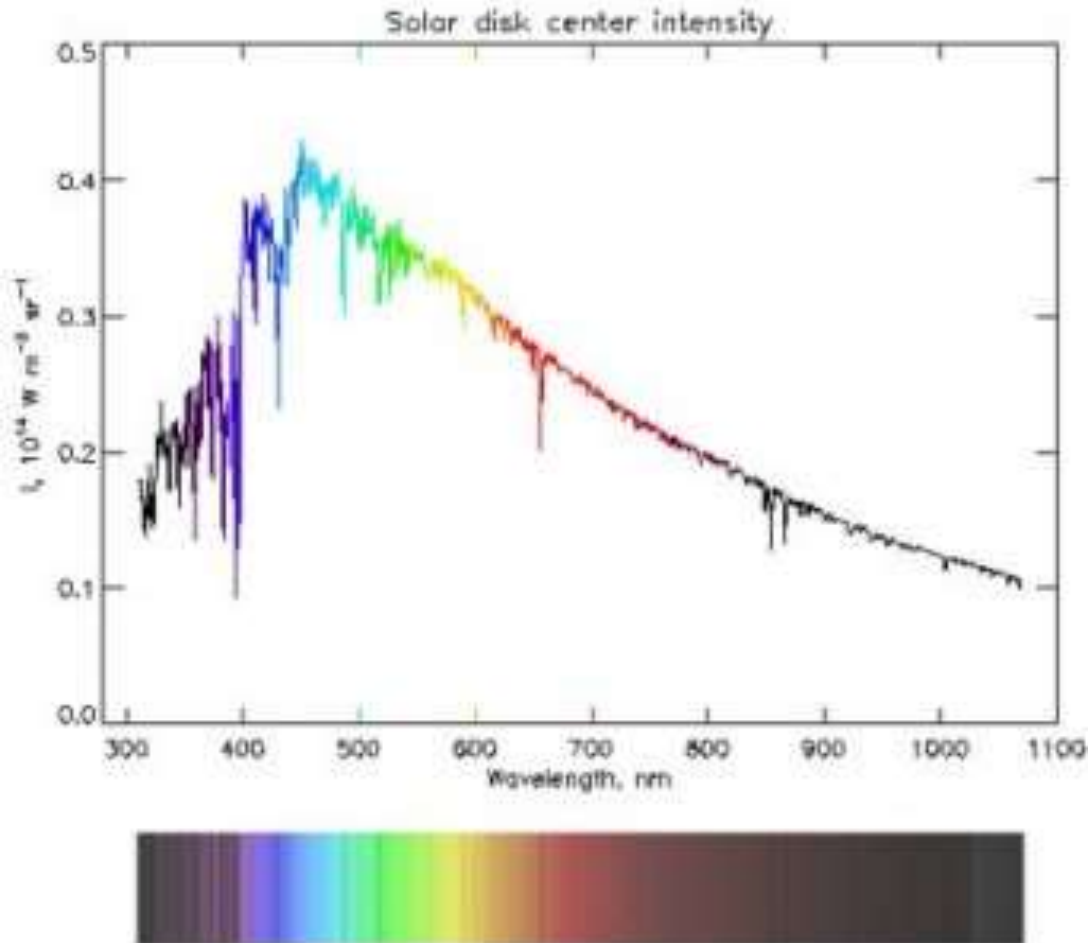
Spectroscopy (absorption)

spectrometer

spectrometer

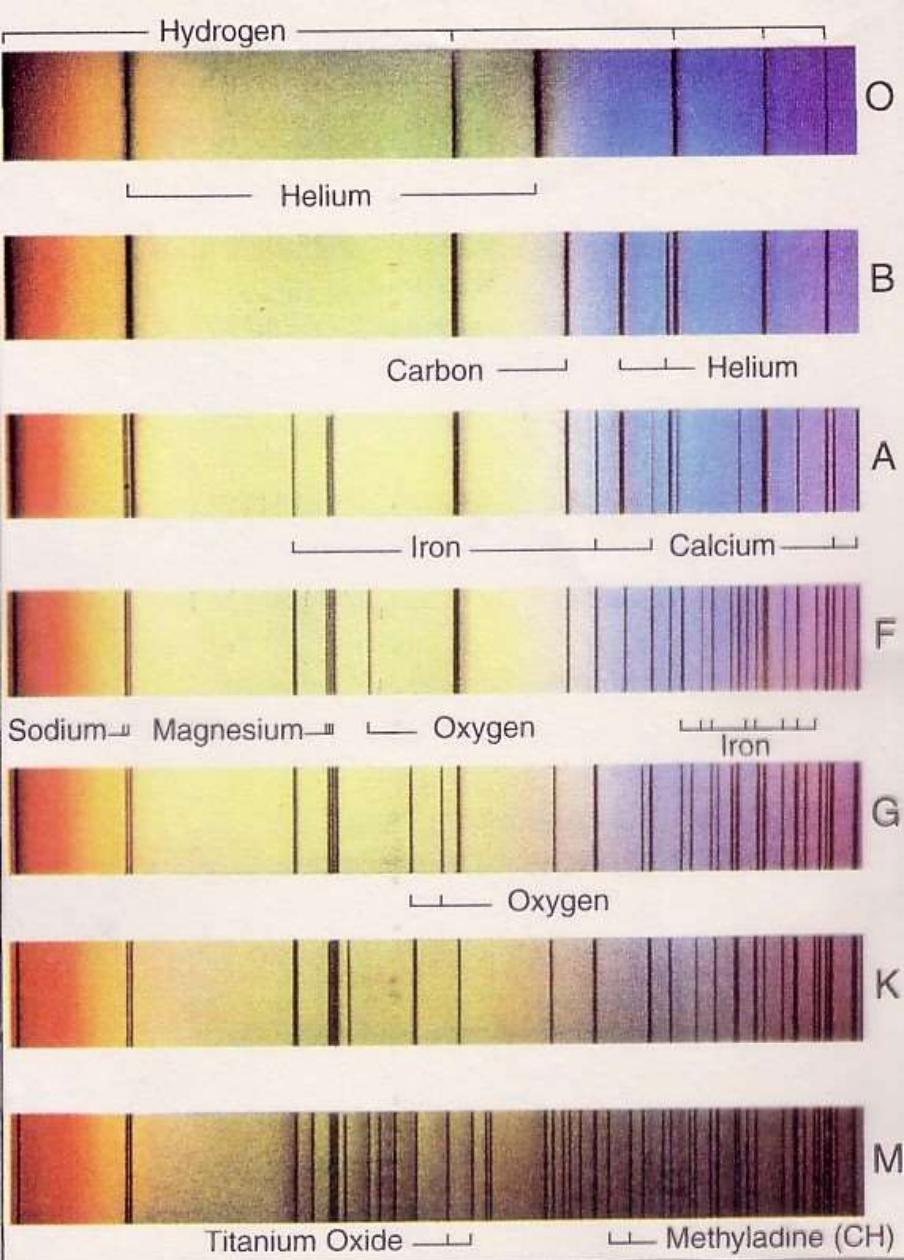


black body spectrum of bulb



absorption lines in Sun's spectrum

11-1.6



absorption lines in spectra of stars
with different surface temperatures (mass)

11-1.6a

Before 1913 – mountains of incredibly precise atomic spectral data.

