

CASCH 131  
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# Chapter 1

## Atomic Theory and the Nature of Modern Chemistry

### 1.1 1.1 - The Nature of Modern Chemistry

#### Definition 1.1.1: Conservation of Energy and Mass

Energy and mass are conserved in ordinary chemical reactions. The total mass of the products equals the total mass of the reactants.

#### Theorem 1.1.1 Macroscopic and Nanoscopic Length Scales

Chemical reactions occur on the scale of nanometers, yet are observed in laboratories on scales of grams and centimeters.

### 1.2 The Atom in Modern Chemistry

#### Note:-

##### Modern Chemistry Timeline

Modern chemistry is approximately 300 years old, with its roots dating back to the late 18th and early 19th centuries. Several foundational laws and principles emerged during this period, forming the basis of modern chemical science.

#### 1.2.1 Lavoisier: Conservation of Mass and Energy

#### Definition 1.2.1: Law of Conservation of Mass and Energy

Antoine Lavoisier (1743–1794) formulated the Law of Conservation of Mass, which states that in a chemical reaction, mass is neither created nor destroyed. This principle was later extended to include energy, particularly after the development of modern physics.

#### Note:-

##### Note on Lavoisier's Contribution

Lavoisier's discovery revolutionized chemistry by providing a quantitative approach to chemical reactions. He is often called the "Father of Modern Chemistry."

### 1.2.2 Proust: Law of Constant Composition

#### Definition 1.2.2: Law of Constant Composition (Definite Proportions)

Joseph Proust (1754–1826) established the Law of Constant Composition, which states that a given chemical compound always contains its component elements in a fixed ratio by mass, regardless of its source or method of preparation.

#### Note:-

Proust's Discovery

This law was critical in distinguishing compounds from mixtures and emphasized the fixed, predictable nature of chemical compounds.

### 1.2.3 Dalton: Law of Multiple Proportions

#### Definition 1.2.3: Law of Multiple Proportions

John Dalton (1766–1844) introduced the Law of Multiple Proportions, which states that when two elements form more than one compound, the masses of one element that combine with a fixed mass of the other are in ratios of small whole numbers.

#### Note:-

Example of Dalton's Law

For example, carbon and oxygen form two compounds: carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). The mass ratio of oxygen in CO<sub>2</sub> to CO is 2:1.

### 1.2.4 Gay-Lussac: Law of Combining Volumes

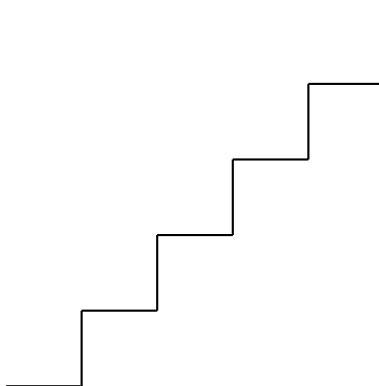
#### Definition 1.2.4: Law of Combining Volumes

Joseph Louis Gay-Lussac (1778–1850) discovered that when gases react together at constant temperature and pressure, the volumes of the reactants and products (if gaseous) are in simple whole number ratios. This is known as the Law of Combining Volumes.

#### Note:-

Gay-Lussac's Contribution

This law played a crucial role in understanding the stoichiometry of gaseous reactions and helped pave the way for Avogadro's hypothesis.



**Note:-**

## Note on Visual Representation

The staircase diagram illustrates the progressive development of chemistry over time, where each step represents a major discovery that builds on the previous one.

### 1.3 1.2 - Elements: The Building Blocks of Matter

**Definition 1.3.1: Mixtures and Compounds**

Mixtures can be separated by physical processes (e.g., filtration, distillation). Compounds are substances that can only be separated into simpler substances by chemical reactions.

### 1.4 1.3 - Indirect Evidence for the Existence of Atoms

**Definition 1.4.1: Dalton's Atomic Theory**

Atoms are indivisible, retain their identity in chemical reactions, and combine in fixed whole-number ratios to form compounds.

**Note:-**

## Laws of Chemical Combination

The laws of definite proportions and multiple proportions form the basis for determining chemical formulas.

### 1.5 1.4 - The Physical Structure of Atoms

**Definition 1.5.1: Cathode Ray Experiment**

Cathode rays are negatively charged particles (electrons) with a charge-to-mass ratio measured by Thomson and charge measured by Millikan.

**Theorem 1.5.1 Planetary Model of the Atom**

The scattering of alpha particles by gold established the planetary model: a dense nucleus surrounded by electrons.

### 1.6 1.5 - Mass Spectrometry and Isotopes

**Note:-**

## Relative Atomic Masses

Elements have isotopes with different masses but identical chemical properties.

### 1.7 1.6 - The Mole: Counting Molecules by Weighing

**Definition 1.7.1: Avogadro's Number**

1 mol =  $6.022 \times 10^{23}$  molecules. Molar mass is used to convert between mass, moles, and the number of molecules.

## Chapter 2

# 19 - Nucleosynthesis of the Elements

## 2.1 19.1 - Mass-Energy in Nuclei

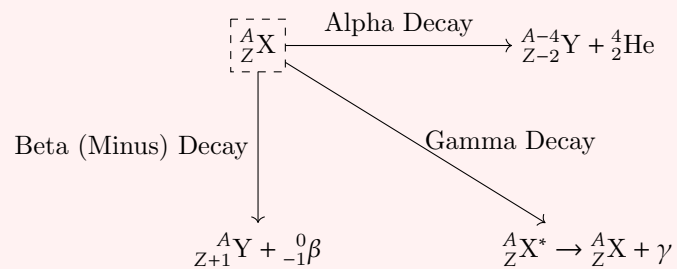
### Definition 2.1.1: Nuclear Symbols

Number of nucleons  $A$   
Number of protons  $Z$



## 2.2 19.2 - Nuclear Decay

### Definition 2.2.1: Nuclear Decay Process



### Definition 2.2.2: Alpha Decay

**Alpha decay** is the most common nuclear decay process.

Alpha decay is most common in nuclei with atomic number greater than 82 (the highest binding energy per nuclei).

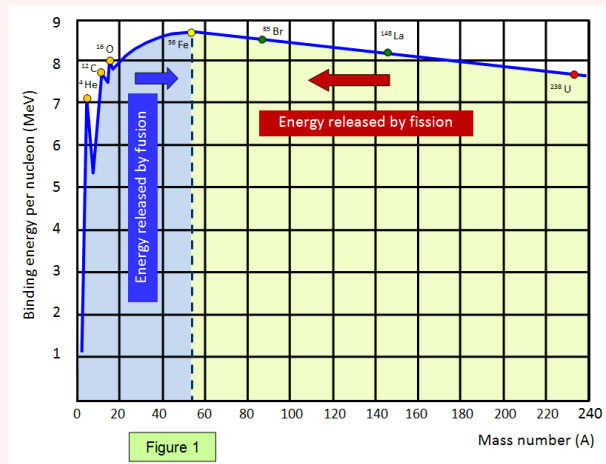
### Definition 2.2.3: Binding Energy per Nucleon

$$\Delta E = \Delta mc^2$$

$$\Delta E = M_{Z,A} - (M_{Z-2} + M_{2,\alpha}) c^2 > 0$$

If  $\Delta E > 0 \Rightarrow$  Decay Occurs

If  $\Delta E < 0 \Rightarrow$  Stable



### Definition 2.2.4: Beta Decay

**Beta decay** occurs when a nucleus emits or absorbs a neutron.  
Beta decay is very common in nuclei with atomic number less than 82.

### Definition 2.2.5: Gamma Decay

**Gamma decay** occurs when a nucleus emits or absorbs a photon.  
Gamma decay is rare, but it can occur in high-energy nuclei.  
Photons of electromagnetic radiation that carry away excess energy when nuclei make  $\gamma$  decay.

## 2.3 19.6 - Nuclear Fusion

### Definition 2.3.1: Origin of elements

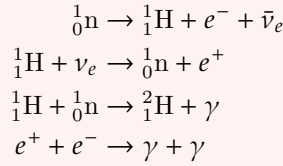
**Fusion of elements** involves 2 nuclei of very low A amalgamating to form a more stable nucleus.  
Getting the A value nearer to 56 (the highest Binding Energy per nucleon).

#### Note:-

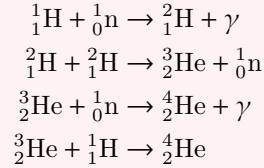
Hubble's observations of red shift in further galaxies and knowledge of fusion leads us to predict the existence of a singularity at the start of the current universe. What came before this is not known, but it is believed to be a singularity of the same type as the one at the end of the universe.

**The Steady State model** states that the density of the expanding universe should remain constant. As the universe expands, the density of matter stays the same as more matter is created.



**Definition 2.3.2: Initial Events of Big Bang**

Then



Helium 3 (weird particle due to its quantum behavior) and helium 4 are created 1/10 of the time

**Note:-**

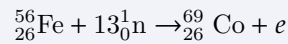
The fusion of 1 gram deuterium and helium 3 gives about 350 billion joules of energy. Reason for which we are trying to reproduce fission on earth

**Theorem 2.3.1 Clusters**

Ripples in the helium and tritium gas clouds form denser regions, which group further due to gravity → hydrogen burn → HE is formed in a star cycle of reactions (proton-proton cycle) and heavier elements move towards the center. Outer portions do proton-proton burn, inner denser portions of the star do helium burn. → Helium 4's combine to make Beryllium  ${}^8_4\text{Be}$ . Beryllium and Helium combine to make carbon  ${}^{12}_6\text{C}$ . → CARBON CYCLE occurs as  ${}^{12}_6\text{C}$  is the catalyst. By adding helium  ${}^4_2\text{He}$  to all the elements in the dense cores, all the elements up to iron  ${}^{56}_{26}\text{Fe}$  formed, and then stopped due to it having the highest binding energy per nucleon.

**Theorem 2.3.2 After Iron**

A 14 particle collision is needed to make elements after Iron, which is very unlikely.

**Note:-**

Fusion only gets us 26 elements (in stars).

## Chapter 3

# Chemical Structures

### 3.1 Drawing Lewis Dot Structures

Lewis dot structures are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Here's a step-by-step guide on how to draw Lewis dot structures:

#### 3.1.1 Steps to Draw a Lewis Dot Structure

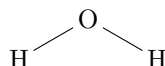
1. **Count the Valence Electrons:** Find the total number of valence electrons in the molecule by adding up the valence electrons of all atoms.
2. **Arrange the Atoms:** Write the atoms in the molecule with the least electronegative atom as the central atom (except for hydrogen, which is always terminal).
3. **Form Bonds Between Atoms:** Connect the atoms with single bonds. Each bond represents a pair of shared electrons.
4. **Distribute Remaining Electrons:** Distribute the remaining valence electrons as lone pairs around the atoms to satisfy their octet (or duet for hydrogen).
5. **Complete Octets:** Make sure that each atom (except hydrogen) has 8 electrons around it by sharing additional pairs of electrons to form double or triple bonds if necessary.
6. **Check Formal Charges:** If necessary, minimize formal charges to ensure that the most stable structure is drawn.

