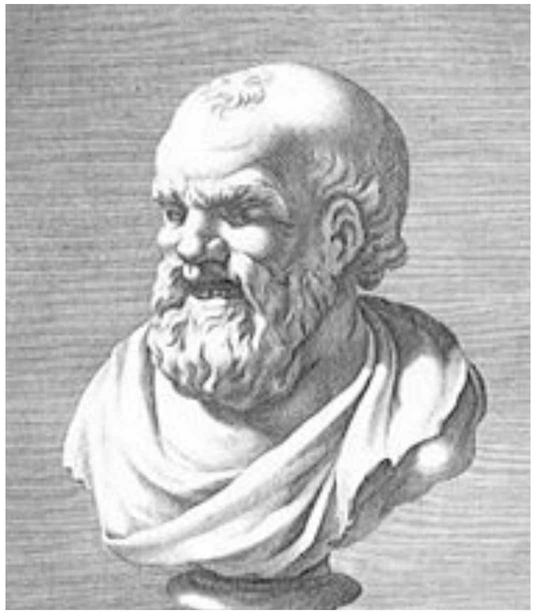
Part 2: Atomic theory from 400 BC to 1913

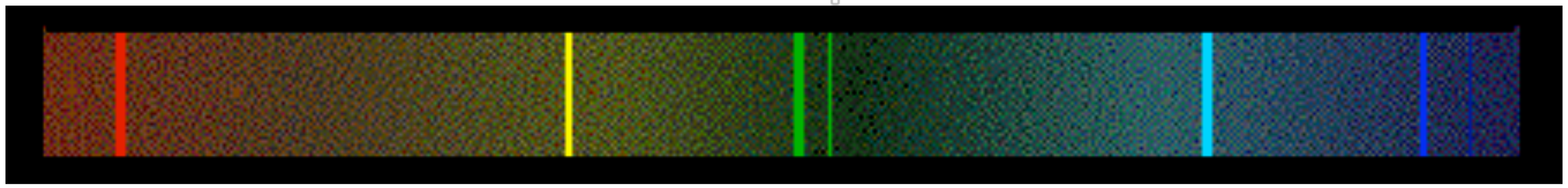
Today's Lecture

- Pre-quantum Atomic Models (from Democritus 433 A.D. to Bohr 1913)

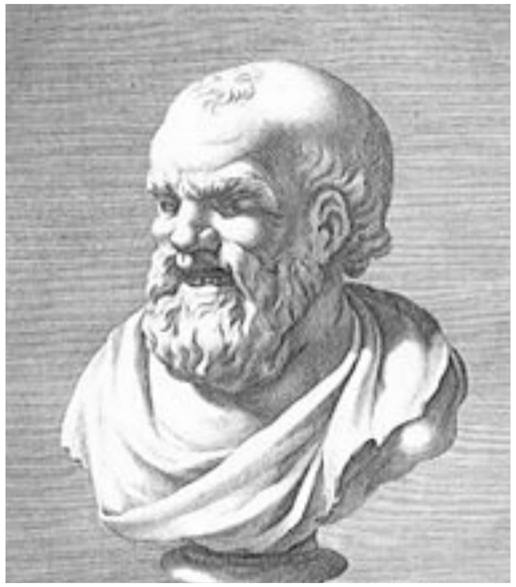


- Atomic Spectra (unique signatures of the elements)

Emission Spectrum



History of the Atom



Democritus

John Dalton

- Democritus: c. 400 BC
  - All matter composed of indivisible "atoms".
    (No experimental evidence to support this)
- John Dalton: c. 1800
  - All matter is composed of atoms.
  - There are a limited number of "types" of atoms - called elements - which have differing mass.
  - Atoms corresponding to the same element are identical.
  - Evidence: mass ratios in chemical reactions.

Images from Wikipedia

History of the Atom

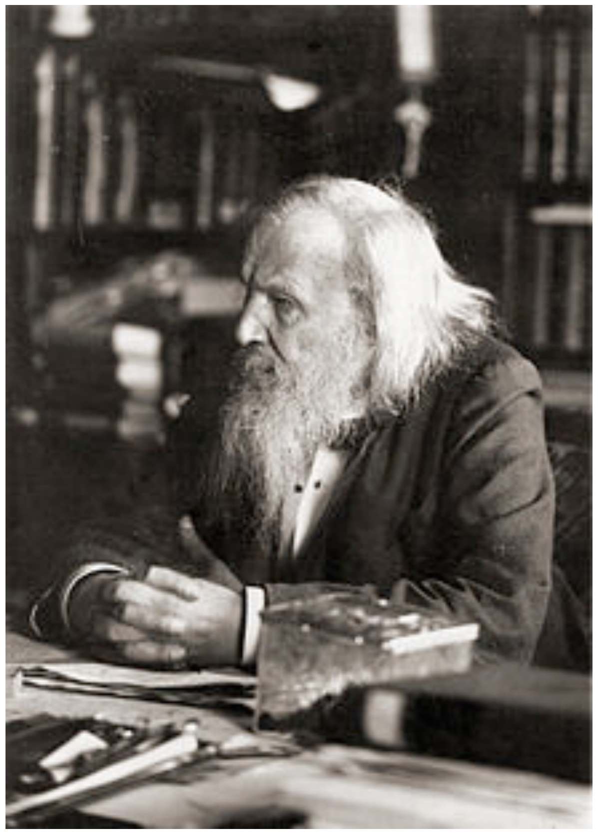
John Dalton

- "Law of multiple proportions"
- Ratio of masses in chemical reactions always very close to **small integers**.
- E.g. Carbon Monoxide
  - 100g Carbon + **133g** Oxygen -> 233g CO
  - ***Carbon Dioxide***
  - 100g Carbon + **266g** Oxygen ->366g CO2
- **Many** other examples across Chemistry.
- Dalton's explanation
  - 1 or 2 Carbon Atoms + 1 Oxygen Atom

Images from Wikipedia

History of the Atom

- 1869: **Periodic Table** of elements developed (Mendeleyev, Meyer).
- No notion of internal atomic structure was known at this time.



Dimitri Mendeleyev

Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Images from Wikipedia

History of the Atom

- J. J. Thomson:
  - **1897**: Discovery of the **electron** as a particle.
  - "Cathode ray" - a stream of electrons.
    In 1890s a puzzle!

J.J. Thomson

Fig. 2.

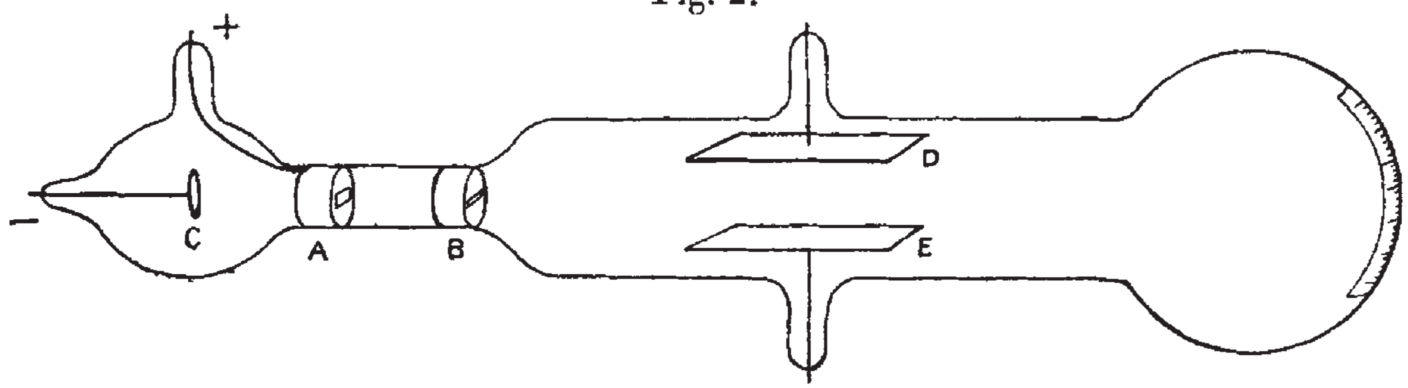


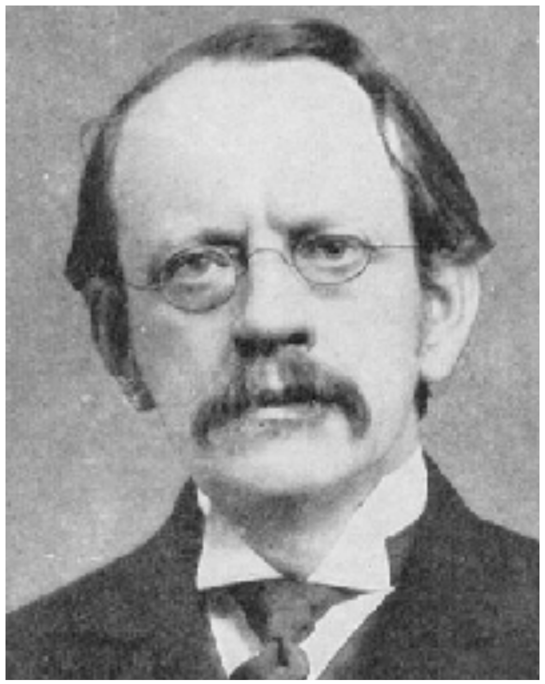
Figure: J.J. Thompson, Philosophical Magazine, 1897.

Cathode "ray" **deflected** by **electric field.**

Same behaviour as predicted by **electromagnetic theory** for **negatively charged particles** with **mass to charge ratio** m_e / e.

History of the Atom

- J. J. Thomson:
  - Proposal for an atomic model:
    - The **plum pudding** model



J.J. Thomson

Fig. 2.

