Introduction to Quantum Chemistry

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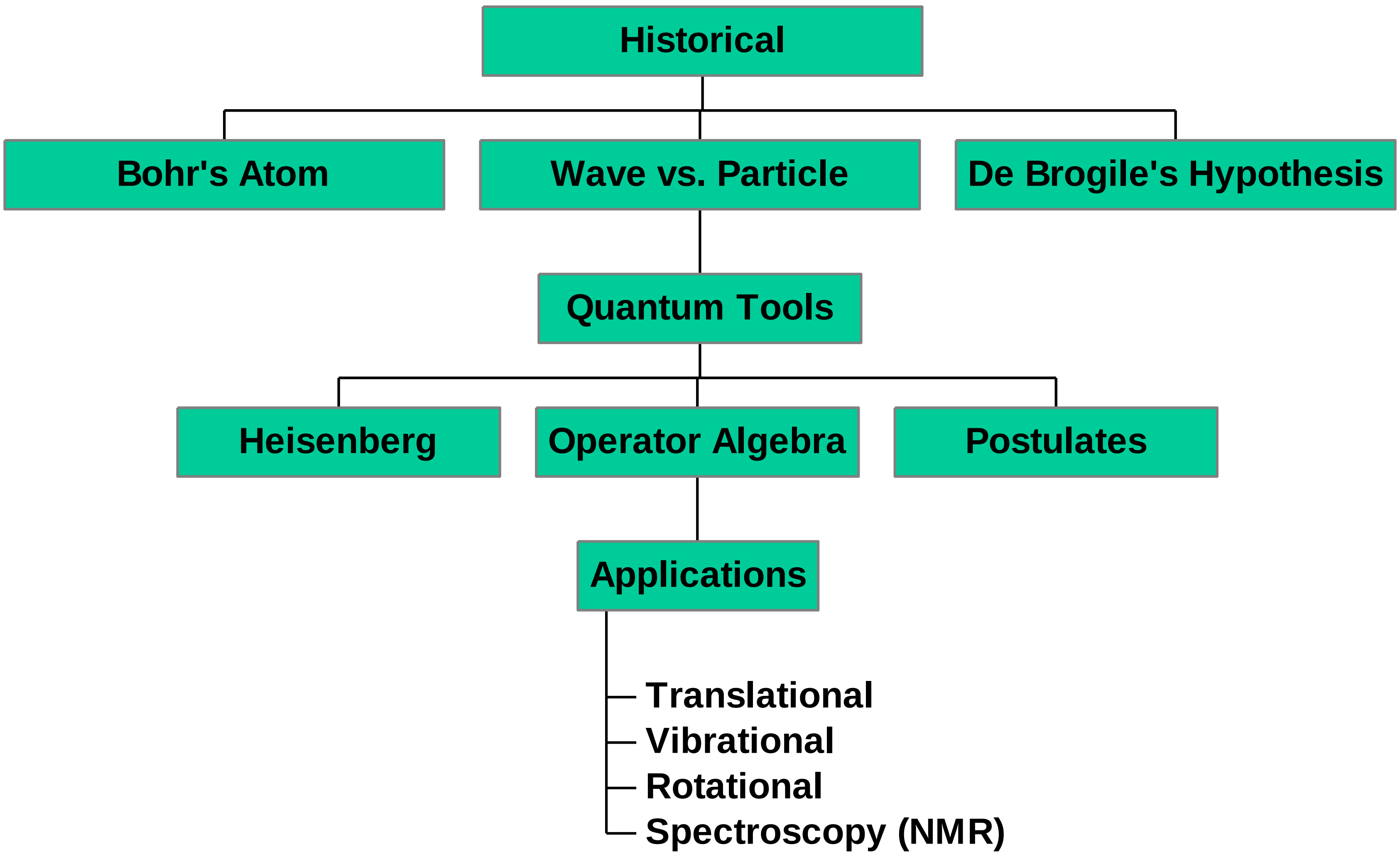
Introductory Quantum Mechanics/Chemistry



Developing the model of the Atom

- electrons discovered by J.J. Thomson in 1857 using an experiment with “cathode rays”
- the atomic nucleus discovered in 1910 by Rutherford
- Bohr model of the energy levels of Hydrogen developed (early 1900’s)
- study of the atom led to the “quantum revolution”

Electromagnetic radiations:

The radiations which are associated with electrical and magnetic fields are called electromagnetic radiations. When an electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves. These waves are called electromagnetic waves or electromagnetic radiations.

