Atomic Structure

Thornton and Rex, Ch. 4

Models of the Atom

Required features:

1. Electrons as constituents.

2. Some positive charges to neutralize the negative charges of the electrons.

3. Some scheme to account for the various different atomic weights.

4. Something to account for the different chemical properties of atoms

The "Plum Pudding" Model

(J.J. Thomson, 1904)

In this model, "a number of negatively-charged corpuscles were enclosed in a sphere of uniform positive electrification"

- A blob of positive "pudding" with electron "plums". The charges cancel.
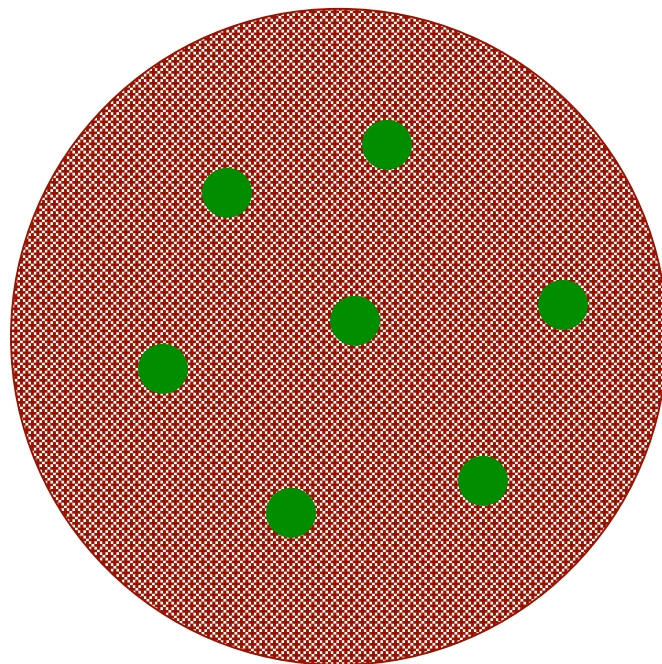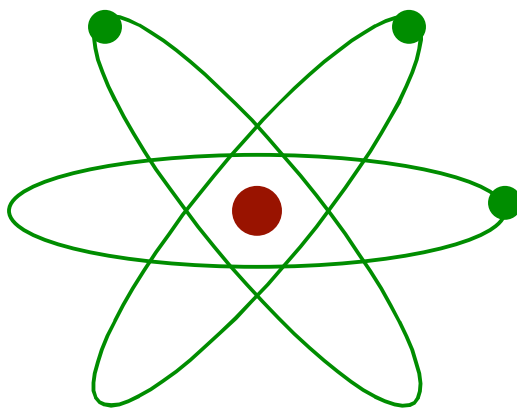
Rutherford Scattering

- Rutherford (1907), with Geiger and Marsden, set out to study scattering of α-rays.

- α-rays can be observed through scintillation. A screen coated with ZnS emits a short, faint flash of light when struck by an α-ray.

- To the amazement of all, the α-rays were scattered through very large angles.
(1 in 20,000 even bounced back in the direction from which they had come - a scattering angle of 180°.) This was an incredible result!

-In 1910 Rutherford calculated how close the positive α-ray must get to the positive charge in the gold atom for it to stop and reverse direction.

- The calculation showed a distance of about 1 x 10^{-14} m, about 1/10,000 the size of the atom.

The "plum pudding" model was wrong. The positive charge in the atom must be concentrated only at the very center.

Rutherford Scattering

Experiment of Geiger and Marsden:

α-rays scattered from thin gold target at large angles.


1911 - Rutherford:

- Results inconsistent with scattering from a homogeneous structure.

- Atom must contain central charge in small volume.

Rutherford worked out the scattering expected for the α-rays as a function of angle, thickness of material, velocity, and charge.

Rutherfords formulae verified by Geiger and Marsden in 1913.

Rutherford coins the term nucleus: central positively-charged core of the atom.

Popular picture of atom today is due to Rutherford:
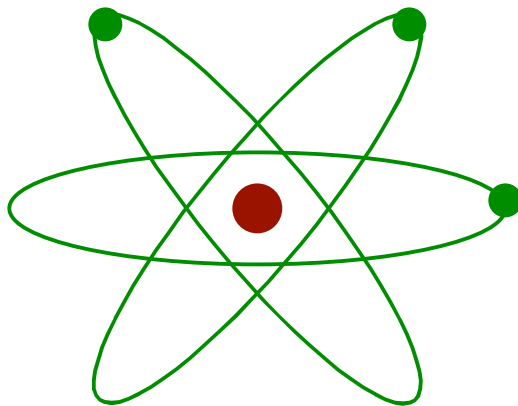
Impact parameter b vs. scattering angle θ:

$$b = (r_{min}/2) \cot(\theta/2)$$

where

$$r_{min} = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 K}$$

is the distance of closest approach for head-on collision.

Any particle hitting an area πb^2 around the nucleus will be scattered through an angle of θ or greater.

This area is called the cross section (for angle > θ). It is written:

$$\sigma = \pi b^2$$

(common unit of σ : barn = 10^{-28} m^2
$= 100$ fm^2)

THE MINIMUM SEPARATION OF THE INCIDENT PARTICLE AND THE SCATTERING NUCLEUS IS GIVEN BY:-

$$ENERGY = K + \sim 0$$

$$ENERGY = 0 + \frac{1}{4\pi\varepsilon_0} \frac{z_1 z_2 e^2}{R_{MIN}}$$

CONSERVATION OF ENERGY $\Rightarrow$

$$K = \frac{1}{4\pi\varepsilon_0} \frac{z_1 z_2 e^2}{R_{MIN}}$$

$$\therefore R_{MIN} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 K}$$

RUTHERFORD USED 7.7 MeV α-RAYS SCATTERED FROM GOLD

$$\therefore R_{MIN} = \frac{(8.99E9) . 2.79 . (1.6E-19)^2}{(7.7E6)(1.6E-19)}$$

$$= 2.95 E-14 \, m$$

WHERE $Z_1 e$ AND $Z_2 e$ ARE THE SIZES OF THE COLLIDING CHARGES, AND K IS THE KINETIC ENERGY OF THE INCIDENT PARTICLE.