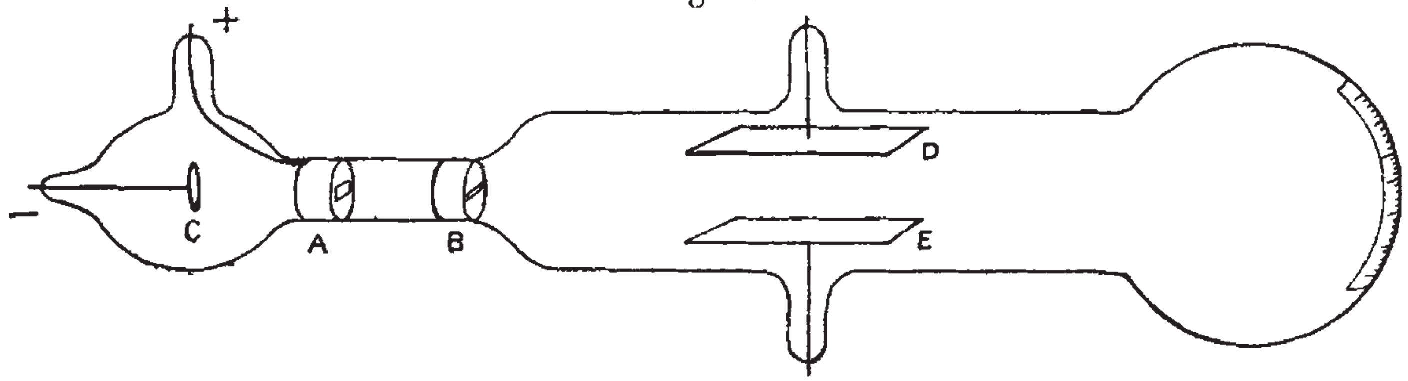
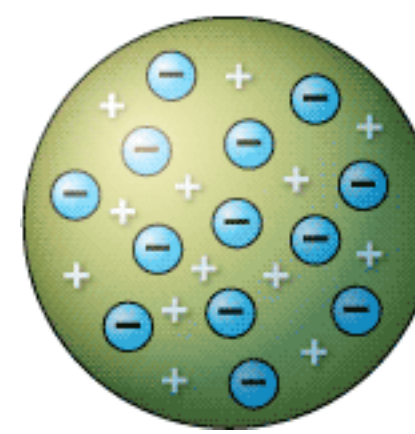


Figure: J.J. Thompson, Philosophical Magazine, 1897.

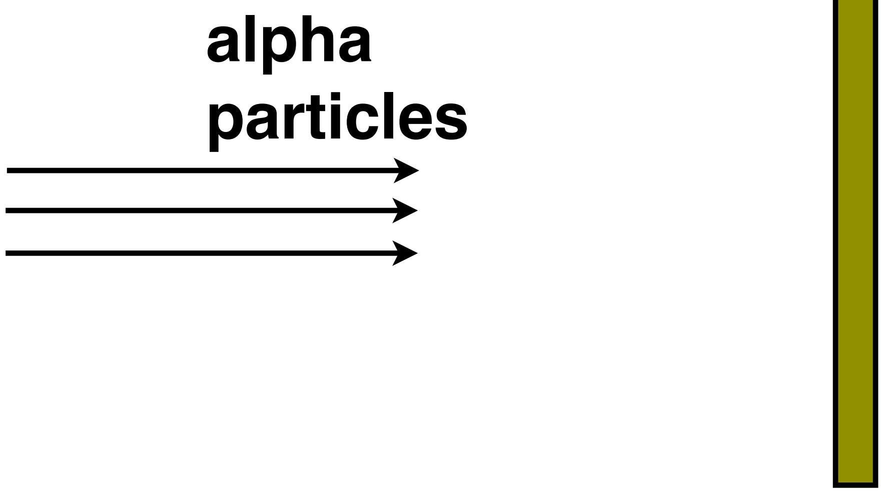
- **The plum pudding atomic model:**
  - **Atoms neutrally charged, but can release negative electrons.**
  - **So atoms are a "plum pudding" structure of electrons surrounded by positively charged "liquid".**



History of the Atom

- Rutherford: 1907
  - Geiger–Marsden experiment
  - Alpha particles (He^{2+} ions) scattered from Gold foil.

Ernest Rutherford



Images from Wikipedia

History of the Atom

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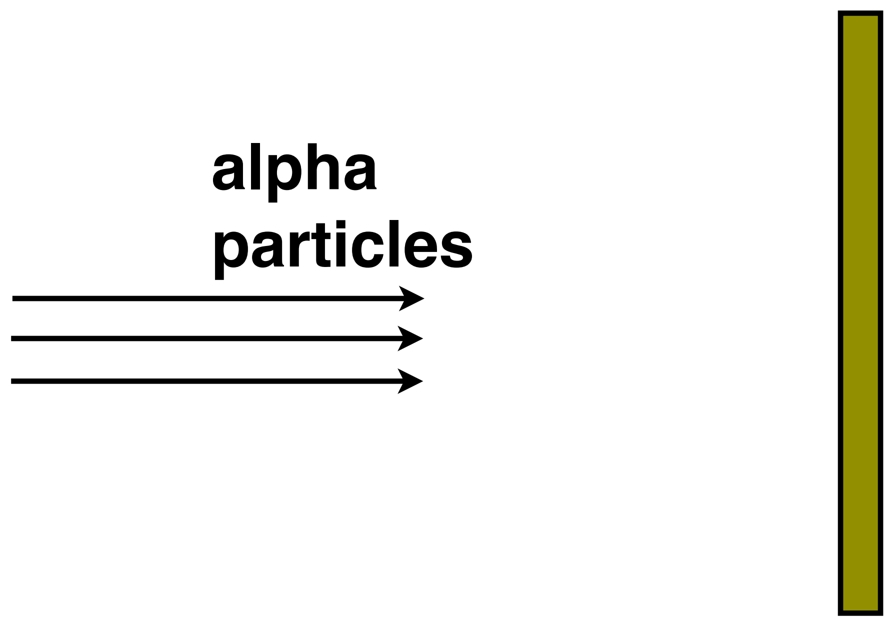
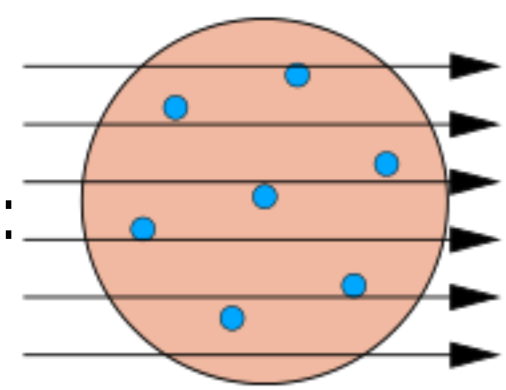
Ernest Rutherford



Prediction of **plum pudding** model:



Positive charge "smeared out"
Little deflection

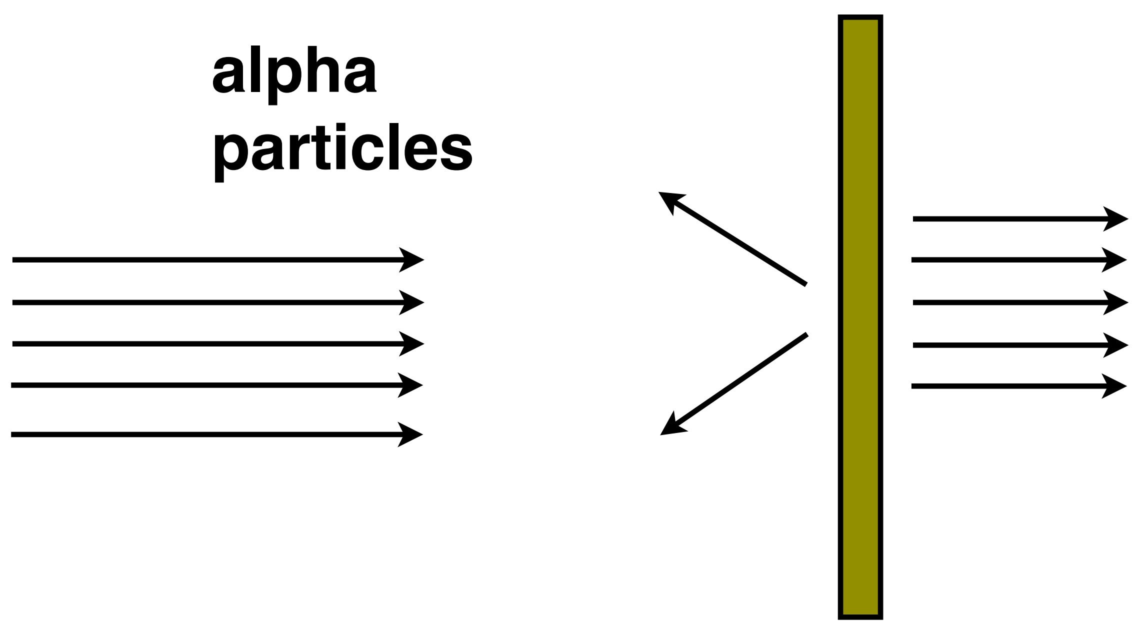
Images from Wikipedia

History of the Atom

- Rutherford: 1907
    - Geiger–Marsden experiment
    - Alpha particles (He^{2+} ions) scattered from Gold foil.