#### 3.1.2 Example Structures

##### Water ( $\text{H}_2\text{O}$ )

The water molecule consists of two hydrogen atoms and one oxygen atom. Oxygen has 6 valence electrons, and each hydrogen has 1 valence electron, making a total of 8 valence electrons.

The Lewis structure is drawn as follows:

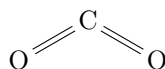


In this structure, the oxygen atom forms single bonds with each hydrogen atom and has two lone pairs of electrons.

##### Carbon Dioxide ( $\text{CO}_2$ )

The carbon dioxide molecule consists of one carbon atom and two oxygen atoms. Carbon has 4 valence electrons, and each oxygen has 6, making a total of 16 valence electrons.

The Lewis structure is drawn as follows:



In this structure, the carbon atom forms double bonds with each oxygen atom, and each oxygen has two lone pairs of electrons.

## 3.2 Common Molecular Shapes

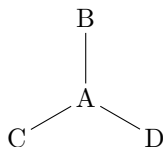
### 3.2.1 2 Electron Pairs - Linear - $AX_2$

In molecules with 2 bonding pairs and no lone pairs, the atoms are arranged in a straight line, resulting in a bond angle of  $180^\circ$ .



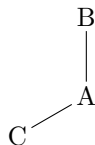
### 3.2.2 3 Electron Pairs - Trigonal Planar - $AX_3$

When there are 3 bonding pairs and no lone pairs, the atoms are positioned around the central atom in a single plane, forming a bond angle of  $120^\circ$ .



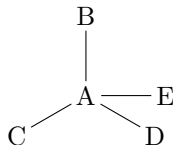
### 3 Electron Pairs (1 Lone Pair) - Bent - $AX_2E$

If there are 2 bonding pairs and 1 lone pair, the lone pair causes a repulsion that slightly decreases the bond angle to less than  $120^\circ$ .



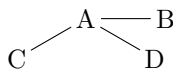
### 3.2.3 4 Electron Pairs - Tetrahedral - $AX_4$

For 4 bonding pairs and no lone pairs, the atoms are arranged in a tetrahedral shape with bond angles of  $109.5^\circ$ .



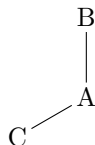
### 4 Electron Pairs (1 Lone Pair) - Trigonal Pyramidal - $AX_3E$

When there are 3 bonding pairs and 1 lone pair, the structure becomes trigonal pyramidal, and the lone pair repulsion decreases the bond angles to slightly less than  $109.5^\circ$ .



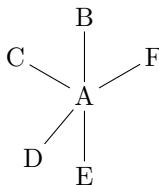
### 4 Electron Pairs (2 Lone Pairs) - Bent $AX_2E_2$

With 2 bonding pairs and 2 lone pairs, the shape is bent, with bond angles further reduced to less than  $109.5^\circ$ .



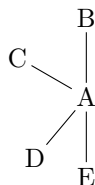
### 3.2.4 5 Electron Pairs - Trigonal Bipyramidal

For 5 bonding pairs and no lone pairs, the shape is trigonal bipyramidal, with bond angles of  $90^\circ$  (axial) and  $120^\circ$  (equatorial).



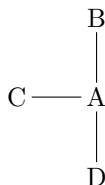
#### 5 Electron Pairs (1 Lone Pair) - Seesaw

With 4 bonding pairs and 1 lone pair, the structure becomes a seesaw, and the bond angles are slightly adjusted due to lone pair repulsion.



#### 5 Electron Pairs (2 Lone Pairs) - T-Shaped

When there are 3 bonding pairs and 2 lone pairs, the shape is T-shaped, with bond angles around  $90^\circ$ .



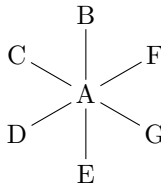
#### 5 Electron Pairs (3 Lone Pairs) - Linear

With 2 bonding pairs and 3 lone pairs, the shape reverts to linear with a bond angle of  $180^\circ$ .



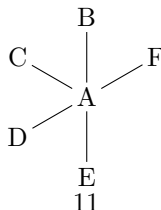
### 3.2.5 6 Electron Pairs - Octahedral

In a molecule with 6 bonding pairs and no lone pairs, the atoms are arranged in an octahedral shape with bond angles of  $90^\circ$ .



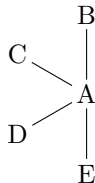
#### 6 Electron Pairs (1 Lone Pair) - Square Pyramidal

For 5 bonding pairs and 1 lone pair, the structure is square pyramidal, with slightly less than  $90^\circ$  bond angles due to lone pair repulsion.



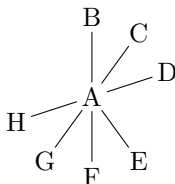
### 6 Electron Pairs (2 Lone Pairs) - Square Planar

With 4 bonding pairs and 2 lone pairs, the molecule is square planar, maintaining bond angles of  $90^\circ$ .



### 3.2.6 7 Electron Pairs - Pentagonal Bipyramidal

For 7 bonding pairs and no lone pairs, the atoms are arranged in a pentagonal bipyramidal shape with bond angles of  $72^\circ$  (within the pentagon) and  $90^\circ$  (between axial and equatorial positions).



## 3.3 Dipole Moment

The dipole moment is a measure of the separation of positive and negative charges in a molecule. It is a vector quantity, possessing both magnitude and direction. Molecules with polar bonds may have a net dipole moment if their molecular geometry does not cancel out the individual bond dipoles. The dipole moment influences many physical properties such as solubility, boiling point, and reactivity.

### 3.3.1 Examples

#### Carbon Tetrachloride ( $\text{CCl}_4$ )

Carbon tetrachloride is a symmetric molecule where the four C–Cl bonds are directed towards the corners of a tetrahedron. Although each C–Cl bond is polar due to the difference in electronegativity between carbon and chlorine, the symmetry of the molecule causes the bond dipoles to cancel out, resulting in a net dipole moment of zero.

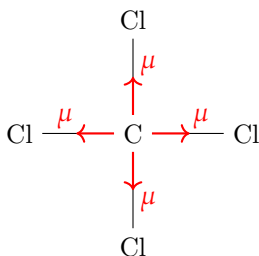


Figure 3.1: Molecular structure of  $\text{CCl}_4$  showing bond dipoles cancelling out.

#### Chloroform ( $\text{CHCl}_3$ )

Chloroform has a similar tetrahedral geometry as carbon tetrachloride but with one hydrogen atom replacing one of the chlorine atoms. This asymmetry results in bond dipoles that do not completely cancel out, giving chloroform a net dipole moment.

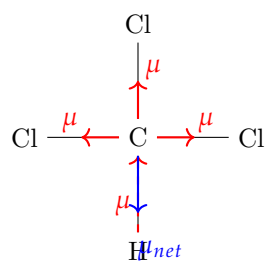


Figure 3.2: Molecular structure of CHCl<sub>3</sub> showing bond dipoles and net dipole moment.

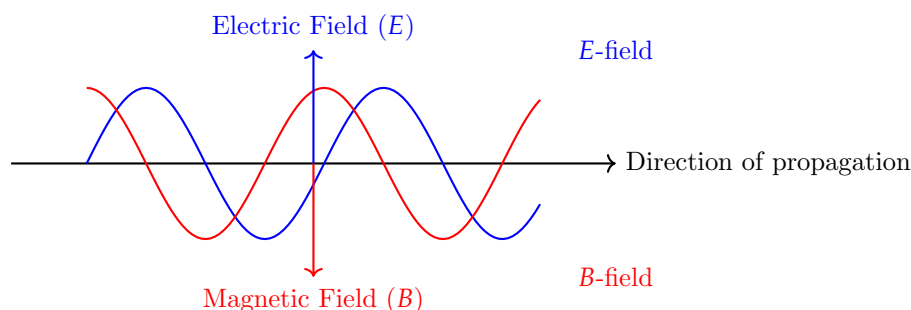
# Chapter 4

## Quantum Mechanics

### 4.1 Electromagnetic Fields in Light

Electromagnetic (EM) waves are composed of electric and magnetic fields oscillating perpendicularly to each other and to the direction of wave propagation. Light is an example of an EM wave, and it travels at the speed of light in a vacuum.

The electric field ( $E$ ) and magnetic field ( $B$ ) are perpendicular to each other, and both are perpendicular to the direction of wave propagation. Below is a simplified representation of an electromagnetic wave:



In this diagram, the electric field ( $E$ ) oscillates in one plane, while the magnetic field ( $B$ ) oscillates in a perpendicular plane. Both fields are sinusoidal and propagate together in the direction shown.

### 4.2 The Wave Equation: $c = f\lambda$

The relationship between the speed of light ( $c$ ), the frequency ( $f$ ), and the wavelength ( $\lambda$ ) of an electromagnetic wave is given by the equation:

$$c = f\lambda$$

where:

- $c$  is the speed of light in a vacuum, approximately  $3 \times 10^8$  m/s,
- $f$  is the frequency of the wave (in Hz),
- $\lambda$  is the wavelength of the wave (in meters).

This equation shows that the speed of light is the product of its frequency and wavelength. As the frequency of a wave increases, its wavelength decreases, and vice versa.

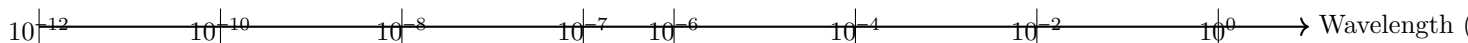
### 4.3 The Electromagnetic Spectrum

The electromagnetic spectrum encompasses all types of electromagnetic radiation, ranging from low-frequency radio waves to high-frequency gamma rays. Below is a diagram showing the range of the spectrum:

Decreasing Frequency  $\rightarrow$

Gamma Ray	X-Ray	Ultraviolet	Visible	Infrared	Microwave	Radio
-----------	-------	-------------	---------	----------	-----------	-------

Increasing Wavelength  $\leftarrow$



The electromagnetic spectrum ranges from long-wavelength, low-frequency waves like radio waves to short-wavelength, high-frequency waves like gamma rays. Visible light is a small portion of the spectrum, spanning from approximately 400 nm (violet) to 700 nm (red) in wavelength.

## 4.4 Absorption Spectrum of Elements

The absorption spectrum of an element is a unique pattern of dark lines or bands that appear when white light passes through a gas or vapor composed of the element. These dark lines correspond to specific wavelengths of light that have been absorbed by the element's atoms. Understanding absorption spectra is crucial in fields like astronomy and spectroscopy, as they allow scientists to identify elements in stars and distant galaxies.

### 4.4.1 How Absorption Spectra Work

When white light (which contains all visible wavelengths) passes through a sample of an element in its gaseous state, the electrons in the atoms of that element absorb specific amounts of energy. This energy corresponds to the difference between specific energy levels or orbits of the electrons.