Properties of electromagnetic radiations:

- ❖ Oscillating electric and magnetic field are produced by oscillating charged particles. These fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
- ❖ They do not need a medium to travel. That means they can even travel in vacuum.

Characteristics of electromagnetic radiations:

Wavelength: It may be defined as the distance between two neighbouring crests or troughs of wave. It is denoted by λ.

Frequency (ν): It may be defined as the number of waves which pass through a particular point in one second.

Velocity (v): It is defined as the distance travelled by a wave in one second. In vacuum all types of electromagnetic radiations travel with the same velocity. Its value is 3 X10^{8}m sec^{-1}. It is denoted by v

Wave number: Wave number is defined as the number of wavelengths per unit length. It denoted as $(\bar{\nu})$

Velocity = frequency x wavelength $c = \nu\lambda$

Planck's Quantum Theory-

- The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy called ‘quantum’. In case of light , the quantum of energy is called a ‘photon’
- The energy of each quantum is directly proportional to the frequency of the radiation, i.e. $E \alpha \upsilon$ or $E= h\upsilon$ where h= Planck’s constant = 6.626×10^{-27} Js
- Energy is always emitted or absorbed as integral multiple of this quantum. $E=nh\upsilon$ Where n=1,2,3,4,.....

What is Quantum?

The word *quantum* comes from the Latin *quantus*, meaning "how great".

In physics, a **quantum** (plural: **quanta**) is the minimum amount of any physical entity (physical property such as *such as energy or matter*) involved in an interaction.

It is a discrete quantity of energy proportional in magnitude to the frequency of the radiation it represents.

Quantum theory describes matter as acting both as a particle and as a wave.

Quantum Theory of Atoms

The quantum mechanical view of atomic structure maintains some of Rutherford and Bohr's ideas. The nucleus is still at the center of the atom and provides the electrical attraction that binds the electrons to the atom.

- ✓Contrary to Bohr’s theory, however, the electrons do not circulate in definite planet-like orbits.

- ✓The quantum-mechanical approach acknowledges the wavelike character of electrons and provides the framework for viewing the electrons as fuzzy clouds of negative charge.

- ✓Electrons still have assigned states of motion, but these states of motion do not correspond to fixed orbits. Instead, they tell us something about the geometry of the electron cloud—its size and shape and whether it is spherical or bunched in lobes like a figure eight.

- ✓Physicists called these states of motion orbitals.
- ✓Quantum mechanics also provides the mathematical basis for understanding how atoms that join together in molecules share electrons.

✓ Two of the rules of quantum theory that are most important to explaining the atom **are the idea of wave-particle duality and the exclusion principle.**

✓French physicist Louis de Broglie first suggested that particles could be described as waves in 1924.

- Louis de Broglie proposed that all particles could be treated as matter waves with a wavelength λ, given by the following equation:

$$\lambda = \frac{h}{mv}$$

✓ In the same decade, Austrian physicist Erwin Schrödinger and German physicist Werner Heisenberg expanded de Broglie’s ideas into formal, mathematical descriptions of quantum mechanics describing electron as matter wave

$$\mathbf{E = pc} \rightarrow pc = h\nu$$

$$\mathbf{p} = \frac{\mathbf{h\nu}}{\mathbf{c}} = \frac{\mathbf{h}}{\boldsymbol{\lambda}} = \frac{\mathbf{E}}{\mathbf{c}}$$

Where p is the momentum

$$\boldsymbol{\lambda} = \frac{\mathbf{h}}{\mathbf{p}}$$

$$\lambda = \frac{hc}{E} \rightarrow \boldsymbol{\lambda}\ (\mathbf{\AA}):$$

- ✓ The exclusion principle was developed by Austrian-born American physicist Wolfgang Pauli in 1925.
- ✓ The Pauli exclusion principle states that no two electrons in an atom can have exactly the same characteristics.
- ✓The combination of wave-particle duality and the Pauli exclusion principle sets up the rules for filling electron orbitals in atoms.
- ✓ The way electrons fill up orbitals determines the number of electrons that end up in the atom’s valence shell.