Atoms interact with light in highly organized **discrete ways.**

Only some wavelengths “fit”.

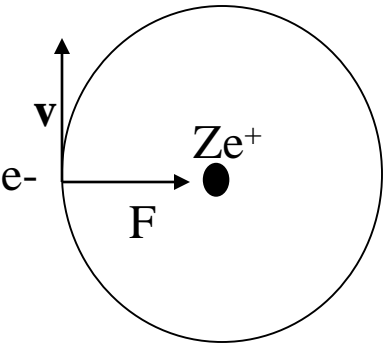
****Totally** un-understandable in classical physics of particles.**

1913 Bohr (“something stinks in Denmark”)

1913 Bohr Atom

Classical first step

Circular orbit



The diagram shows a circular orbit with a central nucleus labeled Ze^+ . A point on the orbit is labeled e^- . A horizontal arrow labeled F points from the e^- point towards the nucleus. A vertical arrow labeled v points upwards from the e^- point, indicating the direction of motion.

$$F = \frac{mv^2}{r} \quad \text{circular motion}$$
$$F = \frac{k(e)(Ze)}{r^2} \quad \text{Coulombs Law}$$

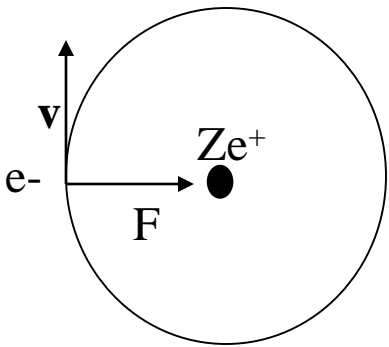
Two arrows point from the right-hand sides of the equations above to the following equation:

$$\therefore \frac{mv^2}{r} = \frac{ke^2Z}{r^2}$$

$$mv^2 = \frac{ke^2Z}{r} \quad (1)$$

1913 Bohr Atom

Circular orbit



$$mv^2 = \frac{ke^2Z}{r} \quad (1)$$

"stationary state"
can't change
continuously

**Angular Momentum conserved
in classical problem**

(Bohr had to assume this!)

Angular Momentum Quantized !!

$$(2) \quad L = mvr = n\hbar \Rightarrow v = \frac{n\hbar}{mr}$$

$$\left[\hbar = \frac{h}{2\pi} \right]$$

2 into 1 $m \left(\frac{n\hbar}{mr} \right)^2 = \frac{ke^2Z}{r} \Rightarrow \frac{n^2\hbar^2}{mr} = ke^2Z \Rightarrow r_n = n^2 \left(\frac{\hbar^2}{ke^2Zm} \right)$

Only quantized orbits allowed!!

$$r_n = n^2 \left(\frac{\hbar^2}{ke^2Zm} \right) = \frac{n}{Z} [0.53(10)^{-10} \text{ m}] = [0.53 \text{ \AA}] \frac{n^2}{Z} = r_n$$

11-1.8a

J. Hand correction

2 Bohr radius \Rightarrow 1 Å = atomic size

Bohr Atom (continued: Energy)

recall

$$mv^2 = \frac{ke^2Z}{r} \quad (1)$$

$$E = KE + PE = \frac{1}{2}mv^2 - \frac{ke^2Z}{r}$$

$$E = \frac{1}{2} \left(\frac{Ke^2Z}{r} \right) - \frac{Ke^2Z}{r} = -\frac{1}{2} \frac{Ke^2Z}{r}$$

But recall

$$r_n = n^2 \left(\frac{\hbar^2}{ke^2Zm} \right)$$

$$\therefore E = -\frac{1}{2} \frac{ke^2Z}{\frac{n^2\hbar^2}{ke^2Zm}}$$

$$E_n = -\left(\frac{k^2e^4Z^2m}{2\hbar^2} \right) \frac{1}{n^2} = -(13.6 \text{ eV}) \frac{Z^2}{n^2} \quad \text{quantized orbits} \Rightarrow \text{quantized energy !}$$

for $Z=1$ H $E_1 = -2.17(10)^{-18} \text{ J} = -13.6 \text{ eV}$

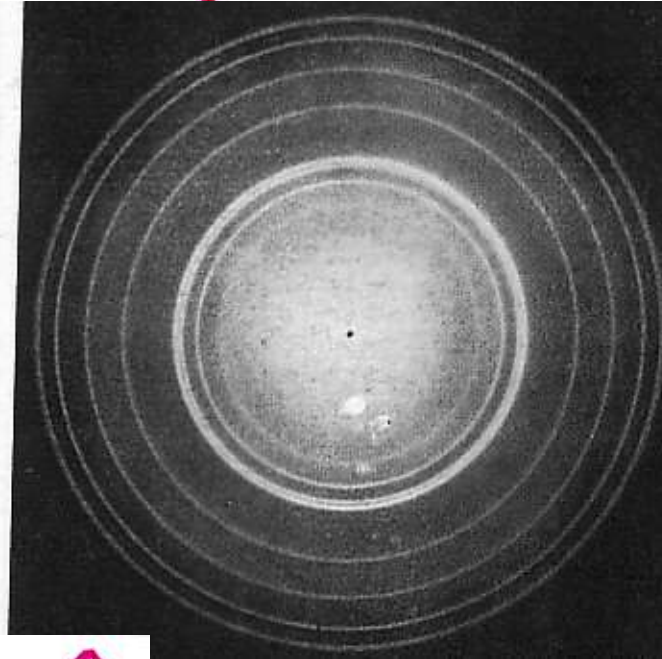
Planck's law + Einstein photons = light has some "particle like" properties
 1901 1905 PE effect