When electrons absorb this energy, they jump from a lower energy level to a higher energy level, creating an absorption event. Each element has a unique set of energy levels, so the wavelengths absorbed (or "dark lines" in the spectrum) are also unique to each element. These dark lines are referred to as **absorption lines**.

### 4.4.2 Relationship to Emission Spectrum

The absorption spectrum is closely related to the **emission spectrum** of an element. When an electron drops from a higher energy level to a lower one, it emits light at a wavelength corresponding to the energy difference between these levels. In contrast, the absorption spectrum is formed when electrons move from lower to higher energy levels by absorbing light.

The emission lines and absorption lines occur at the same wavelengths for any given element, but they appear differently in the spectra:

- **Emission Spectrum:** Bright lines on a dark background, representing wavelengths emitted by electrons falling to lower energy levels.
- **Absorption Spectrum:** Dark lines on a bright (continuous) background, representing wavelengths absorbed by electrons jumping to higher energy levels.

### 4.4.3 Example: Hydrogen Absorption Spectrum

The hydrogen atom, for example, has a simple absorption spectrum. It consists of a series of dark lines in the visible region, corresponding to the specific wavelengths absorbed by electrons as they move to higher energy levels. The Balmer series is a well-known part of hydrogen's absorption spectrum, with lines appearing in the visible light range.

Below is a simplified representation of the absorption spectrum of hydrogen:



The dark lines represent wavelengths absorbed by the hydrogen atoms.



#### 4.4.4 Applications of Absorption Spectra

Absorption spectra are used in a variety of scientific fields to:

- Identify elements present in stars and distant astronomical objects.
- Determine the chemical composition of substances.
- Study the energy levels and quantum mechanics of atoms and molecules.

Since each element has a unique absorption spectrum, this technique allows scientists to detect and analyze the presence of different elements based on the pattern of dark lines that appear in a spectrum.



In this diagram, the gradient from white to black represents the continuous spectrum of light, while the vertical white lines represent absorption lines where specific wavelengths are absorbed by the element.

#### 4.5 Rydberg Equations and Emission Spectra

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:

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

where  $\lambda$  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

$$\Delta E = hf = E_i - E_f, \quad (30.3.22)$$

where  $\Delta E$  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

$$L = m_e v_n r_n = n \frac{h}{2\pi} \quad (n = 1, 2, 3, \dots),$$

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

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

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

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

Furthermore, the energies of hydrogen-like atoms are given by

$$E_n = -\frac{Z^2}{n^2} E_0 \quad (n = 1, 2, 3, \dots),$$

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

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

Thus, for hydrogen,

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

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

### 4.5.1 Applications of Rydberg Equation

The Rydberg equation is not only crucial for predicting the emission spectrum of hydrogen but also for understanding other one-electron systems like  $\text{He}^+$ ,  $\text{Li}^{2+}$ , and so forth. By studying the emission spectra of various elements, scientists can gain insights into the structure of atoms and the quantized nature of their energy levels. The emission spectra are also used in astrophysics to identify the elements present in distant stars and galaxies by comparing observed spectral lines with known values.

## 4.6 Max Planck's 1900 Theory and the Relationship $E = h\nu$

In the early 1900s, Max Planck introduced a revolutionary concept that laid the foundation for quantum mechanics. To address the problem of blackbody radiation, Planck proposed that electromagnetic energy could only be emitted or absorbed in discrete units, or "quanta." This concept was a significant departure from classical physics and led to the development of the famous relationship:

$$E = h\nu,$$

where:

- $E$  is the energy of a quantum (or photon) of electromagnetic radiation.
- $h$  is Planck's constant, with a value of approximately  $6.626 \times 10^{-34} \text{ Js}$ .
- $\nu$  (or  $f$ ) is the frequency of the electromagnetic radiation.

### 4.6.1 The Blackbody Radiation Problem

Classical physics predicted that a blackbody (an idealized physical body that absorbs all incident electromagnetic radiation) would emit radiation with an intensity that increases infinitely as the wavelength decreases (known as the "ultraviolet catastrophe"). However, experimental observations showed that the intensity reaches a peak and then drops off at shorter wavelengths. This discrepancy between theory and experiment led to the need for a new understanding of how radiation is emitted.

### 4.6.2 Planck's Solution: Quantization of Energy

Planck hypothesized that the energy emitted by a blackbody could only take on discrete values, rather than being continuous. He proposed that the energy of each quantum of radiation is proportional to its frequency, leading to the equation:

$$E = h\nu.$$

This assumption meant that electromagnetic radiation is quantized and that the energy levels are spaced in multiples of  $h\nu$ . In essence, energy could only be emitted or absorbed in "packets" or quanta, not as a continuous wave.

### 4.6.3 Implications of Planck's Theory

Planck's theory successfully explained the blackbody radiation spectrum, and the constant  $h$ , later known as Planck's constant, became a fundamental constant in quantum mechanics. This idea of quantization was groundbreaking because it introduced the concept that energy is not infinitely divisible, contradicting the classical wave theory of light.

The relationship  $E = h\nu$  implies that higher frequency (shorter wavelength) radiation has more energy per photon. This paved the way for the development of quantum theory and influenced subsequent discoveries, including:

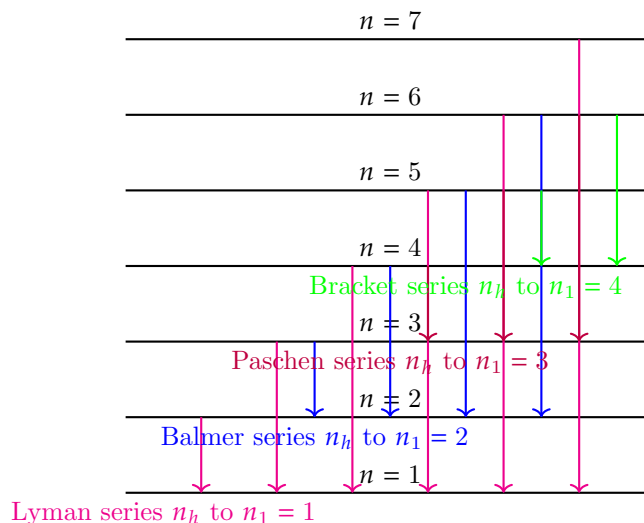
- **Photoelectric Effect:** Albert Einstein used Planck's concept to explain the photoelectric effect in 1905, showing that light can eject electrons from a material if the frequency is above a certain threshold. This provided further evidence of the particle-like behavior of light.
- **Wave-Particle Duality:** Planck's work suggested that light exhibits both wave-like and particle-like properties, an idea that became central to quantum mechanics.
- **Quantum Energy Levels:** The concept of quantized energy levels led to the understanding of atomic structure and the development of quantum mechanical models, where electrons occupy discrete energy states around the nucleus.

### 4.6.4 Applications and Further Developments

Planck's relationship,  $E = h\nu$ , has vast implications in various fields of physics and chemistry. It underpins the understanding of atomic spectra, molecular vibrations, and electronic transitions. It also plays a crucial role in technologies such as lasers, semiconductors, and quantum computing.

Overall, Planck's introduction of the quantization of energy marked the beginning of a new era in physics, laying the groundwork for the development of quantum mechanics and fundamentally changing our understanding of the physical world.

### 4.6.5 Quantized Emission Spectra



## 4.7 The Photoelectric Effect

The photoelectric effect is a phenomenon in which electrons are ejected from the surface of a material (usually a metal) when it is exposed to light of sufficient frequency. The experimental observations of the photoelectric effect could not be explained by classical wave theory and led to the development of quantum theory. Albert Einstein provided the explanation for this effect in 1905 by extending Max Planck's concept of quantization of energy.

### 4.7.1 Einstein's Explanation

According to Einstein, light consists of packets of energy called "photons," each with an energy  $E$  given by:

$$E = hf,$$

where:

- $h$  is Planck's constant ( $6.626 \times 10^{-34}$  Js).
- $f$  is the frequency of the incident light.

When a photon hits the surface of a material, its energy is transferred to an electron. If the photon's energy is greater than a certain minimum energy needed to free the electron (known as the **work function**  $\Phi$  of the material), the electron is ejected from the surface.

### 4.7.2 The Photoelectric Equation

The maximum kinetic energy  $E_{\max}$  of the ejected electron is given by the equation:

$$E_{\max} = hf - \Phi,$$

where:

- $E_{\max}$  is the maximum kinetic energy of the ejected electron.
- $hf$  is the energy of the incident photon.
- $\Phi$  is the work function of the material, which is the minimum energy required to free an electron from the surface.

This equation implies that the kinetic energy of the ejected electron depends linearly on the frequency of the incident light, and there is a threshold frequency  $f_{\text{threshold}}$  below which no electrons are ejected, regardless of the intensity of the light.

### 4.7.3 Stopping Voltage and Kinetic Energy

The kinetic energy of the ejected electrons can be measured experimentally using a stopping voltage  $V_s$ . The stopping voltage is the voltage required to stop the ejected electrons from reaching the detector. The relationship between the stopping voltage and the kinetic energy is given by:

$$E_{\max} = eV_s,$$

where:

- $e$  is the charge of the electron ( $1.602 \times 10^{-19}$  C).
- $V_s$  is the stopping voltage.

By measuring the stopping voltage for different frequencies of light, one can determine the work function  $\Phi$  of the material and verify the linear relationship between  $E_{\max}$  and the frequency  $f$  of the incident light.

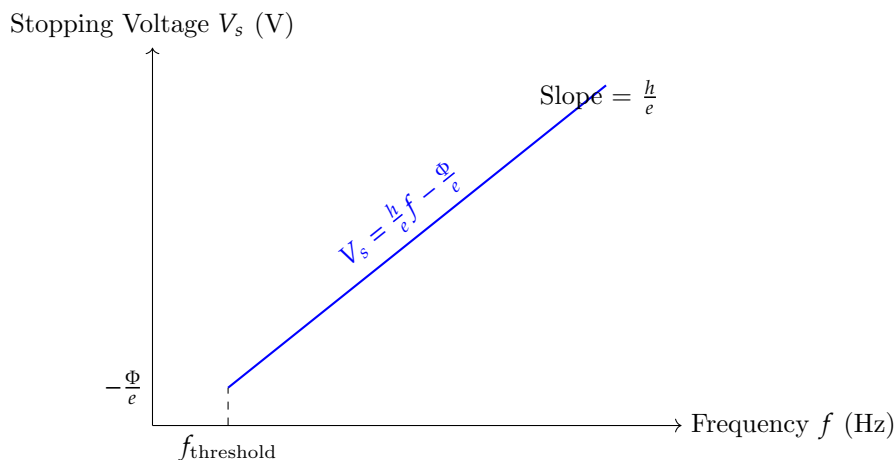
### 4.7.4 Significance of the Photoelectric Effect

The photoelectric effect provided strong evidence for the quantization of light and supported the particle-like behavior of photons. This was a crucial step in the development of quantum mechanics. The effect also showed that the energy of ejected electrons is independent of the light's intensity (which only affects the number of emitted electrons) and is instead solely dependent on the frequency of the incident light.