$$\theta = 0 \qquad \cot \frac{\theta}{2} = \infty \qquad b = \infty$$

$$\theta = 90° \qquad \text{''} \quad = 1$$

$$\theta = 180° \qquad \text{''} \quad = 0 \qquad b = 0$$

i.e. SHOWING THAT SMALLER IMPACT PARAMETERS CORRESPOND TO LARGER SCATTERING ANGLES.
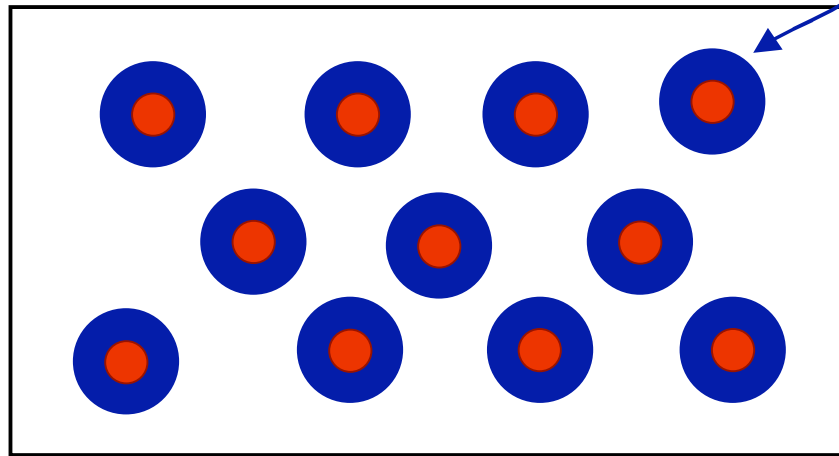
ANY PARTICLE HITTING AN AREA πb^2 CLOSE TO THE NUCLEUS WILL BE SCATTERED THROUGH AN ANGLE OF θ OR GREATER. WE DEFINE THIS AREA AS A CROSS SECTION, σ

$$\sigma = \pi b^2$$

THIS IS RELATED TO THE PROBABILITY OF BEING SCATTERED BY A NUCLEUS.

Probability of scattering (with angle > θ) is

$$f = \frac{(\# \text{ atoms}) \, \sigma}{\text{Total Area}}$$

πb^2

atoms/Area =
   (# atoms/Volume) x thickness
         = n t

$$\left[\begin{array}{l} n = \left(N_A \, \frac{\text{atoms}}{\text{mole}}\right)\left(\frac{1}{A} \, \frac{\text{mole}}{\text{gm}}\right)\left(\rho \, \frac{\text{gm}}{\text{cm}^3}\right) \\[2ex] = \frac{\rho \, N_A}{A} \end{array} \right]$$

So

$$f = nt\pi b^2 = (\pi nt/4) \, r_{min}^2 \cot^2(\theta/2)$$

Size of an atom of Lead

n = atoms/volume = $\rho N_A / A$

$= 19.6 g/cm^3 \times 6 \times 10^{23} / 197 = 6 \times 10^{22} = 1/L^3$

$L = 2.6 \times 10^{-8}$ cm $= 2.6 \times 10^{-10}$ m

$Rmin/(L/2) = 2.9 \times 10^{-14}/1.3 \times 10^{-10} = 2 \times 10^{-4}$

For comparison:

Fly ~ 2 cm $= 2 \times 10^{-2}$ m
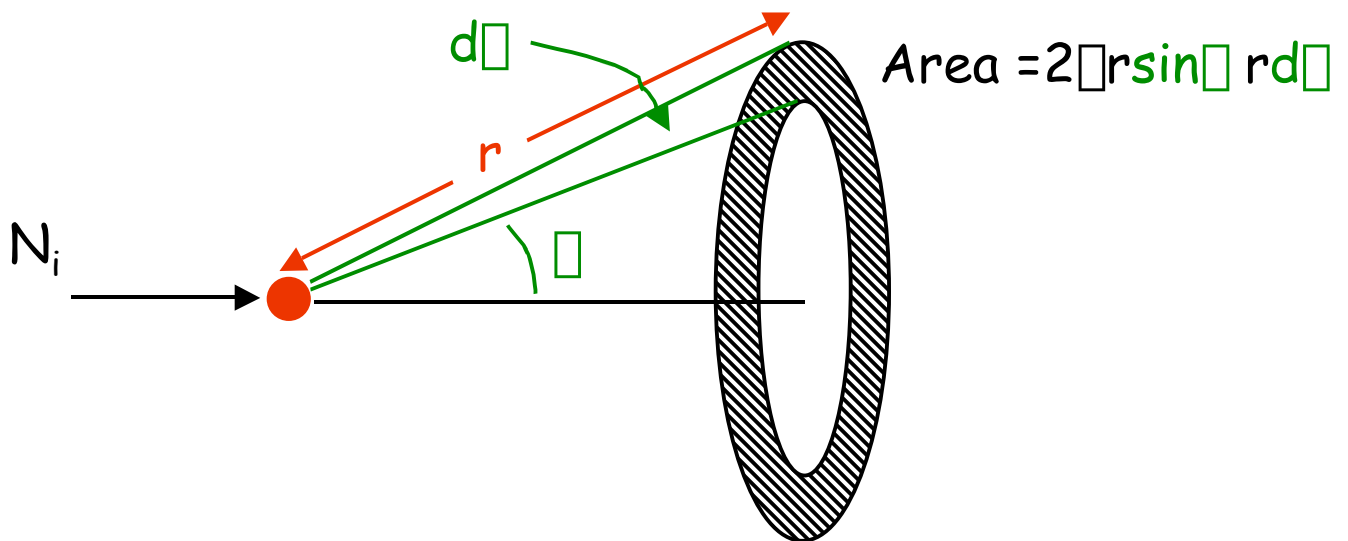
Catherdral ~ 20 m high (Chartres is closer to 40 m)

Fly/Cathedral $= .5 \times 10^{-4}$

In practice, events are measured in range θ to $\theta+d\theta$

Differential probability:

$$df = -(\pi nt/4)\, r_{min}^2 \cot(\theta/2)\mathrm{cosec}^2(\theta/2)\, d\theta$$

For N_i incident particles, # scattered into ring between θ and $\theta+d\theta$ is $N_i|df|$.

