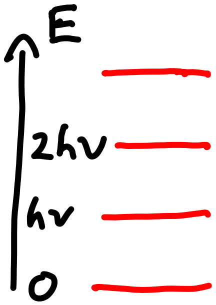
Lecture 6: 01/30/09

- The quantized Atom
  - Evidence for quantized Energy Levels
  - Bohr Atom

Niels Bohr (1885 – 1962): Nobel Prize 1922

$I_{1,4}$ Blackbody Radiation

Recap:



energy level

Planck: Energy in each mode is quantized: $E_n = nh\nu$

quantum number

$\Rightarrow \langle E_{per\ mode} \rangle \longrightarrow 0$ for $h\nu \gg kT$

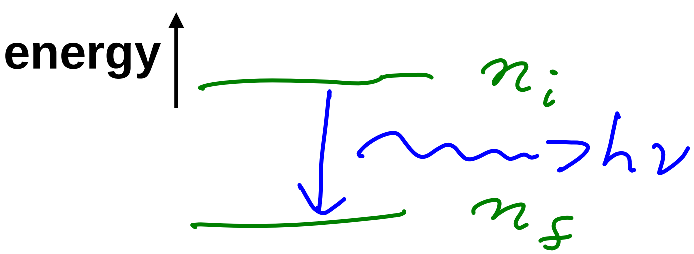
$$\Rightarrow \rho_T(\nu)\,d\nu = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT}-1}\,d\nu$$

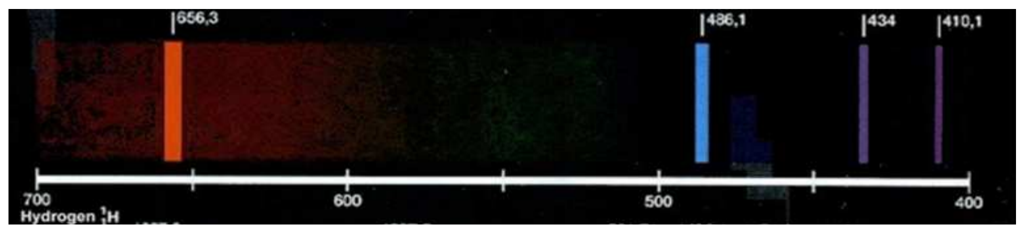
I_2 The Quantized Atom

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

(a) Spectral Lines

Example: Hydrogen





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

Example: Hydrogen

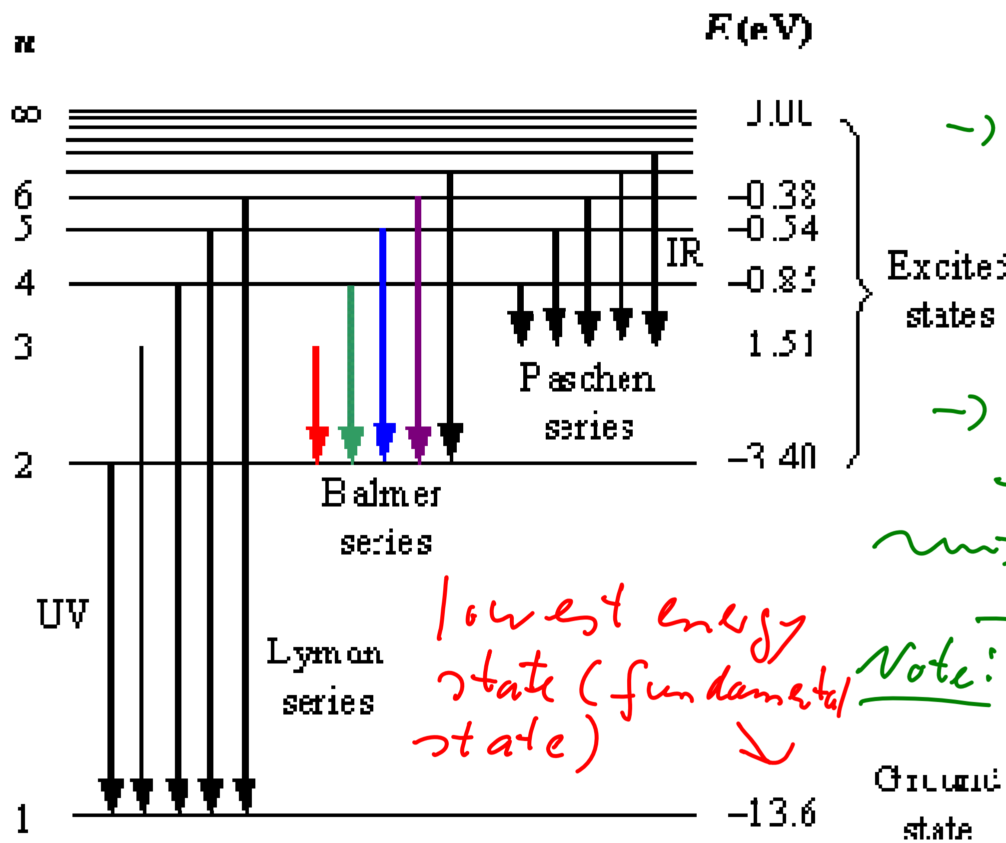
Empirical result: $$E_{photon} = E_i - E_f = hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$\Rightarrow$ Quantized energy levels: $E_n = -hcR_H \frac{1}{n^2}$

