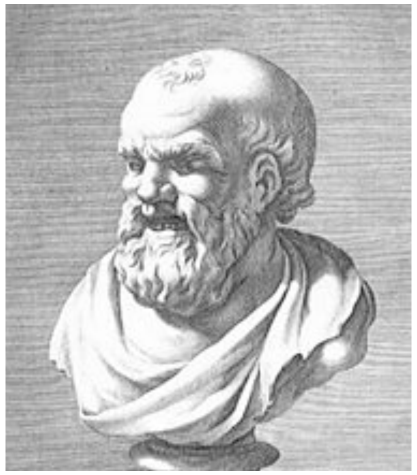
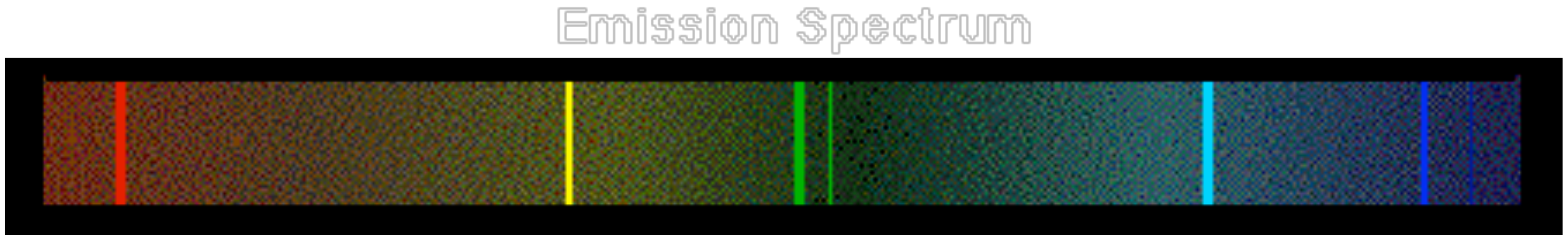
# Part 2: Atomic theory from 400 BC to 1913

# Today's Lecture

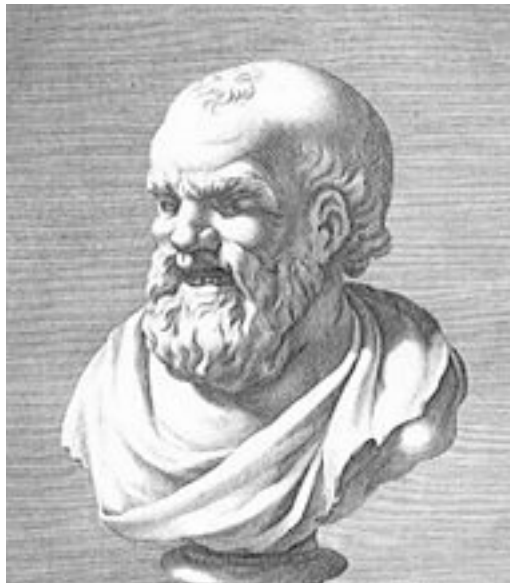
- **Pre-quantum Atomic Models** *(from Democritus 433 A.D. to Bohr 1913 )*



- **Atomic Spectra** *(unique signatures of the elements)*



# 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

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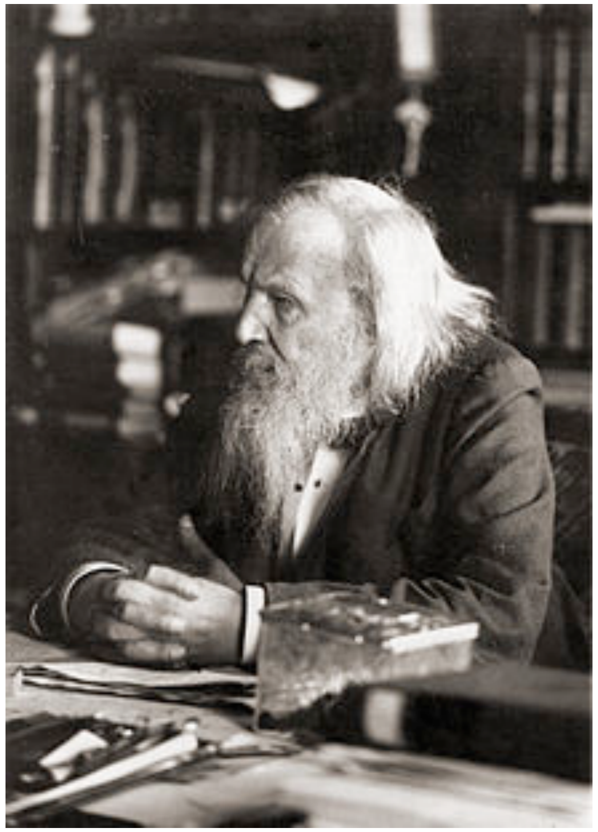
# History of the Atom



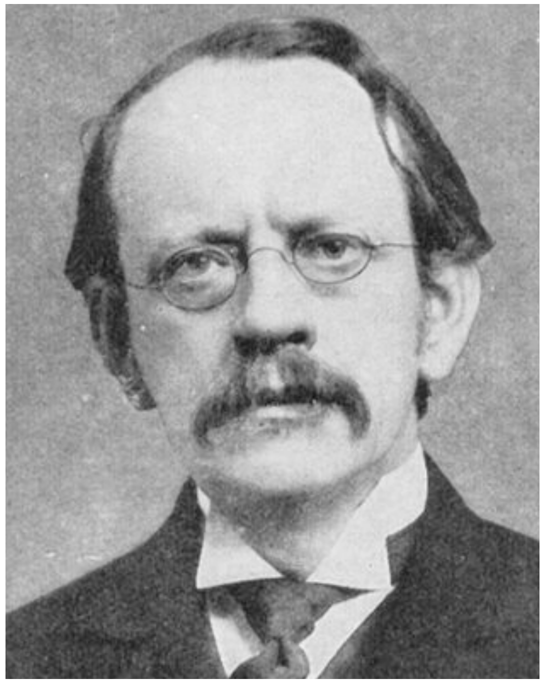
Dimitri Mendeleyev

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

| 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

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

Fig. 2.

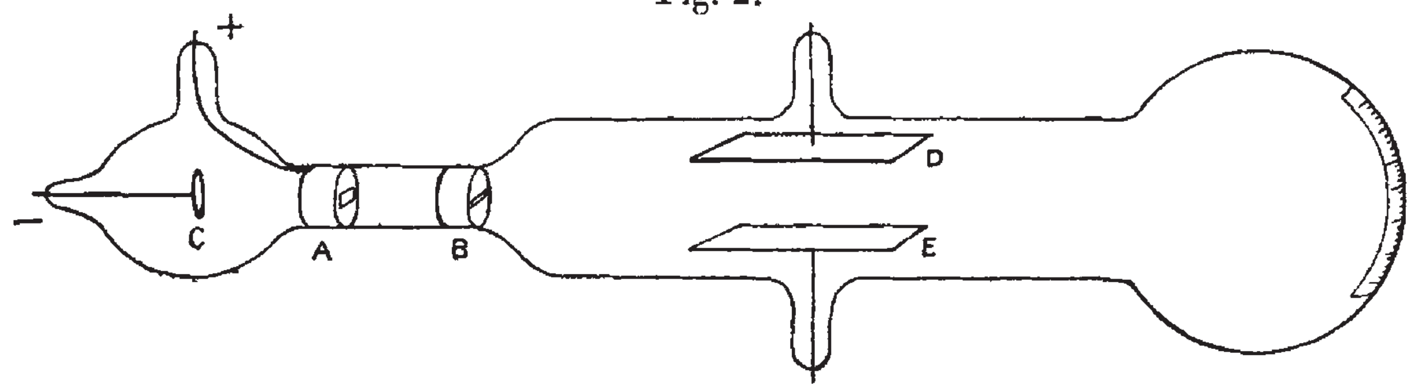
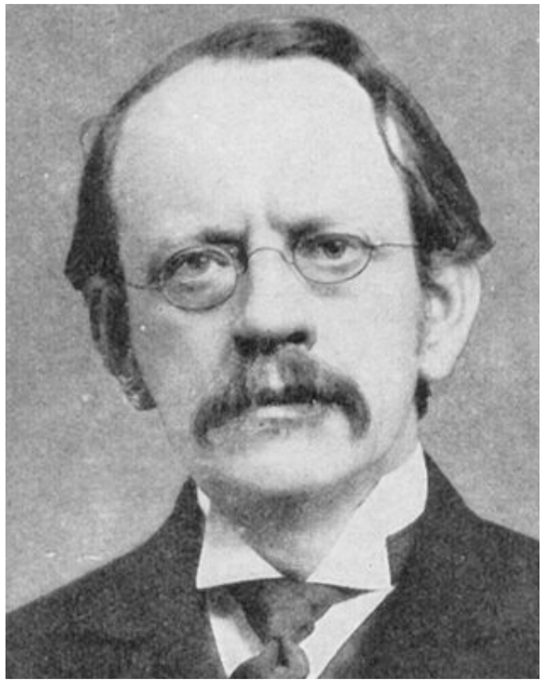



Figure: J.J. Thompson, Philosophical Magazine, 1897.