Area $=2\pi r\sin\theta\, r d\theta$

$d\theta$

r

N_i

θ

per unit area between θ and $\theta+d\theta$

$$= \frac{N_i\,|df|}{2\pi r^2\,\sin\theta\, d\theta}$$

$$N(\theta) = \frac{N_i \, nt}{16 \, r^2} \, (r_{min})^2 \, \frac{1}{\sin^4(\theta/2)}$$

$$= \frac{N_i \, nt}{16 \, r^2} \, (e^2/4\pi\varepsilon_0)^2 \, \frac{Z_1^2 \, Z_2^2}{K^2 \, \sin^4(\theta/2)}$$

The Rutherford Scattering Formula

a) Proportional to Z_1^2 and Z_2^2

b) Proportional to $1/K^2$

c) Proportional to $1/\sin^4(\theta/2)$
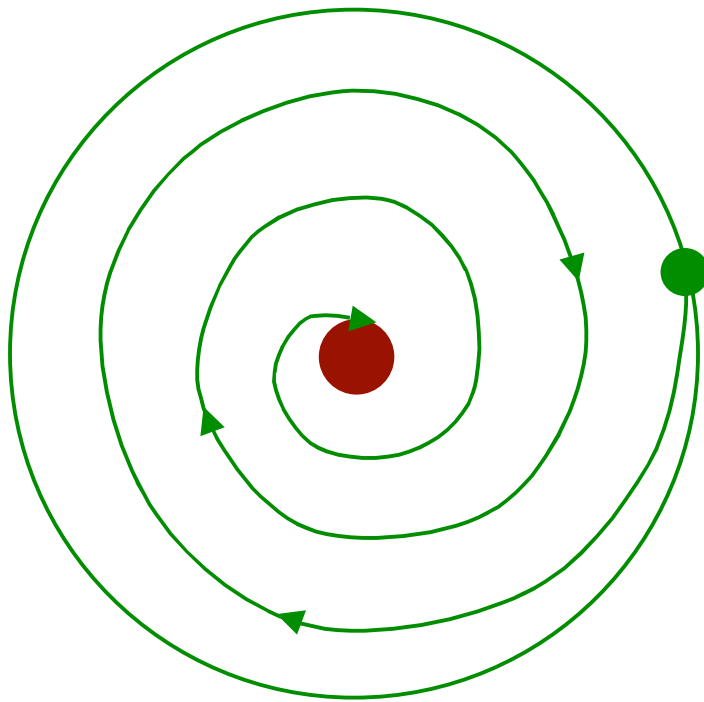
d) Proportional to thickness t
   (for thin targets)

Rutherford's Model of the Atom

+e

-e
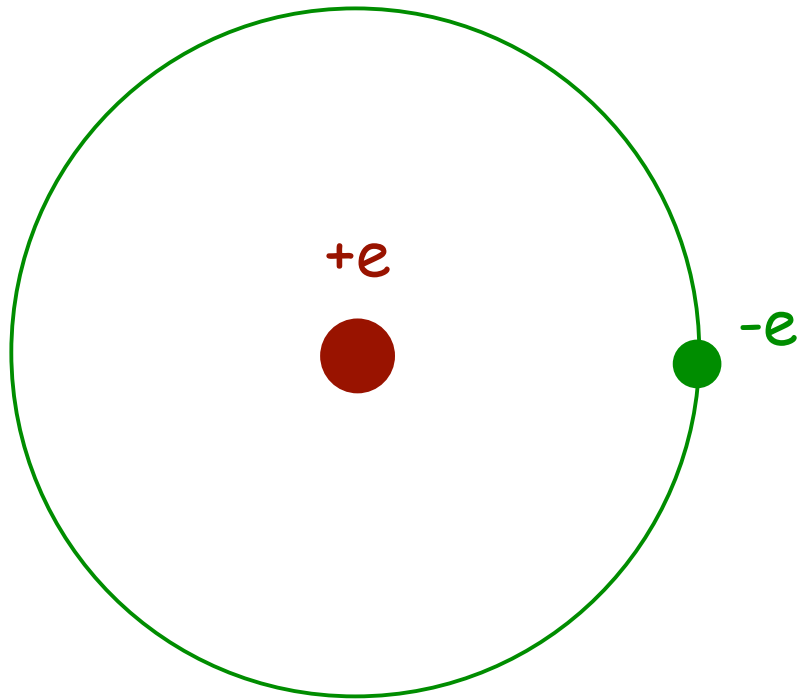
Hydrogen atom

But there are problems . . .

- Accelerating electrons radiate energy. The electron should spiral into the nucleus (in ~10^{-9} seconds!)


- Atoms with > 1 electron are unstable, due to electron repulsion.

Bohr's Model of the Hydrogen Atom

Neils Bohr modified Rutherford's model with some ad-hoc assumptions:

1) Electrons only in special orbits: "Stationary States".

2) An electron in a stationary state obeys classical mechanics (Newton's laws).

3) Transitions between stationary states (i->f) do not obey classical mechanics. They are accompanied by the emission or absorption of radiation of fixed energy $E = E_i - E_f$.
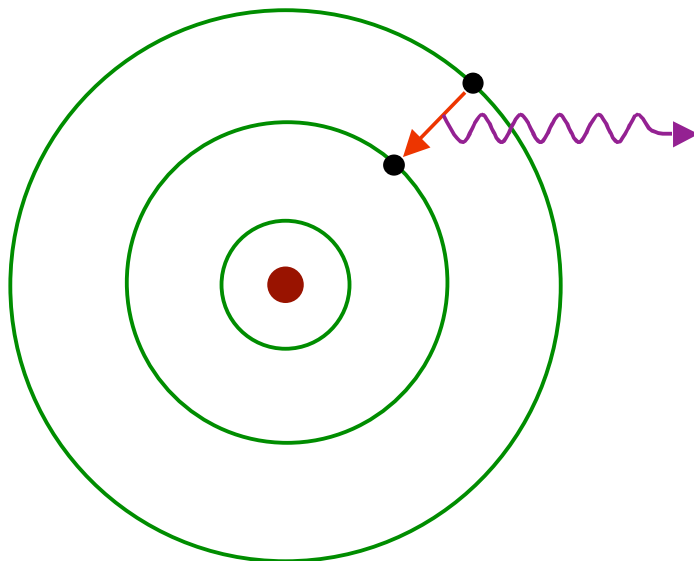
4) The angular momentum of a stationary state is an integer multiple of $h/(2\pi)$. I.e. $L = n\, h/(2\pi)$, where $n = 0,1,2,\ldots$