Ernest Rutherford

Observation:



Small number of particles **reflected back!**

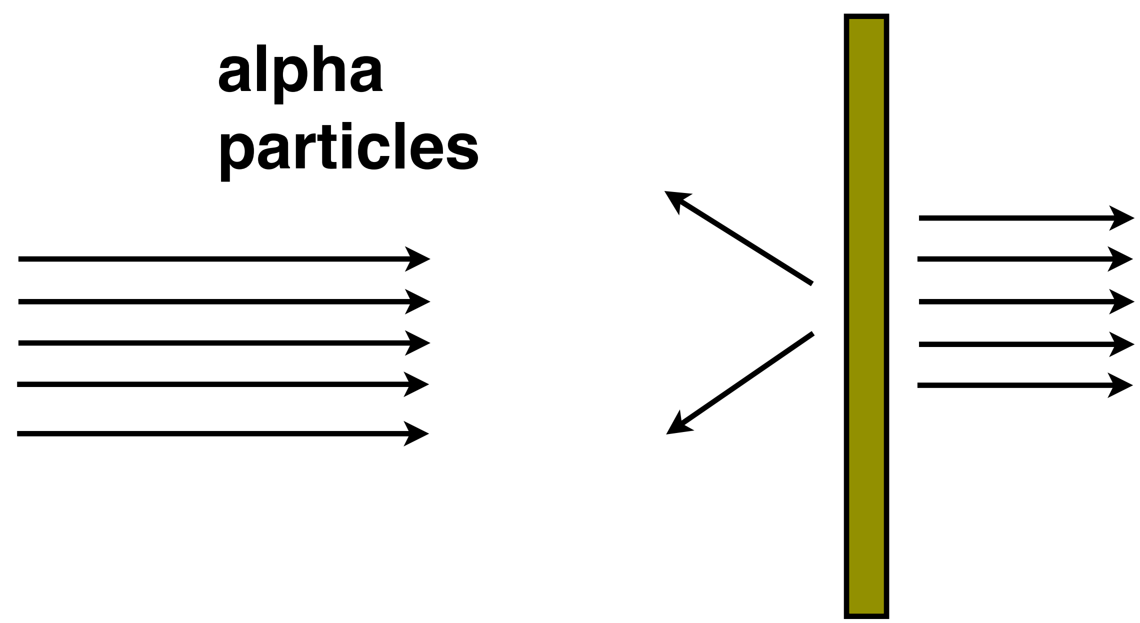
Images from Wikipedia

Quote

- “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.”
  - **Sir Ernest Rutherford**
  - Recalling in 1936 the discovery of the nucleus in 1909, when some alpha particles were observed instead of travelling through a very thin gold foil were seen to rebound backward, as if striking something much more massive than the particles themselves.

History of the Atom

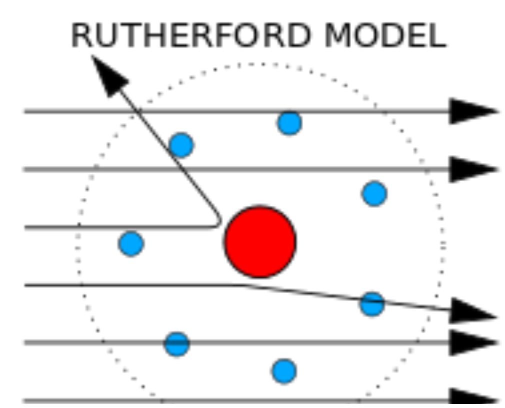
- Rutherford: 1907
    - Alpha particles (He^{2+} ions) scattered from Gold foil.



Au nucleus:
+79 e

Ernest Rutherford

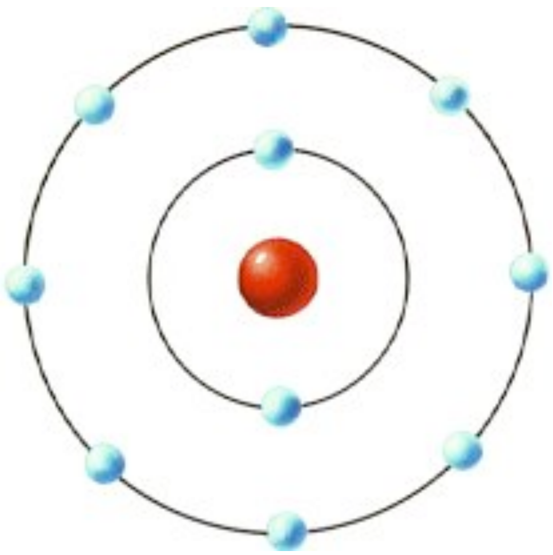
- **Atomic model: “Planetary Model”**
    - **Atom: a tiny positively charged nucleus orbited by electrons.**



Images from Wikipedia

QUIZ

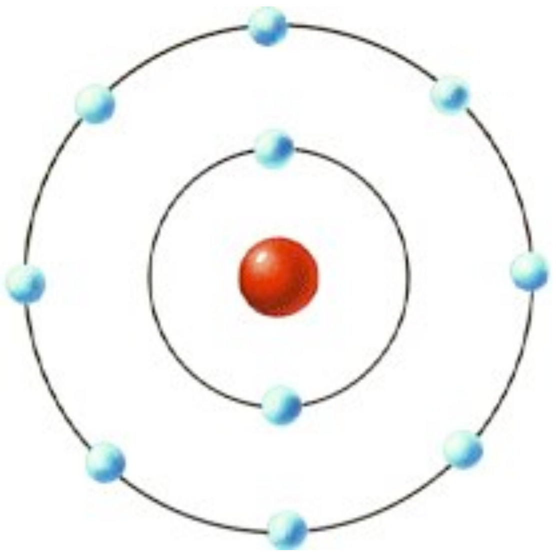
- Rutherford: 1907
  - "Planetary Model"
    - A tiny positively charged nucleus
    - Electrons orbit the nucleus



- The planetary model had some aspects which **contradicted** the known Physics of the time (1907).
- What were they?

Problems with the planetary model

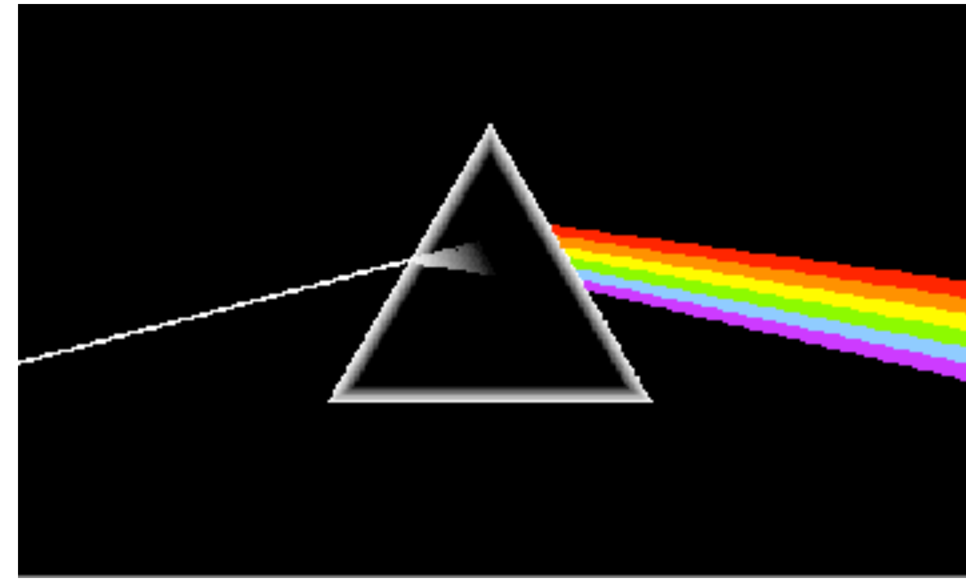
- Rutherford: 1907
  - "Planetary Model"
    - A tiny positively charged nucleus
    - Electrons orbit the nucleus



- **Stability of Matter**
  - **Orbiting electrons** must be **constantly accelerating** (centripetal acceleration).
  - But electromagnetic theory (Maxwell's equations) predict that **accelerating charges** always create **electromagnetic radiation**.
  - Electrons should **lose energy** as they radiate and **spiral** into the nucleus.
- Atomic spectrometry
  - Elements known to have **unique signatures** of emitted light.
  - These spectra **not explained at all** by this model..

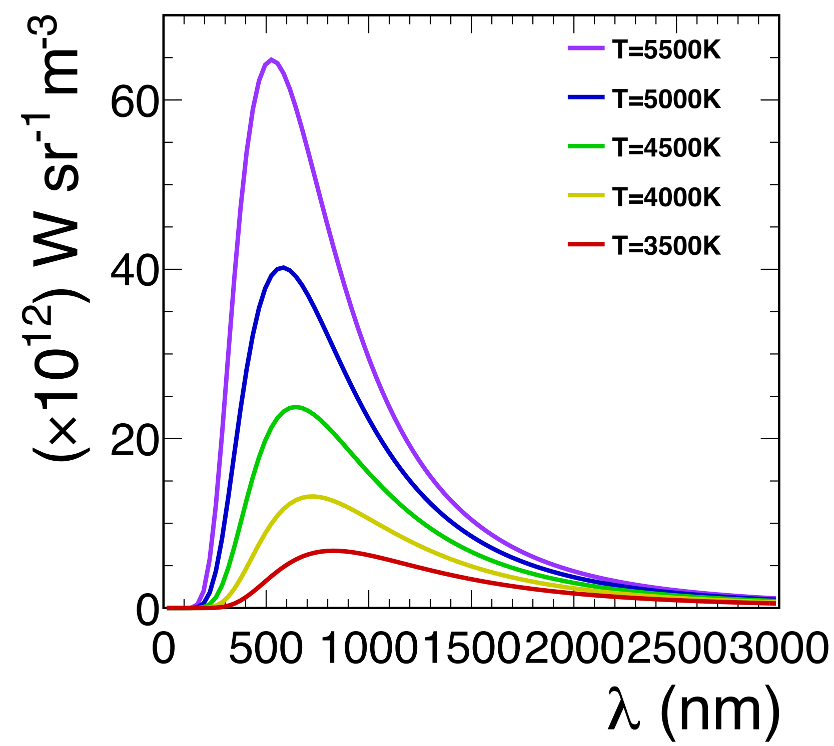
A quick tour of Atomic spectra

- **Prisms** split light into its component frequencies. Key component of a **spectroscope**.
- Two main types of spectra: **absorption spectra** and **emission spectra**.