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

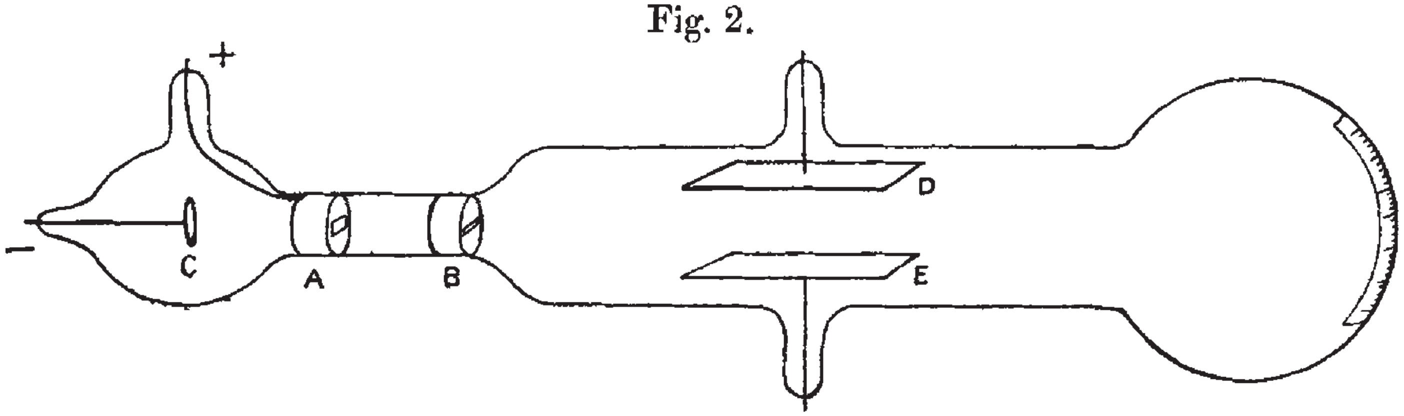
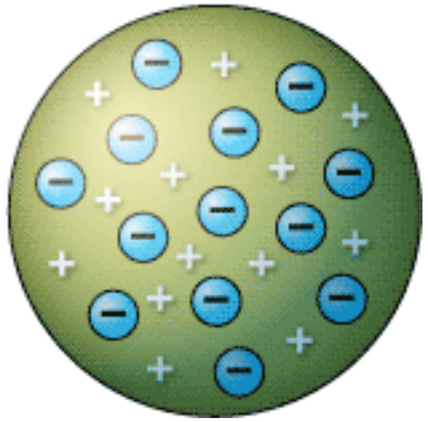



Figure: J.J. Thompson, Philosophical Magazine, 1897.

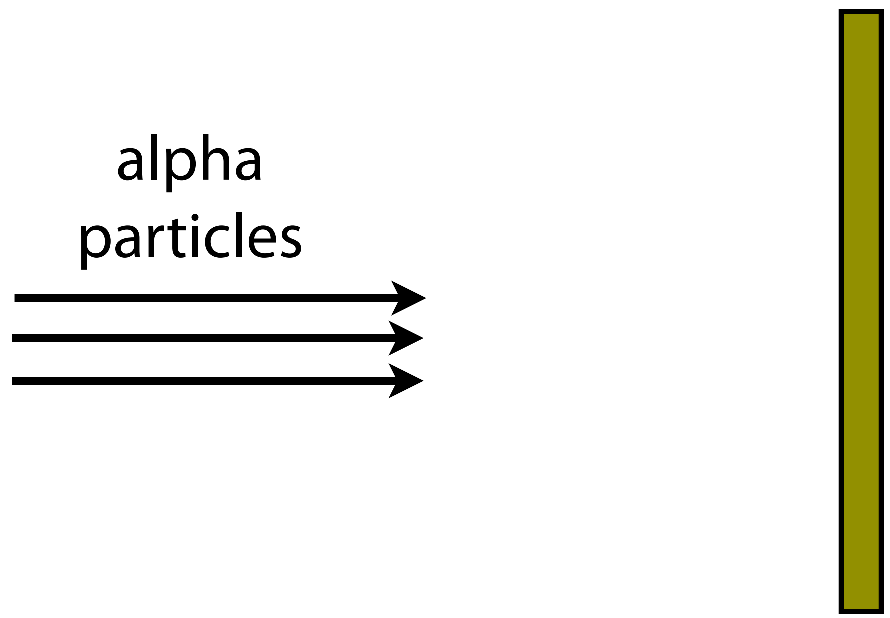
- The plum pudding atomic model:
  - Atoms **neutrally charged**, but can release negative **electrons**.
  - So atoms are a "plum pudding" structure of electrons surrounded by positively charged "liquid".



# History of the Atom

Ernest Rutherford

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




Images from Wikipedia

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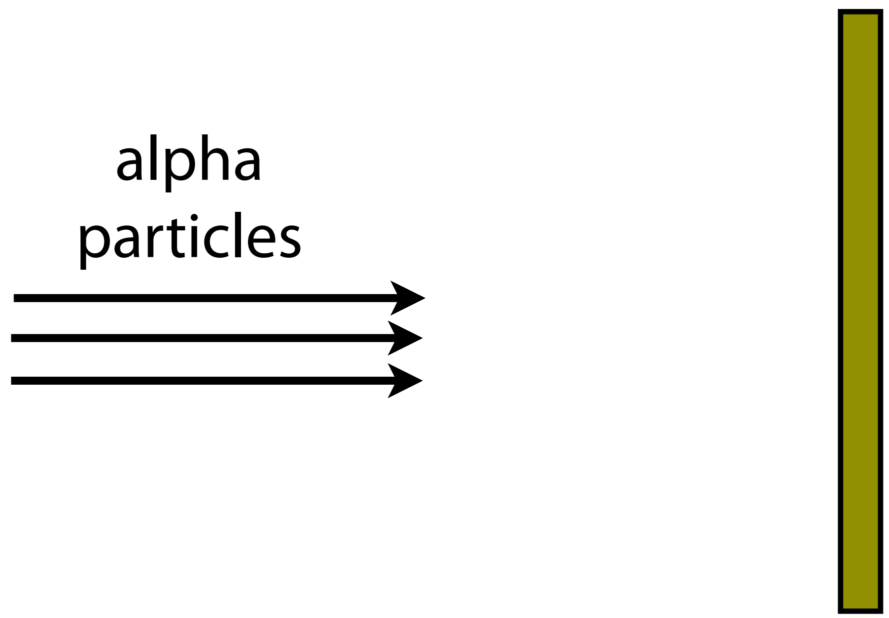
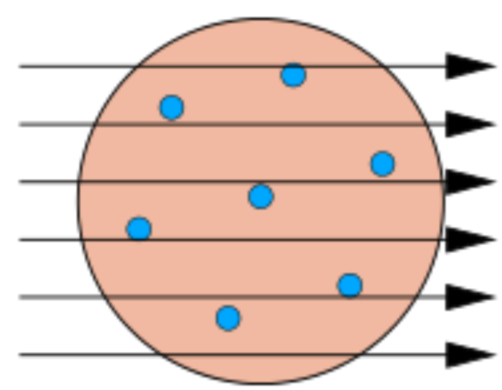