The combination $h/(2\pi)$ occurs so frequently that it is given a special symbol:
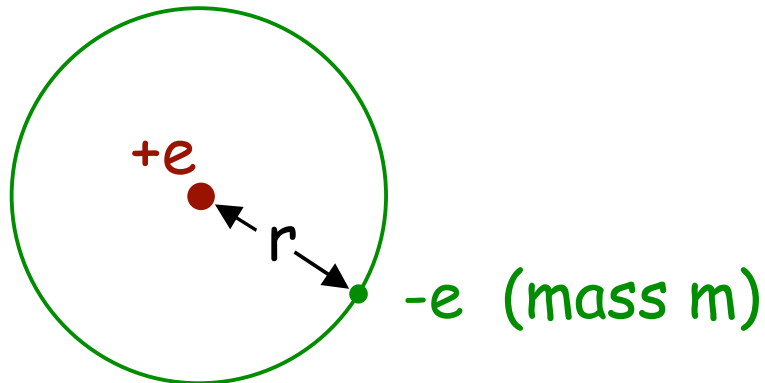
$$\hbar = h/(2\pi)$$

$$\hbar = 1.05 \times 10^{-34}\ \text{J}\cdot\text{s}$$

Assumption 4 (quantization of angular momentum) was the most controversial.

But...

- it accounts for stability of Hydrogen,

- it leads to Rydberg formula for line spectra of Hydrogen.

Hydrogen with electron in circular orbit:

Quantization of L gives:

$$L = mvr = n\hbar$$

$$\Rightarrow v = n\hbar / (mr) \qquad (1)$$

Centripetal force due to Coulomb attraction:

$$\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r^2} = m\, a_{cent} = m\, \frac{v^2}{r}$$

$$\Rightarrow v^2 = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{mr} \qquad (2)$$

Plug (1) into (2) and solve for radius r:

$$\Rightarrow r = 4\pi\varepsilon_0 \; \frac{n^2 \hbar^2}{m \, e^2}$$

$\Rightarrow$ Each stationary state orbits at specific radius, identified by integer n.
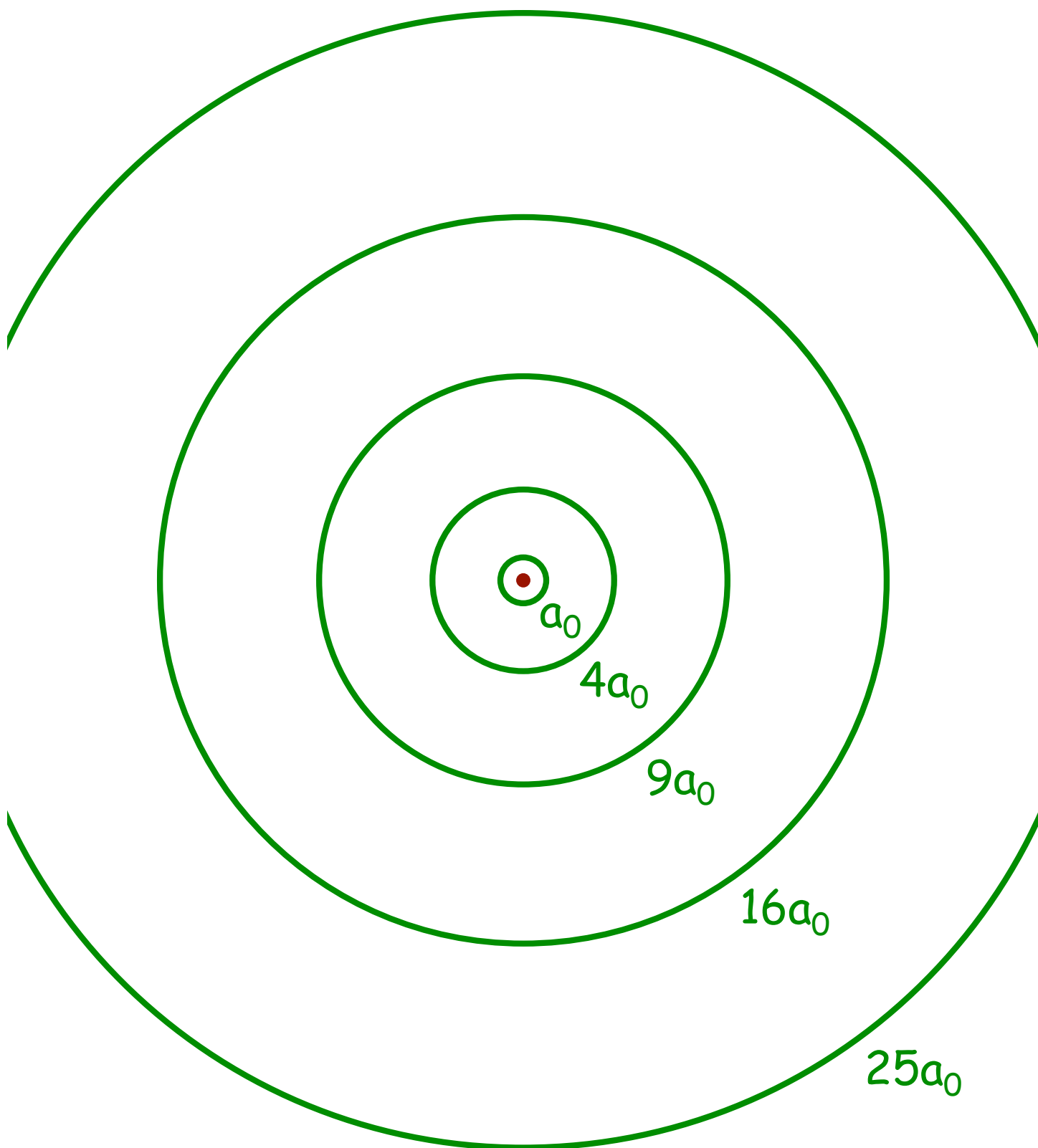
The smallest radius (n=1) is called the "Bohr radius:

$$a_0 = \frac{4\pi\varepsilon_0 \, \hbar^2}{m \, e^2} = 5.3 \times 10^{-11} \, m$$