The energy stored in atoms

- ground state – lowest energy
- excited state – higher energy
- ionization – electron lost

Example 1: Calculating the de Broglie wavelength of an electron

The velocity of an electron in the ground-state energy level of hydrogen is $2.2 \times 10^6\ \frac{\text{m}}{\text{s}}$. If the electron's mass is 9.1×10^{-31} kg, what is the de Broglie wavelength of this electron?

We can substitute Planck's constant and the mass and velocity of the electron into de Broglie's equation:

$$\lambda = \frac{h}{\text{mv}}$$

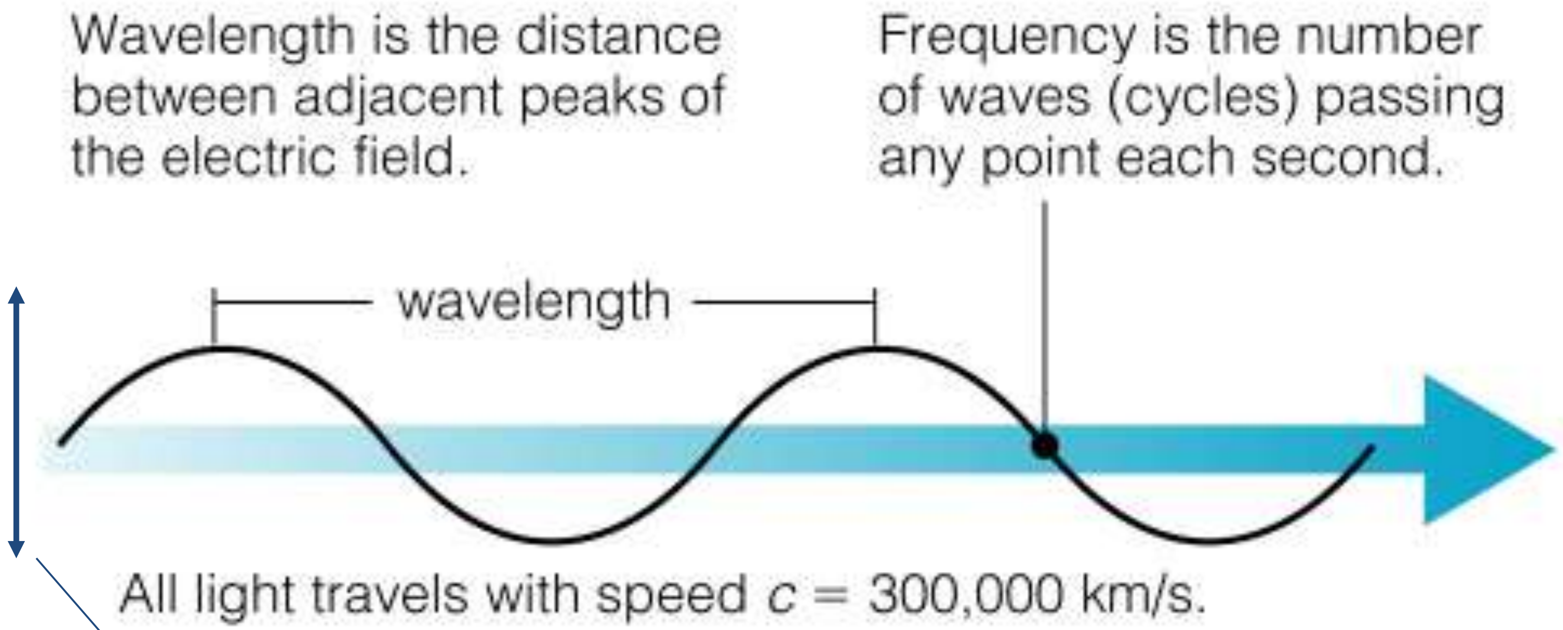
$$= \frac{6.626 \times 10^{-34}\ \frac{\cancel{\text{kg}} \cdot \text{m}^{\cancel{2}}}{\cancel{\text{s}}}}{(9.1 \times 10^{-31}\ \cancel{\text{kg}})(2.2 \times 10^{6}\ \frac{\cancel{\text{m}}}{\cancel{\text{s}}})}$$