**Prediction** of **plum pudding** model:



*Positive charge*
*"smeared out"*
*Little deflection*

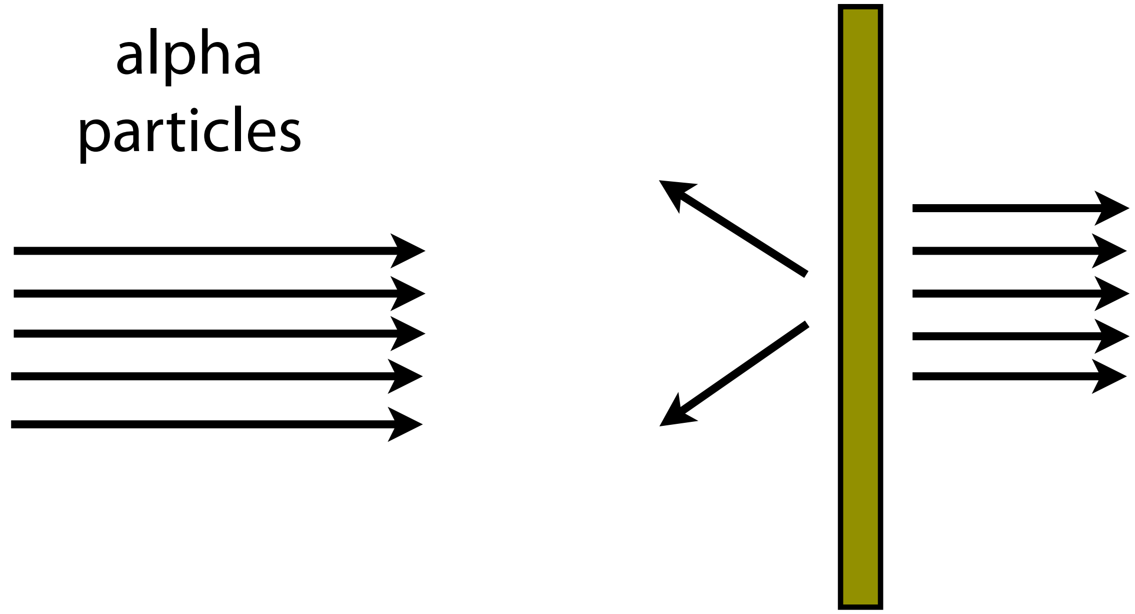
Images from Wikipedia

# History of the Atom

Ernest Rutherford

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

**Observation:**



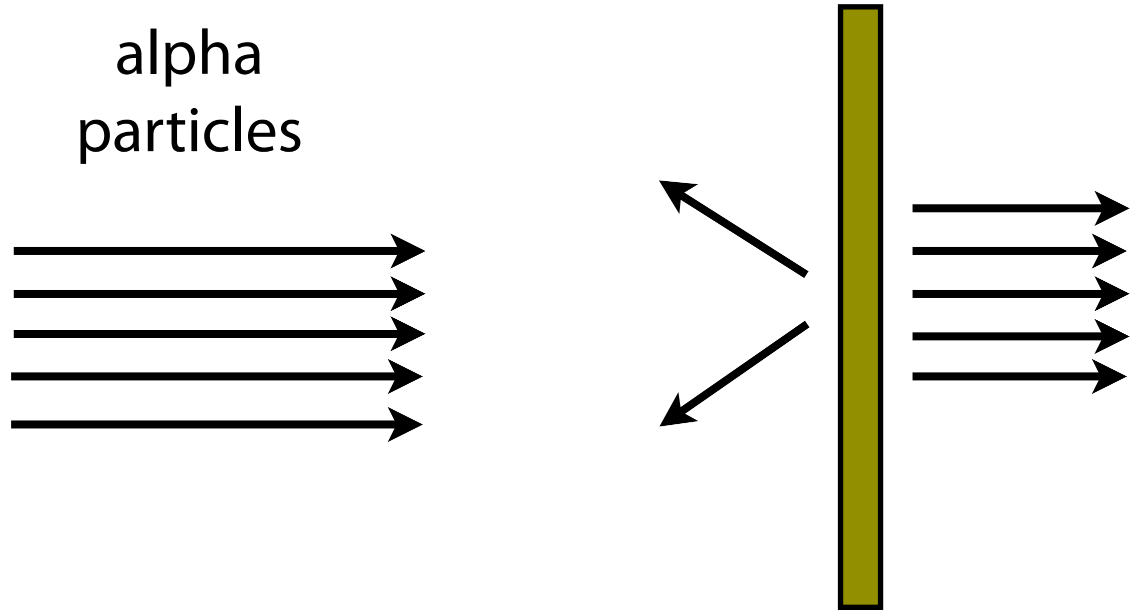

*Small number of particles* **reflected back!**

Images from Wikipedia

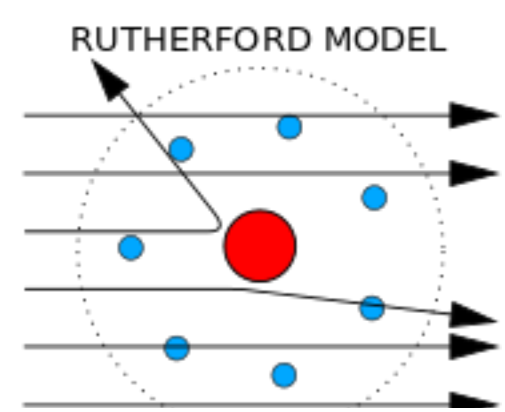
# History of the Atom

Ernest Rutherford

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



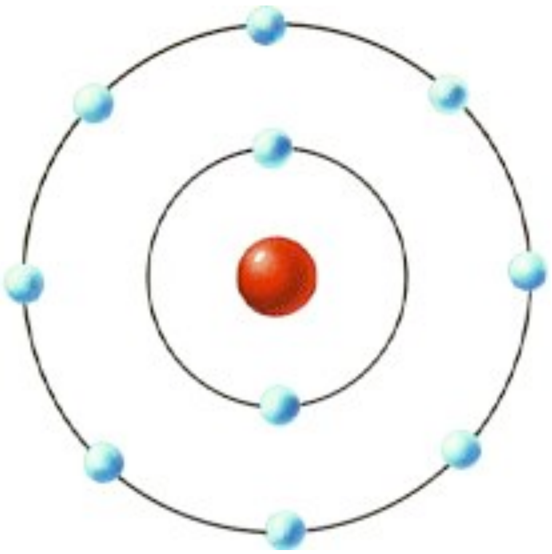

**Au nucleus:**
+79 e




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

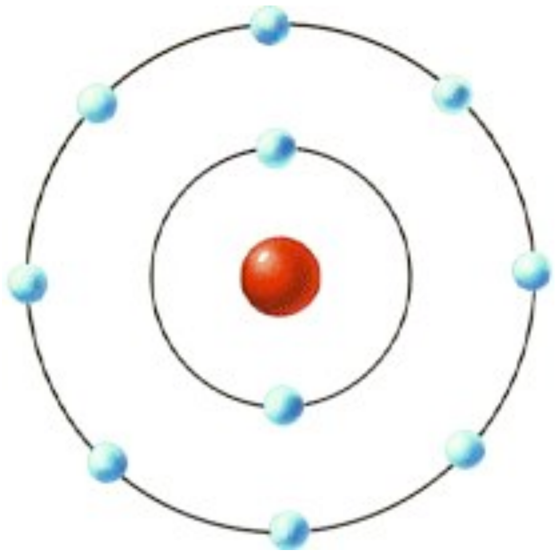
Images from Wikipedia

# QUIZ



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

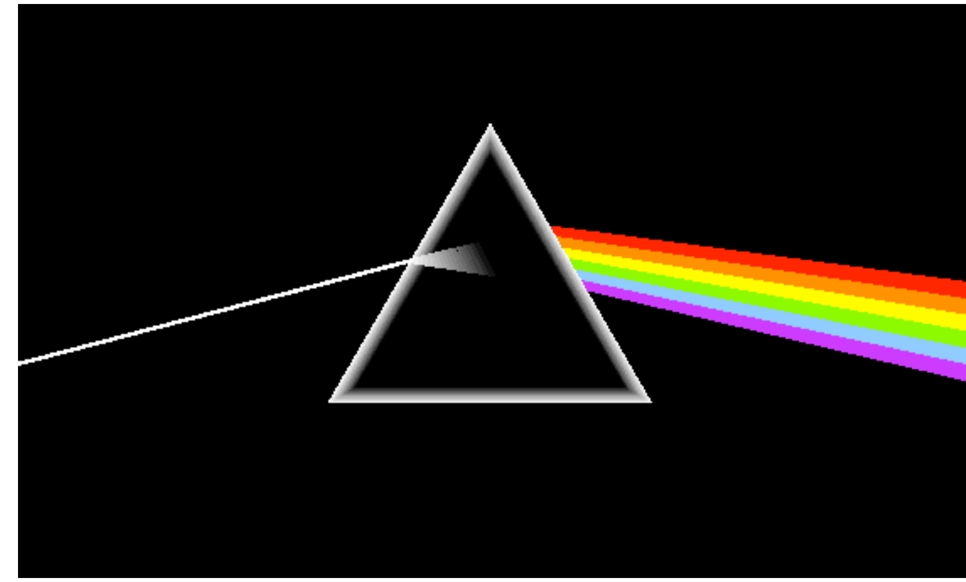
# Problems with the planetary model



- **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..