GP Thompson -1930 – electron has some wave properties

light interference
 ↓

G.P. Thomson¹⁸ electron interference
 ↓

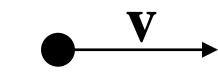
Point source
 coherent light
 0.2 mm
 aperture

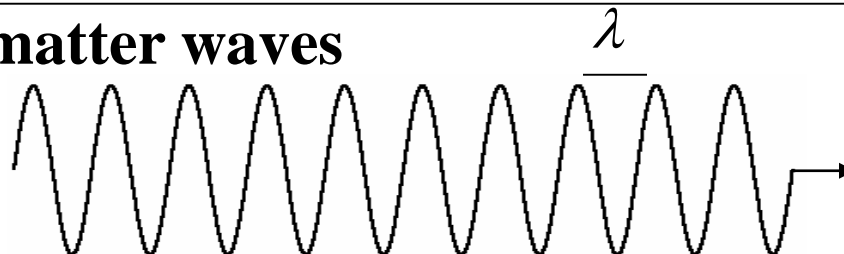


e⁻ beam
 through
 Crystal lattice
 of Be
 polycrystalline
 material

↑ individual photons and electrons have wave character ↑

De Broglie (1924) matter waves


 $m \quad p=mv$

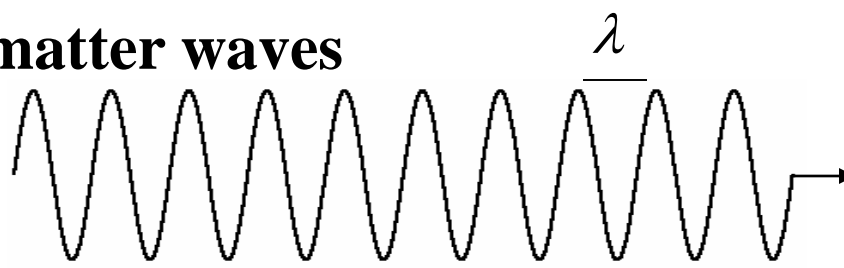


$$p = \frac{h}{\lambda}$$

11-3

De Broglie (1924) matter waves

$$\begin{array}{c} \bullet \xrightarrow{\mathbf{v}} \\ \mathbf{m} \quad \mathbf{p} = \mathbf{mv} \end{array}$$



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

Recall Bohr said for e^- in atomic orbit:

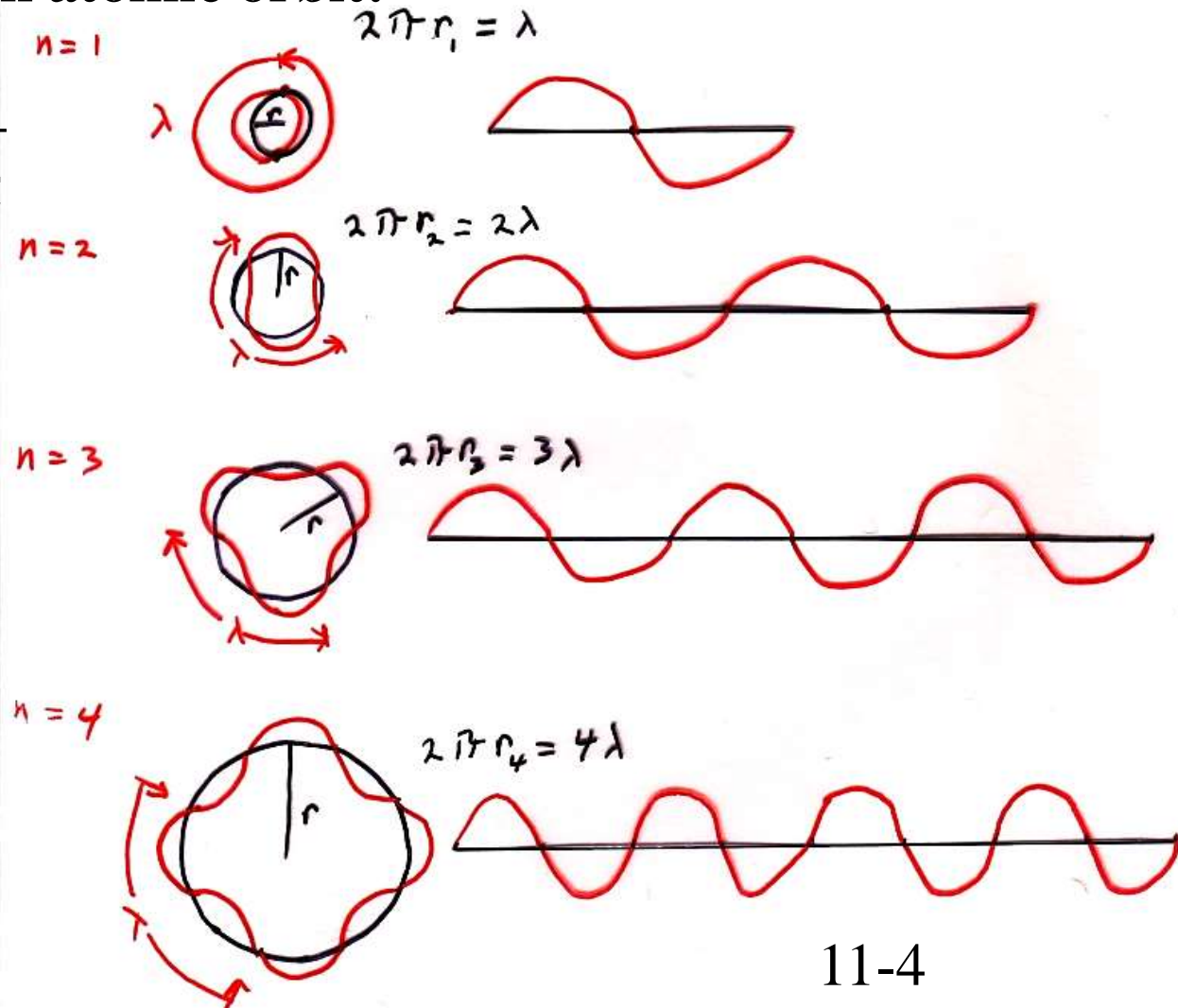
$$L = mvr = pr = n \frac{h}{2\pi}$$

$$\therefore \text{ if } p = \frac{h}{\lambda}$$

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

$$2\pi r = n\lambda$$

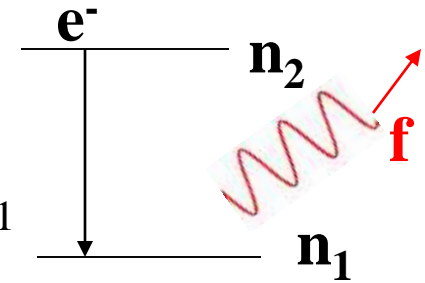
Like standing waves
on a circular orbit.