Applications of the photoelectric effect are found in various technologies, including photodetectors, solar cells, and photoelectron spectroscopy.

### 4.7.5 Graph of Voltage vs. Kinetic Energy

The photoelectric equation  $E_{\max} = hf - \Phi$  shows that the maximum kinetic energy of ejected electrons is linearly dependent on the frequency of the incident light. Experimentally, this relationship can be studied by plotting the stopping voltage  $V_s$  (which is directly proportional to  $E_{\max}$ ) against the frequency  $f$  of the incident light.



Graph of Stopping Voltage  $V_s$  vs. Frequency  $f$

### 4.7.6 Explanation of the Graph

The graph above represents the relationship between the stopping voltage  $V_s$  and the frequency of the incident light  $f$ . The linear equation governing this relationship is:

$$V_s = \frac{h}{e}f - \frac{\Phi}{e},$$

where:

- $h$  is Planck's constant.
- $e$  is the charge of an electron.
- $\Phi$  is the work function of the material.

In this graph:

- The **slope** of the line is  $\frac{h}{e}$ . Since  $h$  is Planck's constant and  $e$  is a known constant (the electron charge), the slope provides a way to determine Planck's constant experimentally.
- The **y-intercept** is  $-\frac{\Phi}{e}$ , which corresponds to the work function of the material divided by the electron charge. This intercept is negative, as it represents the minimum energy needed to eject an electron.
- The point at which the line intersects the  $f$ -axis is the **threshold frequency**  $f_{\text{threshold}}$ . For frequencies below this value, no electrons are emitted because the photon's energy is insufficient to overcome the work function  $\Phi$ .

The linear nature of this graph is a direct consequence of the photoelectric effect and provides evidence for the quantization of energy in photons. By measuring the slope of this line, one can experimentally determine the value of Planck's constant  $h$ .

## 4.8 Quantized Momentum of an Electron and Standing Waves in Orbits

In the Bohr model of the atom, electrons are assumed to occupy discrete orbits around the nucleus. One of the key ideas is that the angular momentum of an electron in these orbits is quantized. Specifically, the angular

momentum  $L$  is given by:

$$L = n\hbar,$$

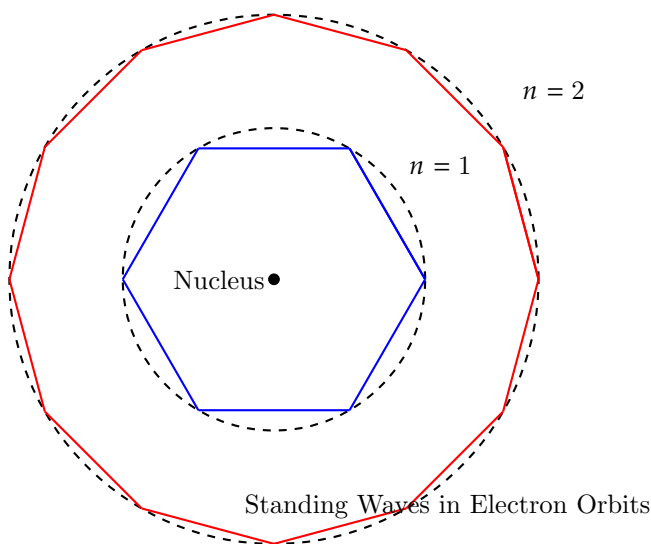
where:

- $n$  is a positive integer (the principal quantum number).
- $\hbar$  is the reduced Planck's constant ( $\hbar = \frac{h}{2\pi}$ ).

This quantization arises because the electron behaves as a standing wave in its orbit. For a stable orbit, the circumference of the orbit must be an integer multiple of the electron's wavelength  $\lambda$ :

$$2\pi r = n\lambda,$$

where  $r$  is the radius of the orbit.



#### 4.8.1 Standing Waves and Quantized Orbits

For each allowed orbit, the electron's de Broglie wavelength  $\lambda$  fits perfectly into the circumference of the orbit, creating a standing wave. This condition ensures that only specific, quantized orbits are possible, corresponding to different values of  $n$ . The quantization of angular momentum restricts electrons to these stable orbits, preventing them from spiraling into the nucleus.

In the diagram:

- The dashed circles represent possible orbits.
- The blue and red standing waves correspond to  $n = 1$  and  $n = 2$ , respectively, showing how the electron's wave fits into each orbit.

#### 4.8.2 Quantized Momentum of an Electron

In the Bohr model of the atom, the momentum of an electron is quantized due to its wave-like nature. The electron behaves as a standing wave around the nucleus, and only certain orbits are allowed where the circumference of the orbit is an integer multiple of the electron's wavelength:

$$2\pi r = n\lambda,$$

where  $r$  is the radius of the orbit,  $n$  is a positive integer (the principal quantum number), and  $\lambda$  is the de Broglie wavelength of the electron.

Since the de Broglie wavelength is related to momentum  $p$  by:

$$\lambda = \frac{h}{p},$$

the quantization condition becomes:

$$p = \frac{n\hbar}{r},$$

where  $\hbar = \frac{h}{2\pi}$ . This shows that the electron's momentum is quantized, allowing only specific values for each orbit.

## 4.9 Heisenberg Uncertainty Principle

The Heisenberg Uncertainty Principle is a fundamental concept in quantum mechanics, stating that it is impossible to simultaneously know the exact position and momentum of a particle. This principle arises due to the wave-like nature of particles at the quantum level. When attempting to measure one property (e.g., position), the wavefunction describing the particle's behavior is disturbed, leading to an increased uncertainty in the complementary property (e.g., momentum). This effect is a direct consequence of the properties of wavefunctions and Fourier transforms.

The principle is mathematically represented by the inequality:

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{4\pi}$$

where: -  $\Delta x$  is the uncertainty in position, -  $\Delta p$  is the uncertainty in momentum, -  $\hbar$  is Planck's constant. In other words, the product of the uncertainties in position and momentum can never be smaller than  $\frac{\hbar}{4\pi}$ . A similar relationship exists between the uncertainties in energy and time, given by:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{4\pi}$$

where: -  $\Delta E$  is the uncertainty in energy, -  $\Delta t$  is the uncertainty in time.

This relationship arises because a particle's energy and the time over which it is measured are also complementary variables, meaning that a precise measurement of one leads to increased uncertainty in the other.

The Heisenberg Uncertainty Principle emphasizes the inherent limitations in our ability to measure certain pairs of physical properties simultaneously, reflecting the fundamental nature of quantum systems.

## 4.10 Schrödinger's Equation and Atomic Orbitals

Schrödinger's equation describes the behavior of quantum particles, particularly electrons in an atom. The time-independent form of the equation is:

$$\hat{H}\psi = E\psi \quad (4.1)$$

where  $\hat{H}$  is the Hamiltonian operator,  $\psi$  is the wavefunction, and  $E$  is the energy of the system. In the context of atoms, solving this equation for electrons leads to quantized energy levels and wavefunctions, known as orbitals.

To reflect the symmetry of the atom, the wavefunction is expressed in spherical coordinates  $(r, \theta, \phi)$  rather than Cartesian coordinates  $(x, y, z)$ . This simplifies the equation due to the spherical symmetry of the Coulomb potential around the nucleus, making it easier to solve for orbitals:

$$\psi_{n,l,m_l}(r, \theta, \phi) = R(r)_{n,l}Y(\theta, \phi)_l \quad (4.2)$$

Here,  $R(r)$  describes the radial part, and  $Y(\theta, \phi)$  represents the angular part of the wavefunction. The quantum numbers  $n$ ,  $l$ , and  $m_l$  arise from these solutions, defining the energy levels and shapes of atomic orbitals.

The quantum numbers have the following values and meanings:

- The principal quantum number  $n$  determines the electron's energy level and the shell in which the electron resides. It takes positive integer values:  $n = 1, 2, 3, \dots$ . The value of  $n$  also correlates with the period (row) of the periodic table in which the element is found, and as  $n$  increases, the electron's average distance from the nucleus and energy both increase.
- The azimuthal quantum number  $l$  determines the shape of the orbital and the subshell, corresponding to the labels  $s$ ,  $p$ ,  $d$ , and  $f$ :

- $l = 0$ :  $s$ -orbital (spherical)
- $l = 1$ :  $p$ -orbital (dumbbell-shaped)
- $l = 2$ :  $d$ -orbital (more complex shapes)
- $l = 3$ :  $f$ -orbital (even more complex shapes)

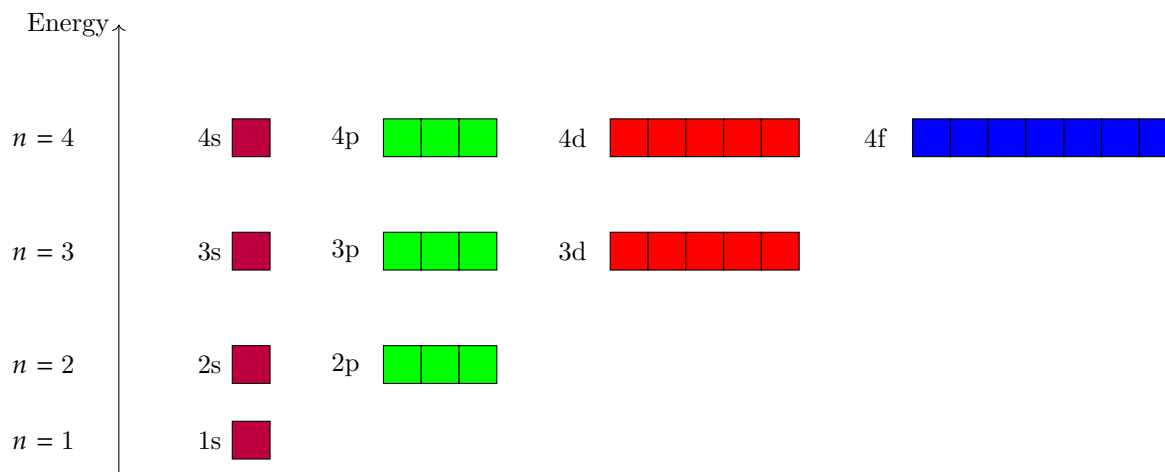
The possible values of  $l$  range from 0 to  $n - 1$  for a given energy level, defining which subshells are present within a shell.

- The magnetic quantum number  $m_l$  defines the orientation of the orbital in space and takes integer values from  $-l$  to  $l$ :  $m_l = -l, -(l-1), \dots, 0, \dots, (l-1), l$ . It specifies the number of orbitals within a subshell, such as the three orientations of the  $p$ -orbitals or the five orientations of the  $d$ -orbitals.