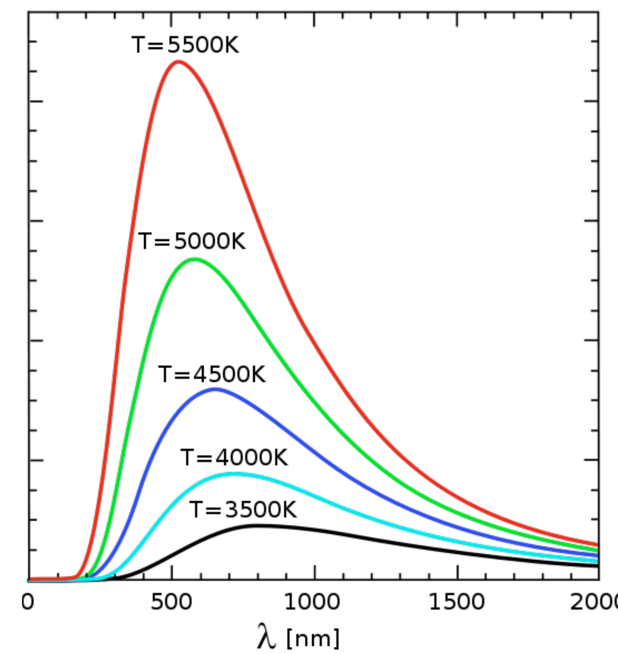
# A quick tour of Atomic spectra

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



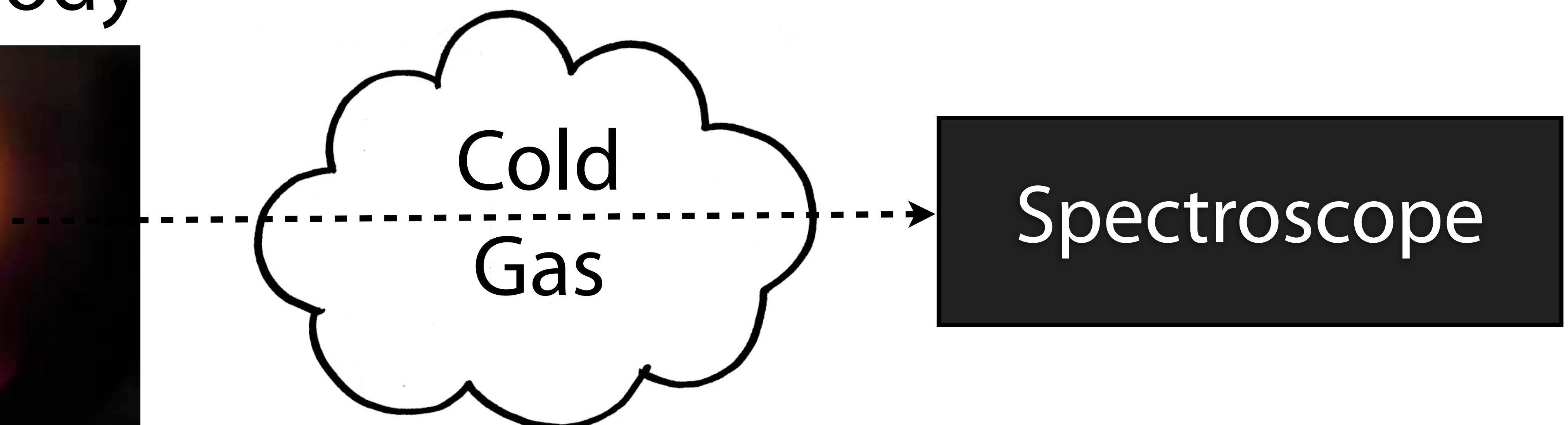
**Black Body Emission Spectrum**

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

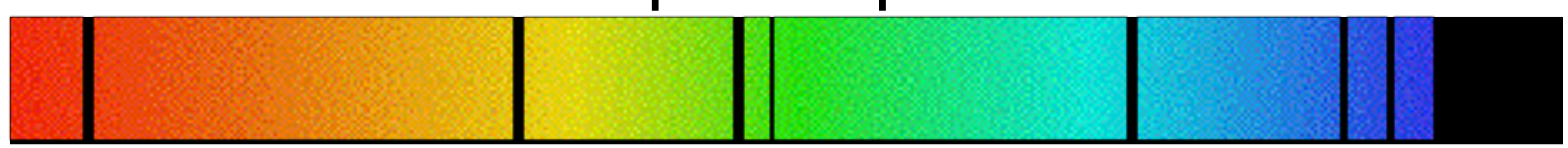



# Absorption spectra

Black body



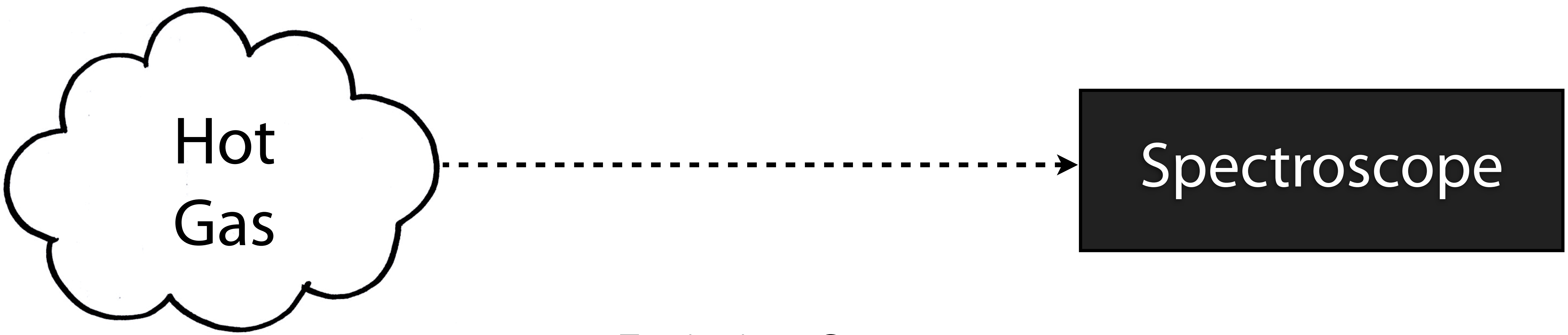

Absorption Spectrum



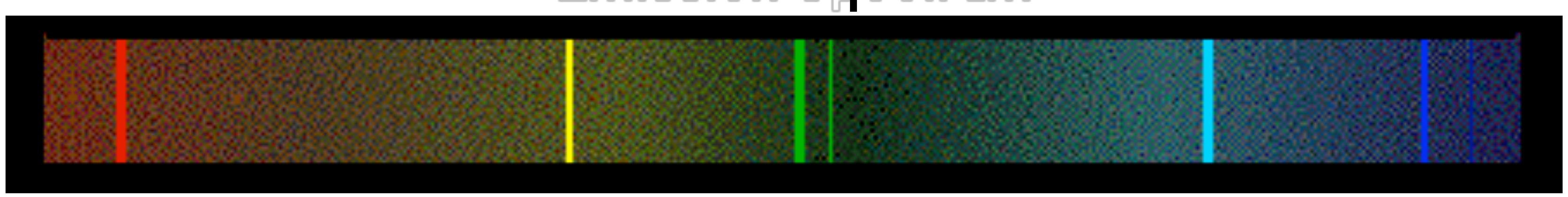
- A black body radiates the over **full spectrum.**
- A **cold gas** placed in front of the light will absorb light, but only absorb **certain frequencies**.
- Viewed beyond the cold gas, the spectrum exhibits **dark lines** at these frequencies.
- For **different gases** we see a **different signature**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

# Atomic spectra

## Emission Spectra



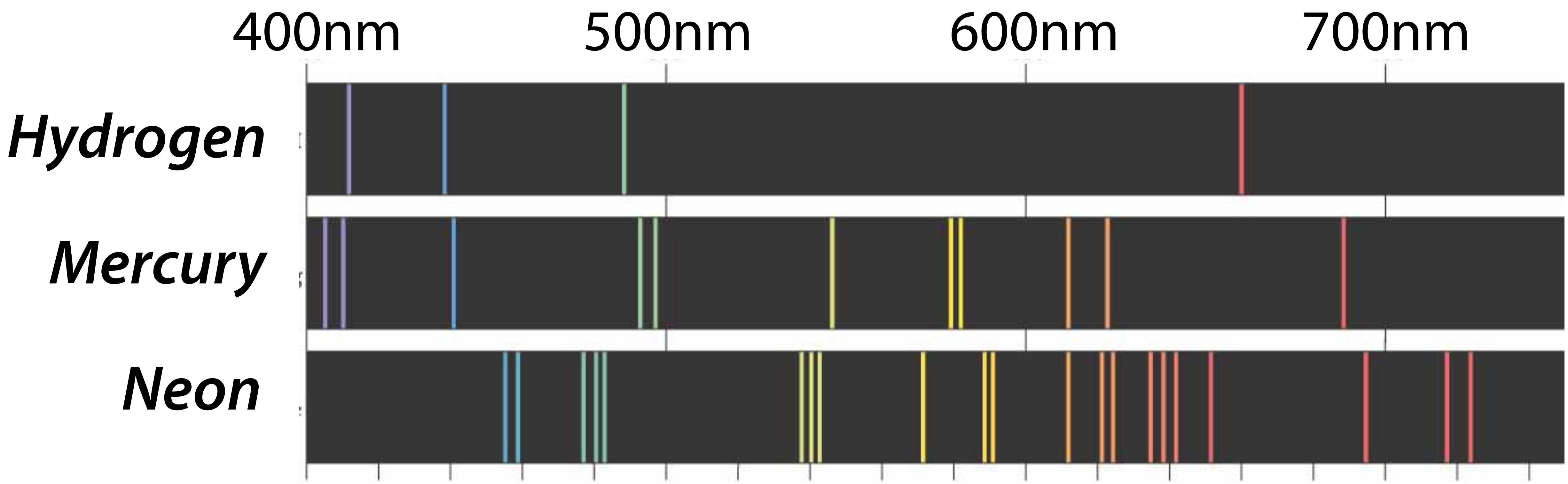

Emission Spectrum



- 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.



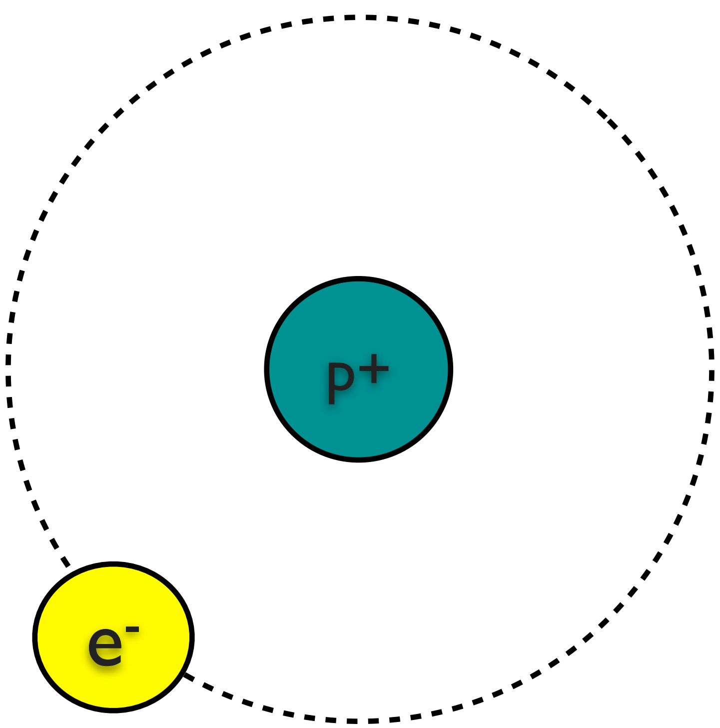

The emission spectra (in visible range) for Hydrogen, Mercury and Neon (from Jewett / Serway, p. 1253).