Bohr Theory – atomic emission spectra

$$E_n = -13.6 \frac{Z^2}{n^2} \quad \begin{array}{l} Z=\text{atomic \#} \\ Z=1 \text{ hydrogen} \end{array}$$

$$hf = E_{n_2} - E_{n_1}$$



Electron drops down \Rightarrow photon emitted

$$\begin{aligned} \left\{ \frac{13.6 \text{ eV}}{hc} \right\} &= \frac{13.6 \cdot 1.6(10)^{-19} \text{ C} \frac{\text{J}}{\text{C}}}{6.626(10)^{-34} \text{ Js} \cdot 3(10)^8 \frac{\text{m}}{\text{s}}} \\ &= \frac{(13.6)(1.6)}{(6.626)(3)} 10^{19-8+34} \text{ m}^{-1} \\ &= 10.973(10)^6 \text{ m}^{-1} = R \\ \frac{1}{\lambda} &= \{R\} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \end{aligned}$$

$$E_{n_2} - E_{n_1} = (13.6) \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = fh$$

$$c = \lambda f \quad \therefore f h = h \frac{c}{\lambda}$$

$$h \frac{c}{\lambda} = (13.6) \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{\lambda} = \left\{ \frac{(13.6)}{hc} \right\} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Rydberg formula from Bohr!!!

$$(\mathcal{R}_H = 10,973,731.534 \text{ m}^{-1}).$$

11-5

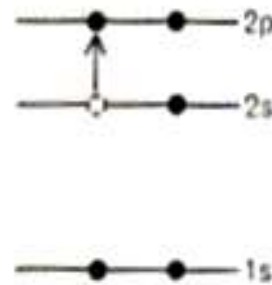
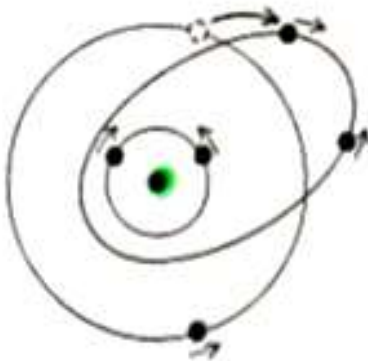
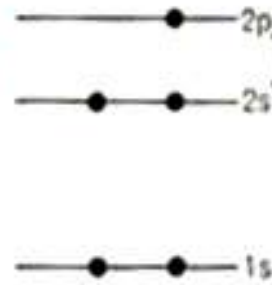
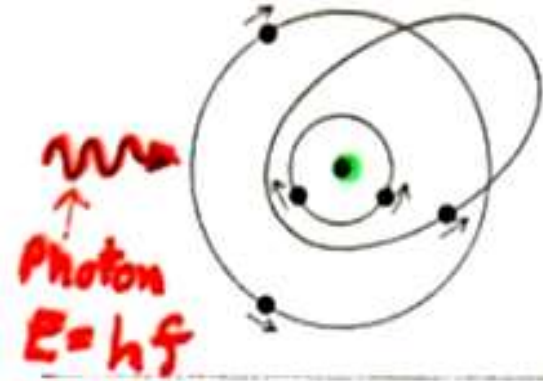
Precision of R unparalleled in history of physics !!!

Picture

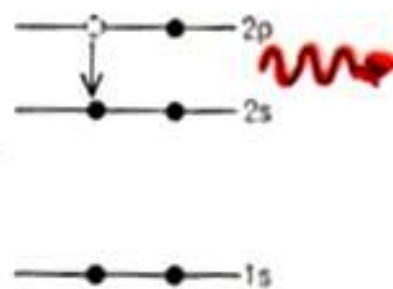
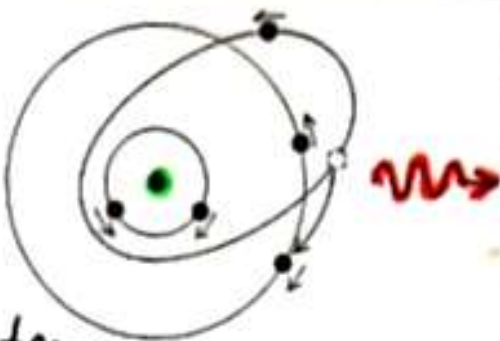
Energy levels

$$hf = \Delta E$$

$E = hf$ of photon
used to kick
electron up
energy ladder
Absorption of photon



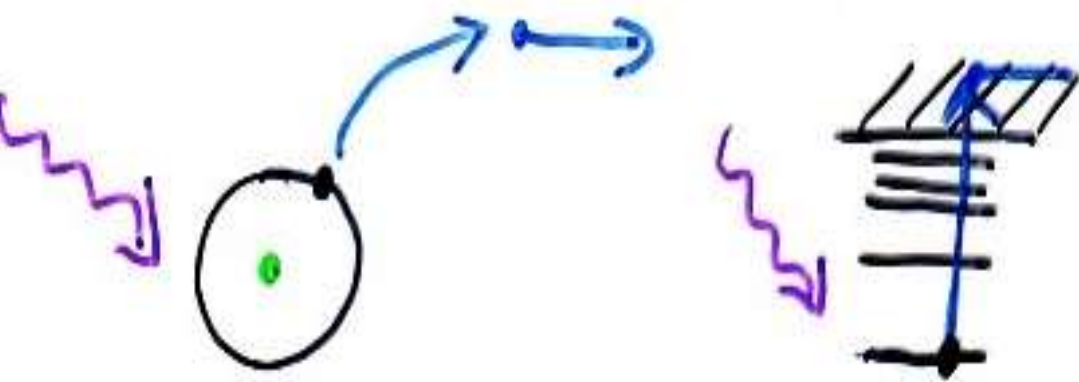
emission of photon
electron drops down
energy ladder
and photon
with $E = hf$
emitted



