

Section Summary

30.1 Discovery of the Atom

- Atoms are the smallest unit of elements; atoms combine to form molecules, the smallest unit of compounds.
- The first direct observation of atoms was in Brownian motion.
- Analysis of Brownian motion gave accurate sizes for atoms (10^{-10} m on average) and a precise value for Avogadro's number.

30.2 Discovery of the Parts of the Atom: Electrons and Nuclei

- Atoms are composed of negatively charged electrons, first proved to exist in cathode-ray-tube experiments, and a positively charged nucleus.
- All electrons are identical and have a charge-to-mass ratio of
- $\frac{q_e}{m_e} = -1.76 \times 10^{11}$ C/kg.
- The positive charge in the nuclei is carried by particles called protons, which have a charge-to-mass ratio of
- $\frac{q_p}{m_p} = 9.57 \times 10^7$ C/kg.
- Mass of electron,
- $m_e = 9.11 \times 10^{-31}$ kg.
- Mass of proton,
- $m_p = 1.67 \times 10^{-27}$ kg.
- The planetary model of the atom pictures electrons orbiting the nucleus in the same way that planets orbit the sun.

30.3 Bohr's Theory of the Hydrogen Atom

- The planetary model of the atom pictures electrons orbiting the nucleus in the way that planets orbit the sun. Bohr used the planetary model to develop the first reasonable theory of hydrogen, the simplest atom. Atomic and molecular spectra are quantized, with hydrogen spectrum wavelengths given by the formula
- $\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$

where λ is the wavelength of the emitted EM radiation and R is the Rydberg constant, which has the value

$$R = 1.097 \times 10^7 \text{ m}^{-1}.$$

- The constants n_i and n_f are positive integers, and n_i must be greater than n_f .

- Bohr correctly proposed that the energy and radii of the orbits of electrons in atoms are quantized, with energy for transitions between orbits given by

$$\Delta E = hf = E_i - E_f,$$

where ΔE is the change in energy between the initial and final orbits and hf is the energy of an absorbed or emitted photon. It is useful to plot orbital energies on a vertical graph called an energy-level diagram.

- Bohr proposed that the allowed orbits are circular and must have quantized orbital angular momentum given by
- $L = m_e v r_n = n \frac{h}{2\pi} (n = 1, 2, 3 \dots),$

where L is the angular momentum, r_n is the radius of the n th orbit, and h is Planck's constant. For all one-electron (hydrogen-like) atoms, the radius of an orbit is given by

$$r_n = \frac{n^2}{Z} a_B (\text{allowed orbits } n = 1, 2, 3, \dots),$$

Z is the atomic number of an element (the number of electrons is has when neutral) and a_B is defined to be the Bohr radius, which is

$$a_B = \frac{h^2}{4\pi^2 m_e k q_e^2} = 0.529 \times 10^{-10} \text{ m}.$$

- Furthermore, the energies of hydrogen-like atoms are given by
- $E_n = -\frac{Z^2}{n^2} E_0 (n = 1, 2, 3 \dots),$

where E_0 is the ground-state energy and is given by

$$E_0 = \frac{2\pi^2 q_e^4 m_e k^2}{h^2} = 13.6 \text{ eV}.$$

Thus, for hydrogen,

$$E_n = -\frac{13.6 \text{ eV}}{n^2} (n = 1, 2, 3 \dots).$$

- The Bohr Theory gives accurate values for the energy levels in hydrogen-like atoms, but it has been improved upon in several respects.

30.4 X Rays: Atomic Origins and Applications

- X rays are relatively high-frequency EM radiation. They are produced by transitions between inner-shell electron levels, which produce x rays characteristic of the atomic element, or by decelerating electrons.
- X rays have many uses, including medical diagnostics and x-ray diffraction.

30.5 Applications of Atomic Excitations and De-Excitations

- An important atomic process is fluorescence, defined to be any process in which an atom or molecule is excited by absorbing a photon of a given energy and de-excited by emitting a photon of a lower energy.

