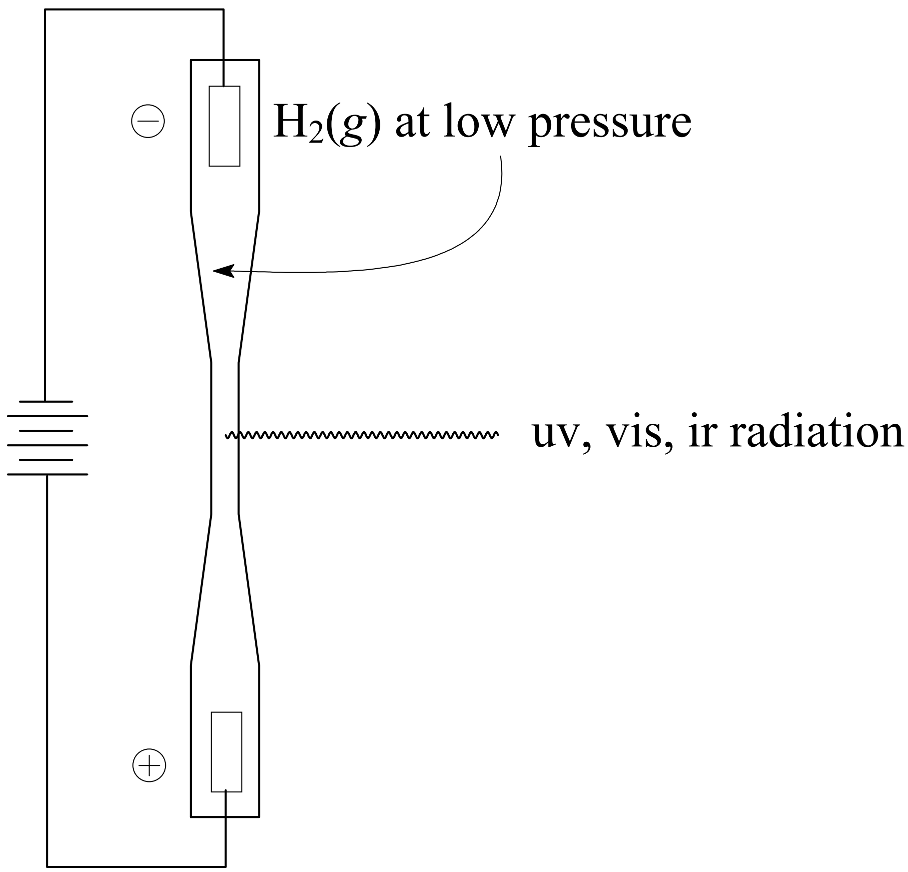
Hydrogen Discharge Tube



Balmer Series (visible light): 656.3 nm (red)
486.1 nm (blue)
434.0 nm (indigo)
410.1 nm (violet)

Balmer Equation for the Visible Line Spectrum of Hydrogen

Johann Balmer - 1885

$$\nu = U\left(\frac{1}{4} - \frac{1}{n^2}\right) \qquad n = 3,\ 4,\ 5,\ ...$$

U = Rydberg constant = $3.29 \times 10^{15}\ s^{-1}$

Bohr's Model of the Atom

1. Electrons can have only certain fixed states of motion about the nucleus, and each state has a corresponding fixed energy.

2. Atoms radiate energy as electromagnetic radiation *only* through a transition from a high energy state to a lower energy state.