Other radii related by:

$$r_n = n^2 \, a_0.$$

Hydrogen atom is stable.

a_0

$4a_0$

$9a_0$

$16a_0$

$25a_0$

Calculation of Energy levels

$$E \quad = \quad KE \quad + \quad PE$$

$$= \frac{1}{2} mv^2 \qquad - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$= \frac{1}{2} m \left(\frac{e^2}{4\pi\varepsilon_0 mr} \right) \quad - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$= - \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0 r}$$

Substituting for r:

$$\Rightarrow E = - E_0 / n^2$$

where

$$E_0 = \alpha^2 m c^2 / 2 = 13.6 \text{ eV}$$

The dimensionless constant α is called the "fine structure constant":

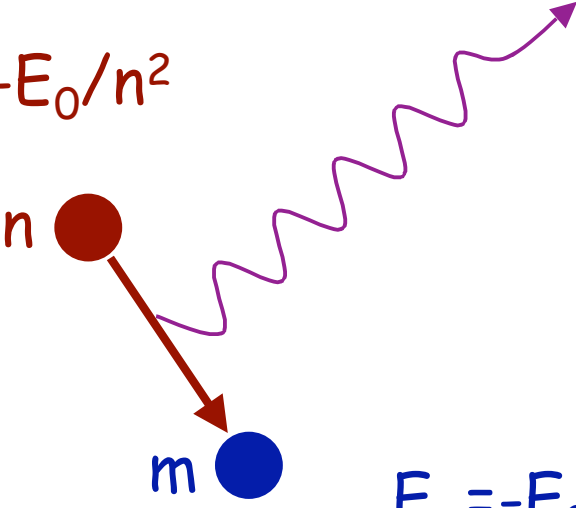$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137.0}$$

$E_n = -E_0/n^2$

n

m

$E_m = -E_0/m^2$

$E = E_n - E_m = \left(\dfrac{1}{m^2} - \dfrac{1}{n^2} \right) E_0$

Emission and Absorption of Radiation

Energy of emitted radiation:

$$E = E_n - E_m$$

$$= E_0 \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

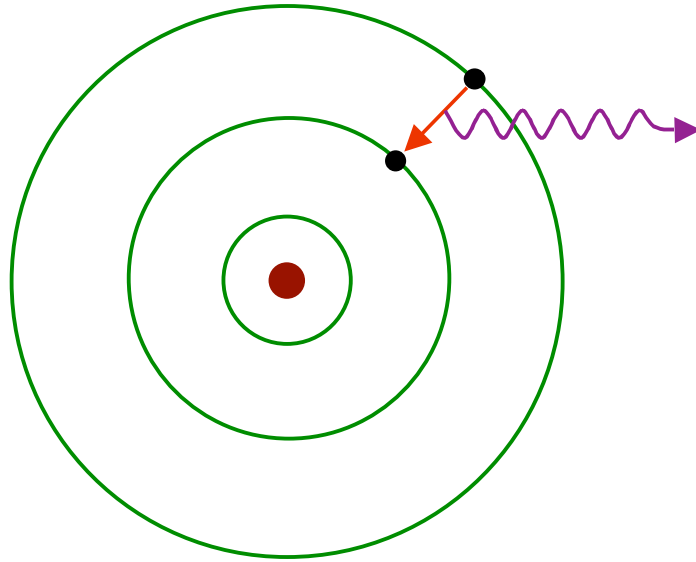Using the Planck formula $E = h\nu = hc/\lambda$, leads to Rydberg formula:

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

With

$$R_H = E_0/(hc) = 13.6 \text{ eV}/(1243 \text{ eV} \cdot \text{nm})$$
$$= 1.09 \times 10^{-7} \text{ m}$$
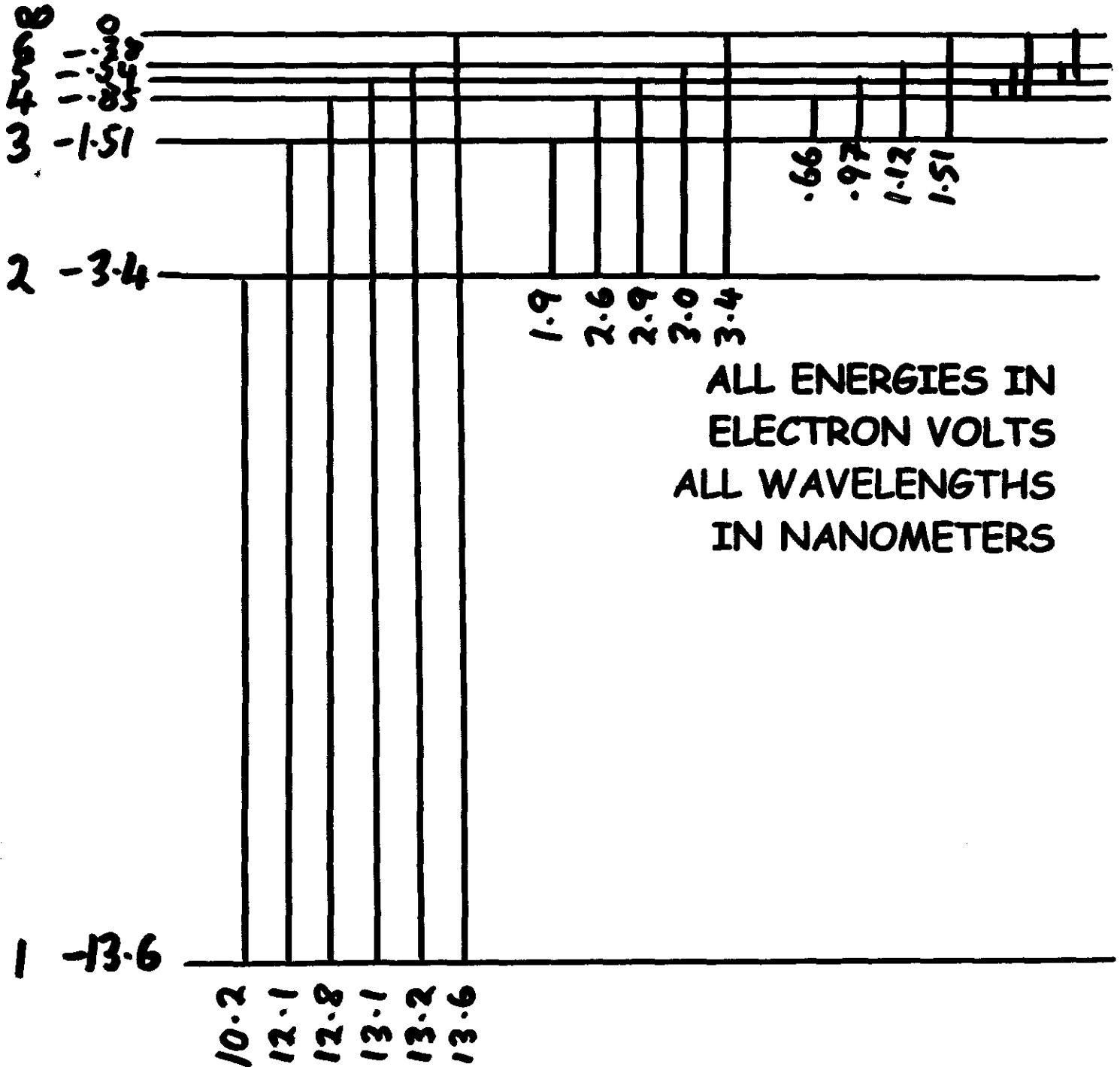
This predicts the Rydberg constant exactly!