- Some states live much longer than others and are termed metastable.
- Phosphorescence is the de-excitation of a metastable state.
- Lasers produce coherent single-wavelength EM radiation by stimulated emission, in which a metastable state is stimulated to decay.
- Lasing requires a population inversion, in which a majority of the atoms or molecules are in their metastable state.

30.6 The Wave Nature of Matter Causes Quantization

- Quantization of orbital energy is caused by the wave nature of matter. Allowed orbits in atoms occur for constructive interference of electrons in the orbit, requiring an integral number of wavelengths to fit in an orbit's circumference; that is,

$$n\lambda_n = 2\pi r_n (n = 1, 2, 3 \dots),$$

where λ_n is the electron's de Broglie wavelength.

- Owing to the wave nature of electrons and the Heisenberg uncertainty principle, there are no well-defined orbits; rather, there are clouds of probability.
- Bohr correctly proposed that the energy and radii of the orbits of electrons in atoms are quantized, with energy for transitions between orbits given by
- $\Delta E = hf = E_i - E_f$,

where ΔE is the change in energy between the initial and final orbits and hf is the energy of an absorbed or emitted photon.

- It is useful to plot orbit energies on a vertical graph called an energy-level diagram.
- The allowed orbits are circular, Bohr proposed, and must have quantized orbital angular momentum given by
- $L = m_e v r_n = n \frac{h}{2\pi} (n = 1, 2, 3 \dots)$,

where L is the angular momentum, r_n is the radius of orbit n , and h is Planck's constant.

30.7 Patterns in Spectra Reveal More Quantization

- The Zeeman effect—the splitting of lines when a magnetic field is applied—is caused by other quantized entities in atoms.
- Both the magnitude and direction of orbital angular momentum are quantized.
- The same is true for the magnitude and direction of the intrinsic spin of electrons.

30.8 Quantum Numbers and Rules

- Quantum numbers are used to express the allowed values of quantized entities. The principal quantum number n labels the basic states of a system and is given by
- $n = 1, 2, 3, \dots$
- The magnitude of angular momentum is given by
- $L = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (l = 0, 1, 2, \dots, n-1),$

where l is the angular momentum quantum number. The direction of angular momentum is quantized, in that its component along an axis defined by a magnetic field, called the z -axis is given by

$$L_z = m_l \frac{h}{2\pi}$$

$$(m_l = -, l, -, l, +, l, +, 1, \dots, -, 1, 0, 1, \dots, l, -, 1, l),$$

L_z is the z -component of the angular momentum and m_l is the angular momentum projection quantum number. Similarly, the electron's intrinsic spin angular momentum s is given by

$$S = \sqrt{s(s+1)} \frac{h}{2\pi} \quad (s = 1/2 \text{ for electrons}),$$

s is defined to be the spin quantum number. Finally, the direction of the electron's spin along the z -axis is given by

$$S_z = m_s \frac{h}{2\pi} \quad (m_s = -\frac{1}{2}, +\frac{1}{2}),$$

where S_z is the z -component of spin angular momentum and m_s is the spin projection quantum number. Spin projection $m_s = +1/2$ is referred to as spin up, whereas $m_s = -1/2$ is called spin down. Table 30.1 summarizes the atomic quantum numbers and their allowed values.

30.9 The Pauli Exclusion Principle

- The state of a system is completely described by a complete set of quantum numbers. This set is written as (n, l, m_l, m_s) .
- The Pauli exclusion principle says that no two electrons can have the same set of quantum numbers; that is, no two electrons can be in the same state.
- This exclusion limits the number of electrons in atomic shells and subshells. Each value of n corresponds to a shell, and each value of l corresponds to a subshell.
- The maximum number of electrons that can be in a subshell is $2(2l+1)$.
- The maximum number of electrons that can be in a shell is $2n^2$.