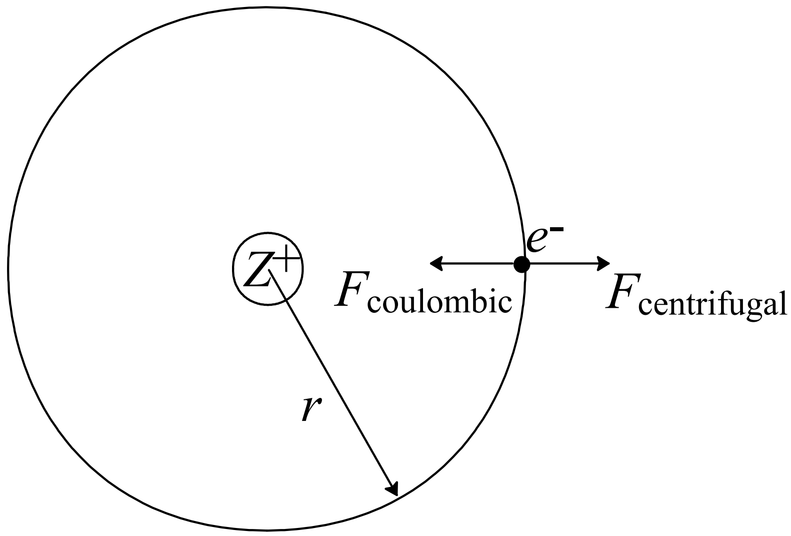
3. Electrons move in circular paths in any fixed state.

4. Allowed states of electron motion are those for which the angular momentum, mvr, is a multiple of $h/2\pi$. This is the *quantum hypothesis*:

   $$mvr = nh/2\pi \qquad n = 1, 2, 3, ...$$

   where n is the quantum number of the state.

Counterbalancing Forces in the Bohr Model



$$F_{\text{centrifugal}} = -mv^2/r$$
$$F_{\text{coulombic}} = -Ze^2/r^2$$

Predicted Relationships from Bohr's Model

Radius of an orbit:

$$r = \frac{n^2 h^2}{4\pi^2 m Z e^2} \qquad n = 1,\ 2,\ 3,\ ...$$

- When $Z = 1$ (hydrogen) and $n = 1$ (lowest state) $r = 0.529$ Å $= a_o$, called the Bohr radius.
- In terms of a_o,

