

Chapter 2: Atomic Structure

Concepts in this Chapter:

- * All matter is composed of atoms.
- * The energies of atoms are quantized.
- * The atom has a shell structure.

Line emission spectrum of hydrogen. All of the observed spectral series of the hydrogen atom were found to obey the Rydberg equation

$$1/\lambda = R_H(1/n_1^2 - 1/n_2^2) \quad R_H \text{ is Rydberg constant} = 1.0974 \times 10^7 \text{ m}^{-1}$$

Bohr's Theory of the Hydrogen Atom. The electron moves about the nucleus in well-defined circular orbits. The angular momenta of the electron in these orbits are:

$$nh/2\pi = mvr$$

m and v are the mass of the electron and its velocity in the orbit, r is the radius of the orbit, and n is a quantum number.

The energy of the electron in the hydrogen atom is therefore quantized (allowed to have only certain values).

$$\text{Radius} \quad r = \epsilon_0 n^2 h^2 / 4\pi^2 m Z e^2$$

where

$$\epsilon_0 = \text{permittivity of a vacuum} = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$$

$$h = \text{Planck constant} = 6.626 \times 10^{-34} \text{ J-sec}$$

$$n = 1, 2, 3, \dots$$

$$m = \text{electron rest mass} = 9.109 \times 10^{-31} \text{ kg}$$

$$e = \text{charge on an electron} = 1.602 \times 10^{-19} \text{ C}$$

$$\text{Energy} \quad E_n = -me^4/8h^2 \epsilon^2 n^2 = -R_H hc/n^2 = -B/n^2 = -2.176 \times 10^{-18}/n^2 \text{ Joules}$$

With one electron system:

$$E_n = -BZ^2/n^2 \text{ where } Z = \# \text{ protons, } B = 2.18 \times 10^{-18} \text{ J/atom or } B = 1312 \text{ J/mole of atoms}$$

$$E_{\text{photon}} = hc/\lambda = \Delta E = E_f - E_i = -B [1/n_f^2 - 1/n_i^2] \text{ where } n = 1, 2, 3, \dots, \infty$$

Bohr: 1) predicted the emission line spectrum of hydrogen

2) gave correct ionization energy of H atom (energy for the removal of an electron)

Failures of the Bohr Model:

1) Electrons don't move in circular orbits

2) Bohr model only works for one-electron systems, Ex: H, He⁺, Li²⁺, Be³⁺ these examples all have 1 electron, but differ in amount of protons (Z).

Wave Particle Duality-Modern Quantum Theory. de Broglie suggested that matter, like light, might exhibit a duality of wave and particle characteristics. de Broglie suggested that the electron is governed by a similar equation as that of a photon:

$$\lambda = h/p \quad (\lambda: \text{wavelength, } p: \text{momentum})$$

$$\Rightarrow \lambda = h/mv \quad (1)$$

The allowed orbits of the hydrogen atom are those in which an integral number of electron wavelengths exactly fits the circumference of the orbit (the electron in the hydrogen atom as a standing wave)

$$n\lambda = 2\pi r \quad (2)$$

$$\text{From (1) and (2):} \quad nh/2\pi = mvr$$

This is exactly Bohr's quantized momentum assumption.

The Schrodinger Wave Equation. Schrödinger model treats electrons as a wave.

Possible states of an electron in the H atom are described by wave functions $\psi_{n, l, m_l}(x, y, z)$ denoted as atomic orbitals.

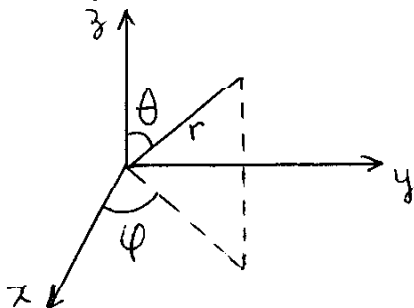
$$-(\hbar^2/8\pi^2m)(\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2) + V\psi = E\psi$$

ψ is the wave function of the electron; ∂ is a partial derivative of wave function; V is the potential energy of the electron in the electric field of the nucleus; and E is the total energy of the electron (potential plus kinetic).

Probability of finding an electron in an atomic orbital (AO) is given by the square of the wave function.

Solution of the Schrodinger equation gives mathematical expressions for the wave functions, ψ , associated with each of the allowed orbitals of the hydrogen atom.

Because the Coulomb term defines a central field potential, it is convenient to solve the above equation using a transformation from Cartesian to Polar coordinate.



$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

Atomic orbitals are characterized by three integral quantum numbers, n , l , and m_l and can be factored into a radial part and two angular components (which are sometimes combined into a single factor, called the Spherical Harmonics):

$$\Psi_{n, l, m_l}(r, \theta, \phi) = R(r) \Phi(\theta) \Phi(\phi) = R(r) Y(\theta, \phi)$$

While the radial function $R(r)$ describes how the electron probability changes with distance from the nucleus, the angular functions $\Phi(\theta)$ and $\Phi(\phi)$ describe the probability changes from point to point at a given distance from the center of the atom; i.e., they determine the shape of the orbitals and their orientation in space.