These quantum numbers collectively describe the unique characteristics of atomic orbitals, such as energy level, shape, orientation, and how they correspond to the organization of elements in the periodic table.

- Total Nodes =  $n - 1$
- Total Angular Nodes =  $l$
- Total Radial Nodes =  $n - l - 1$

## 4.11 Energy Diagram for Atomic Orbitals



### Explanation

The diagram represents the energy levels of atomic orbitals, arranged by the principal quantum number ( $n$ ) and their corresponding subshells.

- **Energy Axis:** The y-axis represents the increasing energy of the orbitals. As the energy increases, the orbitals are arranged vertically.
- **Principal Quantum Number ( $n$ ):** Each horizontal row corresponds to a different value of  $n$ , the principal quantum number, representing different electron shells. For example:
  - $n = 1$ : 1s orbital (lowest energy)
  - $n = 2$ : 2s and 2p orbitals
  - $n = 3$ : 3s, 3p, and 3d orbitals
  - $n = 4$ : 4s, 4p, 4d, and 4f orbitals (highest energy shown)

The value of  $n$  corresponds to the shell and relates to the energy level and the row (period) in the periodic table.

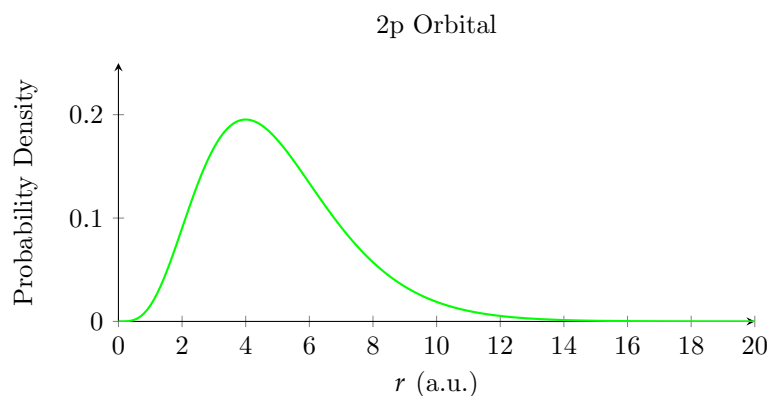
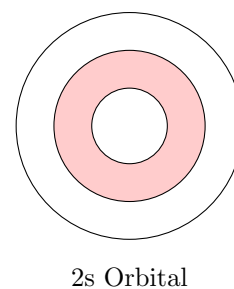
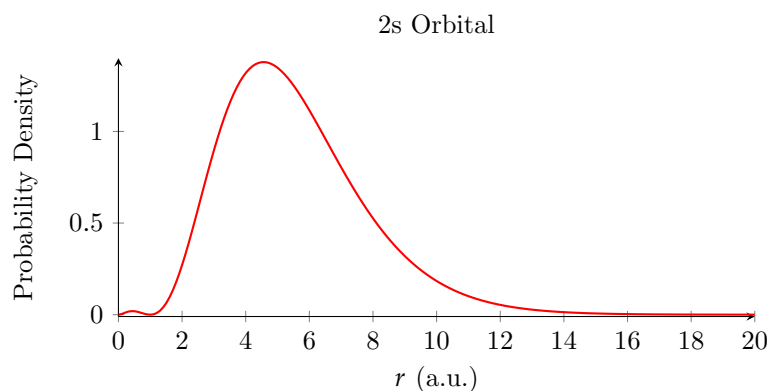
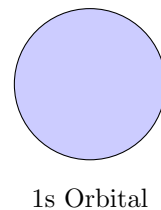
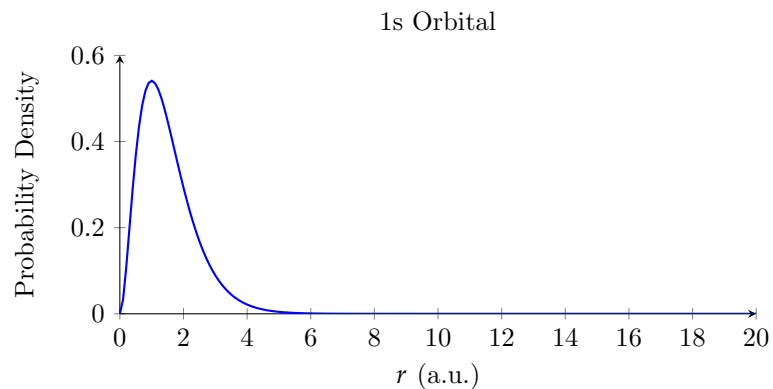


- **Subshells and Orbitals:**

- **s-orbitals** ( $l = 0$ ) are spherical and represented by purple squares. They exist for each value of  $n$  (1s, 2s, 3s, 4s).
- **p-orbitals** ( $l = 1$ ) are dumbbell-shaped and represented by green squares. They appear starting from  $n = 2$  (2p, 3p, 4p) and have three possible orientations, corresponding to three green squares for each  $p$ -subshell.
- **d-orbitals** ( $l = 2$ ) are more complex in shape and represented by red squares. They appear starting from  $n = 3$  (3d, 4d) and have five possible orientations, represented by five red squares for each  $d$ -subshell.
- **f-orbitals** ( $l = 3$ ) are highly complex in shape and represented by blue squares. They appear starting from  $n = 4$  (4f) and have seven possible orientations, represented by seven blue squares for each  $f$ -subshell.

The horizontal arrangement of colored squares shows the degeneracy (number of orbitals) for each subshell, while the vertical arrangement corresponds to increasing energy.

### 4.11.1 Visualization of Electron Probability Density Functions and Orbitals



2p Orbital

## 4.12 Nature of Electrons

Electrons exhibit wave-like properties, a fundamental concept in quantum mechanics. This wave nature is crucial in understanding atomic structure and electron behavior.

### 4.12.1 Delocalization

Delocalization occurs when we attempt to "measure" an electron. It describes an electron's wave that is not 3D localized.

## 4.13 Atomic Structure

### 4.13.1 Electron Configuration

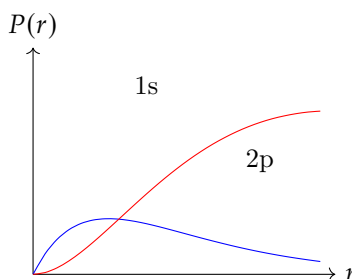
The arrangement of electrons in an atom follows specific patterns:

$$\begin{array}{llll} n = 1 : & 1s \\ n = 2 : & 2s & 2p \\ n = 3 : & 3s & 3p & 3d \\ n = 4 : & 4s & 4p & 4d & 4f \end{array}$$

Where  $n$  represents the principal quantum number.

### 4.14 Radial Probability

The radial probability distribution shows the likelihood of finding an electron at a certain distance from the nucleus.



This graph shows the radial probability distributions for 1s and 2p orbitals.

Shielding occurs when inner electrons partially shield outer electrons from the full nuclear charge. This leads to the concept of effective nuclear charge ( $Z_{\text{eff}}$ ).

For outer core levels:

$$90\% \cdot (3 - 2) = 0.9 \quad (\text{eff})$$

This means that .9 of the charge difference between the actual nuclear charge and the next lower noble gas configuration contributes to the effective nuclear charge.

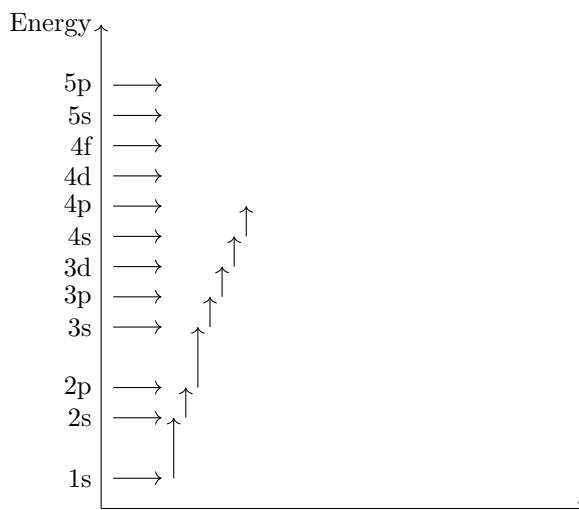
For 2s, which is not shielded by 1s:

$$100\% \cdot (3 - 0) = 3$$

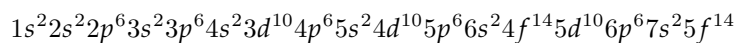
The full charge difference contributes to  $Z_{\text{eff}}$ .

### 4.15 Electron Configuration

The arrangement of electrons in an atom follows the Aufbau principle, Pauli exclusion principle, and Hund's rule. The diagram below illustrates the order of filling orbitals:

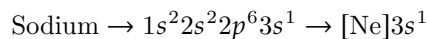


The full electron configuration for elements up to atomic number 87 (Francium) is:

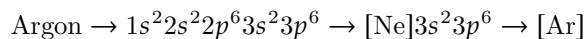


### 4.15.1 Example Configurations

**Sodium**



**Argon**



## 4.16 Quantum Numbers

For the principal quantum number  $n = 3$ :

- $\ell = \{s = 0, p = 1, d = 2, f = 3\dots\}$
- $m_\ell = -\ell, \dots, 0, \dots, +\ell$
- $m_s = -\frac{1}{2}, +\frac{1}{2}$

## 4.17 Hund's Rule

Hund's rule states that electrons in degenerate orbitals (same energy) will occupy different orbitals with the same spin before pairing up. For example, in the  $2p$  orbital:

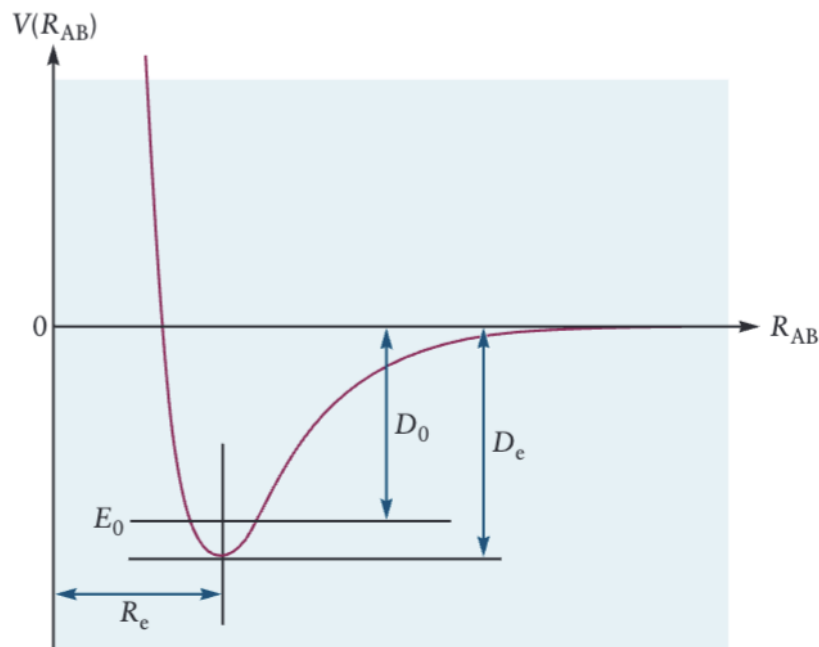


This configuration has  $m_s = +\frac{1}{2}$  for each unpaired electron.