# 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**.

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# Spectrum of Hydrogen

## Balmer series

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

Jacob Balmer


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

where $R_H = 1.1 \times 10^7 \mathrm{m}^{-1} \ (2 \text{ s.f.})$ 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,…,

## 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,…,
and ***n*** = m+1,m+2,…,

- 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 **all** 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.

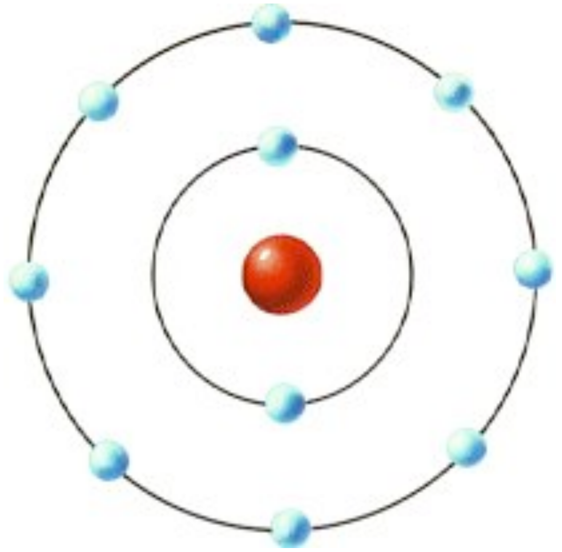
| ***m*** | Series name | year observed | spectral region |
|---|---|---|---|
| 1 | Lyman | 1914 | UV |
| 2 | Balmer | 1814 | visible / UV |
| 3 | Paschen | 1908 | IR / microwave |
| 4 | Brackett | 1922 | microwave |
| 5 | Pfund | 1924 | microwave |

# 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

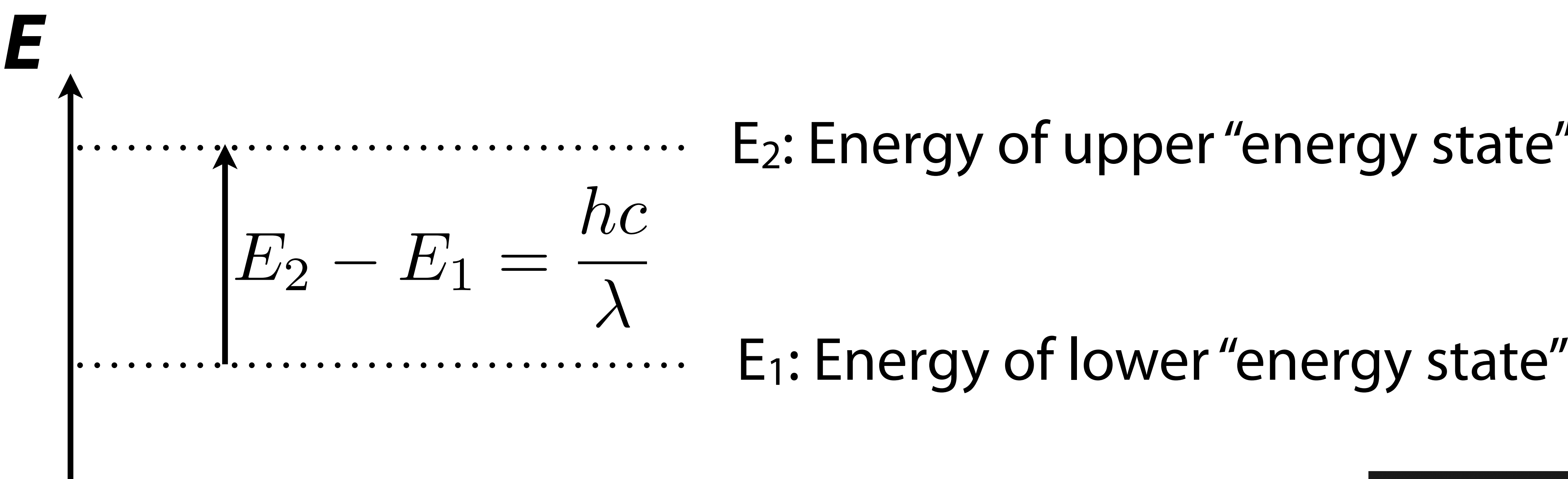
## Understanding the Rydberg formula

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

for $\boldsymbol{m}$ = 1,2,3,4,5,…
and $\boldsymbol{n}$ = m+1,m+2,…

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

- Each **spectral line** corresponds to a “jump” 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,…

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

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

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

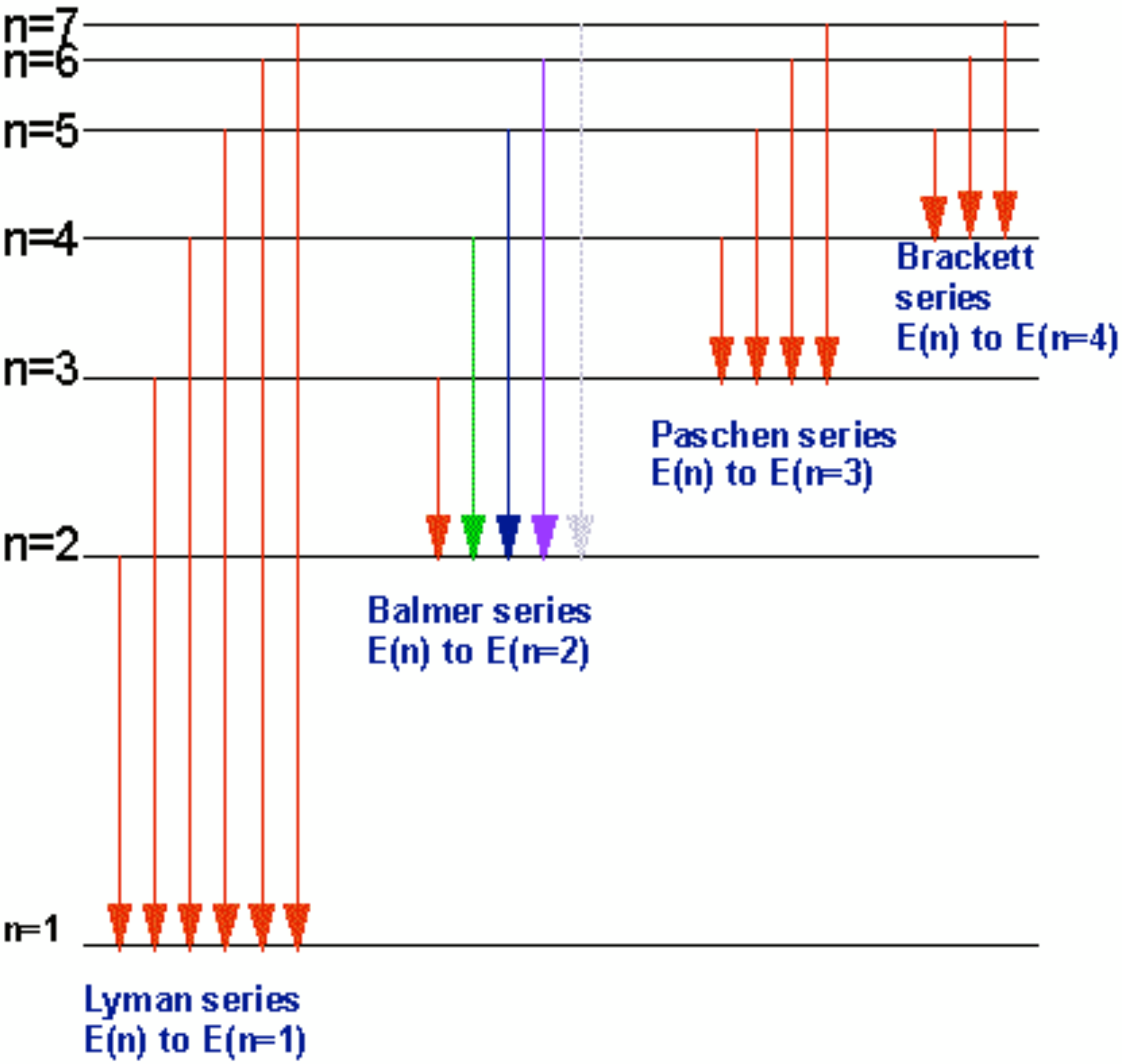
where ***k*** is an integer from 1 to infinity.