• = electrons
● = nucleus

$$hf = \Delta E$$

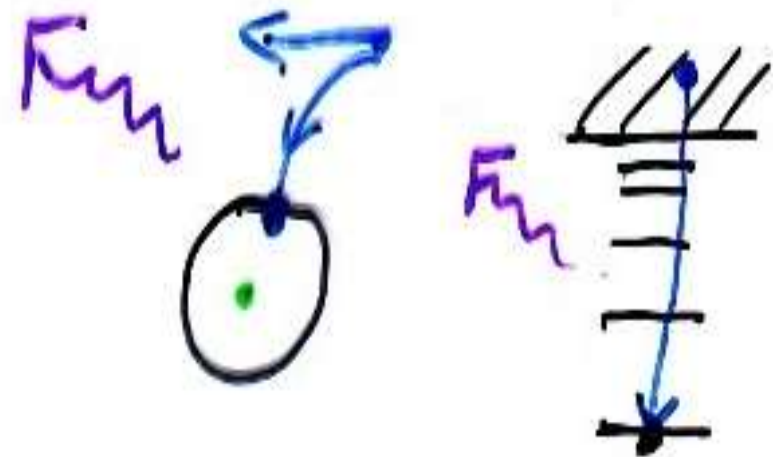
Ionization



electron kicked out
of atom

[any energy above
ionization energy possible]

Recombination



electron drops in

Energy (discrete set) levels of H (all atoms) are unique
 \Rightarrow photons absorbed /emitted unique finger print of atom

11-8

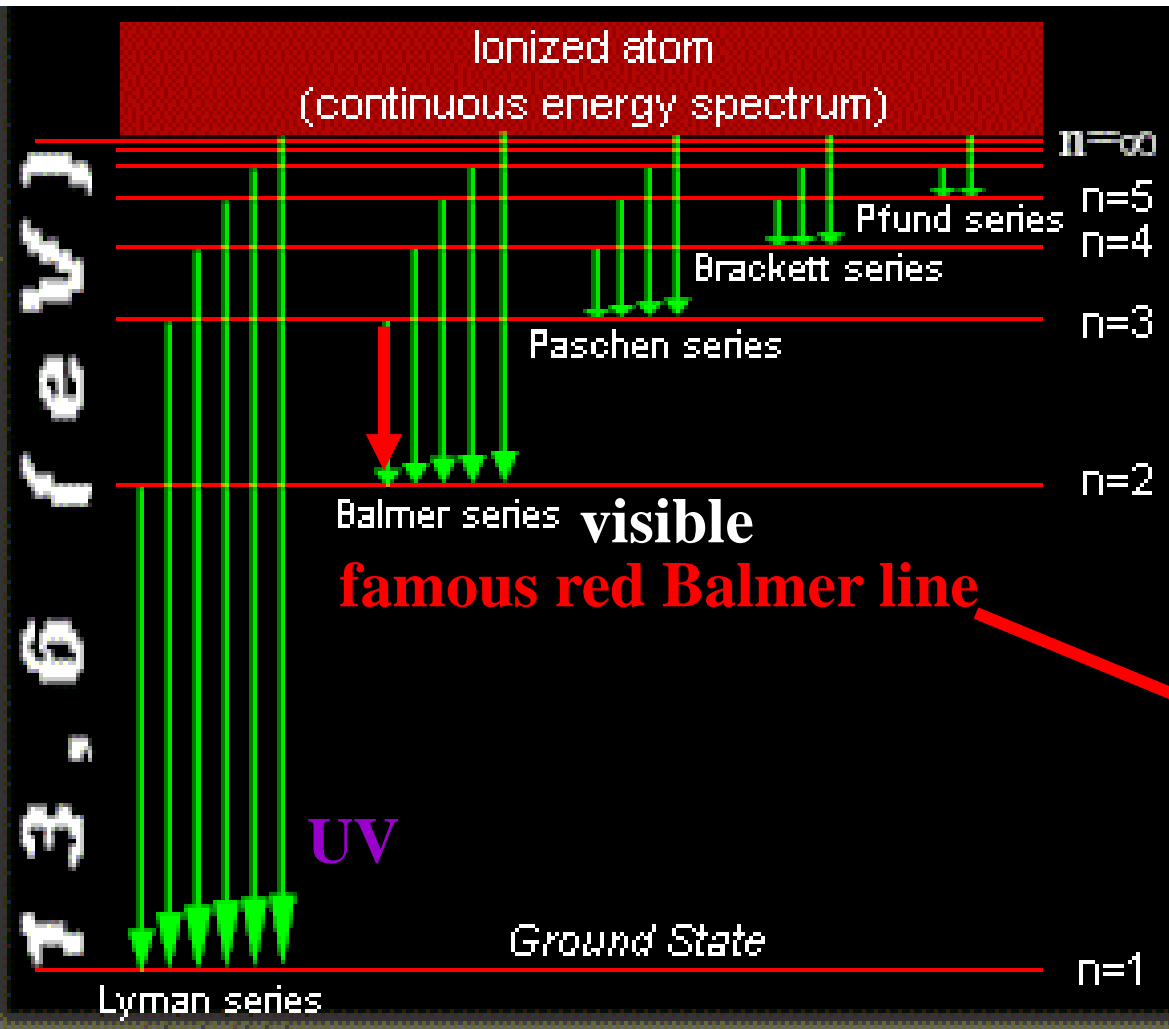
1889 Rydberg generalized to other H emission lines:

