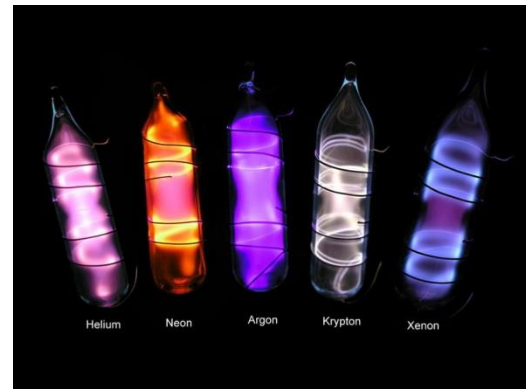
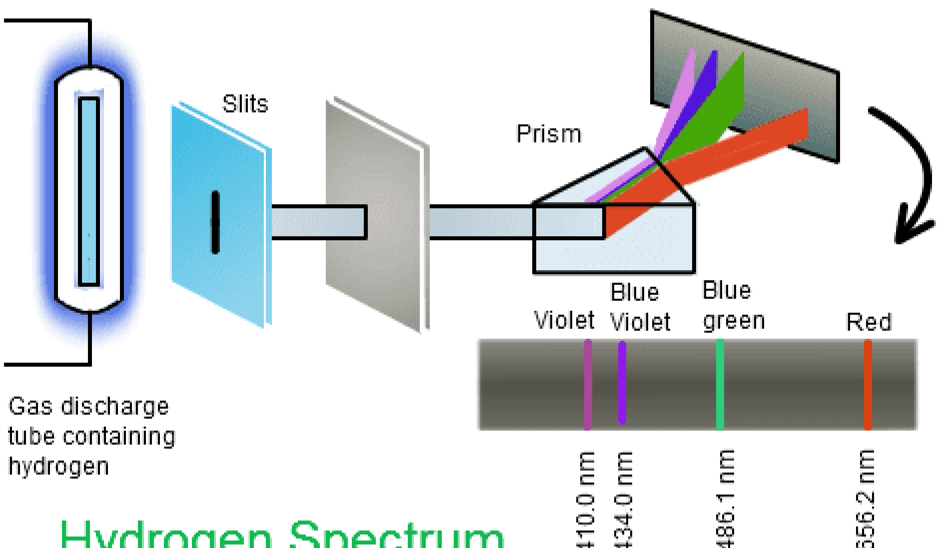
Atomic spectra

Radiation from atom: classified into two kinds spectra.

What are these?