quantum number $n = 1, 2, 3, \ldots$

$\Rightarrow$ Energy level diagram:

H



lowest energy state (fundamental state)

$\rightarrow$ Photon emission:

$n_i \rightarrow n_f$: $h\nu = E_{n_i} - E_{n_f}$

$\rightarrow$ Photon absorption:

$n_i \rightarrow n_f$: $h\nu = E_{n_f} - E_{n_i}$

Note: if $h\nu \neq E_n - E_n$ nothing will happen!

In a transition from which excited state will hydrogen atoms emit at the longest wavelength in the Balmer series ($n_f = 2$)?

A. $n_i = 2$

B. $n_i = 3$

C. $n_i = 4$

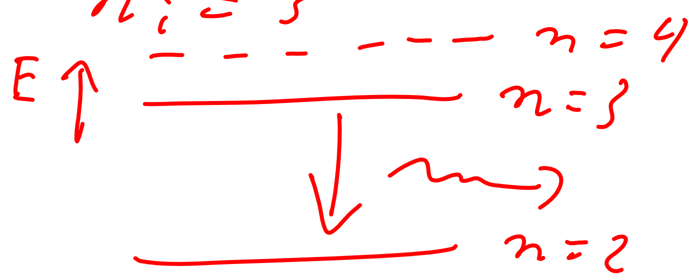
D. $n_i = \infty$

E. Something else

longest λ ⇒ smallest photon energy

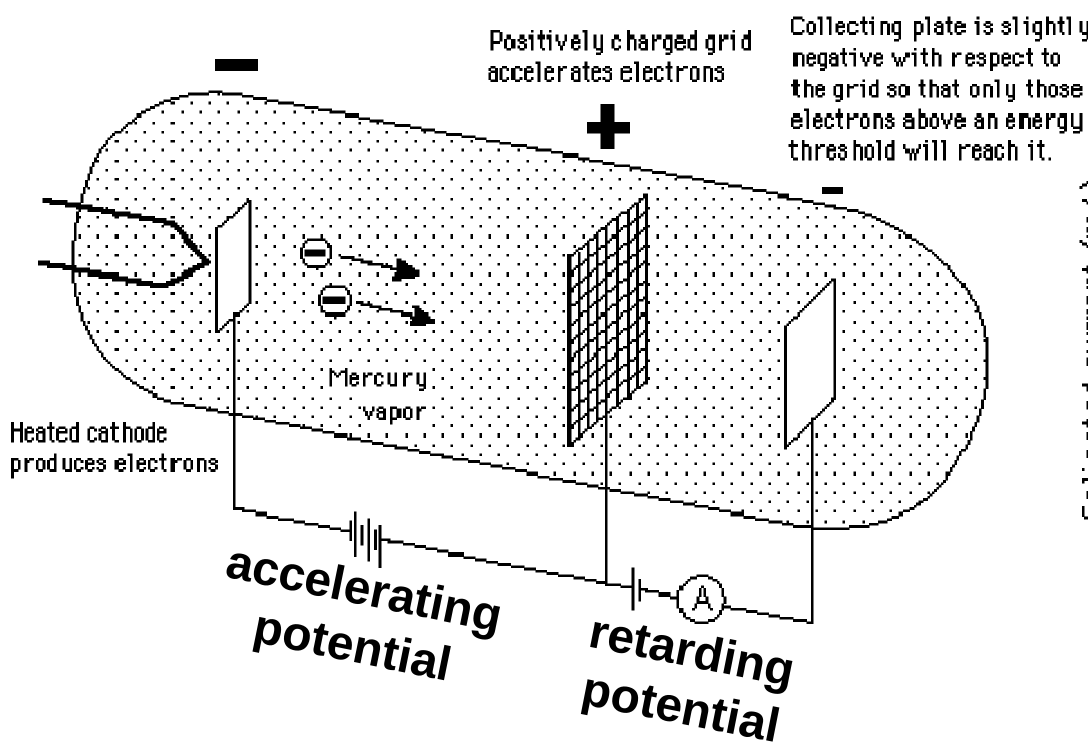
$E_{ph} = h\nu = h\frac{c}{\lambda}$

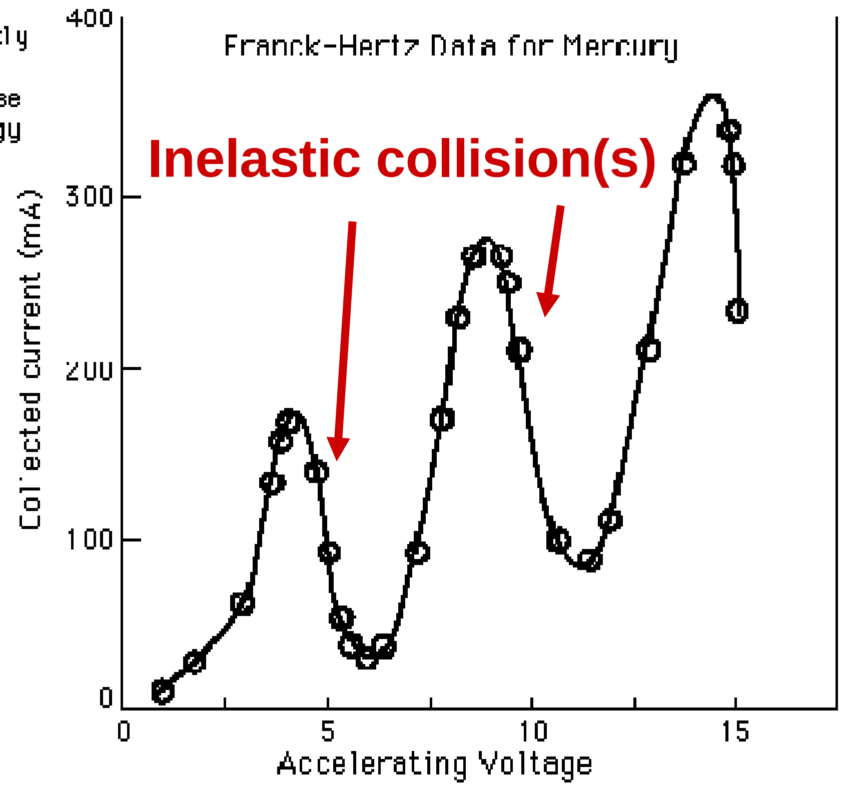
$n_i = 3$



More Evidence for Quantized Energy Levels in Atoms

(b) Franck-Hertz Experiment (1914):





Emission spectrum shows strong ultraviolet line of wavelength 2537 Å

$\Rightarrow E_{photon} = 4.9$ eV.