$$= 3.3 \times 10^{-10}\ \text{m}$$

THE QUANTUM MECHANICAL MODEL OF THE ATOM

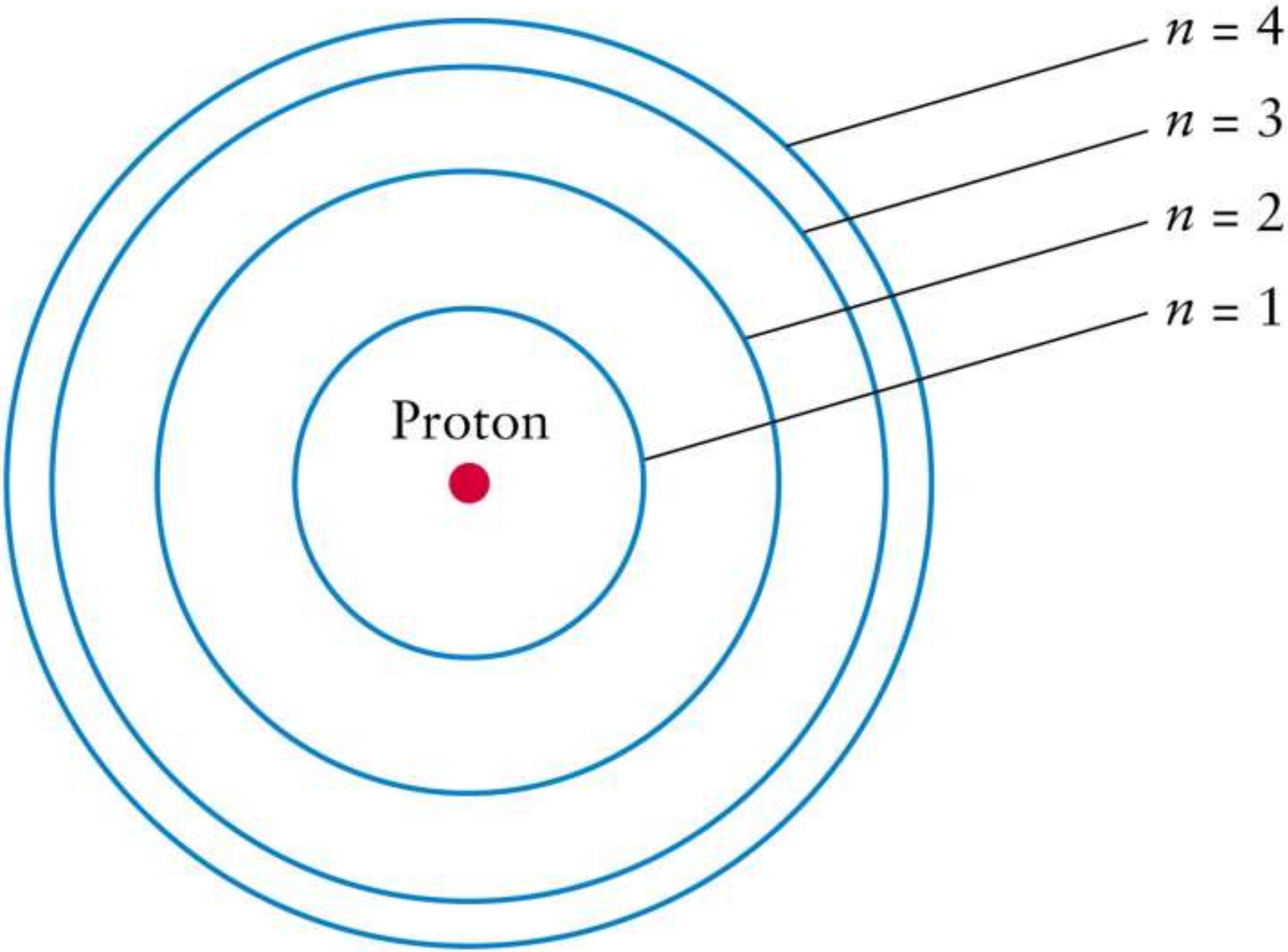
A major problem with Bohr's model was that it treated electrons as particles that existed in precisely-defined orbits. Based on de Broglie's idea that particles could exhibit wavelike behavior, Austrian physicist Erwin Schrödinger theorized that the behavior of electrons within atoms could be explained by treating them mathematically as matter waves. This model, which is the basis of the modern understanding of the atom, is known as the *quantum mechanical* or *wave mechanical* model.