Summary of the Bohr Model of Hydrogen

- L quantized: $L = n\hbar = n\,h/(2\pi)$

- Stationary State orbits: $r = a_0\,n^2$

- Stationary State energies: $E = -E_0/n^2$

- Predicts Rydberg formula and constants: a_0, E_0, R_H

THE ENERGY LEVELS

n   E(eV)

∞ 0
6 −.38
5 −.54
4 −.85

3 −1.51

2 −3.4

1 −13.6

.66
.97
1.12
1.51

1.9
2.6
2.9
3.0
3.4

10.2
12.1
12.8
13.1
13.2
13.6

ALL ENERGIES IN
ELECTRON VOLTS
ALL WAVELENGTHS
IN NANOMETERS

WHILE BOHR WAS DEVELOPING HIS MODEL HE REVIEWED THE FORMULAE OF BALMER AND RYDBERG.

$$1/\lambda = R_H(1/m^2 - 1/n^2)$$

THE RYDBERG CONSTANT HAD A PRECISELY MEASURED VALUE OF $R_H = \underline{10{,}967{,}760}\ m^{-1}$

"AS SOON AS I SAW BALMER'S FORMULA," HE SAID AFTERWARD, *"THE WHOLE THING WAS IMMEDIATELY CLEAR TO ME."*

HE CALCULATED THAT THE FREQUENCIES OF LIGHT CORRESPONDING TO TRANSITIONS BETWEEN HIS ORBITS COULD BE CALCULATED AS FOLLOWS:-
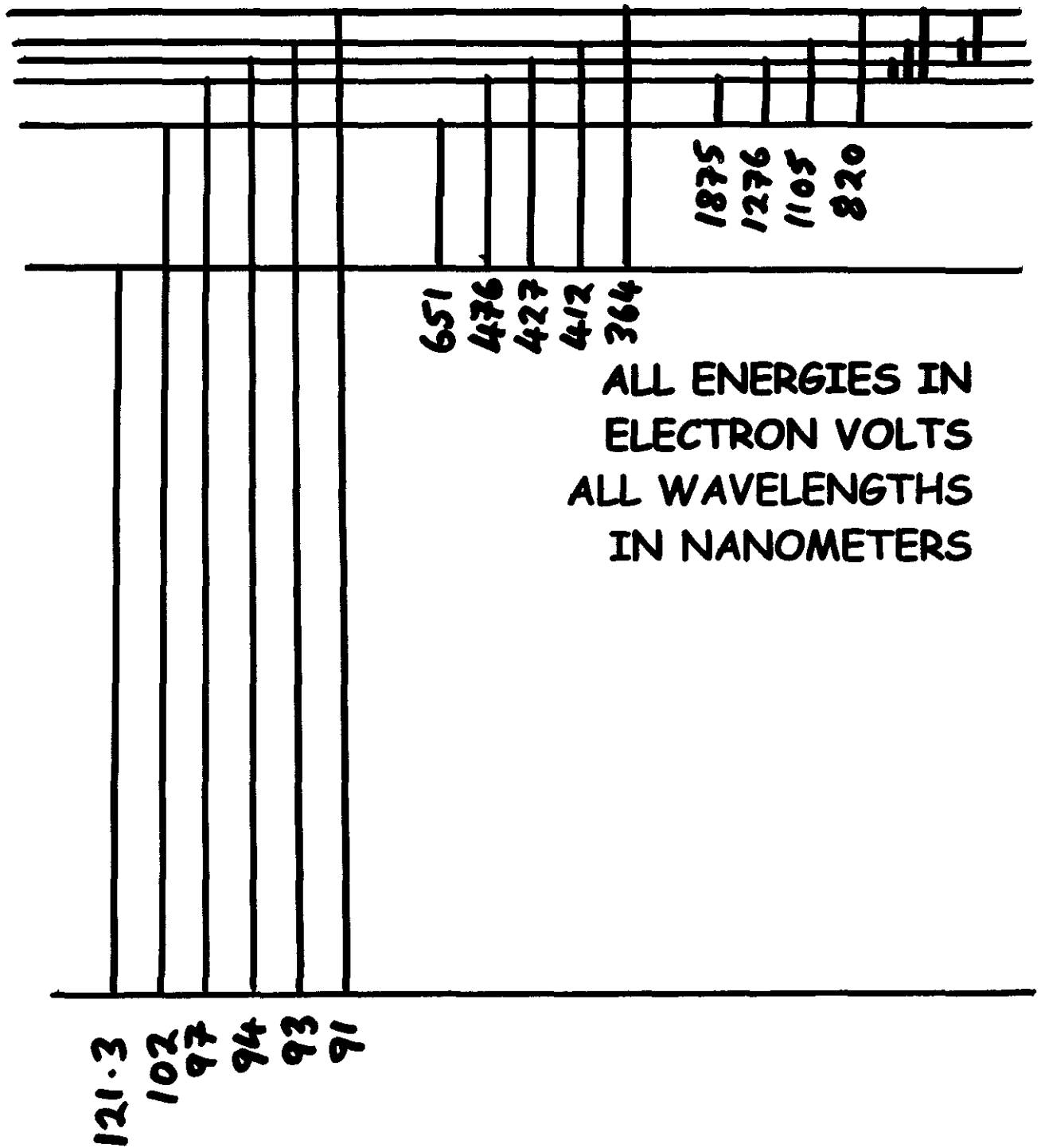
THE ENERGY LEVELS