$e^- \rightarrow$

KE > 4.9 eV

gr. state + 4.9 eV

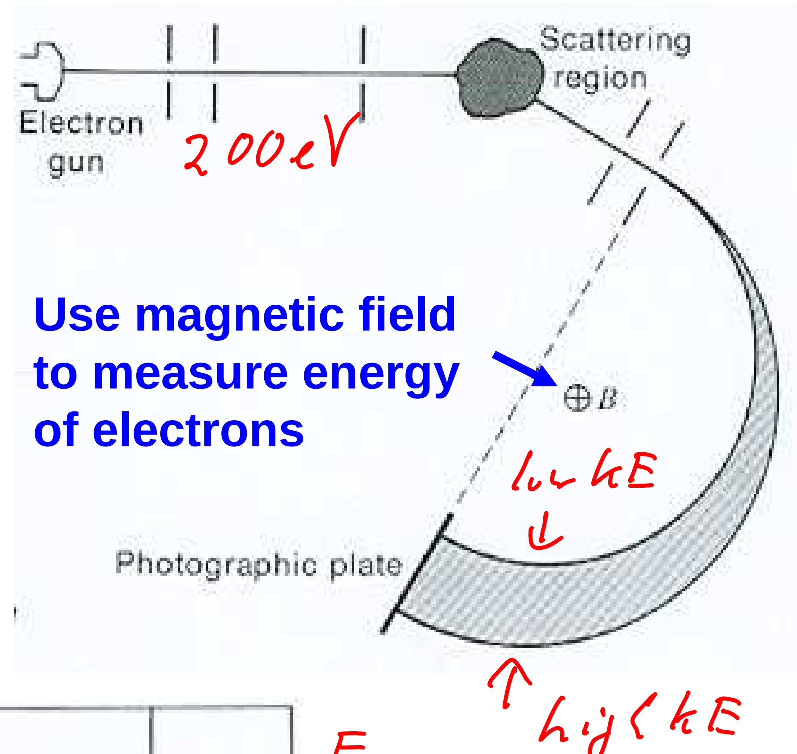
ground state

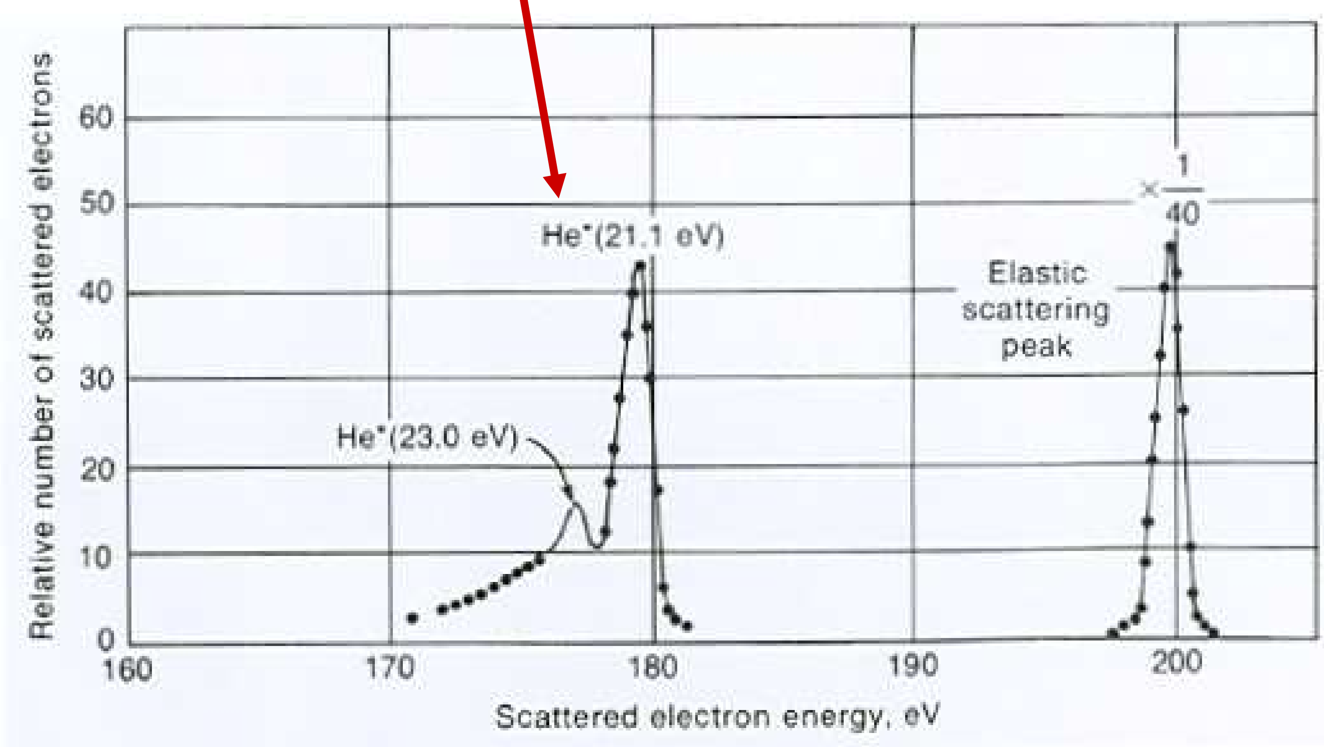
=>