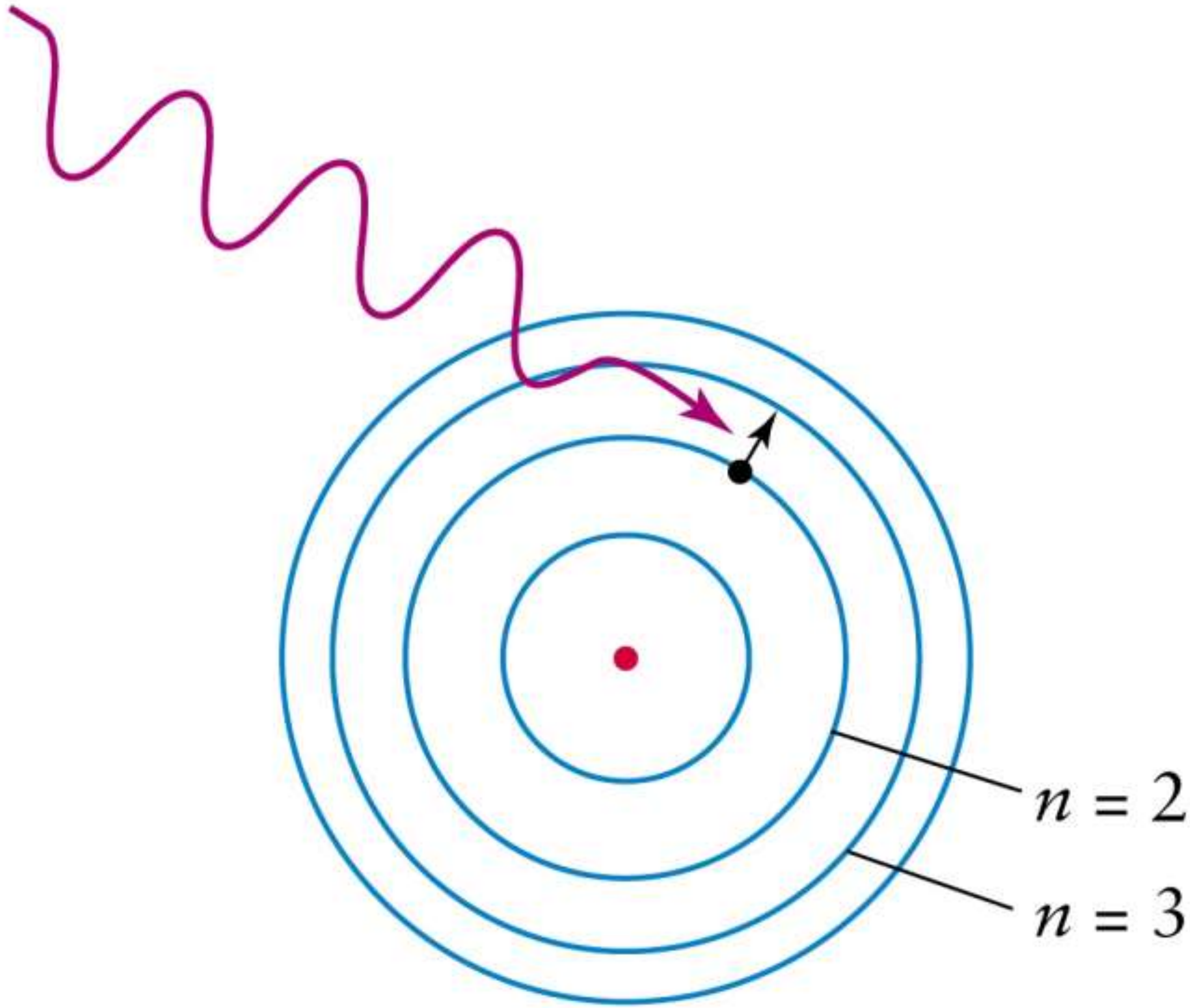
Wavelength, Frequency, and Amplitude



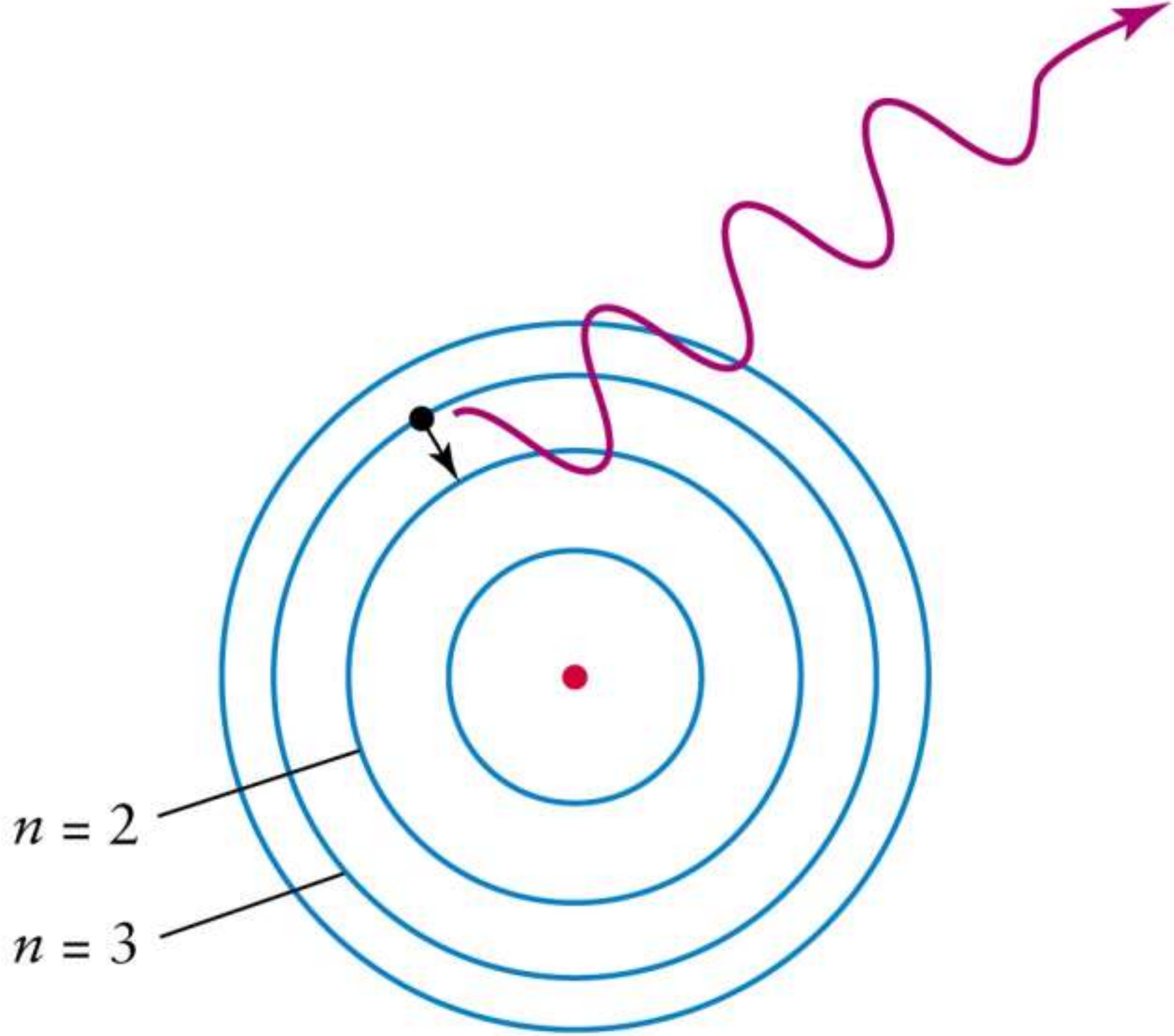
amplitude is the height of the wiggles

The Bohr Model of the Hydrogen Atom





a Absorption



b Emission

Bohr's equation for Hydrogen

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

λ = wavelength
n = number of inner orbit
m = number of outer orbit
R = Rydberg constant