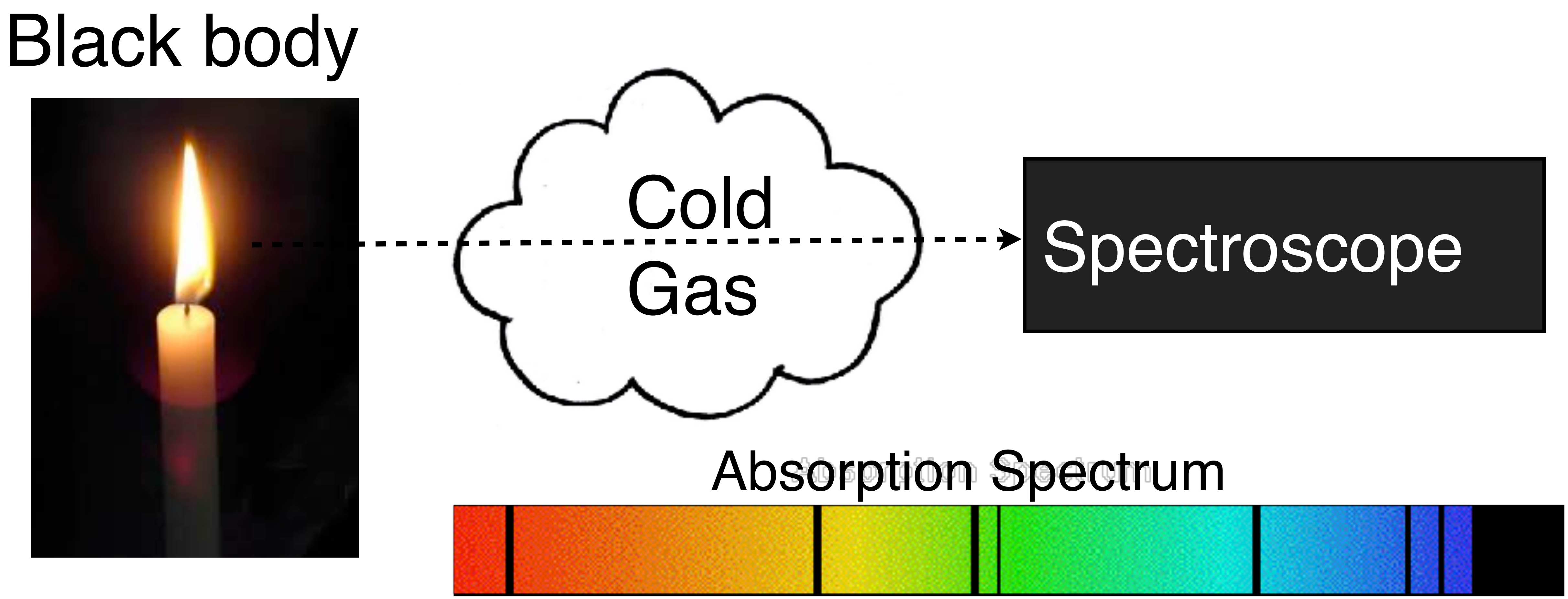


Black Body Emission Spectrum

- Recall the Black Body spectrum.
- Light emitted over **all wavelengths** (Planck Law).



Absorption spectra

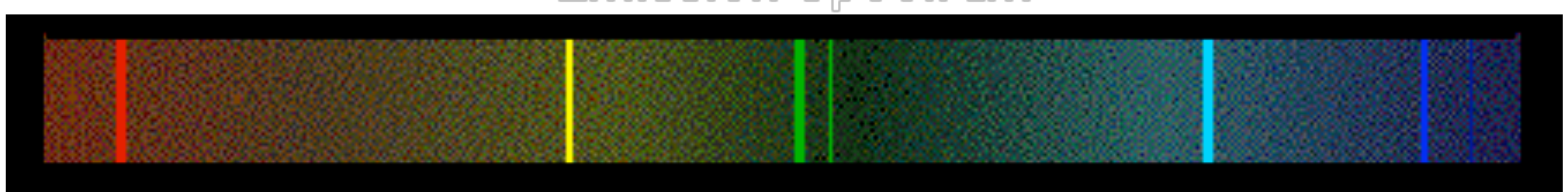


- A black body radiates the over **full spectrum**.
- A **cold gas** placed in front of the light will absorb light, but only absorb **certain frequencies**.
- Viewed beyond the cold gas, the spectrum exhibits **dark lines** at these frequencies.
- For **different gases** we see a **different signature** of lines.
- Lines first observed in solar radiation (Frauenhofer **1814**).

Atomic spectra

Emission Spectra

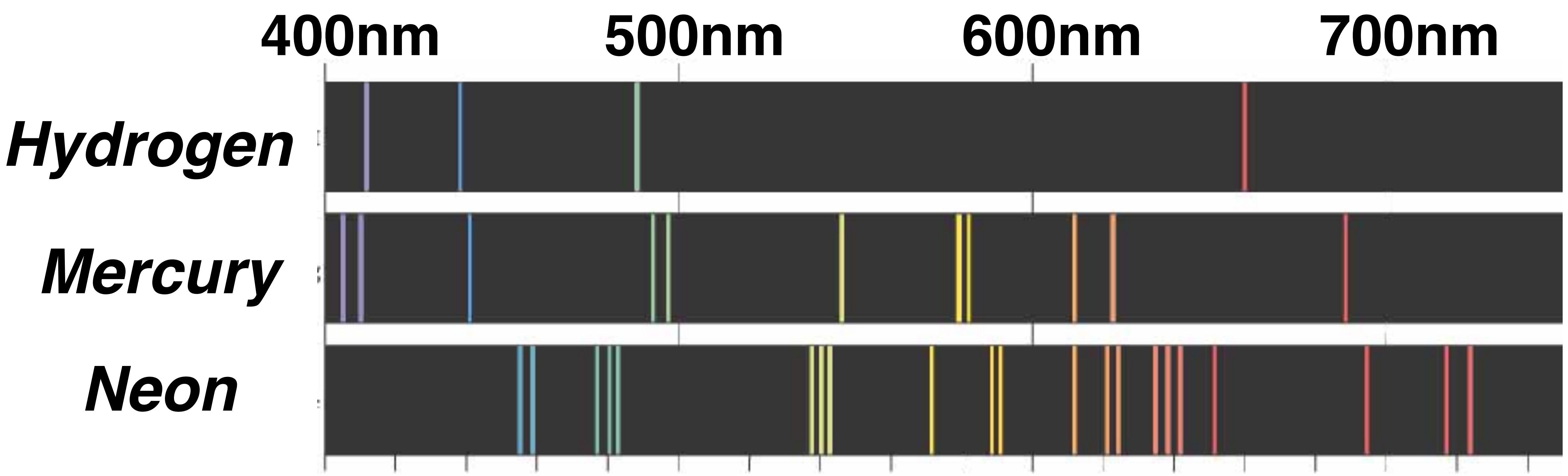
Emission Spectrum



- In **emission spectroscopy**, we heat the gas and look at light emitted by the gas itself.
- This spectrum is **not a continuous black body spectrum**.
- Light is only emitted at **certain frequencies**.
- These are the **same frequencies** absorbed by the gas in **absorption spectroscopy.**

Atomic spectra

- We call the frequencies at which a gas absorbs and emits light its **spectrum**.
- The spectrum differs from element to element, from molecule to molecule.
- It is a **unique signature** which helps us, for example, study the chemical composition of distant stars.

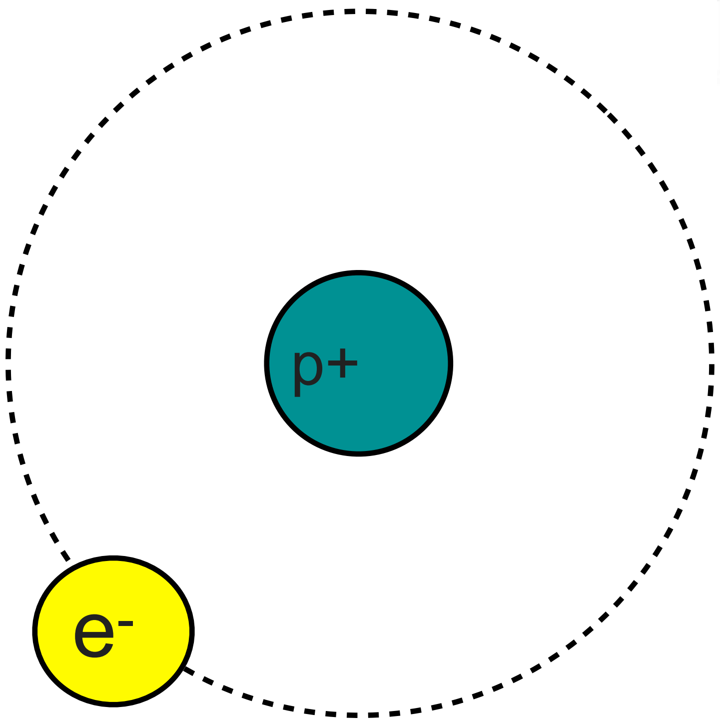


The emission spectra (in visible range) for Hydrogen, Mercury and Neon (from Jewett / Serway, p. 1253).

Spectrum of Hydrogen

- **Hydrogen** was found to have the simplest spectrum, with just 4 lines in the visible spectrum.
- It therefore became the focus of the first **theoretical studies**.

Planetary Model of Hydrogen



- Hydrogen is indeed the **simplest element**, consisting of a nucleus (we now know is a **single proton**) and a **single electron**.

Spectrum of Hydrogen

Balmer series

- In **1885**, Jacob Balmer realised a **remarkably simple** formula can predict the spectrum of **Hydrogen**.