- 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:

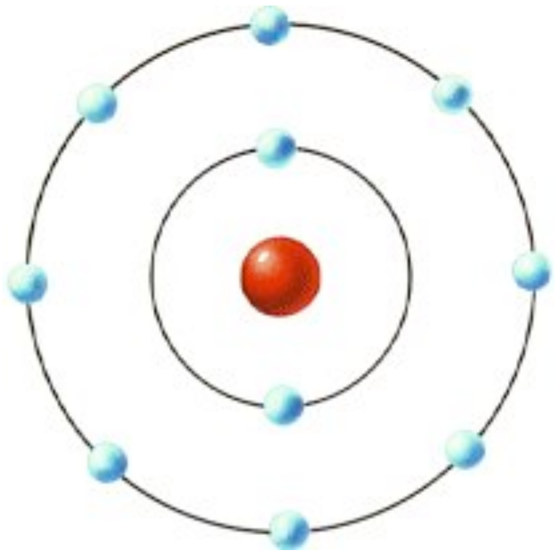



$$\frac{1}{\lambda} = R_H \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$$

for $\boldsymbol{m}$ = 1,2,3,4,5,…

and $\boldsymbol{n}$ = m+1,m+2,…

# The Bohr Atom

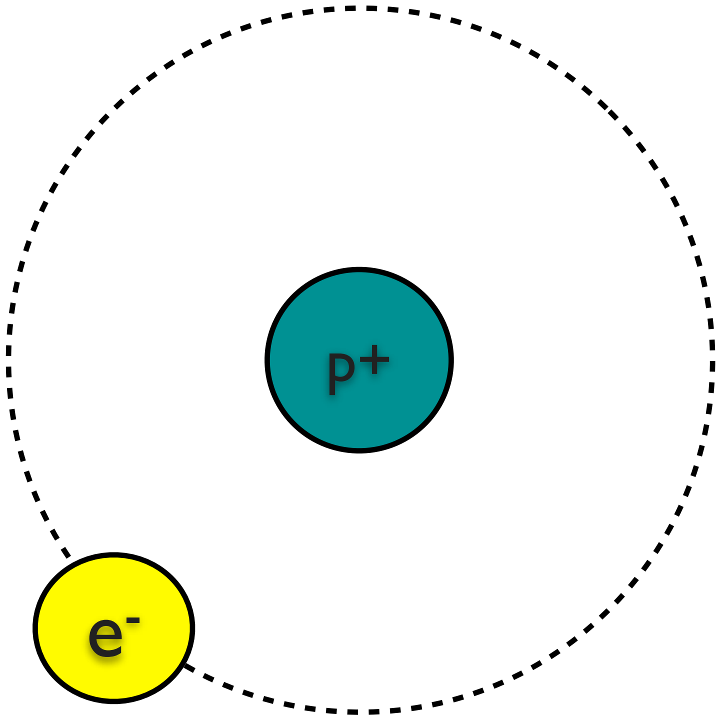


- **1907 - Rutherford's planetary model**
  - Best yet model of atomic structure, **but**:
    - **Not** a **stable model** (electrons should radiate and spiral in).
    - Does **not** predict the **Rydberg equation**, or even the existence of spectral lines.
- **1913 - Niels Bohr**
  - A new atomic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

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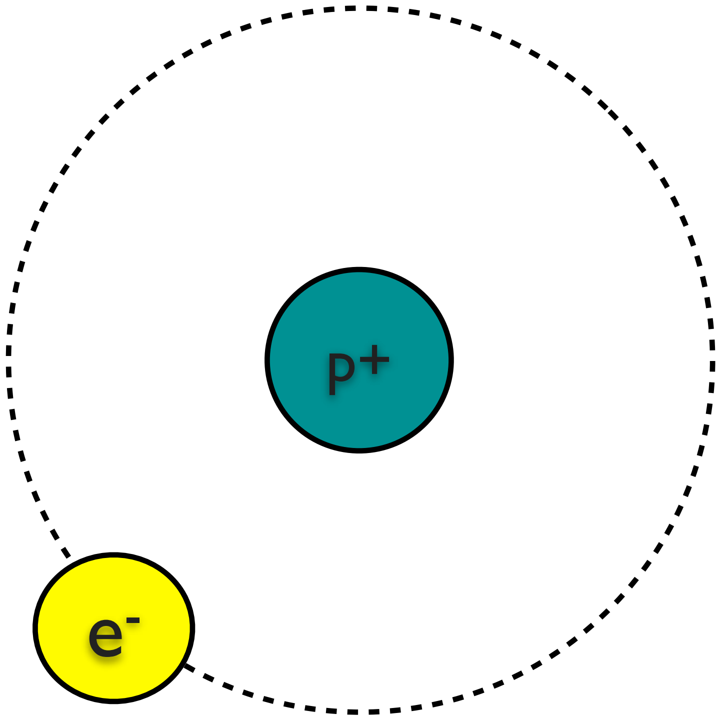
# The Bohr Atom




- 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

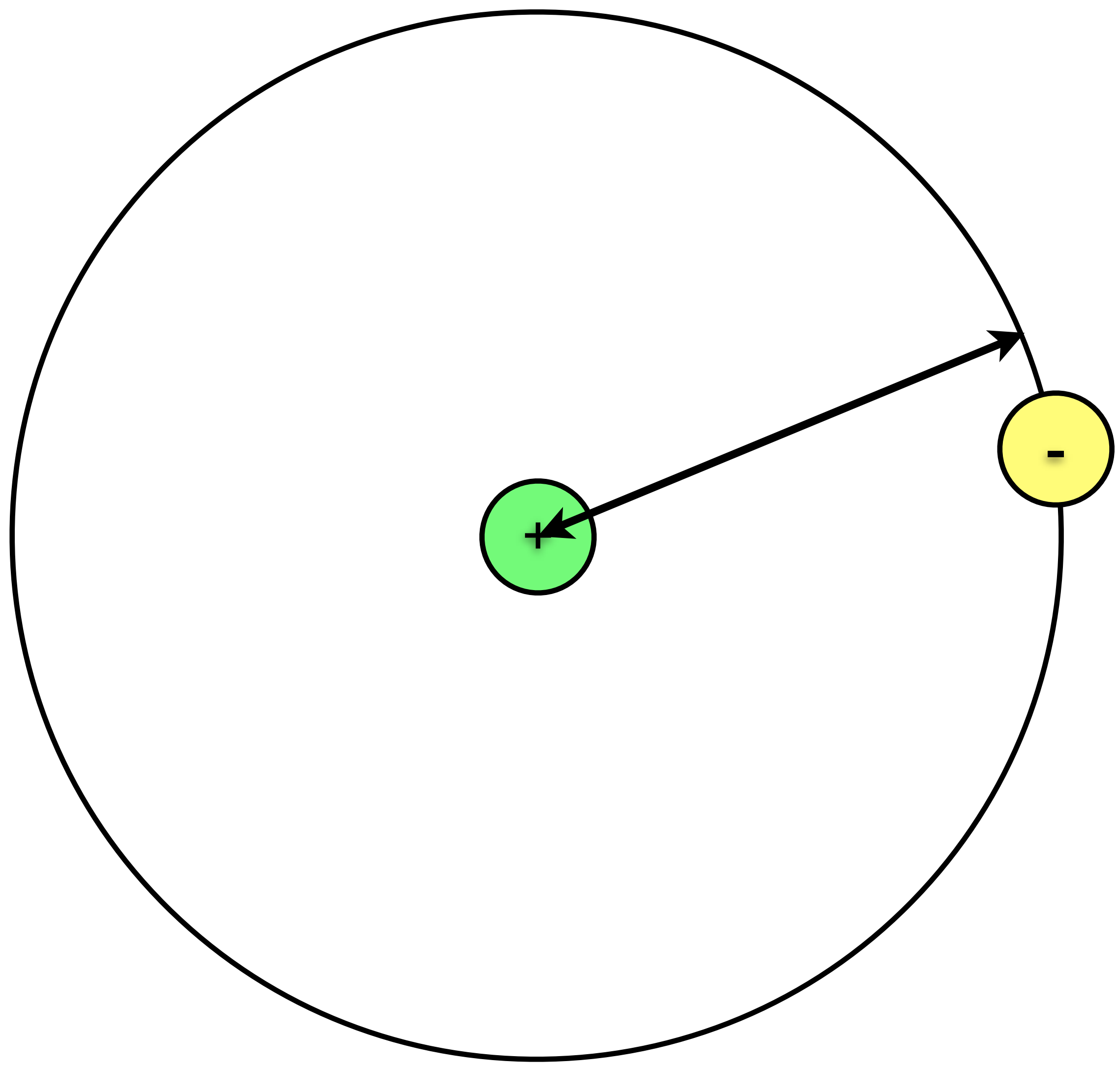
# Straw poll

- Have you studied the electrostatic Coulomb potential before?

# Straw poll

- Have you studied circular motion before?