→ reduces to Balmer's formula when n=2

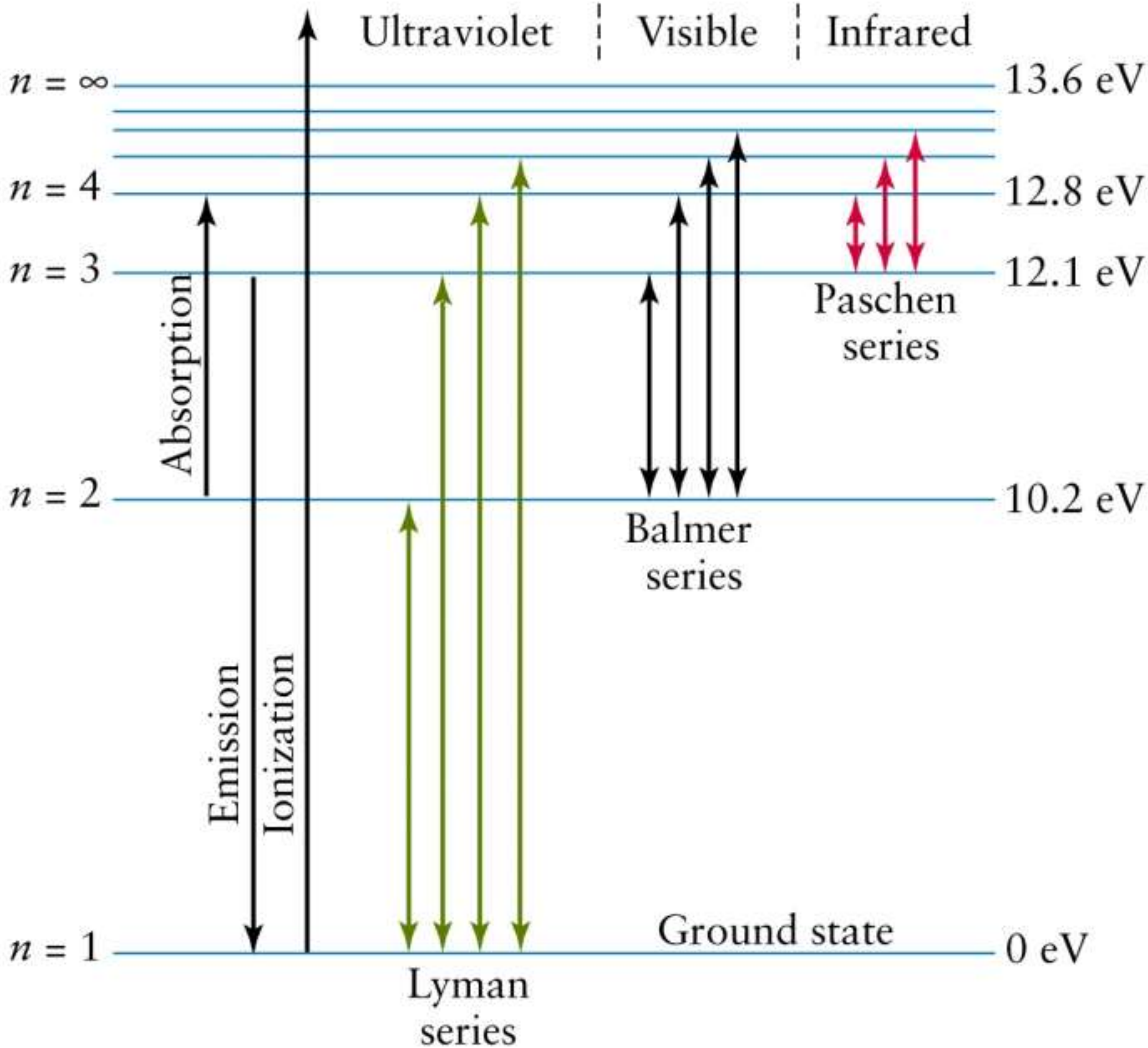
Atomic Spectroscopy

Absorption or Emission

$$\frac{1}{\lambda_{\mathrm{vac}}} = R_{\mathrm{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Johannes Rydberg 1888
Swedish

$n_1 \rightarrow n_2$	name	Converges to (nm)
$1 \rightarrow \infty$	Lyman	91
$2 \rightarrow \infty$	Balmer	365
$3 \rightarrow \infty$	Pashen	821
$4 \rightarrow \infty$	Brackett	1459
$5 \rightarrow \infty$	Pfund	2280
$6 \rightarrow \infty$	Humphreys	3283



Ultraviolet
Visible
Infrared
n = ∞
13.6 eV
n = 4
12.8 eV
n = 3
12.1 eV
Absorption
Paschen
series
n = 2
10.2 eV
Balmer
series
Emission
Ionization
n = 1
Ground state
0 eV
Lyman
series

Summary of quantum view of the atom

- observation: An atom will only absorb or release light at discrete frequencies
- explanation:
  - absorption or emission of light is caused by electron energy transitions within the atom
  - the energy carried by light is connected with its frequency
  - electrons are only allowed to move between discrete energy levels in the atom