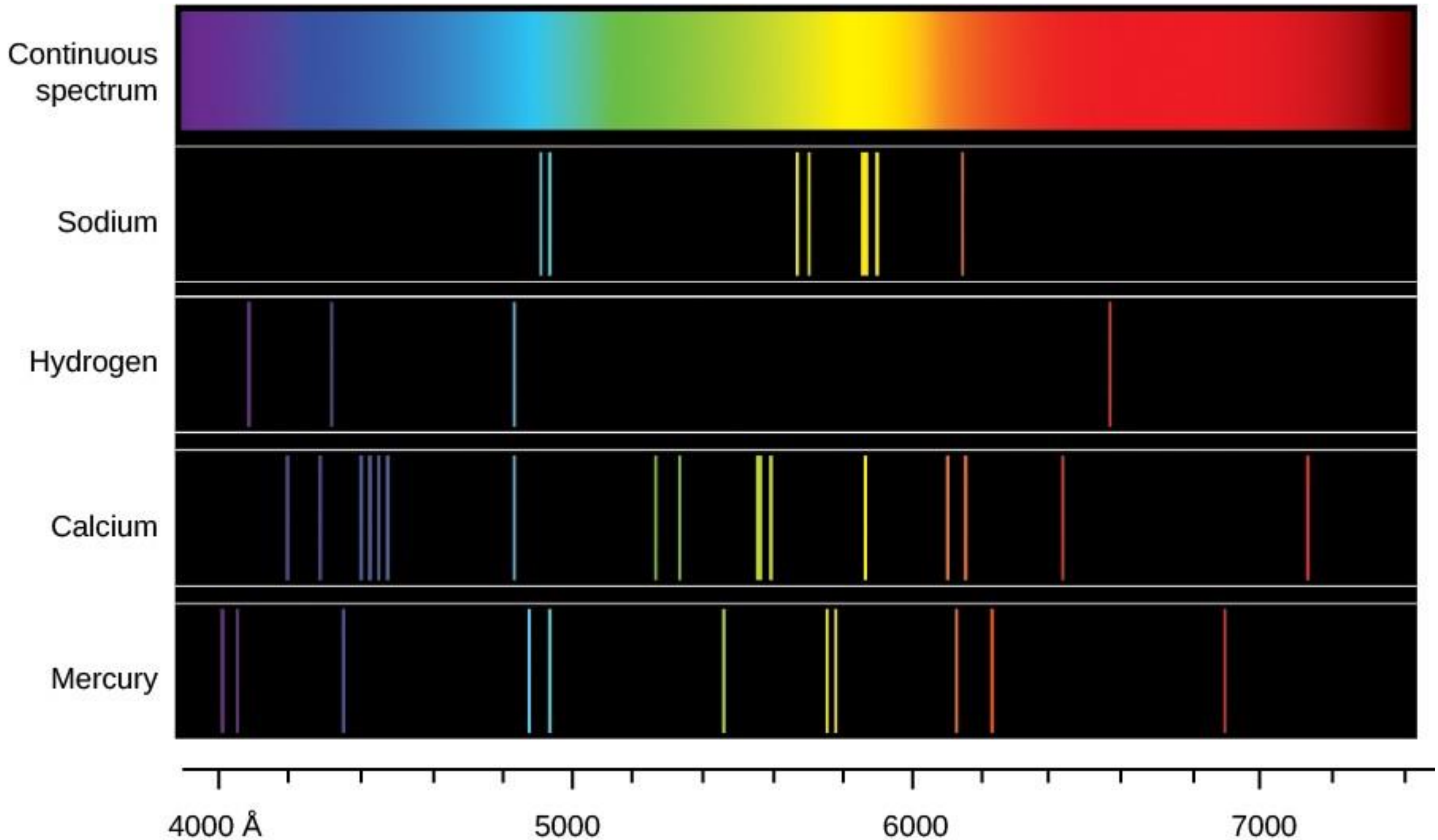




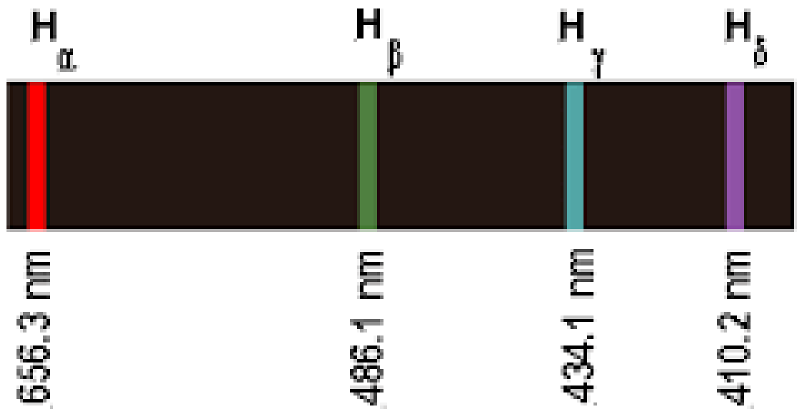
Hydrogen Spectrum

How does it work?