Jacob Balmer

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

for $n = 3,4,5,\ldots,$

where $R_H = 1.1 \times 10^7 \mathrm{m}^{-1}$ (2 s.f.) is now called the Rydberg constant.

n	λ (nm)
3	656
4	486
5	434
6	410
7	396

- Balmer's formula predicts **further** (ultra-violet) **lines** outside the visible region.
- These were later **confirmed** in experiment.
- These spectral lines are now called the **Balmer series**.

Spectrum of Hydrogen

Johannes Rydberg

Balmer Formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$ for $n = 3,4,5,\ldots,$

Rydberg Formula

- In 1888, **Rydberg** proposed a generalisation of Balmer's formula:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$ for $m = 1,2,3,4,5,\ldots,$ and $n = m+1, m+2, \ldots,$

- The **Balmer** series corresponded to the **m=2** case.
- Rydberg's formula predicts many (infinitely!) more spectral lines but none in the visible spectrum, all are **ultraviolet** or **infrared**.
- **None** of the non-visible spectral lines predicted had been observed prior to **1888**.
- But they were subsequently confirmed.

Spectrum of Hydrogen

Rydberg Formula

- Different values of m lead to different families of spectral lines.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$ for m = 1,2,3,4,5,…, and n = m+1,m+2,…,

- In most cases, the families (**series**) of spectral lines (for each value of m) are given names after the lead scientist who verified their existence.

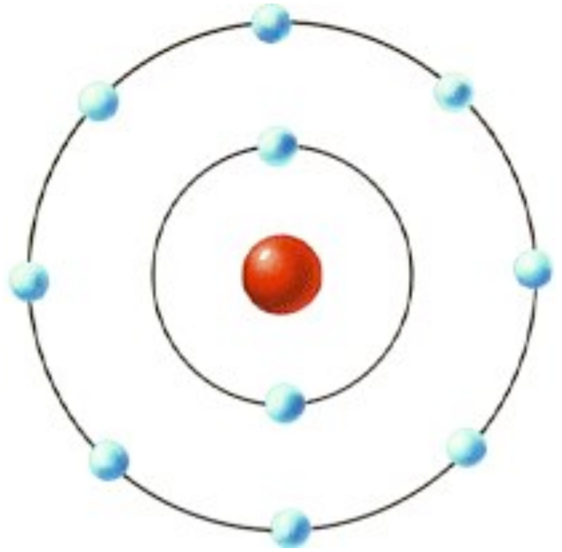
m	Series name	year observed	spectral region
1	Lyman	1914	UV
2	Balmer	1814	visible / UV
3	Paschen	1908	IR
4	Brackett	1922	IR
5	Pfund	1924	IR
6	Humphreys	1953	IR

The challenge of the Rydberg formula

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

for m = 1,2,3,4,5,…,
and n = m+1,m+2,…,

- The Rydberg formula presents a **simple test** of any atomic model. Can the model derive this formula?
- Rutherford's planetary model **resolutely fails!**



- According to classical electromagnetism, orbiting electrons should absorb and emit at **all frequencies**, spiralling in and out as they do so.

The challenge of the Rydberg formula

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

for *m* = 1,2,3,4,5,…
and *n* = m+1,m+2,…

- If we take Planck / Einstein's **quantization of light** on board, this helps us unlock the implications of the Rydberg formula.
- The energy of a photon is

$$E = hf = \frac{hc}{\lambda}$$

- The **specific frequencies** of spectral lines correspond to emission and absorption of photons with a **specific energy**.
- We can understand this if the **energy levels** of the atom are **quantised**, i.e. just like light, the atom is only allowed to take **certain energy values**.
- Each **spectral line** corresponds to a "**jump in energy**" from one "**energy state**" to **another**.

Spectrum of Hydrogen

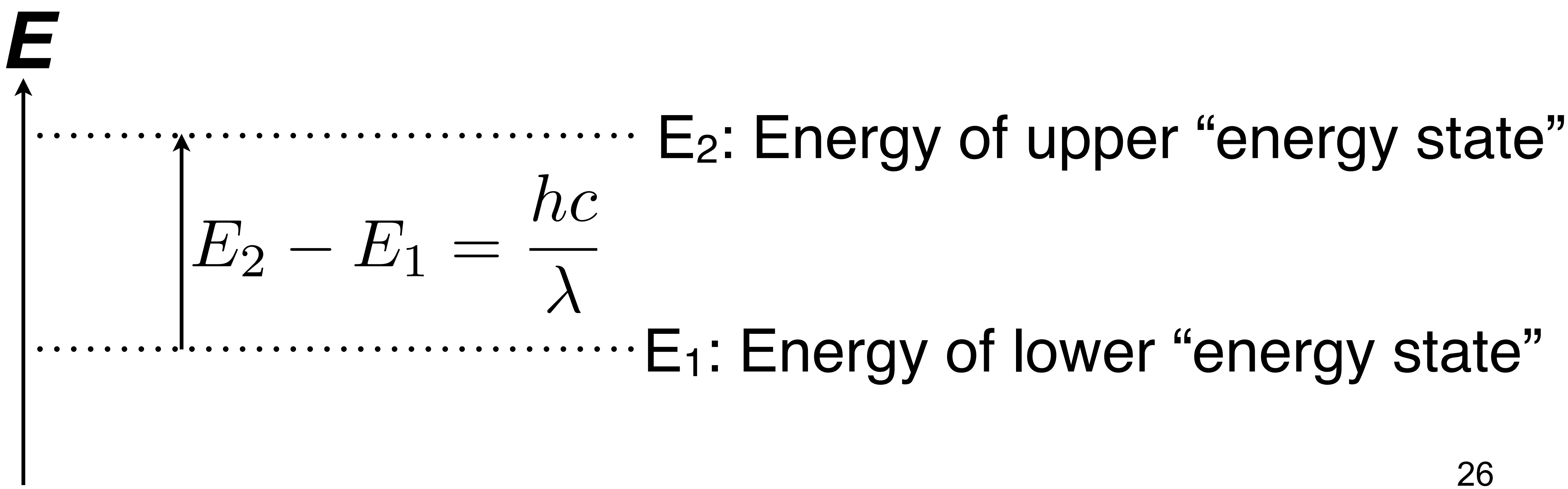
Understanding the Rydberg formula

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

for m = 1,2,3,4,5,…
and n = m+1,m+2,…

$$E = hf = \frac{hc}{\lambda}$$

- Each **spectral line** corresponds to a “jump” from one “energy state” to another.



Understanding the Rydberg formula

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

for *m* = 1,2,3,4,5,…
and *n* = m+1,m+2,…

$$E = hf = \frac{hc}{\lambda}$$

- The Rydberg formula is therefore consistent with the Hydrogen atom possessing "energy states" with energies

$$E_k = -hc\frac{R_H}{k^2}$$

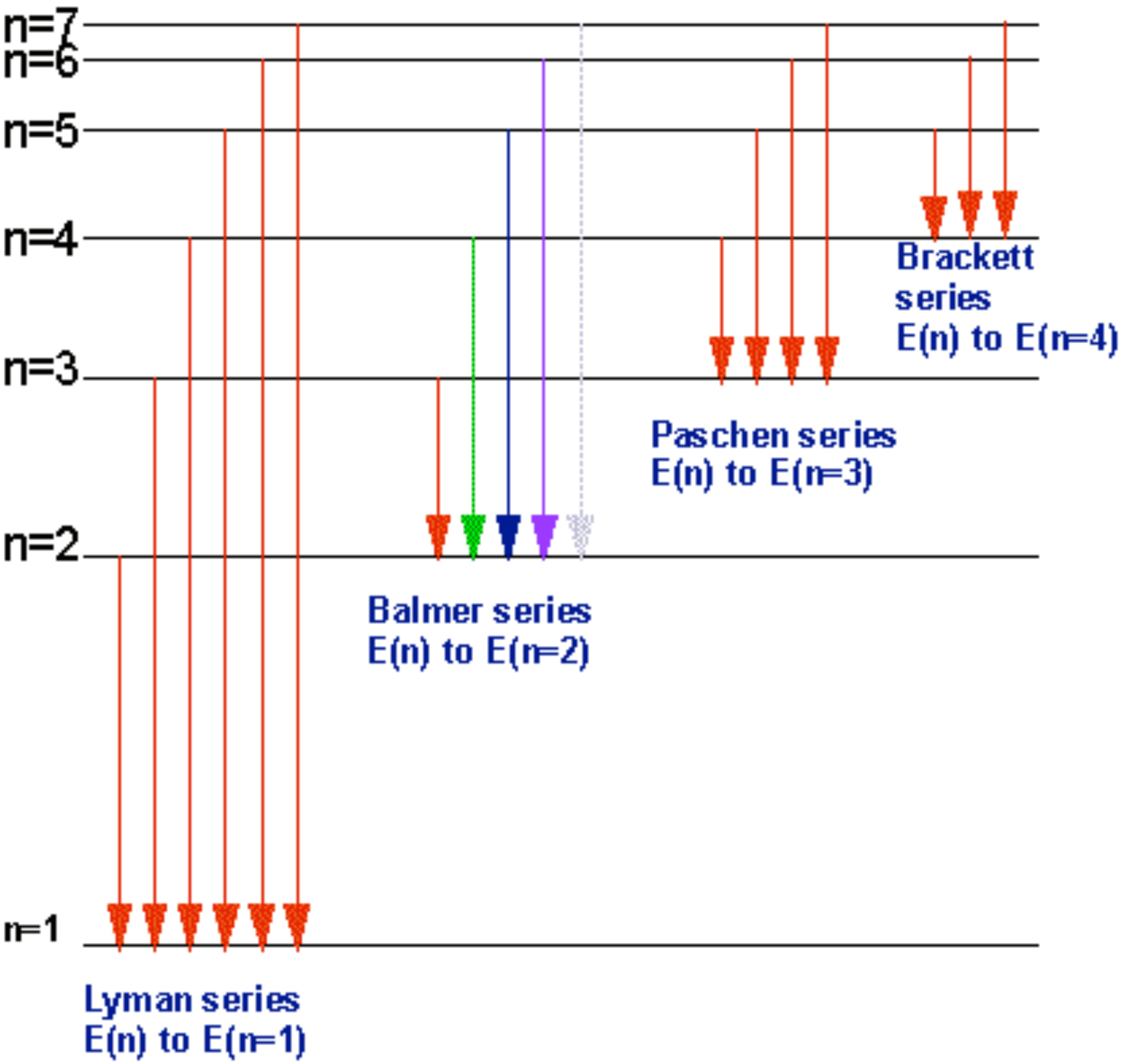
where ***k*** is an integer from 1 to infinity.