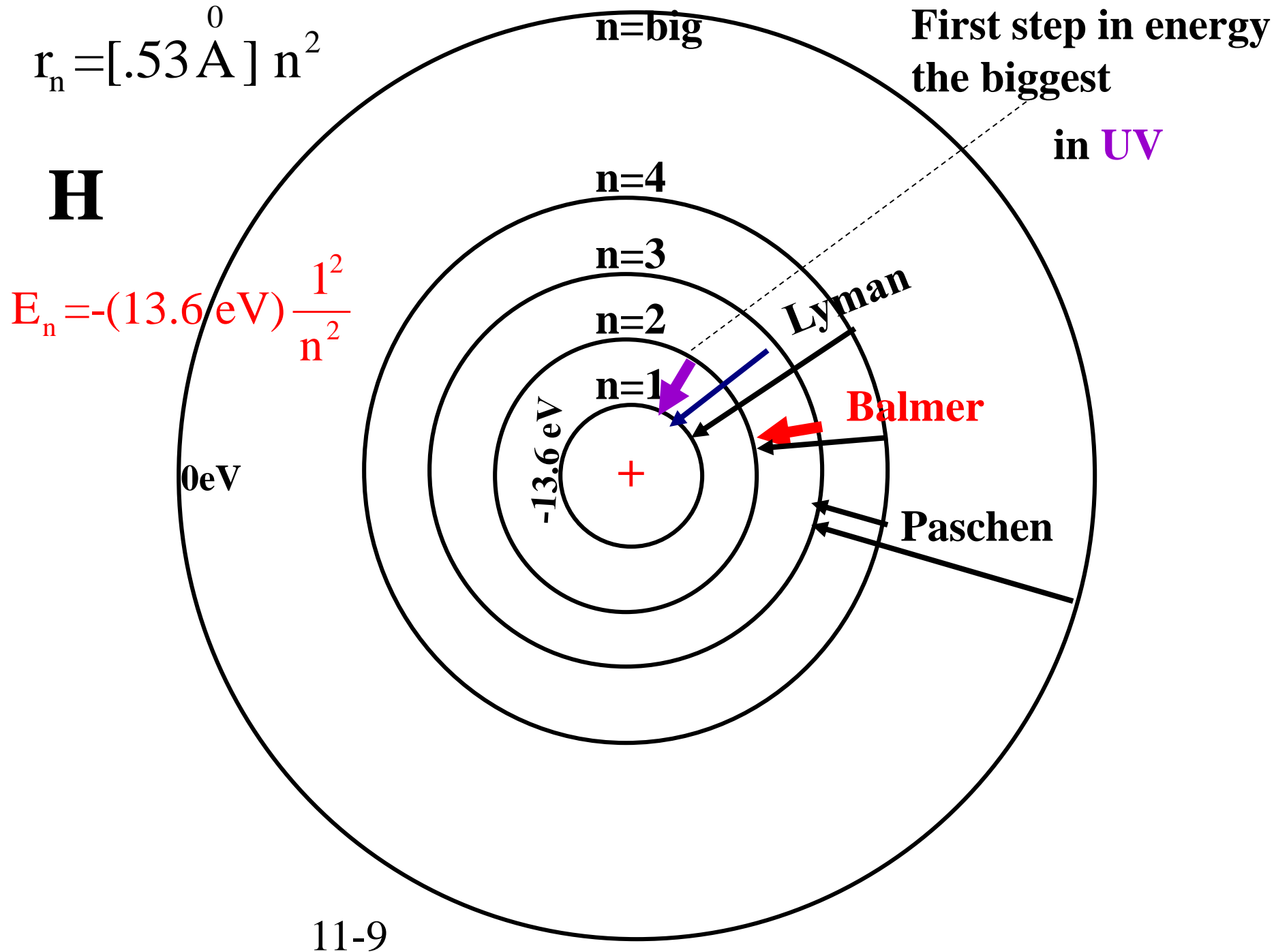
$$\frac{1}{\lambda} = \mathfrak{R}_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) : n_1 < n_2$$

specifically $n_2 = n_1+1, n_1+2, \dots$

\mathfrak{R}_H is the *Rydberg constant*

($\mathfrak{R}_H = 10,973,731.534 \text{ m}^{-1}$).





X-Rays and X-Ray Emission

Roentgen 1895 X-rays (X-Strahlung)

Max von Laue diffraction 1912-1913 (diffraction from planes of atoms in crystal)

**Barkla 1911 x-ray emission – “hardness” = penetrating power hard & soft x-rays
different targets – differing x-ray hardness emitted
(gave us K, L, M, N x-ray emission lines)**

**Bragg 1912/13 x-ray diffraction $n\lambda=2d\sin(\theta)$
[can use θ to measure interatomic distances d in solids !!!!!]**

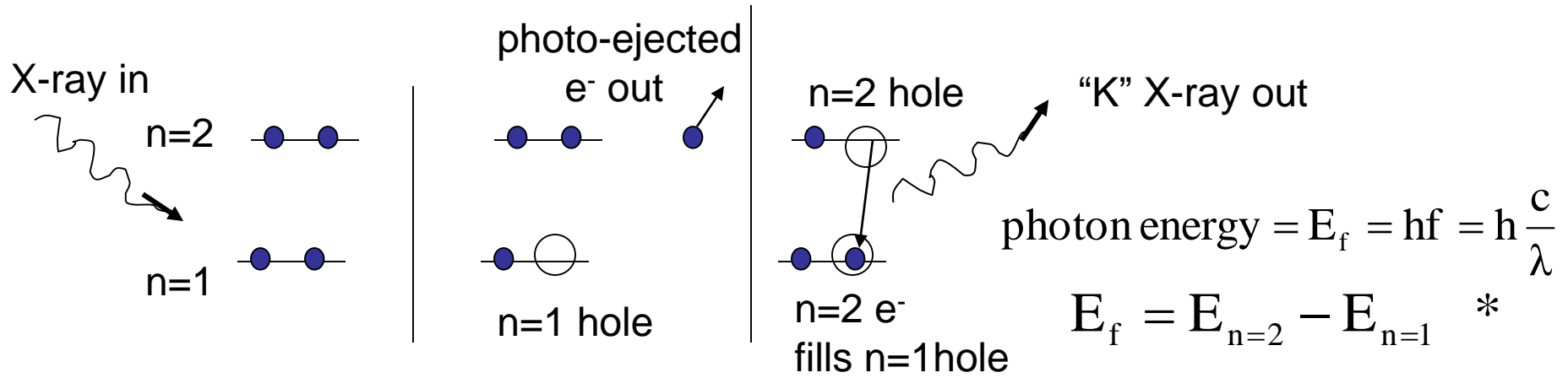
**Mosely (demonstrator in Rutherford’s lab at Manchester)
- Bohr visits Rutherford – Mosely told of new Atomic theory**

**1913- Mosely used Bragg reflection to determine λ of x-ray emission of various
elements $n\lambda=2d\sin(\theta)$ --- know d of crystal – measure θ to determine λ**