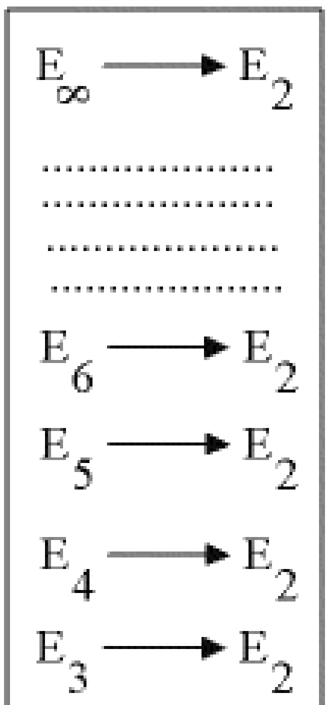
Line spectra



Spectral series of hydrogen atom



Spectrogram of visible lines in the Balmer series of hydrogen as obtained with a constant-deviation spectrograph.



The formula for Balmer Series is

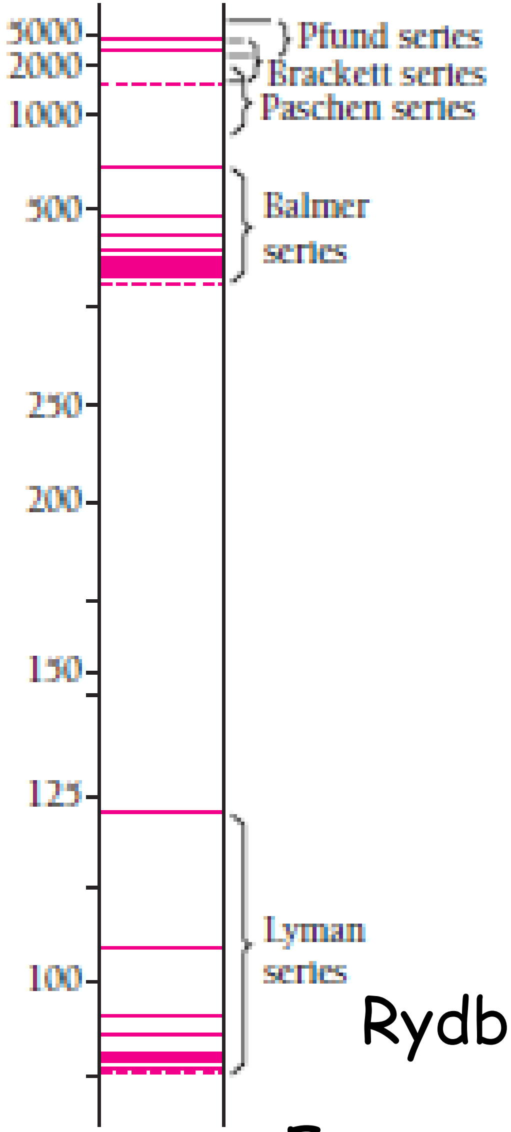
$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

where $n = 3, 4, 5, \ldots$, and

R is the Rydberg Constant.

These transitions emit visible photons.