- Each Rydberg line represents a transition from energy state **k=n** to state **k=m**

or vice versa.

Spectrum of Hydrogen

The origin of the different series can be clearly seen:

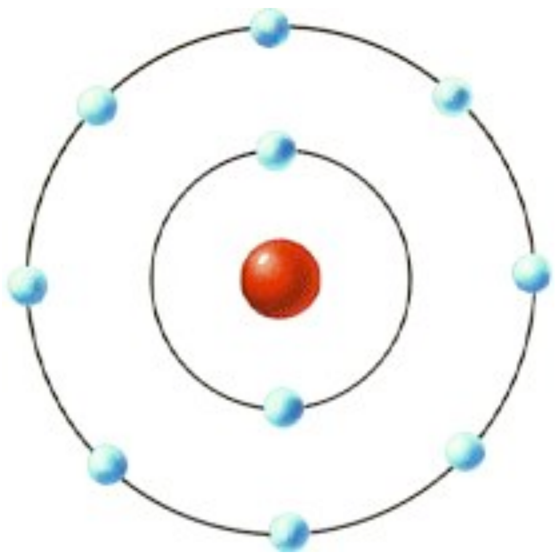


$$\frac{1}{\lambda} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

for $m = 1,2,3,4,5,\ldots$

and $n = m+1, m+2, \ldots$

The Bohr Atom

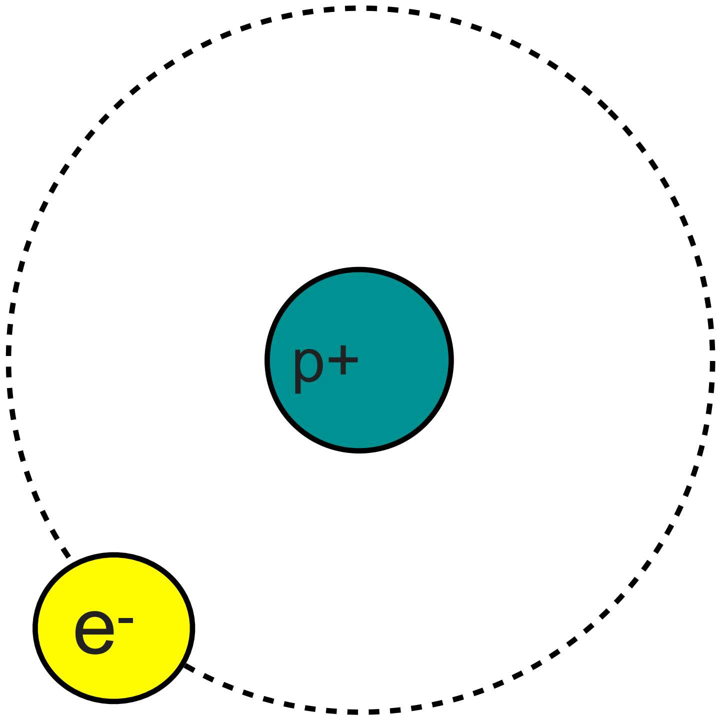


- 1907 - Rutherford's planetary model
  - Best yet model of atomic structure, **but**:
    - **Not** a **stable model** (electrons should radiate and spiral in).
    - Does **not** predict the **Rydberg equation**, or even the existence of spectral lines.
- 1913 - Niels Bohr
  - A new atomic model (the **Bohr model)**.
  - A stepping stone between Rutherford's model and **quantum mechanics**.

Ernest Rutherford

Niels Bohr

The Bohr Atom

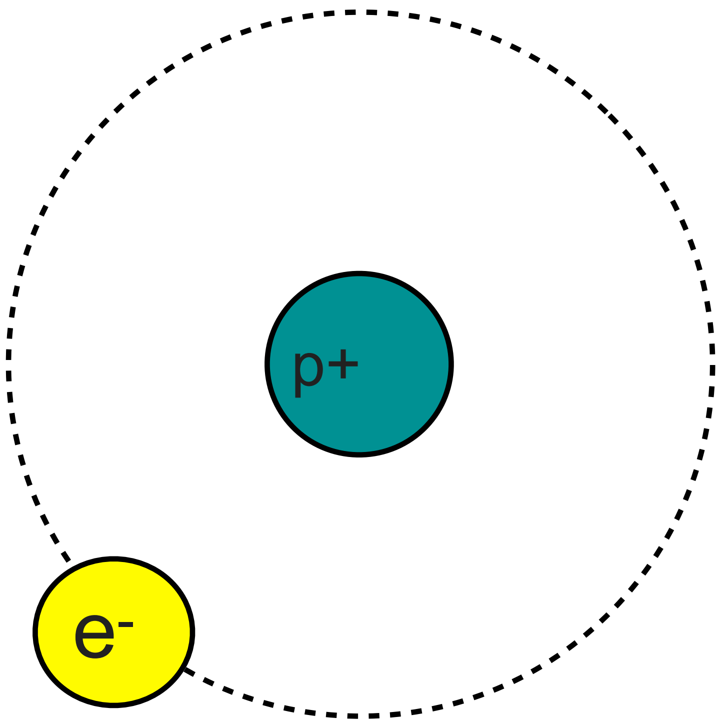


- Starting point: Rutherford's planetary model for **Hydrogen**
  - **Single electron** has a **circular orbit** around the **nucleus**.

Ernest Rutherford

Niels Bohr

The Bohr Atom



- Starting point: Rutherford's planetary model for **Hydrogen**
  - **Single electron** has a **circular orbit** around the **nucleus**.
- But some extra rules:
  - Electron orbits are **quantised.**
    - Only orbits of **specific radius** allowed.
  - Bohr devised a quantisation rule based on **angular momentum.**

Ernest Rutherford

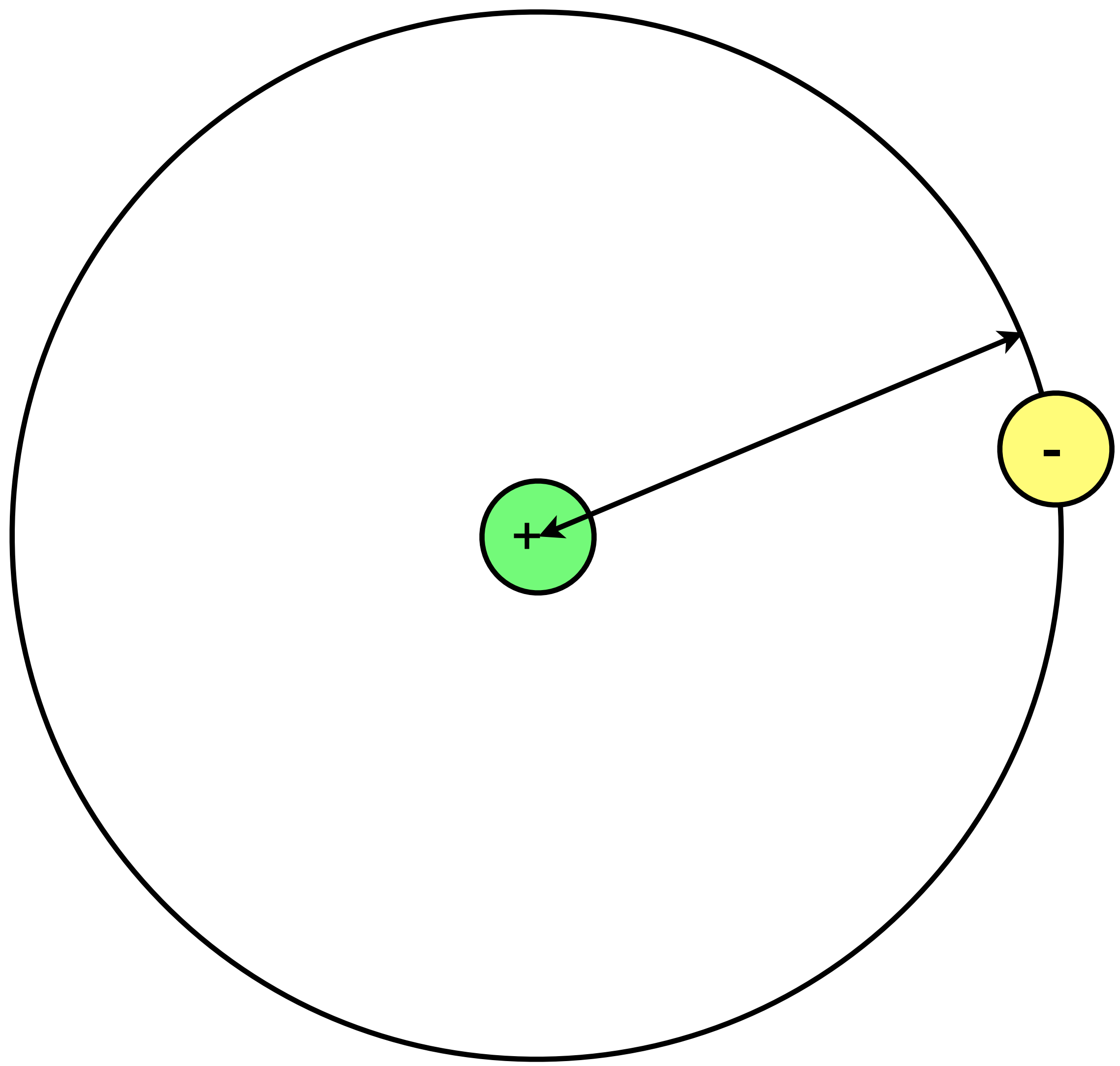
Niels Bohr

Straw poll

Have you studied the electrostatic Coulomb potential before?