## 4.18 Molecular Orbital Theory

Molecular Orbital (MO) theory explains the electronic structure of molecules by considering the combination of atomic orbitals (AOs) into molecular orbitals. These molecular orbitals extend over the entire molecule and can hold electrons from multiple atoms. MO theory provides a more accurate understanding of the bonding and antibonding interactions in a molecule compared to Valence Bond Theory.

### 4.18.1 Potential Energy of Hydrogen Molecule



*Schematic representation of the potential energy of two hydrogen atoms as a function of the distance between them. As distance decreases, the potential energy reaches a minimum value of  $-458 \text{ kJ mol}^{-1}$  at a distance of  $0.74 \text{ \AA}$ . The value of  $D_0$  for  $\text{H}_2$  is  $432 \text{ kJ mol}^{-1}$  or  $4.48 \text{ eV molecule}^{-1}$ .*

The graph above highlights the potential energy curve for the interaction between two hydrogen atoms. The minimum point represents the equilibrium bond length,  $R_e$ , where the potential energy is at its lowest and most stable. The depth of the well,  $D_e$ , reflects the bond dissociation energy, and it illustrates the energy required to break the bond and separate the atoms to infinity.

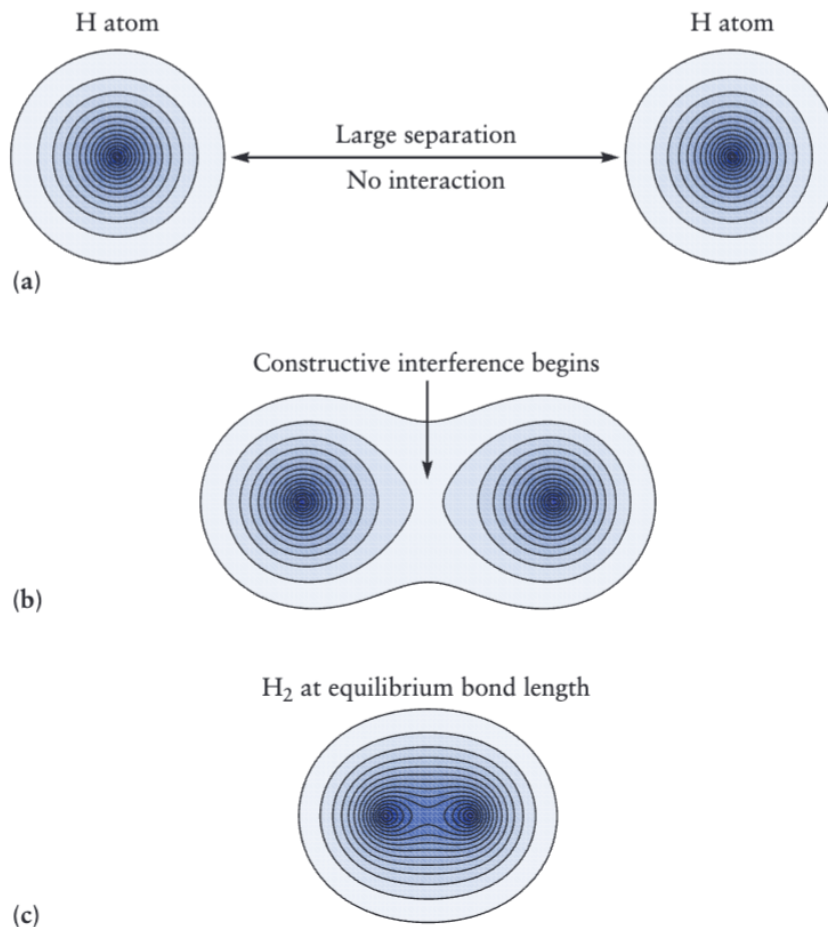
#### **Bond Energy and Stability:**

- $R_e$ : The equilibrium bond length where attractive and repulsive forces balance.
- $D_0$ : The dissociation energy that corresponds to the strength of the bond between hydrogen atoms.
- The deeper the well in the graph, the stronger the bond between atoms.

In the context of Molecular Orbital Theory, the bonding molecular orbital (MO) formed from the constructive interference of atomic orbitals leads to the stabilization and energy minimization observed at  $R_e$ . On the other hand, destructive interference can lead to an antibonding orbital, which increases the potential energy as  $R_{AB}$  approaches zero.

### 4.18.2 Electron Probability Density in $\text{H}_2$ Molecule

The electron probability density in a molecule is crucial to understanding the behavior of molecular orbitals. In MO theory, electrons are not confined to individual atoms but are distributed over the entire molecule. The following figure illustrates the probability density for finding an electron in the  $\text{H}_2$  molecule at three different internuclear distances.



The probability density for finding an electron in the  $H_2$  molecule, plotted at three internuclear distances: (a)  $8a_0$ , (b)  $3.5a_0$ , and (c)  $1.4a_0$ . At the equilibrium bond length (c), a significant buildup of electron density between the nuclei is visible.

This diagram shows three different stages of electron probability density as two hydrogen atoms approach each other:

1. **Large Separation ( $8a_0$ ) - No Interaction:** At large distances, as shown in (a), the two hydrogen atoms do not interact, and the electron densities remain localized around each nucleus. This represents a situation where the atomic orbitals are too far apart to overlap.
2. **Constructive Interference Begins ( $3.5a_0$ ):** As the atoms move closer, as shown in (b), constructive interference between the atomic orbitals begins. This is the first sign of bond formation as electron density starts to accumulate between the nuclei. This constructive overlap is essential in forming bonding molecular orbitals, which results in the lowering of energy and the stabilization of the molecule.
3. **H<sub>2</sub> at Equilibrium Bond Length ( $1.4a_0$ ):** At the equilibrium bond length, illustrated in (c), the overlap of the atomic orbitals is maximal, leading to significant electron density between the nuclei. This concentration of electron density between the two hydrogen atoms is what holds them together in a covalent bond. The bonding molecular orbital created by this overlap has a lower energy than the individual atomic orbitals, contributing to the stability of the  $H_2$  molecule.

#### Key Points to Note:

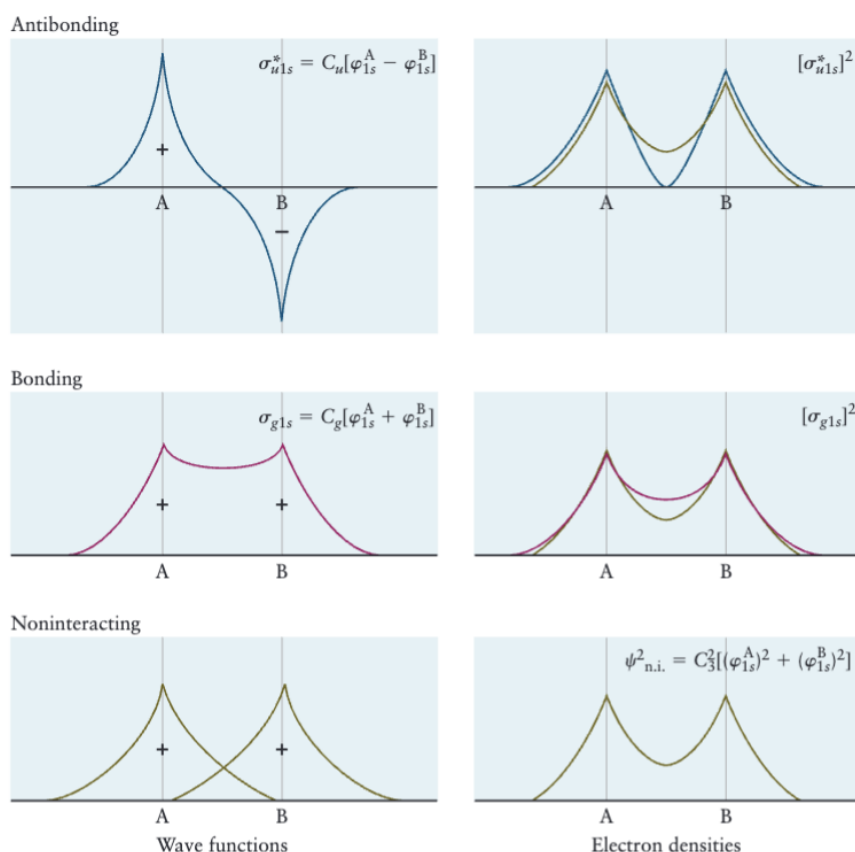
- As the hydrogen atoms approach one another, the electron density starts to build between the nuclei due to constructive interference, forming a bonding molecular orbital.

- At the equilibrium bond length, this bonding interaction is at its strongest, resulting in the maximum overlap of atomic orbitals.
- The behavior of the electron density between the atoms is a direct consequence of quantum mechanical principles that govern molecular orbital formation.

In the case of  $H_2$ , both electrons occupy the bonding molecular orbital, leading to the observed covalent bond. This distribution of electron density provides a qualitative understanding of why the molecule is stable at this bond length.

### 4.18.3 Bonding and Antibonding Molecular Orbitals of $H_2$

In MO theory, the combination of atomic orbitals (AOs) can result in the formation of either bonding or antibonding molecular orbitals (MOs). The following figure depicts the wave functions and electron densities for the  $H_2$  molecule, illustrating the bonding and antibonding interactions along the internuclear axis.



*Antibonding and bonding molecular orbitals of  $H_2$  along the internuclear axis in the linear combination of atomic orbitals (LCAO) approximation. The bonding orbital shows increased probability density between the nuclei, while the antibonding orbital shows decreased probability density.*

The diagram above presents a comparison between:

- The independent atomic orbitals (non-interacting case)
- Bonding molecular orbitals ( $\sigma_{g1s}$ )
- Antibonding molecular orbitals ( $\sigma_{u1s}^*$ )

In MO theory, atomic orbitals combine based on the principles of constructive and destructive interference:

- **Non-interacting Orbitals:** When the atoms are far apart and non-interacting, the electron density is localized around each nucleus. The wave functions, shown in the bottom row, remain independent and do not show any overlap. The electron density is confined to each atom.
- **Bonding Orbitals:** Constructive interference of the wave functions from atomic orbitals leads to the formation of a bonding orbital. In this case, the wave functions ( $\sigma_{g1s}$ ) combine additively, leading to an increased electron density between the two nuclei, as illustrated in the middle row. This increased electron density stabilizes the molecule, lowering its energy.
- **Antibonding Orbitals:** Destructive interference results in the formation of antibonding orbitals ( $\sigma_{u1s}^*$ ). The wave functions subtract from each other, leading to a node between the nuclei where electron density is reduced to zero, as shown in the top row. This decrease in electron density destabilizes the molecule and raises its energy.