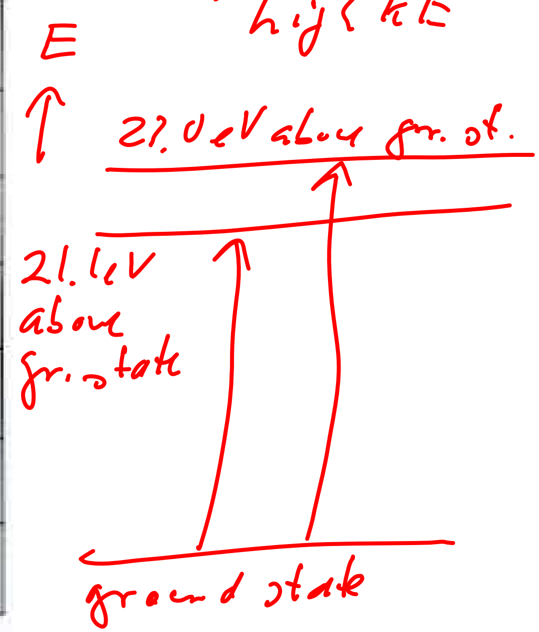
$\leadsto h\nu$

(c) Electron Scattering on a Helium Gas Target

Inelastic scattering: He electrons are excited to