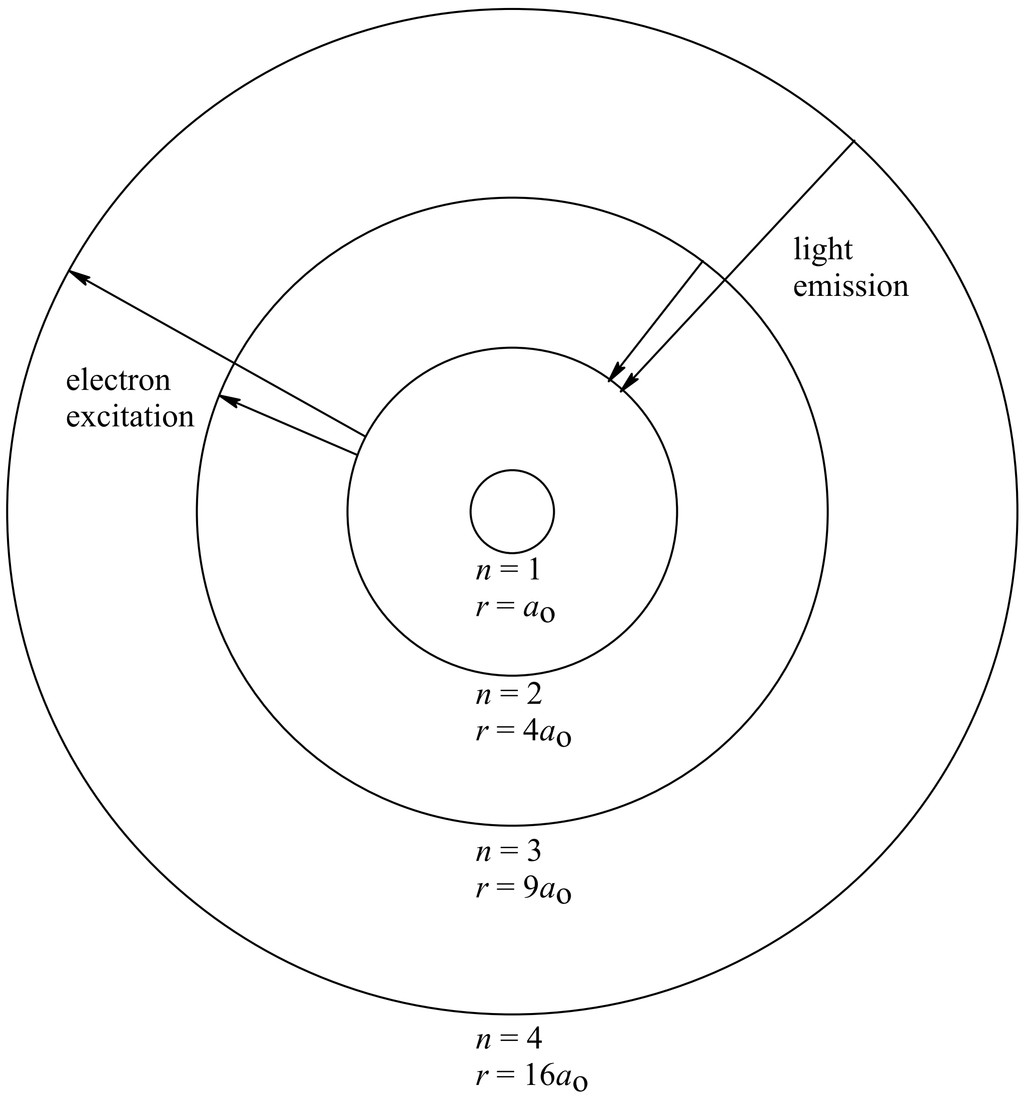
$$r = n^2 a_o / Z$$

Energy of a state:

$$E = \frac{-2\pi^2 m Z^2 e^4}{n^2 h^2} = \frac{-BZ^2}{n^2}$$

The Bohr Model of the Balmer Series

(Not to scale)



Energy of Light Emitted in a Transition Between Energy States

$$E_{\text{light}} = |E_{\text{final}} - E_{\text{initial}}| = |E_{\text{low}} - E_{\text{high}}|$$

$$E_{\text{light}} = \left| \frac{-BZ^2}{n_{\text{low}}^2} - \frac{-BZ^2}{n_{\text{high}}^2} \right| = BZ^2 \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$$

But $E = h\nu$, so

$$\nu = \frac{BZ^2}{h} \left[\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right]$$