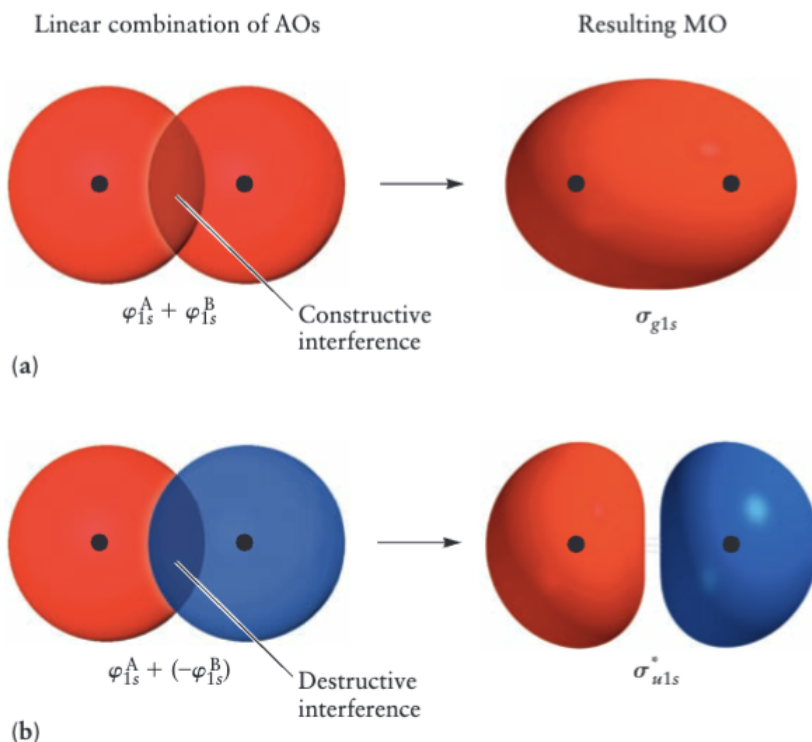
#### Key Features:

- In the bonding orbital, the electron probability density ( $\sigma_{g1s}^2$ ) is concentrated between the nuclei, facilitating covalent bonding.
- In contrast, the antibonding orbital ( $\sigma_{u1s}^{*2}$ ) shows a significant decrease in electron density between the nuclei, resulting in repulsion and higher energy.
- The molecular orbital approximation allows us to predict the relative stability of molecules. Bonding orbitals lower the total energy, while antibonding orbitals raise it.

The balance between the population of bonding and antibonding orbitals determines the overall stability of the  $H_2$  molecule. In stable molecules, bonding orbitals are filled, and antibonding orbitals remain unfilled.

### 4.18.4 Graphical Representation of Bonding and Antibonding MOs

In Molecular Orbital theory, the combination of atomic orbitals (AOs) can lead to the formation of bonding or antibonding molecular orbitals depending on whether the interference is constructive or destructive. The following figure shows a graphical representation of these combinations.





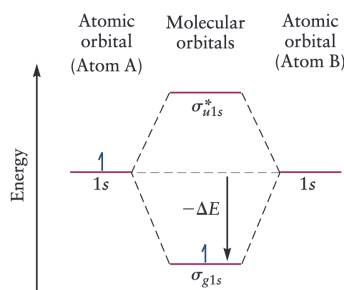
Graphical representation of the linear combination of atomic orbitals (AOs) resulting in a bonding molecular orbital (a) and an antibonding molecular orbital (b). The black dots show the approximate positions of the nuclei.

- In (a), constructive interference between the AOs leads to the formation of a bonding molecular orbital ( $\sigma_{g1s}$ ), where electron density is concentrated between the nuclei, stabilizing the molecule.
- In (b), destructive interference results in an antibonding molecular orbital ( $\sigma_{u1s}^*$ ), where electron density is reduced between the nuclei, leading to destabilization.
- The positions of the nuclei are represented by the black dots, emphasizing that electron density is more concentrated between the nuclei in bonding orbitals, while in antibonding orbitals, it is concentrated outside the internuclear region.

These graphical representations highlight the qualitative differences in electron distribution between bonding and antibonding molecular orbitals.

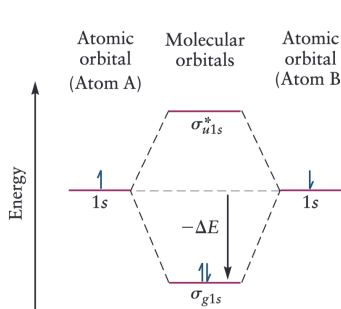
#### 4.18.5 Correlation Diagrams for First-Period Diatomic Molecules

Molecular orbitals for diatomic molecules are constructed from the atomic orbitals of each atom. The following diagrams show the energy correlation for different molecules, starting with  $H_2^+$ ,  $H_2$ , and  $He_2^+$ .

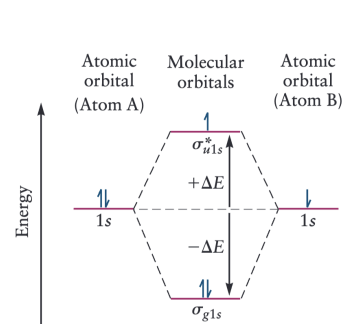


Correlation diagram for  $H_2^+$  in the LCAO approximation. The bonding orbital is stabilized relative to the noninteracting system.

$E_{1s} + (-\Delta E) = E_{\sigma_{g1s}}$ , so  $\Delta E$  is a positive number.



Correlation diagram for  $H_2$  in the LCAO approximation. The blue arrows indicate electron filling in accordance with the Aufbau principle.



Correlation diagram for  $He_2^+$ . The additional electron in the antibonding orbital reduces the bond order compared with that in  $H_2$ .

#### Key Points:

- In  $H_2^+$ , the bonding orbital is stabilized by the energy difference  $-\Delta E$ .
- For  $H_2$ , the bonding orbital  $\sigma_{g1s}$  is filled by two electrons, leading to bond formation.
- In  $He_2^+$ , an additional electron occupies the antibonding orbital  $\sigma_{u1s}^*$ , reducing the bond order and making the bond weaker than in  $H_2$ .

#### 4.18.6 Table: Electron Configurations and Bond Orders for First-Row Diatomic Molecules

<b>TABLE 6.2</b>				
Electron Configurations and Bond Orders for First-Row Diatomic Molecules				
Species	Electron Configuration	Bond Order	Bond Energy (kJ mol <sup>-1</sup> )	Bond Length (Å)
H <sub>2</sub> <sup>+</sup>	( $\sigma_{g1s}$ ) <sup>1</sup>	$\frac{1}{2}$	255	1.06
H <sub>2</sub>	( $\sigma_{g1s}$ ) <sup>2</sup>	1	431	0.74
He <sub>2</sub> <sup>+</sup>	( $\sigma_{g1s}$ ) <sup>2</sup> ( $\sigma_{u1s}^*$ ) <sup>1</sup>	$\frac{1}{2}$	251	1.08
He <sub>2</sub>	( $\sigma_{g1s}$ ) <sup>2</sup> ( $\sigma_{u1s}^*$ ) <sup>2</sup>	0	~0	Large

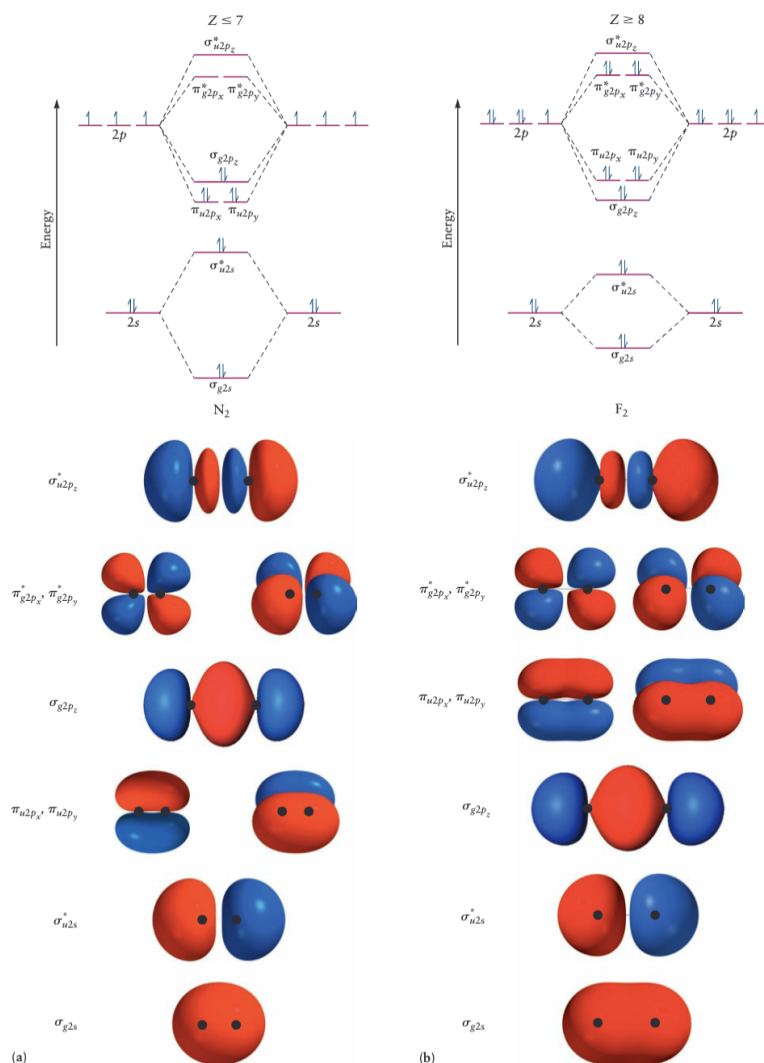
*Electron configurations and bond orders for first-row diatomic molecules. This table summarizes the electron configurations, bond orders, bond energies, and bond lengths for H<sub>2</sub><sup>+</sup>, H<sub>2</sub>, He<sub>2</sub><sup>+</sup>, and He<sub>2</sub>.*

From the table, we can observe:

- H<sub>2</sub><sup>+</sup> has a bond order of  $\frac{1}{2}$  with bond energy 255 kJ mol<sup>-1</sup> and bond length of 1.06 Å.
- H<sub>2</sub> has a bond order of 1, with a bond energy of 431 kJ mol<sup>-1</sup> and bond length of 0.74 Å.
- He<sub>2</sub><sup>+</sup> has a bond order of  $\frac{1}{2}$ , a bond energy of 251 kJ mol<sup>-1</sup>, and bond length of 1.08 Å.
- He<sub>2</sub> has a bond order of 0, indicating no stable bond between two helium atoms.