higher energy levels



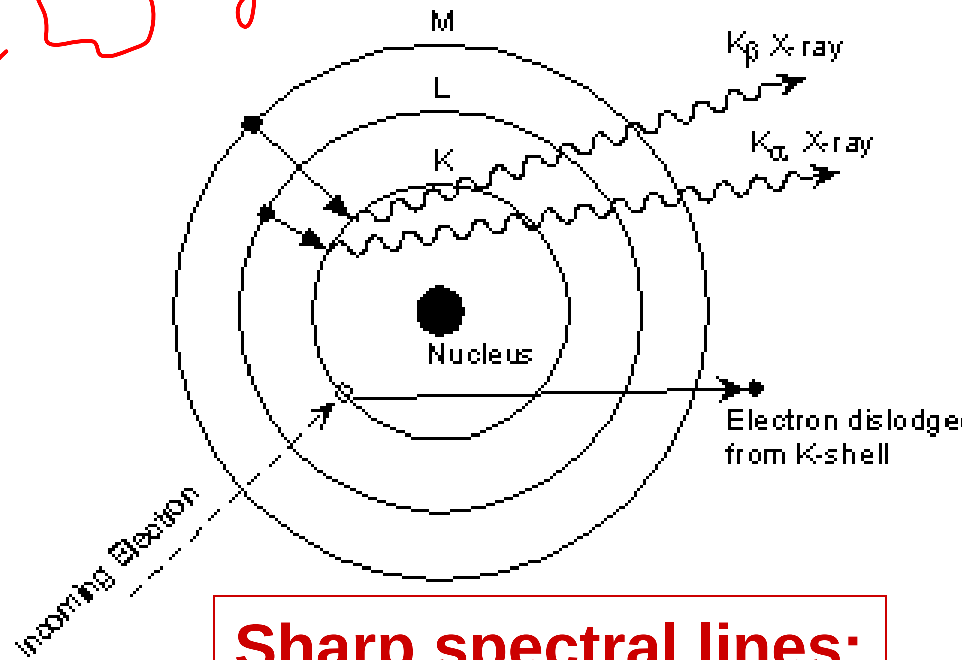




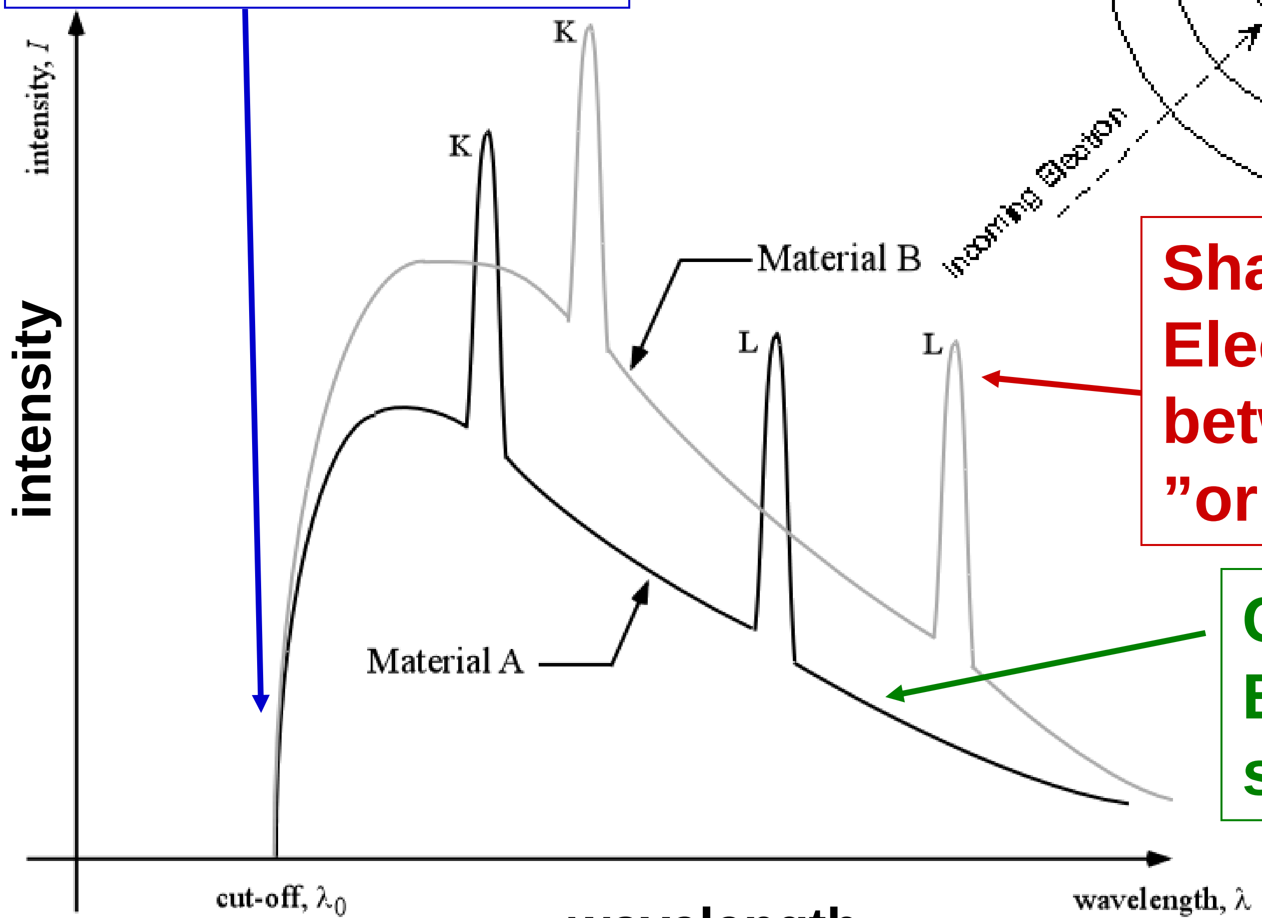
(d) X-Ray Spectra: Bremsstrahlung, Lines