Line spectra of hydrogen



Lyman: $$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4\cdots$$

Balmer: $$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5\cdots$$

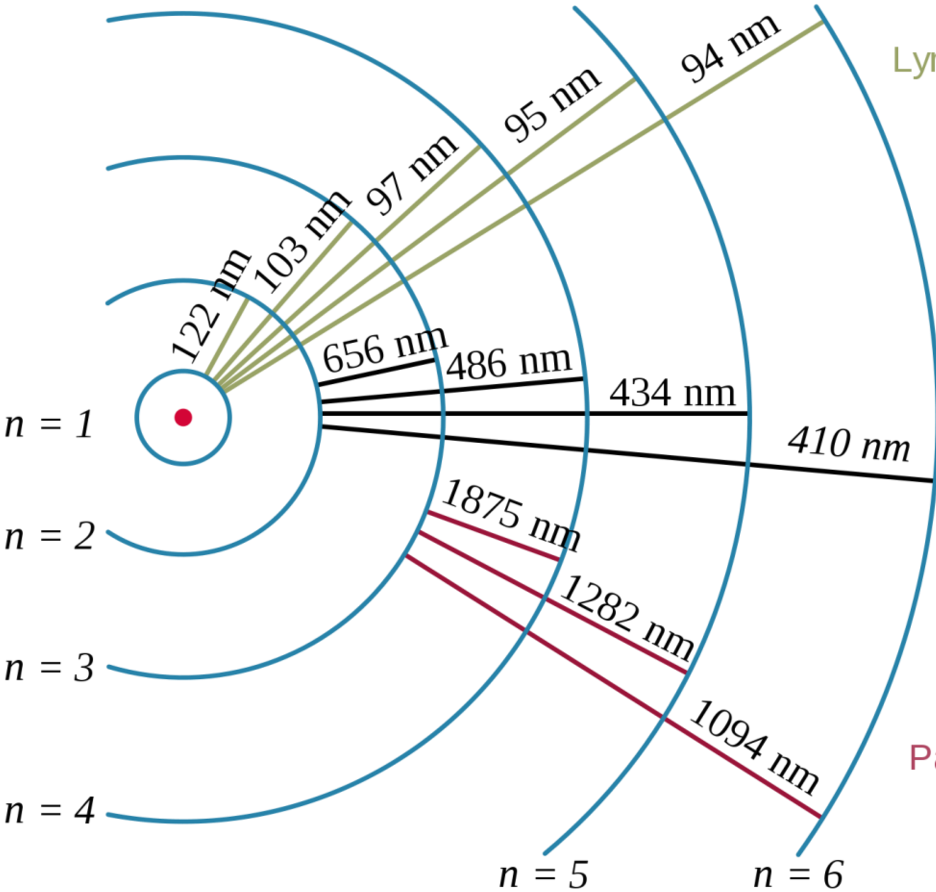
Paschen: $$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6\cdots$$

Brackett: $$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad n = 5, 6, 7\cdots$$

Pfund: $$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \quad n = 6, 7, 8\cdots$$