ALL ENERGIES IN
ELECTRON VOLTS
ALL WAVELENGTHS
IN NANOMETERS

$\lambda(nm) = 1240/E_{phot}$ OR $\lambda(m) = 1240E-9/E_{phot}$

$1/\lambda(m) = E_{phot}/1240E-9 = 13.6/1240E-9\ (1/m^2-1/n^2)$

$1/\lambda(m) = \underline{10,967,742}\ (1/m^2-1/n^2)$

A PRETTY GOOD AGREEMENT!!

BOHR HAD SUCCESSFULLY CALCULATED THE RYDBERG CONSTANT STARTING FROM A TOTALLY NEW THEORY.

"THERE IS NOTHING IN THE WORLD WHICH IMPRESSES A PHYSICIST MORE," AN AMERICAN PHYSICIST COMMENTED, "THAN A NUMERICAL AGREEMENT BETWEEN EXPERIMENT AND THEORY, AND I DO NOT THINK THAT THERE CAN EVER HAVE BEEN A NUMERICAL AGREEMENT MORE IMPRESSIVE THAN THIS ONE."

Generalization of the Bohr Model

Applies to any <u>single electron atom</u>
(H, He$^+$, Li^{++}, …) by changing nuclear charge
from +e to +Ze.

Radius of orbit is now
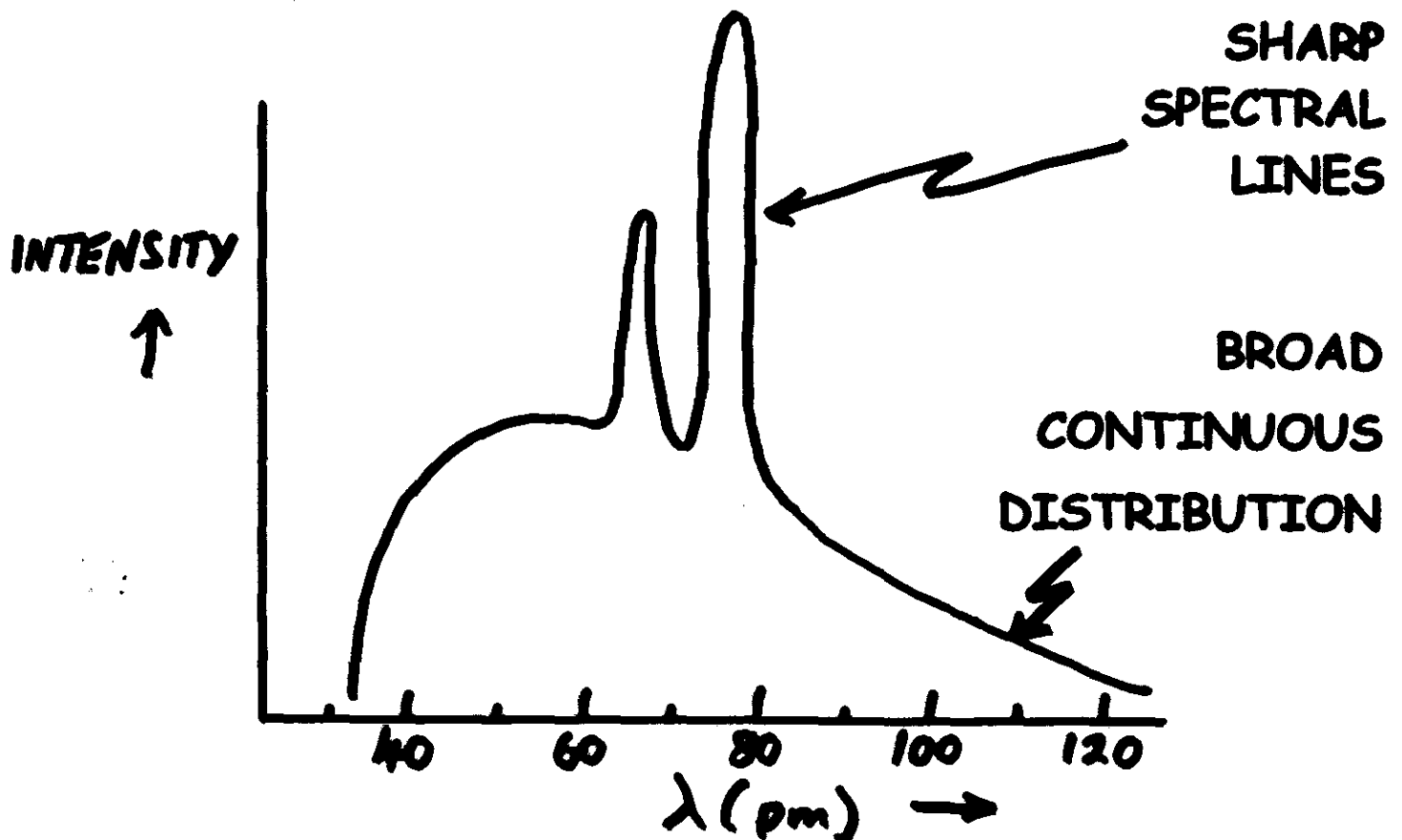
$$r_n = n^2 \, a_0 \, / \, Z$$

and energy is

$$E_n = - Z^2 \, E_0 \, / \, n^2.$$

Stronger electric fields:

$\Rightarrow$ Smaller orbits

$\Rightarrow$ More tightly bound electrons

CHARACTERISTIC X-RAY LINES

IF WE LOOK AT THE WAVELENGTH DISTRIBUTION
OF X-RAYS PRODUCED BY BOMBARDING
ELECTRONS ON A HIGH-Z TARGET.