# The Bohr Model



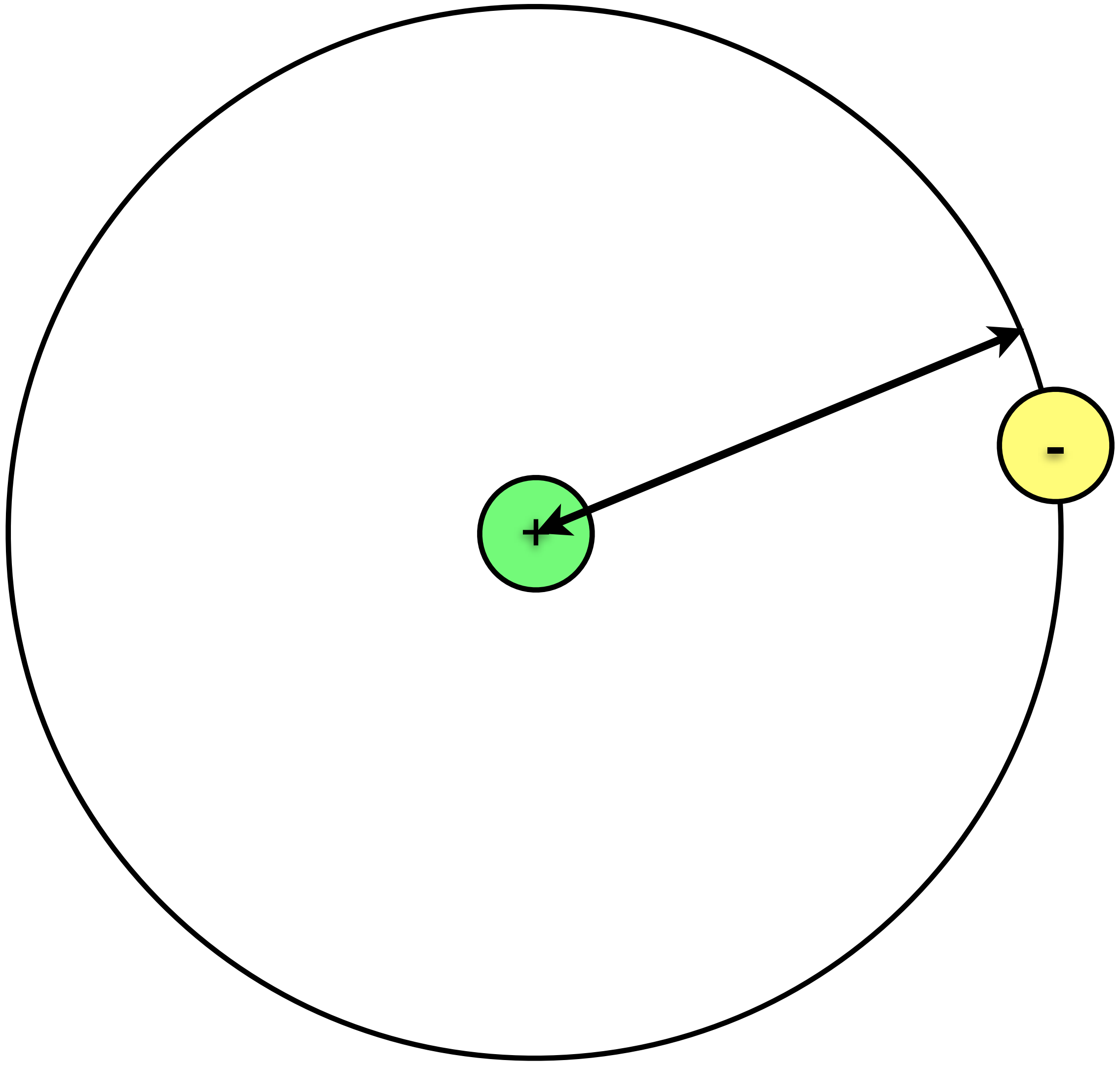

- 1. Electrons travel in **stable** circular orbits.
- 2. Orbits are **quantised.** The only allowed orbits satisfy an **angular momentum rule:**

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

where $\boldsymbol{n}$ = 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.

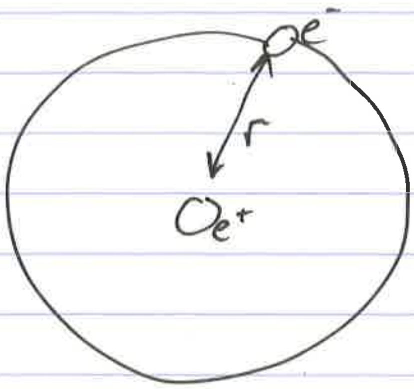
# The Bohr Model




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

*Hand-written Calculations*

## Bohr model




$r$: radius of orbit

Angular momentum:

$l = mvr$

**Balance forces:** Coulomb Force = centripetal force.

Coulomb force $F = -k\dfrac{q_1 q_2}{r^2} = -\dfrac{1}{4\pi\varepsilon_0}\dfrac{q_1 q_2}{r^2}$

$q_1 = e \quad q_2 = -e$

$$\frac{mv^2}{\cancel{r}} = \frac{1}{4\pi\varepsilon_0}\frac{ee}{r\cancel{^2}} \xrightarrow[\text{rewrite}]{} \boxed{v^2 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{m}\frac{1}{r}} \; *$$

**Bohr's quantisation rule** $l = \hbar n \qquad n = 1, 2, 3, \ldots$

$l = mvr = \hbar n$

$$v = \frac{\hbar n}{mr} \rightarrow \boxed{v^2 = \frac{\hbar^2 n^2}{m^2 r^2}} \; **$$

Equate * and **

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\cancel{m}}\frac{1}{\cancel{r}} = \frac{\hbar^2 n^2}{m^{\cancel{2}} r^{\cancel{2}}}$$

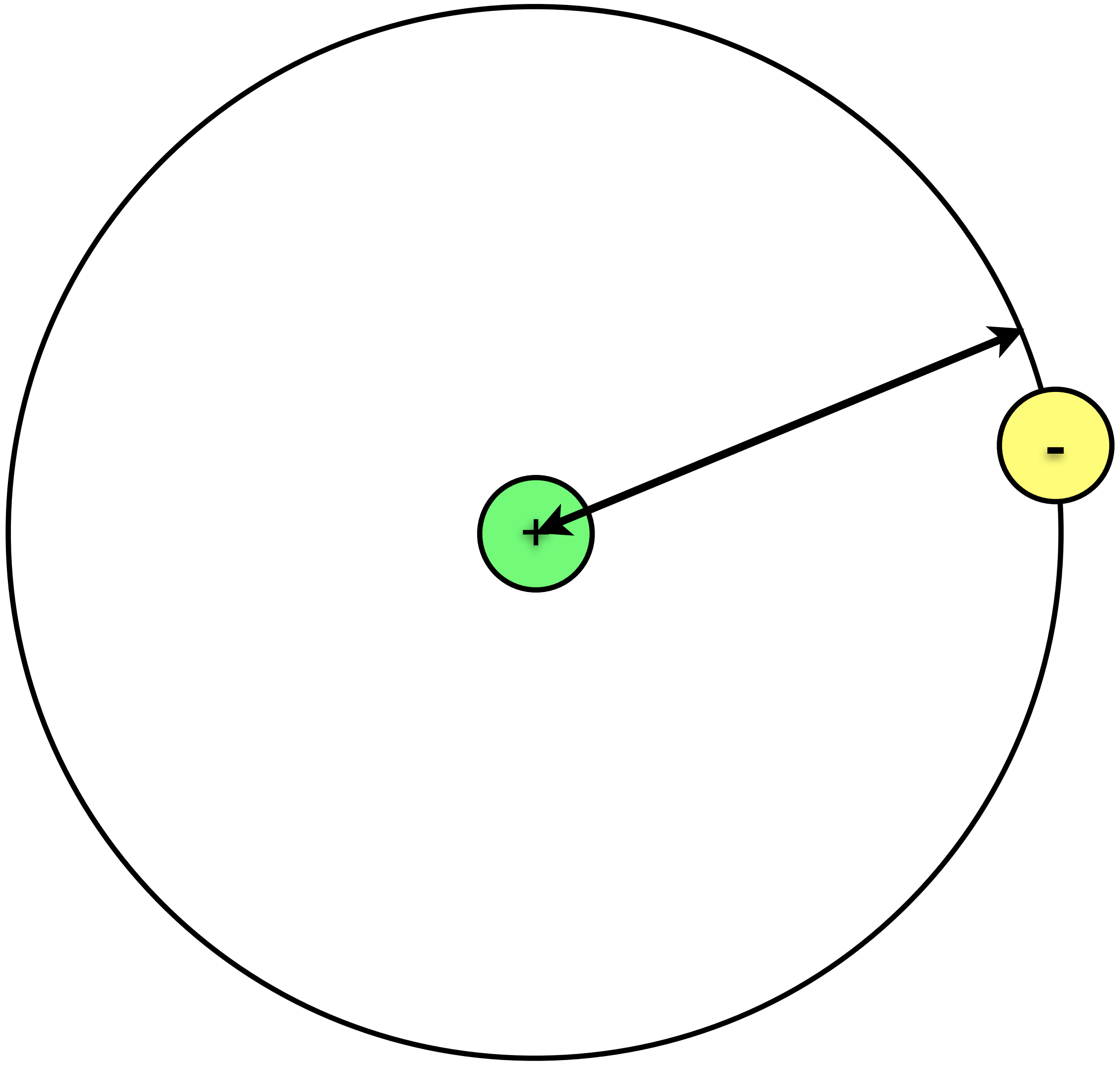
$$r = \overbrace{\left(\frac{\hbar^2(4\pi\varepsilon_0)}{me^2}\right)}^{a_0} n^2$$

$= a_0 n^2$

$a_0$: radius of n=1 orbit "Bohr radius"

$a_0 = 5.3 \times 10^{-11}\,m$
$\simeq \frac{1}{2}$ Å $\qquad$ Å $= 10^{-10}\,m$.