Rydberg constant: $R = 1.097\times10^7\ m^{-1} = 0.01097\ nm^{-1}$

Energy of hydrogen ➡ Discrete states



Lyman series

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4\cdots$$

Balmer series

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5\cdots$$

Paschen series

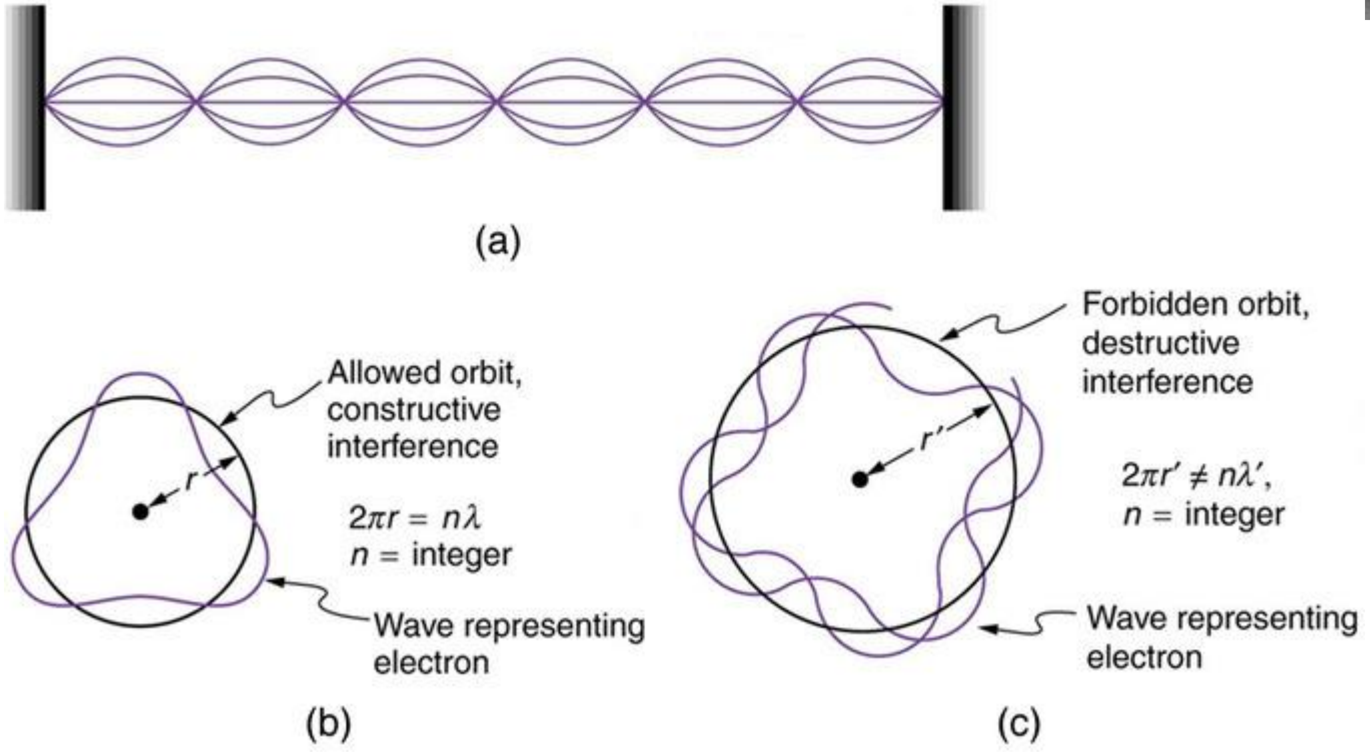
$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6\cdots$$

Bohr atom Niels Bohr (1913)

Following Rutherford's proposal that the mass and positive charge are concentrated in a small region at the center of the atom, ...

A miniature planetary system

Stationary state of electrons:



Bohr model: stationary states

Introducing stationary state of electrons:

De Broglie wave + **Angular momentum**

+ Standing wave in orbits

De Broglie wave: $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

Angular momentum: $L = rp$

Standing wave: $2\pi r = n\lambda \quad (n = 1, 2, \cdots)$

$$L = \frac{nh}{2\pi} \quad (n = 1, 2, 3, \cdots)$$

$$\lambda = \frac{h}{e}\sqrt{\frac{4\pi\varepsilon_0 r}{m}}$$

$$r_n = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2} = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} n^2 = n^2 a_0 \quad (n = 1, 2, 3, \cdots)$$

$$a_0 = r_1 = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} = 5.292 \times 10^{-11} m$$

$$E_n = -\frac{m e^4}{8\pi\varepsilon_0^2 h^2}\frac{1}{n^2} = \frac{E_1}{n^2} \quad (n = 1, 2, 3, \cdots)$$