high KE e^- → Target

10 - 100 keV



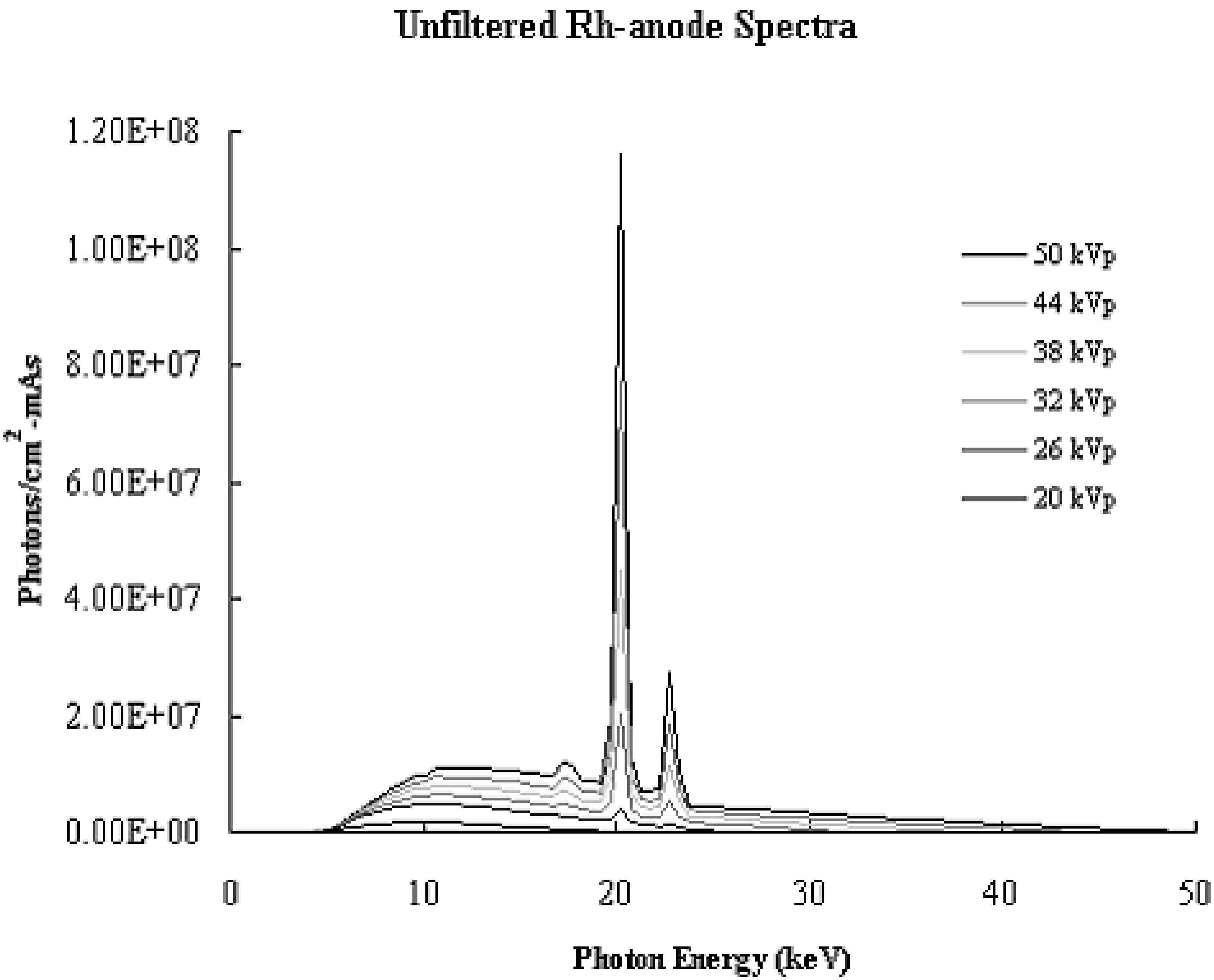
Cut-off:
$h\nu$ = KE of electron



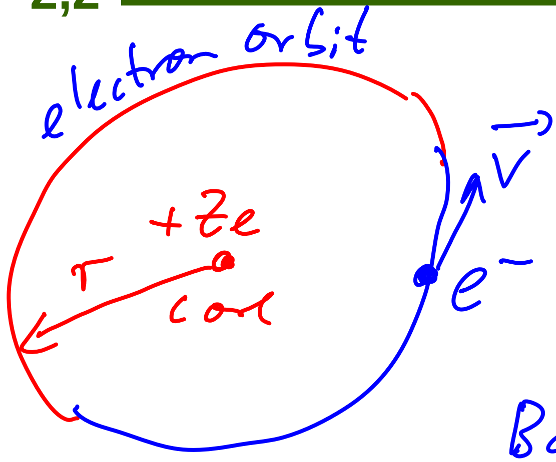
Sharp spectral lines: Electron transition between innermost "orbits": $h\nu = E_m - E_n$

Continuous Bremsstrahlung spectrum

Measured x-ray spectra from a rhodium-anode x-ray tube



$I_{2,2}$ The Bohr Atom (1913)



Rutherford (1909): atoms consist of small positive central core ($r < 10^{-14}m$) with lighter electrons outside

- e^- in orbit around core?

But: classical physics: unstable! orbiting e^- is accelerated ⇒ should radiate ⇒ lose energy ⇒ fall into nucleus

- Bohr Postulates: "patch work model"

I "stationary orbits" according to laws of Newtonian mechanics, but electron does not radiate while on orbit

II when electron passes from one orbit to another, a photon is emitted: $E_{photon} = E_i - E_f = h\nu$

1st: apply classical mechanics to electron in circular orbit around charge $Q = Ze$ nucleus:

- total energy: $$E = \underbrace{\frac{1}{2} m v^2}_{KE} - \underbrace{\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r}}_{\text{Coulomb pot.}} \qquad (1)$$

- Newton's law:

$$F = ma = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2} \stackrel{!}{=} m \frac{v^2}{r}$$

circular motion $\left(a = \frac{v^2}{r}\right)$

$$\Rightarrow \quad m v^2 = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} \qquad (2)$$

(1), (2)

$$E = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} - \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} = -\frac{1}{2} \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} = \frac{1}{2} U$$

< 0 takes energy to remove e^- $\Rightarrow$ <u>bound</u>!