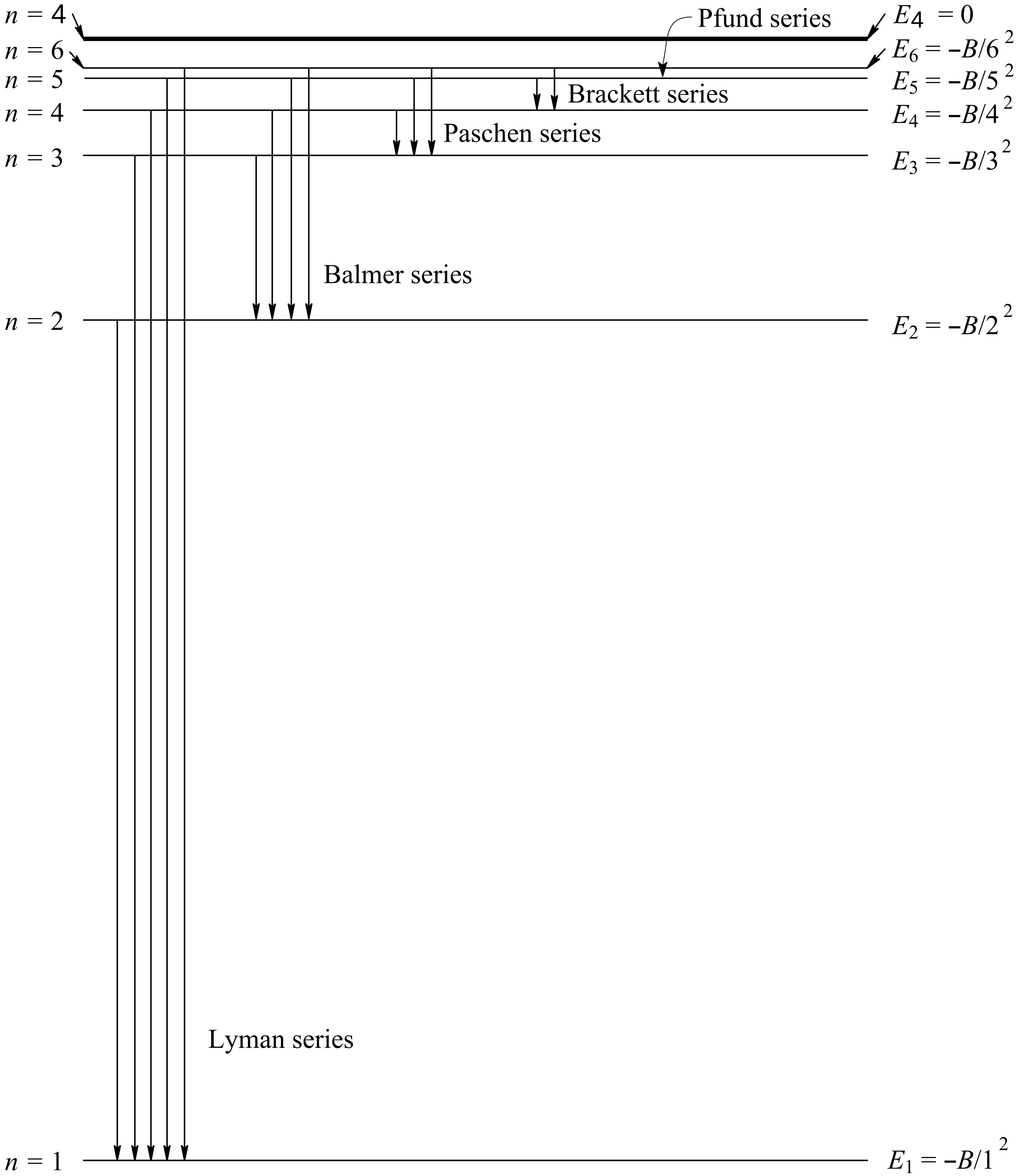
where $BZ^2/h = \Re$, the Rydberg constant. For the Balmer series, then

$$\nu = \frac{BZ^2}{h} \left[\frac{1}{2^2} - \frac{1}{n_{\text{high}}^2} \right] = \Re \left[\frac{1}{4} - \frac{1}{n_{\text{high}}^2} \right]$$

Series of Line Spectra for Hydrogen Predicted by the Bohr Equation

n_{low}	n_{high}	Region	Series Name
1	2, 3, ..., 4	ultraviolet	Lyman
2	3, 4, ..., 4	visible	Balmer
3	4, 5, ..., 4	infrared	Paschen
4	5, 6, ..., 4	infrared	Brackett
5	6, 7, ..., 4	infrared	Pfund

Energy Level Diagram for the Hydrogen Atom



Problems With The Bohr Model

The ability to predict the frequencies of these series gave credibility to the Bohr model. But it had a number of limitations that lead to its complete abandonment by about 1935:

1. It could not satisfactorily explain the spectra of multi-electron atoms, even with extensive mathematical modification.

2. It could not explain the characteristic appearances of some lines in the various series, which spectroscopists routinely labeled with the following notations:

   s = sharp
   p = principal
   f = fundamental
   d = diffuse

3. It was fundamentally inconsistent with some newly discovered principles of physics.