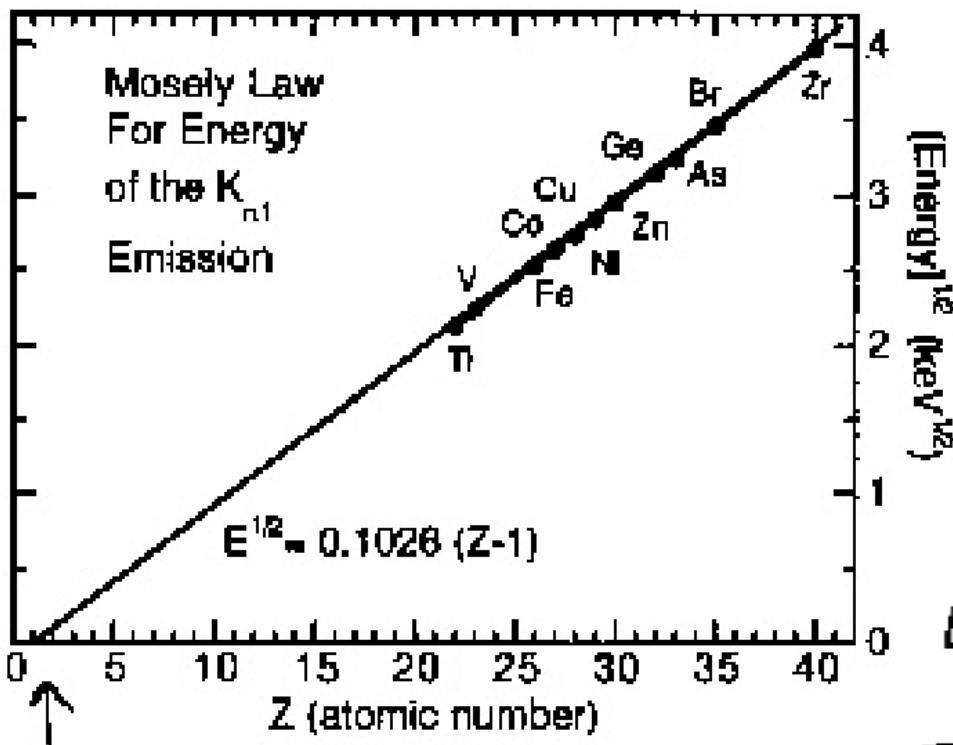
**1913- Mosely’s Law $1/\lambda = K [Z-\sigma]^2$ $\sigma_K=1$ $\sigma_L=1$
 Z =atomic number !!!!!**

“Mosely and the Numbering of the Elements”- by Jaffe – Doubleday NY 1971

**1915 - Mosely- killed in WWI – Dardanelles Campaign- (against Turkey)
{Winston Churchill’s idea (1’st Lord of the Admiralty)
– blood bath and WC didn’t come back till WWII}**



Z^* = effective charge including screening = Atomic No. - 1



$$E_f = \frac{-13.6 Z^{*2}}{2^2} - \frac{-13.6 Z^{*2}}{1^2} \quad \{\text{eV}\}$$

$$E_f = 10.2 Z^{*2} \quad \{\text{eV}\} \quad Z^* = (Z-1)$$

$$E_f (\text{K-edge}) = 10.2 (Z-1)^2 \quad \{\text{eV}\}.$$

Z = Atomic No.

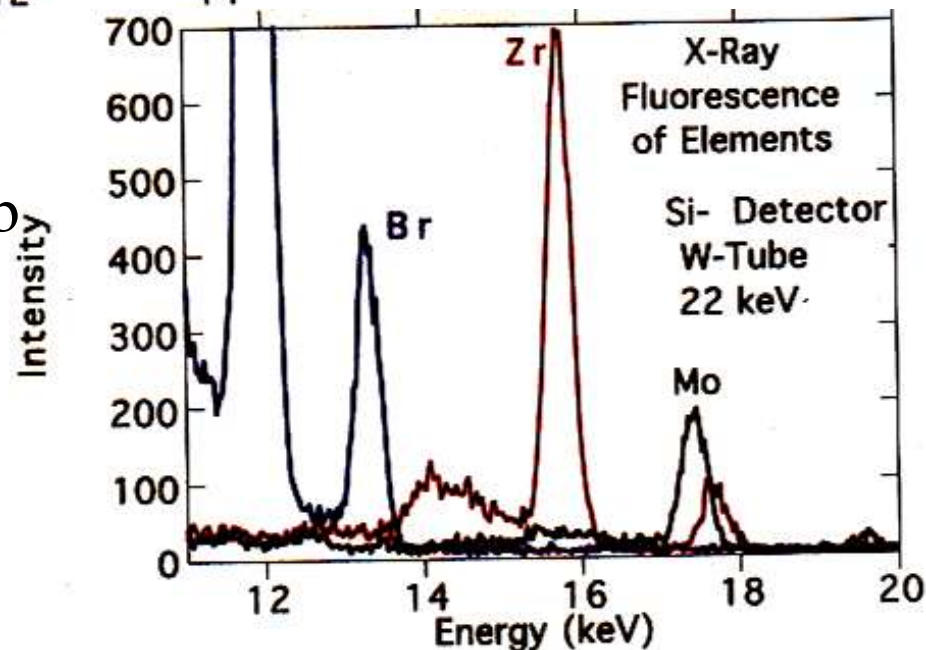
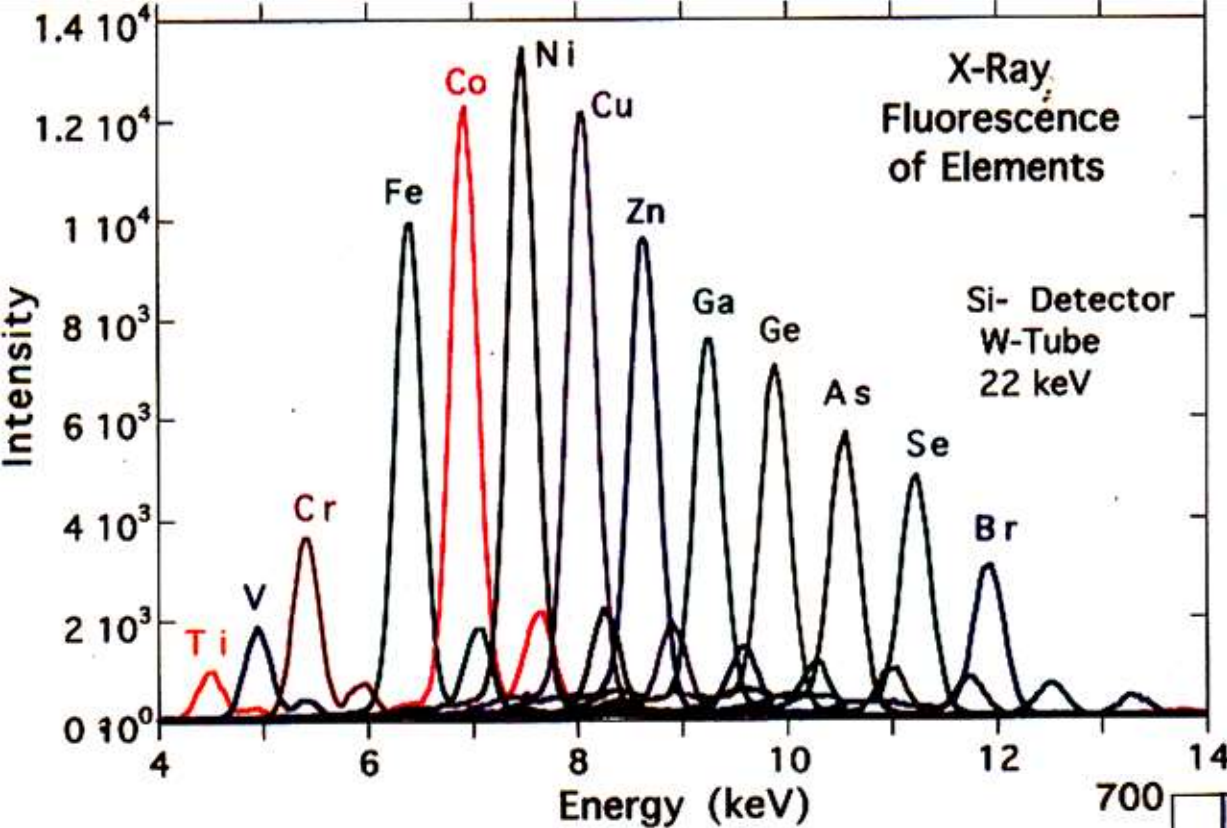
$$E_f (\text{K-edge}) = 0.102 (Z-1)^2 \quad \{\text{keV}\}$$