$\underline{2^{nd}}$: Consider a quantum jump from an initial orbit to (low energy) final orbit:

- have: $E_{photon} = h\nu = E_i - E_f = \frac{1}{8\pi\varepsilon_0} Ze^2 \left(\frac{1}{r_f} - \frac{1}{r_i} \right)$
- need to be consistent with empirical Balmer series:

$$E_{photon} = h\nu = E_i - E_f = hc R_H \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right)$$

$\Rightarrow$ Introduce quantized energy levels and quantized electron orbits:

Energy levels: $E_n = -hcR_H \frac{1}{n^2} \overset{?}{=} -\frac{1}{8\pi\varepsilon_0} \frac{Ze^2}{r_n}$

$\Rightarrow$ allowed, quantized electron orbits: $\underline{\underline{r_n}} = \frac{Ze^2}{8\pi\varepsilon_0 hcR_H} n^2 = \underline{\underline{a_0 n^2}}$

with $\underline{\text{Bohr radius}} = a_0 = \frac{Ze^2}{8\pi\varepsilon_0 hcR_H} = \underset{\text{about right size?}}{\underbrace{0.5}}\,\text{Å}$ for $Z=1$

radius of e^- in ground state $(n=1)$

$\Rightarrow$ allowed, quantized electron energies (energy levels / states) : $\underline{\underline{E_n}} = -\frac{1}{8\pi\varepsilon_0}\frac{Ze^2}{a_0 n^2} = \underline{\underline{-13.6\,eV\frac{Z^2}{n^2}}}$

$n = 1, 2, 3 \ldots$

$\rightsquigarrow$ ground state energy ($n=1$) : $E_1 = -13.6\,eV$ for $Z=1$

$\rightsquigarrow$ $n > 1$: excited states of hydrogen

$\rightsquigarrow$ $n \to \infty$ $\Rightarrow$ $E_n \to 0$

$r_n \to \infty$

Can the electron in the ground state of the hydrogen atom absorb a photon of energy *<u>less</u>* than 13.6 eV?

A. Yes

B. No

C. It depends

only if excited state E_f exists such that

$E_f - E_i = h\nu = E_{photon}$

Can the electron in the ground state of the hydrogen atom absorb a photon of energy ***more*** than 13.6 eV?

A. Yes

B. No

C. It depends

$E_{photon} > |E_1|$

$\Rightarrow$ ionizes hydrogen atom

(e^- is no longer bound)

3rd: Derive value for a_0:

- use "correspondence principle":

Predictions of quantum theory should agree with predictions of classical physics for large quantum numbers!

• Bohr:

$n+1 \to n$

$$E_{photon} = h\nu = \frac{Ze^2}{8\pi\varepsilon_0}\left(\underbrace{\frac{1}{a_0 n^2}}_{1/r_f} - \underbrace{\frac{1}{a_0(n+1)^2}}_{1/r_i}\right)$$

$$= \frac{Ze^2}{8\pi\varepsilon_0 a_0}\left\{\frac{1+2n}{n^2(n+1)^2}\right\} \xrightarrow[\text{large } n]{} \frac{Ze^2}{8\pi\varepsilon_0 a_0}\frac{2}{n^3}$$

$$\Rightarrow \text{for large } n: \ \nu^2 \simeq \frac{Z^2e^4}{(4\pi\varepsilon_0)^2 a_0^2 n^6 h^2} \quad (a)$$

• classically: frequency of radiation = orbital frequency of e^- = $1/T_{orbit}$

$$\Rightarrow \nu^2 = \left(\frac{1}{T}\right)^2 = \left(\frac{v}{2\pi r_n}\right)^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{m r_n}\left(\frac{1}{2\pi r_n}\right)^2$$

from ②

$$= \frac{Ze^2}{4\pi\varepsilon_0 m (2\pi)^2 a_0^3 n^6} \leftarrow r_n = a_0 n^2 \qquad (b)$$

• (a) = (b) if:

$$\frac{Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2 a_0^2 n^6} = \frac{Ze^2}{4\pi\varepsilon_0 m (2\pi)^2 a_0^3 n^6}$$

$$\Rightarrow a_0 = \frac{h^2 (4\pi\varepsilon_0)}{(2\pi)^2 m Z e^2}$$

$\Rightarrow R_H$, theoretical = 109700 cm^{-1}

R_H, measured = 109700 cm^{-1}