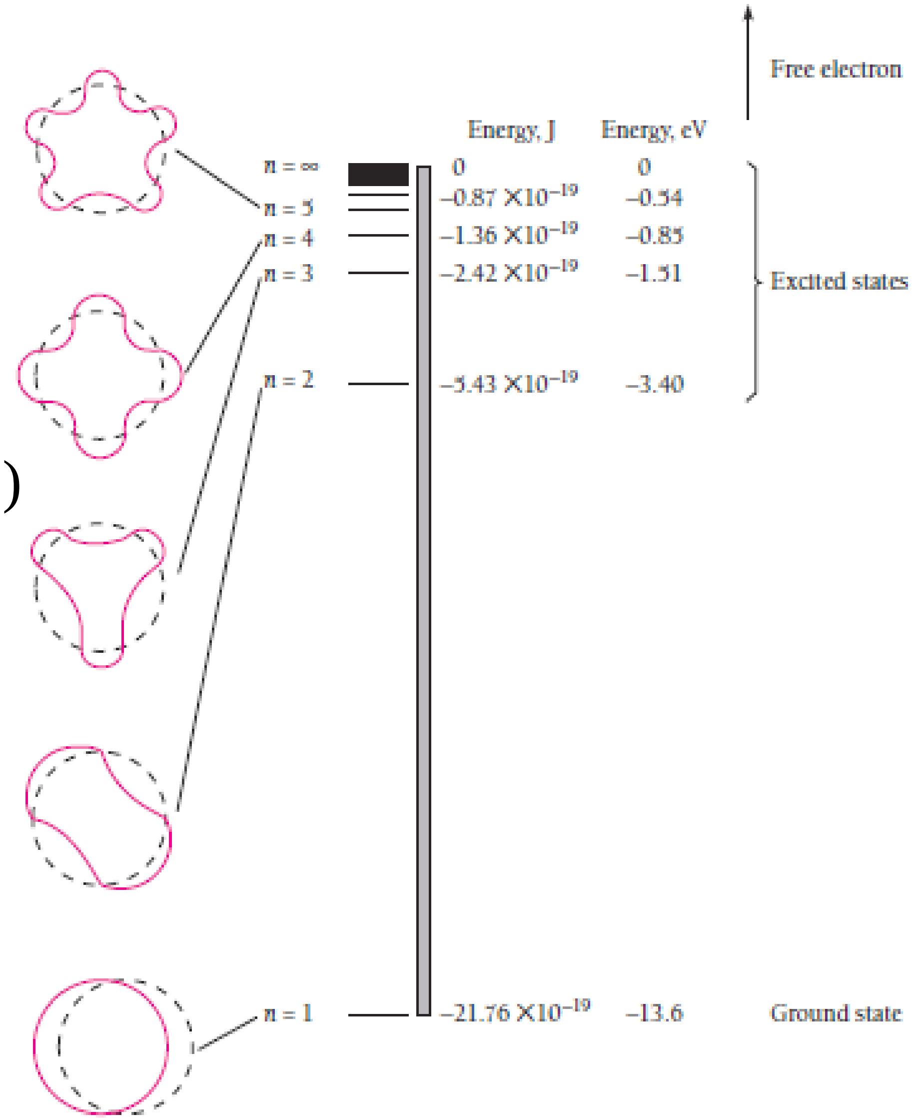
$$E_1 = -2.18 \times 10^{-18} J = -13.6 eV$$