NOTE: ABOUT 1000 TIMES SHORTER THAN
VISIBLE LIGHT

IF A HIGH-Z MATERIAL IS BOMBARDED BY ENERGETIC ELECTRONS THEN ONE OF THE TIGHTLY BOUND n = 1 ELECTRONS MAY BE KNOCKED OUT OF THE ATOM.

IMMEDIATELY AN ELECTRON FROM A HIGHER LEVEL ORBIT (n = 2, n = 3 OR HIGHER) WILL DROP DOWN TO THE LOWER ENERGY AND RADIATE AN X-RAY OF FREQUENCY,

$$f = (E_n - E_1)/h$$
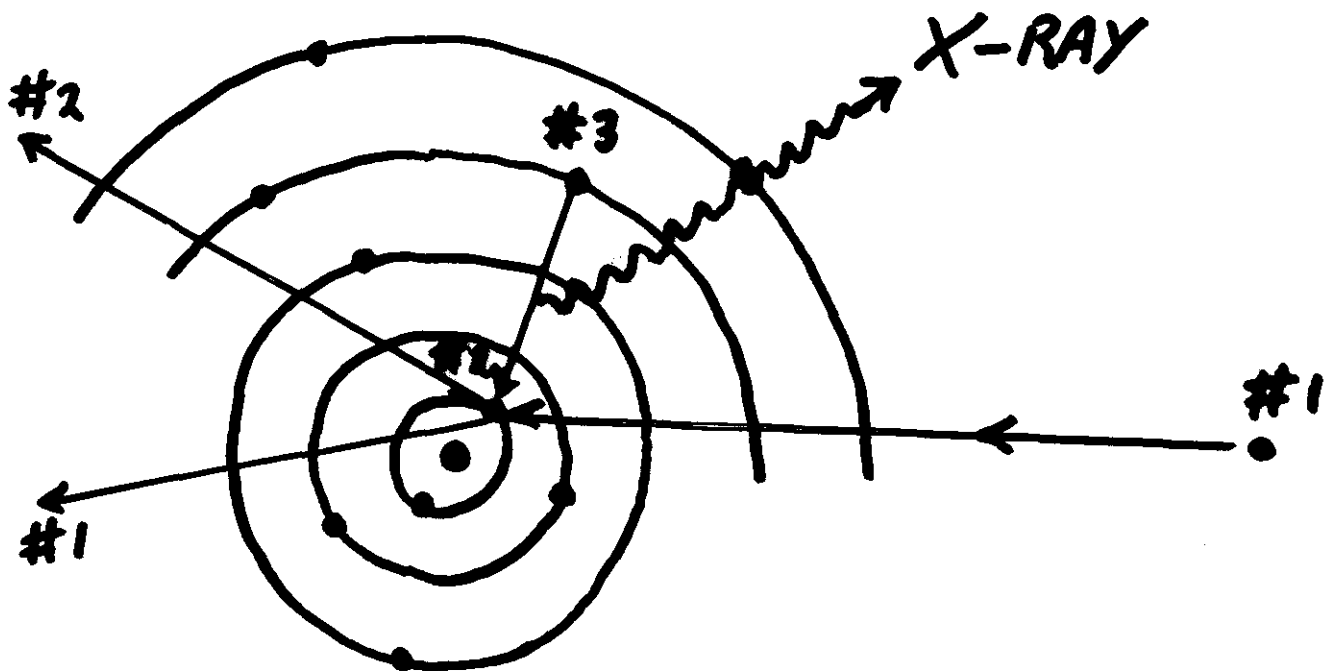
ELECTRON #1 IS ACCELERATED WITH A HIGH VOLTAGE AND IT STRIKES THE ELECTRONS IN A HEAVY (HIGH Z) METAL TARGET.

ELECTRON #2 IS KNOCKED OUT OF THE ATOM.

ELECTRON #3 "FALLS DOWN" FROM A HIGHER ORBIT TO REPLACE #2 AND LOSES ENERGY IN THE FORM OF AN X-RAY.

IF THE FREQUENCIES OF THE X-RAYS ARE MEASURED THEN THESE CAN BE CONVERTED INTO ENERGIES AND THEN INTO ENERGY DIFFERENCIES BETWEEN THE ELECTRON ORBITS FOR THE ATOM.

BECAUSE THESE ENERGY DIFFERENCES ARE PROPORTIONAL TO THE Z^2 OF THE ATOM, A PRECISE MEASUREMENT OF THE X-RAY SPECTRUM OF A SUBSTANCE IS A GOOD WAY OF MEASURING ITS Z (i.e. THE NUMBER OF ELECTRONS AND THE SIZE OF THE CHARGE OF THE CENTRAL NUCLEUS).

THIS NUMBER BECAME KNOWN AS <u>THE ATOMIC NUMBER</u> OF THE ELEMENT.

THIS WAS FIRST REALIZED BY A YOUNG ENGLISH PHYSICIST, HENRY GWYN JEFFREYS MOSELEY. HARRY MOSELEY, AS HE WAS CALLED, PERFORMED A SERIES OF EXPERIMENTS IN 1913 AND 1914 THAT MEASURED THE FREQUENCY OF X-RAYS OF MANY ELEMENTS IN THE PERIODIC TABLE, FROM ALUMINUM (Z = 13) UP TO GOLD (Z = 79).

MOSELEY CONDUCTED HIS RESEARCH AT THE SAME TIME THAT NIELS BOHR WAS DEVELOPING HIS MODEL OF THE ATOM, AND THE TWO OF THEM CONFERRED OFTEN AND EXCHANGED INFORMATION. MOSELEY'S DATA PROVIDED A SPECTACULAR CONFIRMATION OF BOHR'S HYPOTHESES.

THE REGULARITY OF X-RAY FREQUENCIES ENABLED MOSELEY TO ORDER THE ELEMENTS BY THEIR ATOMIC NUMBER (Z). HE SAW THAT ATOMIC NUMBERS WERE ALL INTEGERS. IN SOME CASES HIS CAREFUL WORK SHOWED THAT MENDELEEV'S ORDERING (BY ATOMIC WEIGHT) WAS INCORRECT.