$$E = 0.102 (Z-1)^2 \text{ keV}$$

verified!

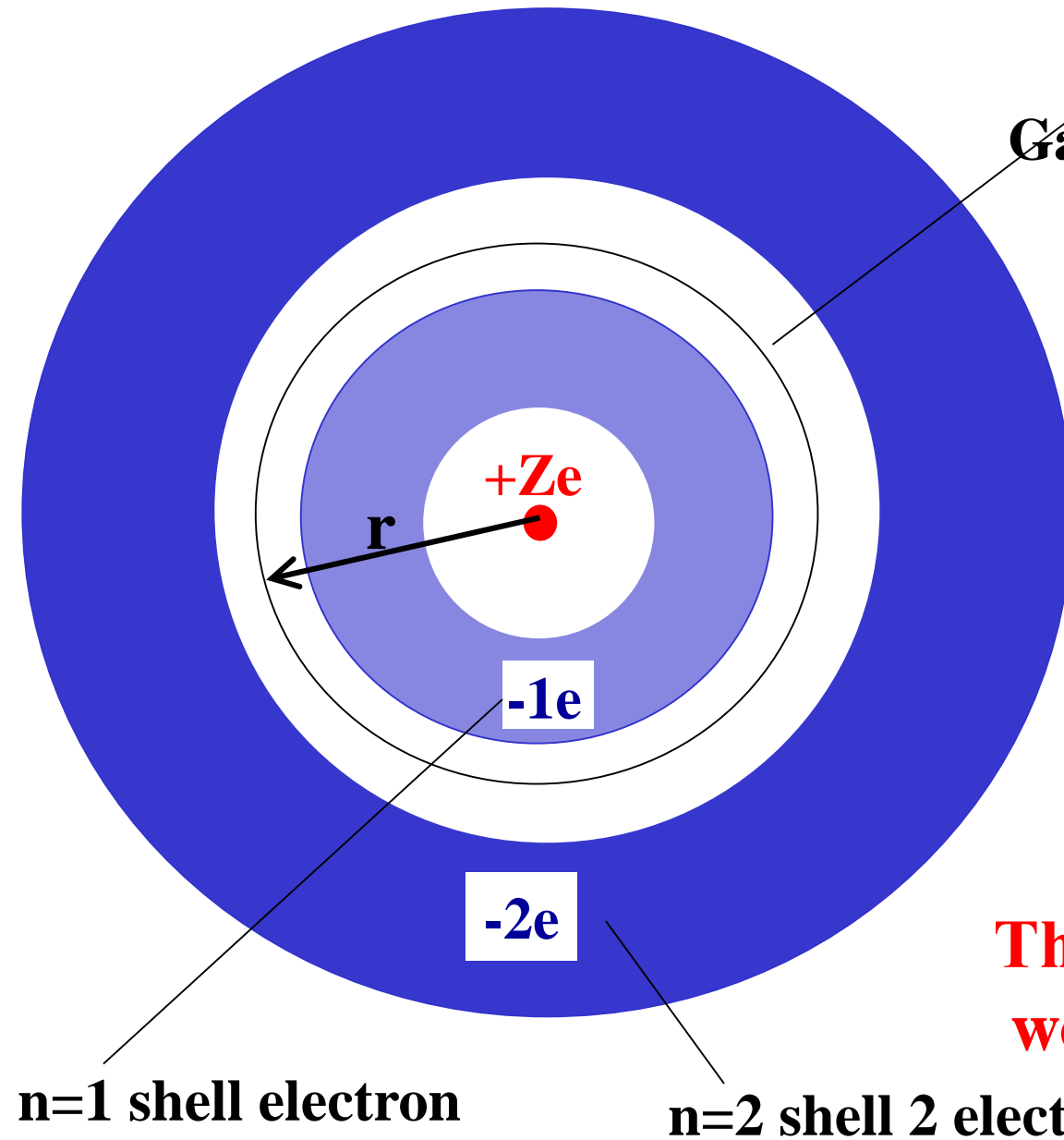
$Z=1$ intercept!

Fig 3b mosmosely copy 2



Actual data from previous page
taken in Rutgers senior undergrad lab

~ charge distribution in atom interior



$$\sum_{\text{surf}} \mathbf{E}_{\perp} \Delta A = \frac{Q_{\text{inside}}}{\epsilon_0}$$

Gaussian surf.

$$Q_{\text{inside}} = +Ze - 1e$$

$$Q_{\text{inside}} = (Z - 1)e$$

$$\mathbf{E} 4\pi r^2 = \frac{(Z - 1)e}{\epsilon_0}$$

$$\mathbf{E} = \frac{(Z - 1)e}{4\pi\epsilon_0 r^2}$$

This is why Mosley's Law worked with (Z-1) !!