Energy levels and spectra

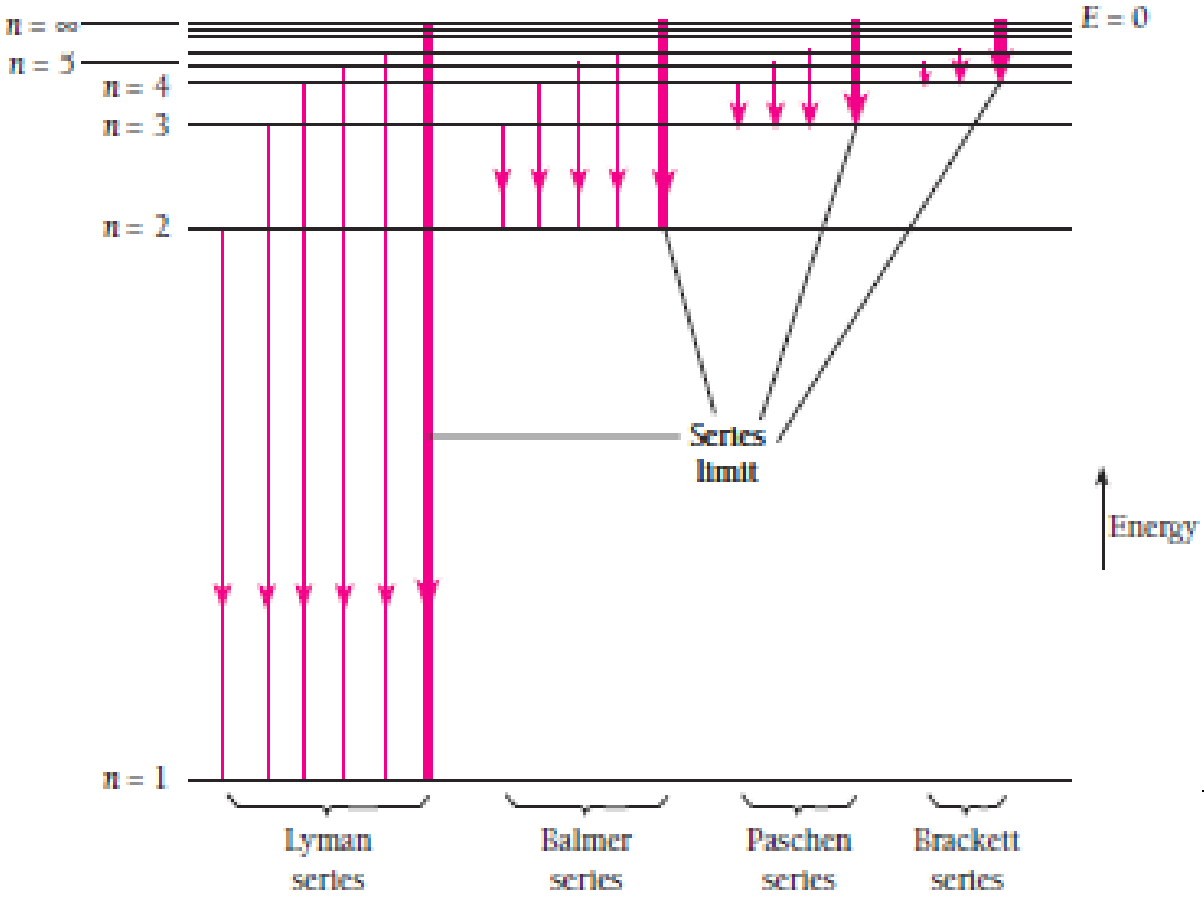
A photon is emitted when an electron jumps from one energy level to a lower level.

$$E_n = -\frac{me^4}{8\pi\varepsilon_0^2 h^2}\frac{1}{n^2} = \frac{E_1}{n^2} \quad (n = 1, 2, 3, \cdots)$$

$$E_1 = -2.18\times10^{-18} J = -13.6 eV$$



Hydrogen wavelengths in the Bohr model



$$E_i - E_f = h\nu$$

$$E_i - E_f = E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= -E_1\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{\lambda} = -\frac{E_1}{ch}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$-\frac{E_1}{ch} = \frac{me^4}{8\varepsilon_0^2 ch^3} 1.097 \times 10^7\, m^{-1}$$