Have you
studied circular
motion before?

The Bohr Model



– 1. Electrons travel in **stable** circular orbits.

– 2. Orbits are **quantised**. The only allowed orbits satisfy an **angular momentum rule:**

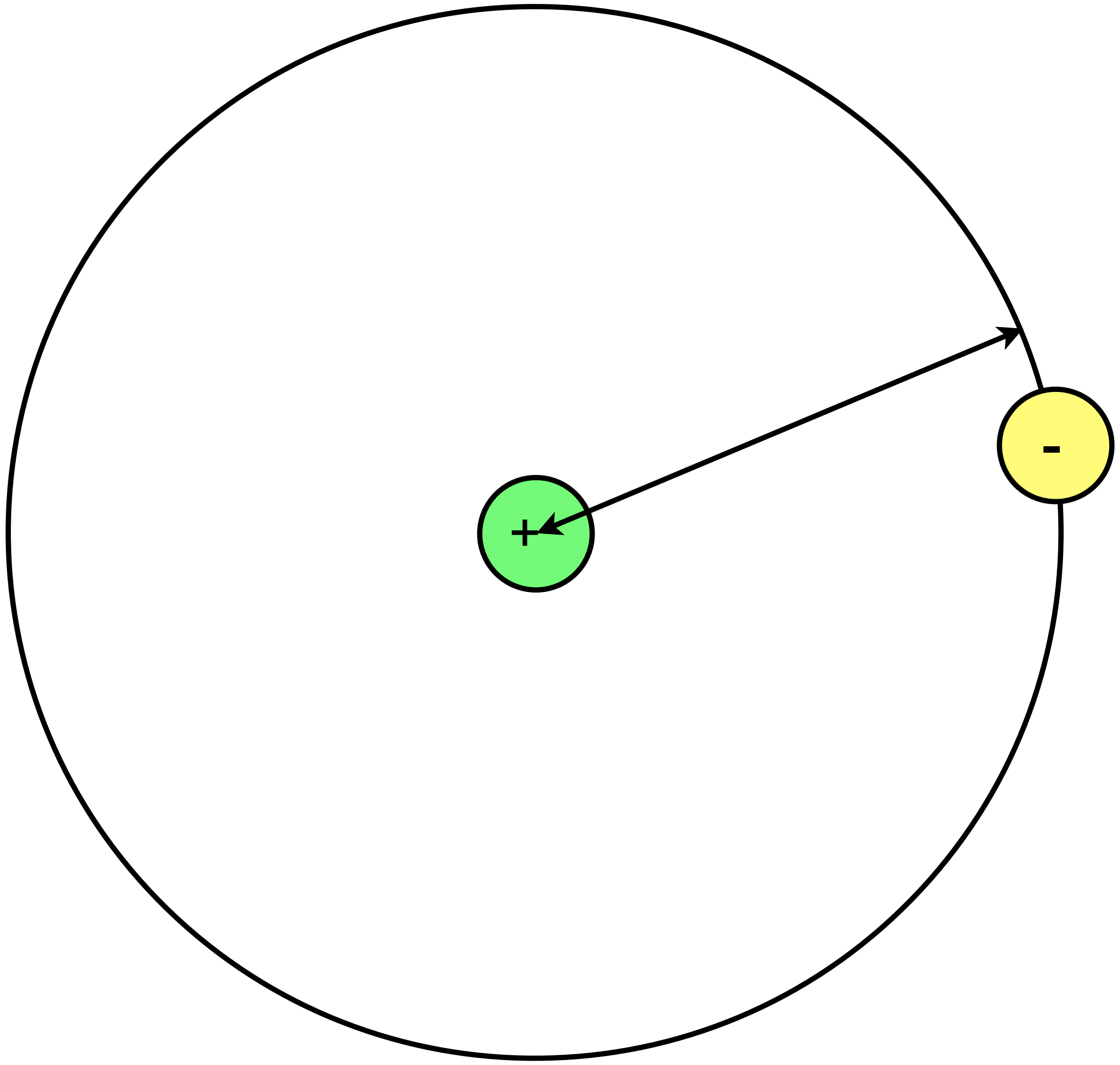
$$l = mvr = \hbar n = \frac{h}{2\pi} n$$

where ***n*** = 1,2,3,…

– 3. Electrons in an orbit **do not** emit light due to their **acceleration**, and their orbit does not decay.

– 4. Electrons may change orbits by **absorbing** or **emitting** a photon of **equal energy** to the **energy difference** between the orbits.