# The Bohr Model




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

Energy of electron

Energy = Kinetic energy + Potential Energy.

$$= \frac{1}{2}mv^2 + \left( -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \right)$$

Substitute * for $v^2$:

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

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

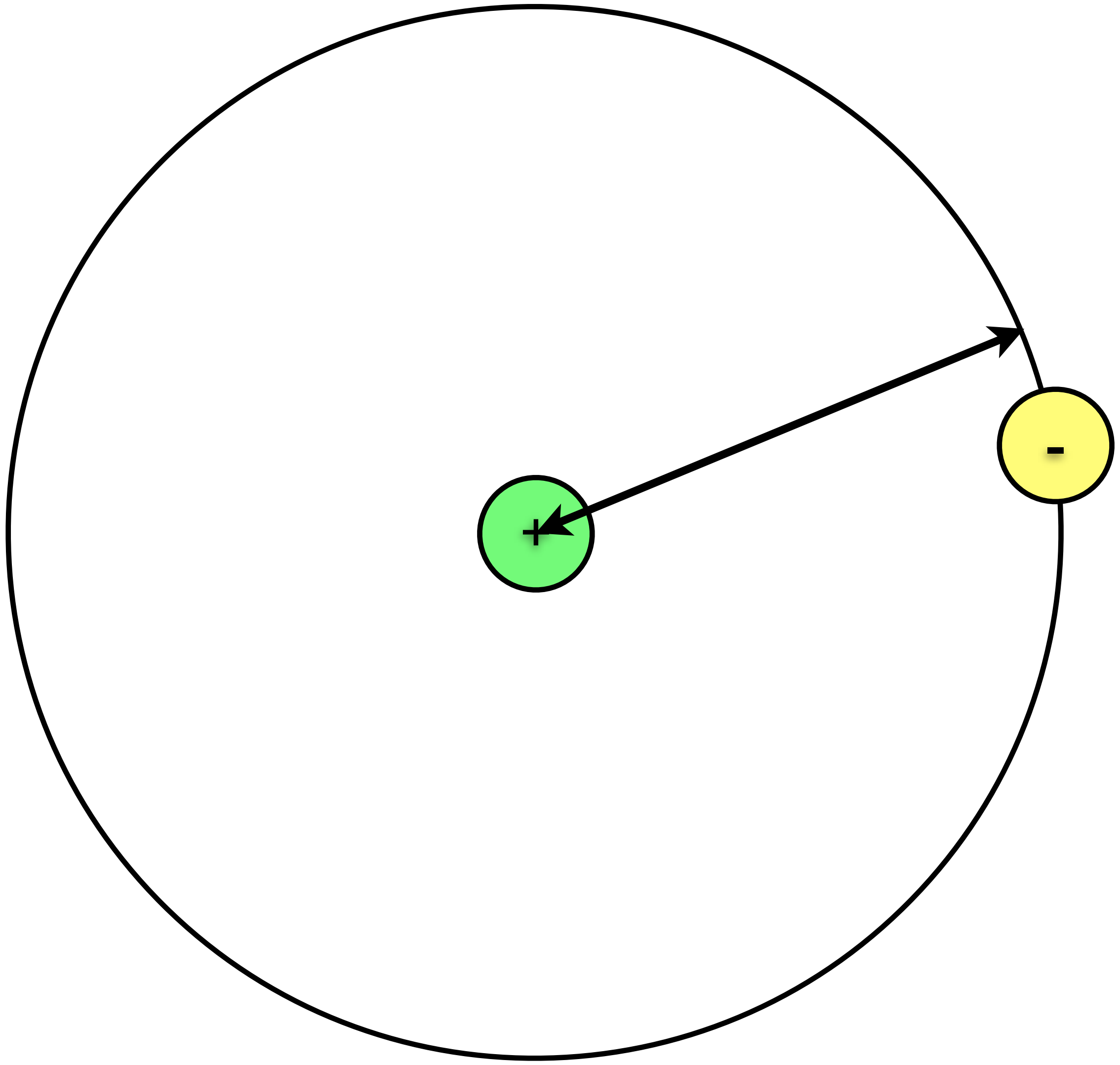
Use: $r = a_0 n^2$

$$= \underbrace{\frac{-1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{e^2}{a_0}}_{\text{Fundamental constants}} \frac{1}{n^2}$$

$$= \frac{-2.2 \times 10^{-18}\ \text{J}}{n^2} = \frac{-13.6\ \text{eV}}{n^2}$$

# *Hand-written Calculations*

# The Bohr Model




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

where $n = 1,2,3,\ldots$

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

- Orbital radius:

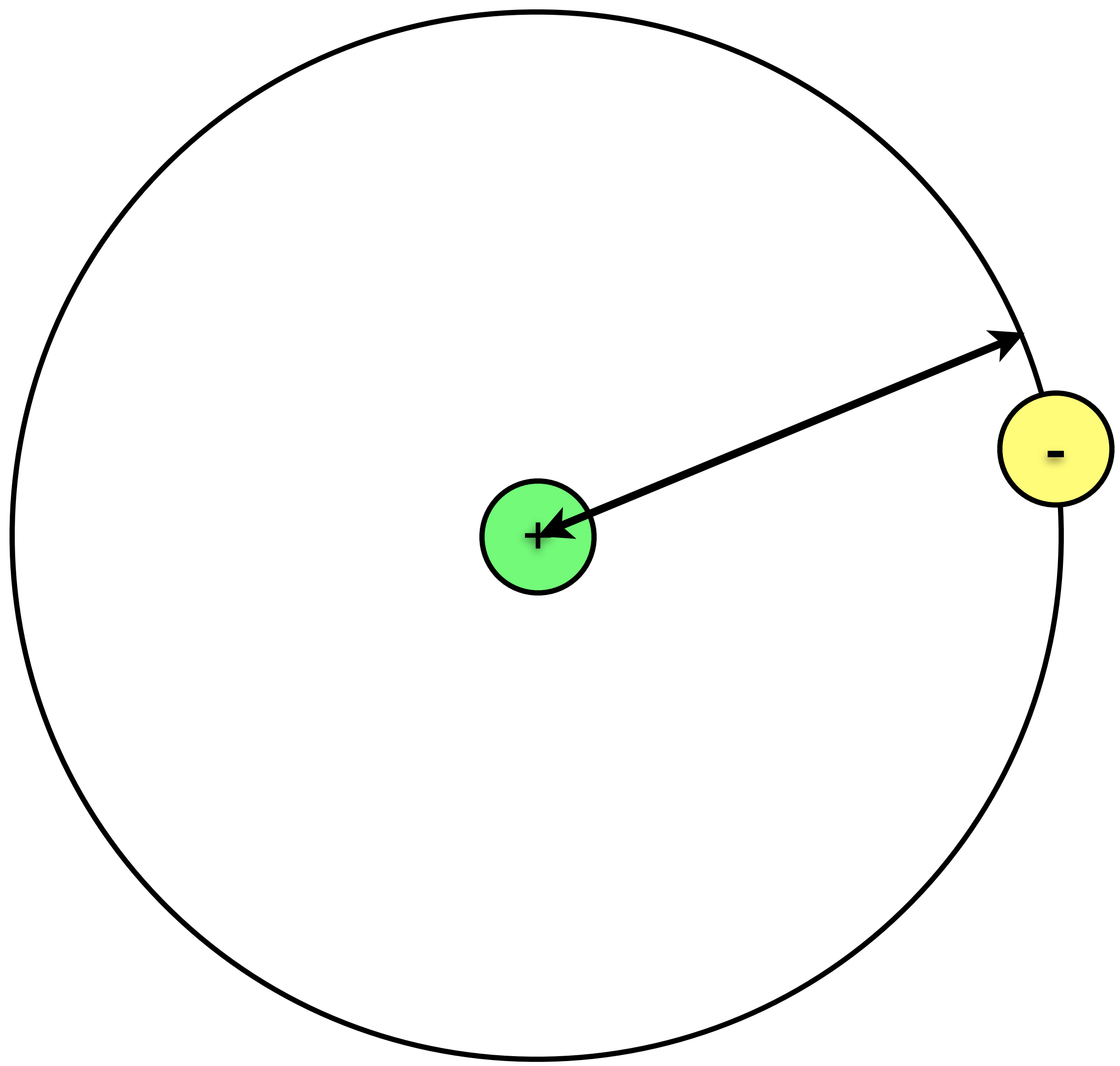
$$r_n = a_0 n^2$$

- 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 $\boldsymbol{n}$ = 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.

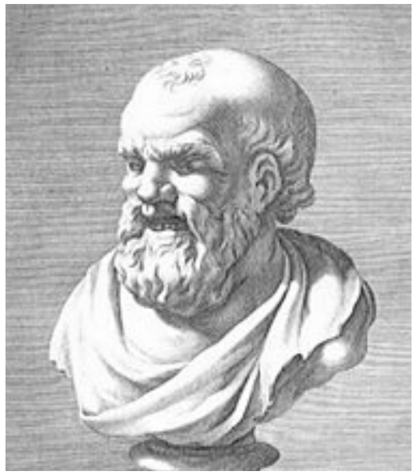
# The Bohr Model

- **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**.