Atoms with Z > 1

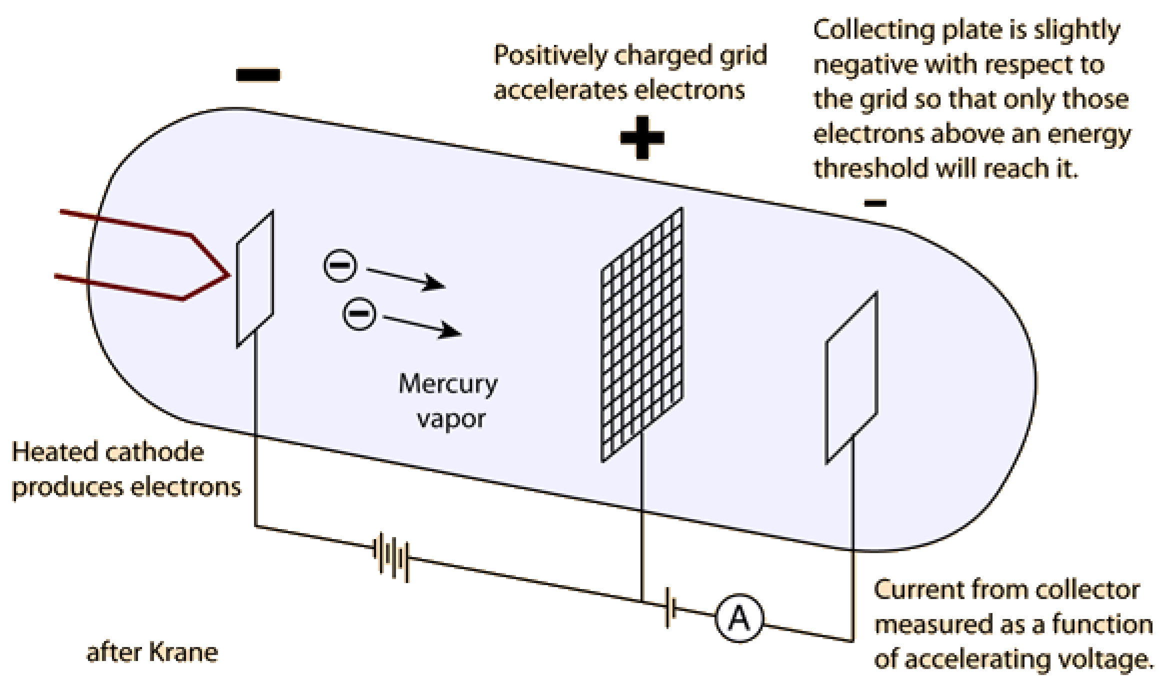
The Bohr theory for hydrogen can be used for any atom with a single electron, even if the nuclear charge is greater than 1.

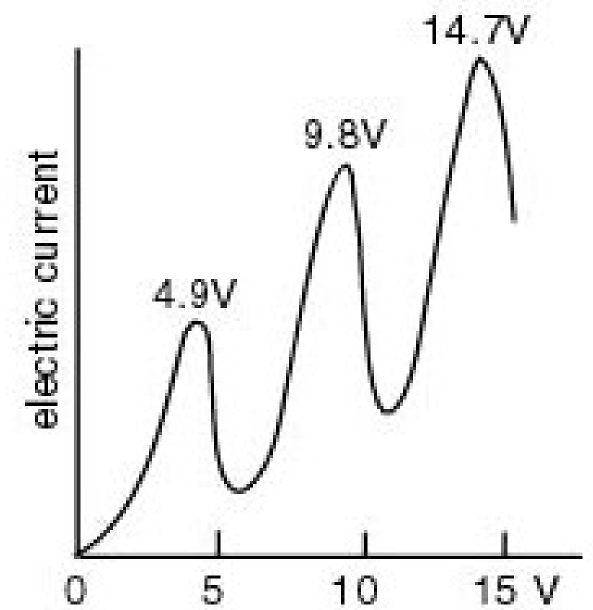
$$F = \frac{1}{4\pi\varepsilon_0}\frac{|q_1||q_2|}{r^2} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}$$

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{Zme^2}n^2 = \frac{n^2 a_0}{Z} \quad (n = 1, 2, 3, \cdots)$$

$$E_n = -\frac{m(Ze^2)^2}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} = -(13.6\ eV)\frac{Z^2}{n^2} \quad (n = 1, 2, 3, \cdots)$$

Franck-Hertz experiment





Problems with Bohr's model

Bohr's "planetary system" of the atom did explain a lot…, but not everything. In particular,

✔ **Multi-electron atoms:**

- do not have energy levels predicted by the model. It does not even work for neutral helium.

✔ **Doublets and triplets:**

- appear in the spectra of some atoms: very close pairs or trios of lines. Bohr's model cannot explain why some energy levels should be very close together.

✔ **Violation of the uncertainty principle:**

- Only certain values of r are permitted: $\Delta r=0$

- Since orbits are circular, the radial components of velocity and momentum are zero: $\Delta p_r=0$