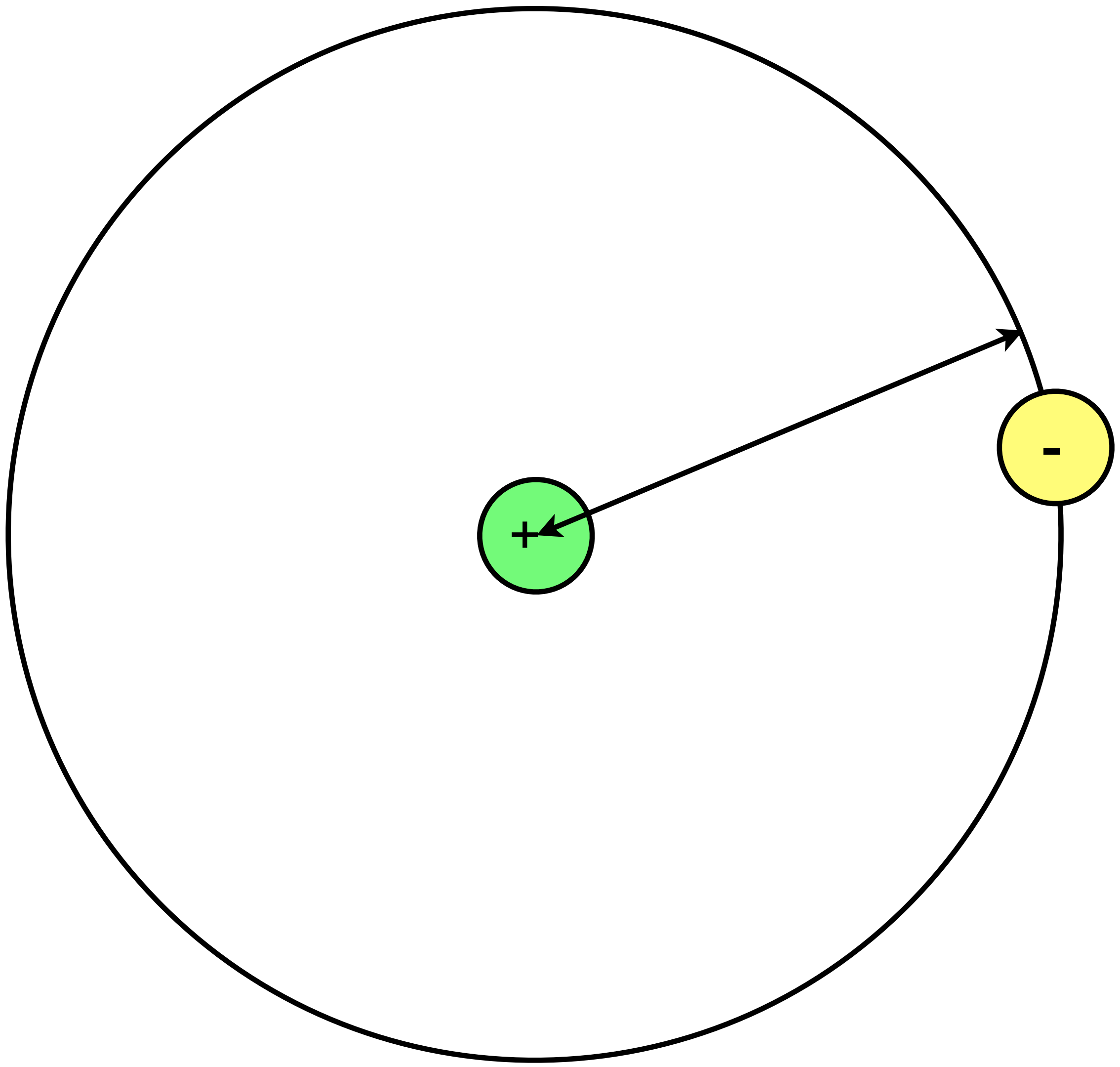
The Bohr Model



– First let's consider the **radius** of orbits ***r*** in Bohr's Model***.***

Hand-written Calculations

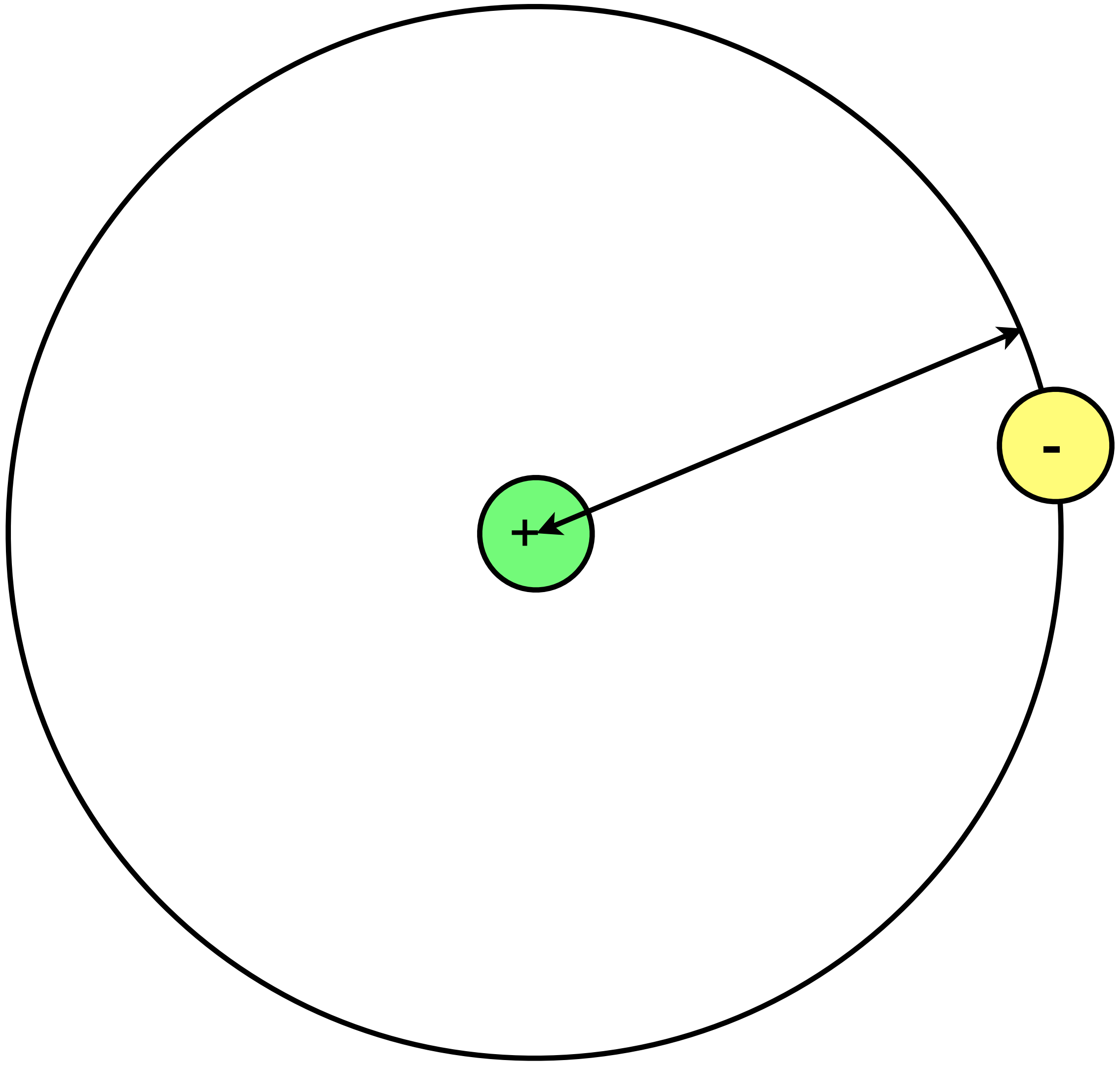
The Bohr Model



– Now let's consider the **energy** of the orbits in Bohr's Model.

Hand-written Calculations

The Bohr Model



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

where n = 1,2,3,…

– Using this **angular momentum quantisation rule** together with the classical mechanics of a charged particle in a circular orbit, we derived:

– Orbital radius:

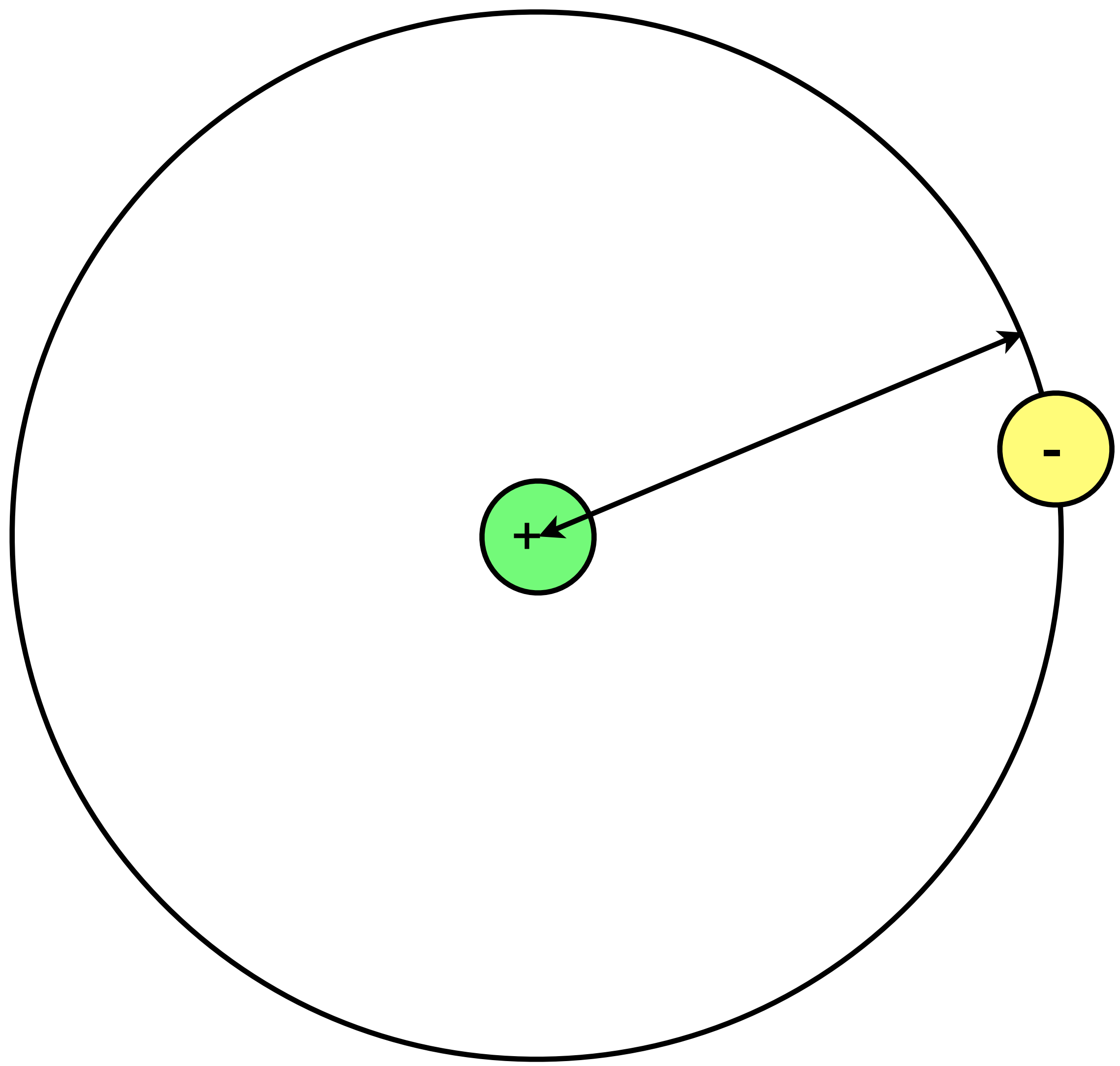
$$r_n = a_0 n^2$$

– where a_0 is the **Bohr radius**

$$a_0 = \frac{\hbar^2 (4\pi\epsilon_0)}{me^2}$$

- which depends only on constants of nature:
  - **hbar** (Planck's constant), **epsilon$_0$** (permittivity of free-space), **m** (electron mass) and **e** (electron charge).

The Bohr Model



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

where n = 1,2,3,…

– We also used it to derive an **energy** for each allowed orbit (i.e. each value of n).

$$E_n = -\left(\frac{1}{2}\frac{1}{4\pi\epsilon_0}\frac{e^2}{a_0}\right)\frac{1}{n^2}$$

$$= -\frac{2.2 \times 10^{-18}}{n^2} \text{ Joules}$$

$$= -\frac{13.6}{n^2} \text{ eV}$$

- which precisely coincides with the predictions of **Rydberg's formula** plus **Planck's** photon energy:

$$E_n = -\frac{hcR_H}{n^2} \approx -\frac{2.2 \times 10^{-18}}{n^2} \text{ Joules}$$

The Bohr Model

– **Successes of the Bohr Model**

- Atoms are **stable** (stable orbits built in to the model).
- The **Rydberg formula** for spectral lines can be **fully derived**.
- And the **Rydberg constant** expressed in terms of **fundamental constants.**
- **Bohr radius** gives a “size scale” to atoms (which is a useful order of magnitude approximation).
- Bohr model gives an **“intuition”** to our quantum atomic models.

The Bohr Model

- **Failures of the Bohr Model**
  - Only works for **Hydrogen**. Generalised (with some but limited success) by Sommerfeld.
  - Model is **adhoc** - not based on any underlying theory. No explanation or justification for axioms.
    - Important point - Bohr model is **not quantum mechanics!**
  - Experiments show that **some predictions** of Bohr model are incorrect.
    - e.g. **finer features** of atomic spectra (e.g. line splittings) seen in modern experiments.
    - **angular momentum** of Hydrogen ground state is **zero**, not hbar.
    - Electron is **not** a **classical particle**!

The Bohr Model

– Beyond the Bohr Model

- The Bohr model is a **hybrid**, a **stepping stone**.
- It is built on **classical physics**, but with some quantum elements (e.g. **energy quantisation**).
- To find a better atomic model, we need to leave behind **classical physics** altogether.
- We need a new theory - **quantum mechanics**!

Summary of Part 2

- We saw how the development of the pre-quantum models of the atom, from **Democritus** to **Bohr**.
- **Atomic spectroscopy** provided the key test. No models prior to Bohr could derive **Rydberg's formula**.
- **Bohr model** could do so - but it had **many failings**.
- To do **better** than Bohr,
  - to develop a **modern theory** of the atom compatible with **all** spectroscopic predictions and other experiments
  - we need a new theory - **quantum mechanics**.