#### 4.18.7 Correlation Diagrams and Molecular Orbitals for Second-Period Diatomic Molecules

For second-period diatomic molecules, the molecular orbitals (MOs) are constructed from the atomic orbitals of the constituent atoms, including the 2s and 2p orbitals. The following figure shows the correlation diagrams and the molecular orbitals for N<sub>2</sub> and F<sub>2</sub>.



Correlation diagrams and molecular orbitals for second-period diatomic molecules. (a) Correlation diagram and molecular orbitals calculated for N<sub>2</sub>. (b) Correlation diagram and molecular orbitals calculated for F<sub>2</sub>.

#### Key Points:

- In the case of N<sub>2</sub>, where  $Z \leq 7$ , the  $\pi_{2p}$  orbitals are lower in energy than the  $\sigma_{2p_z}$  orbital. The filling of bonding orbitals ( $\sigma_{2s}$ ,  $\sigma_{2s}^*$ ,  $\pi_{2p_x}$ ,  $\pi_{2p_y}$ ,  $\sigma_{2p_z}$ ) leads to a strong triple bond.
- For F<sub>2</sub>, with  $Z \geq 8$ , the  $\sigma_{2p_z}$  orbital is lower in energy than the  $\pi_{2p_x}$  and  $\pi_{2p_y}$  orbitals. The addition of electrons to the antibonding orbitals ( $\pi_{2p_x}^*$ ,  $\pi_{2p_y}^*$ ,  $\sigma_{2p_z}^*$ ) weakens the bond, resulting in a single bond.
- The diagrams also show the molecular orbital isosurfaces, which enclose the regions of highest electron density. Red and blue areas represent the positive and negative phases of the wave function, showing nodal planes where the wave function changes sign.

#### Bonding in N<sub>2</sub>:

- The bond order is 3, as there are six bonding electrons and no electrons in antibonding  $\pi_{2p}^*$  orbitals.
- This leads to a very strong and stable triple bond in N<sub>2</sub>.

#### Bonding in F<sub>2</sub>:

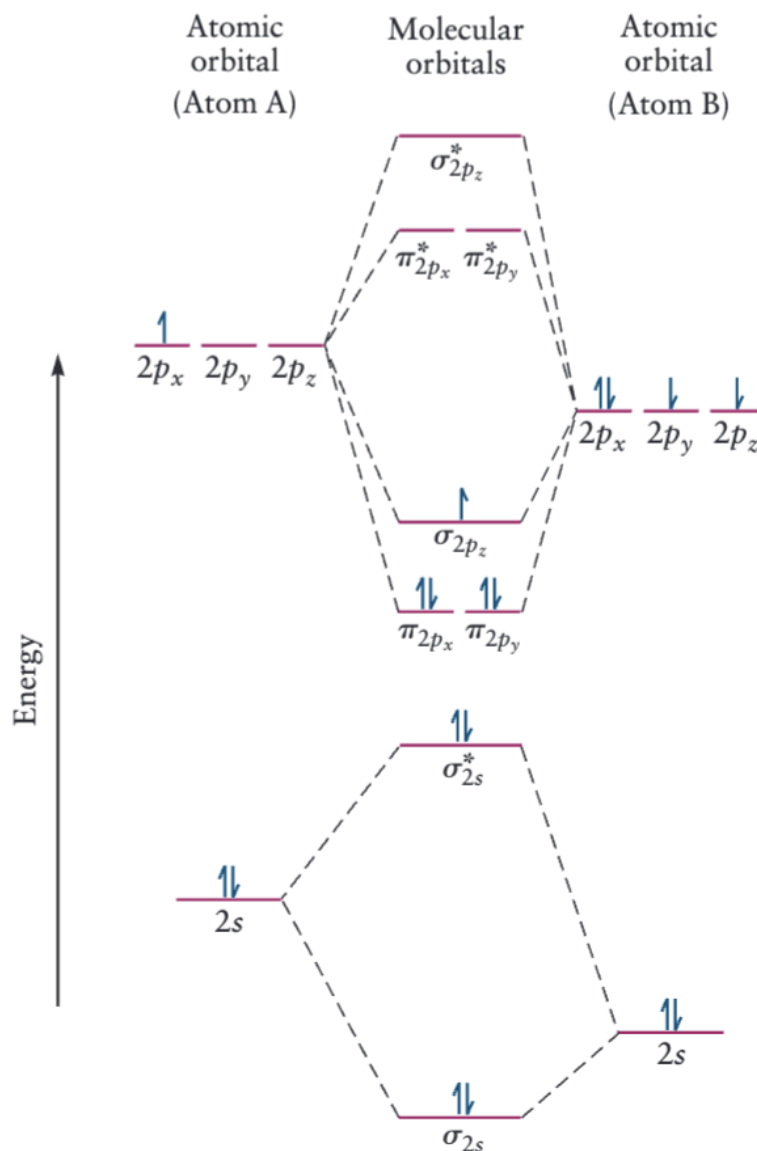
- The bond order is 1, as two bonding electrons are canceled by two electrons in antibonding orbitals ( $\pi_{2p_x}^*$  and  $\pi_{2p_y}^*$ ).

- This results in a much weaker single bond compared to  $\text{N}_2$ .

This diagram emphasizes the energy ordering of orbitals and how electron filling impacts bond strength in second-period diatomic molecules.

#### 4.18.8 Correlation Diagram for Heteronuclear Diatomic Molecules

Heteronuclear diatomic molecules consist of two atoms with different electronegativities. In such molecules, the atomic orbitals of the more electronegative atom (B) are lower in energy compared to those of atom A. The diagram below shows the correlation diagram and orbital filling for boron monoxide (BO).



Correlation diagram for heteronuclear diatomic molecules, AB. The atomic orbitals for the more electronegative atom (B) are displaced downward because they have lower energies than those for A. The orbital filling shown is for boron monoxide (BO).

##### Key Features:

- In heteronuclear diatomic molecules, the atomic orbitals of the more electronegative atom (B) are lower in energy. This causes an asymmetry in the molecular orbitals' energy levels.

- The  $\sigma_{2p_z}$  orbital, formed from the combination of  $2p$  orbitals of both atoms, is lower in energy compared to the  $\pi_{2p_x}$  and  $\pi_{2p_y}$  orbitals, as seen in BO.
- The bonding orbitals are filled following the Aufbau principle. In this case, bonding occurs in the  $\sigma_{2p_z}$ ,  $\pi_{2p_x}$ , and  $\pi_{2p_y}$  orbitals, while antibonding occurs in the  $\sigma_{2s}^*$  and  $\pi_{2p_x}^*$ ,  $\pi_{2p_y}^*$  orbitals.
- Due to the energy disparity between the atoms' orbitals, the contributions of each atom to the bonding molecular orbitals are unequal, with the more electronegative atom (B) contributing more to the lower-energy bonding orbitals.

#### Bonding in BO:

- The orbital filling diagram shows that bonding occurs primarily in the  $\pi$  orbitals and the  $\sigma_{2p_z}$  orbital.
- The bond order is determined by the number of bonding and antibonding electrons, and in the case of BO, there is significant bonding between the two atoms due to the partially filled bonding orbitals.

Heteronuclear diatomic molecules often exhibit polar bonds due to the difference in electronegativity, which further affects the molecular properties.

### 4.18.9 Paramagnetic and Diamagnetic

In chemistry and physics, **paramagnetic** and **diamagnetic** refer to the magnetic properties of atoms or molecules:

- **Paramagnetic:** Paramagnetic substances have unpaired electrons, which give rise to a magnetic moment. When an external magnetic field is applied, these unpaired electrons align with the field, causing the material to be weakly attracted to it. This effect is temporary; once the field is removed, the magnetic alignment disappears. Examples include oxygen ( $O_2$ ) and ions with unpaired electrons, such as  $Fe^{3+}$  and  $Mn^{2+}$ .
- **Diamagnetic:** Diamagnetic substances have all electrons paired, resulting in no permanent magnetic moment. These substances are slightly repelled by an external magnetic field, and this repulsion is also temporary. Examples include nitrogen ( $N_2$ ) and most organic compounds.

Paramagnetic and diamagnetic properties are essential in fields like magnetic resonance imaging (MRI) and magnetic material design, where the behavior of materials in magnetic fields is crucial.

### 4.18.10 Bond Length

**Bond length** is the distance between the nuclei of two bonded atoms in a molecule. It depends on various factors, including:

- **Bond Order:** Higher bond orders (e.g., double or triple bonds) typically result in shorter bond lengths due to the stronger attraction between atoms.
- **Atomic Size:** Larger atoms tend to form longer bonds since their electron clouds are more spread out.
- **Electron Distribution:** Bonding versus antibonding electron populations influence bond length. Electrons in bonding orbitals shorten the bond, while electrons in antibonding orbitals lengthen it.
- **Resonance and Delocalization:** In molecules with delocalized electrons, such as benzene, bond lengths may be intermediate between those typical for single and double bonds.

Understanding bond length is important in determining molecular shape, strength of bonds, and reactivity in chemical reactions.

# Chapter 5

## Gasses

### 5.1 Introduction to Gases

Gases are a state of matter characterized by their lack of fixed shape or volume. Gas particles are in constant, rapid motion and are spaced far apart compared to the particles in solids or liquids. Here are some fundamental properties of gases:

- **No Significant Intermolecular Forces:** In an ideal gas, particles are assumed to have no significant intermolecular forces between them. This means that gas particles neither attract nor repel each other, allowing them to move independently. This assumption simplifies gas behavior, especially under low-pressure and high-temperature conditions.
- **Pressure and Collisions:** Gas pressure is primarily caused by collisions between gas particles and the walls of their container. The force exerted by these collisions per unit area defines the pressure of the gas. In an ideal gas, we assume elastic collisions, meaning the total kinetic energy of particles remains constant.

### 5.2 Boyle's Law

Boyle's Law states that the pressure  $P$  of a given amount of gas is inversely proportional to its volume  $V$ , at constant temperature:

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = \text{constant}.$$

**Explanation:** As the volume of a gas decreases, particles have less space to move, resulting in more frequent collisions with the container walls, which increases pressure. Conversely, increasing the volume decreases the frequency of collisions, lowering the pressure.

### 5.3 Non-Uniform Collisions and Energy Distribution

The collisions between gas particles are non-uniform, meaning not all particles collide with the same energy. This variability in collision energy results in an uneven distribution of kinetic energy among gas particles, leading to what is known as the Maxwell-Boltzmann distribution of speeds.

### 5.4 Charles's Law

Charles's Law states that the volume  $V$  of a gas is directly proportional to its absolute temperature  $T$  when pressure is kept constant:

$$\frac{V}{T} = \text{constant}.$$

**Explanation:** When the temperature of a gas increases, the kinetic energy of the gas particles also increases, causing them to collide with greater force and frequency. To maintain constant pressure, the volume of the gas must increase to allow particles more space.

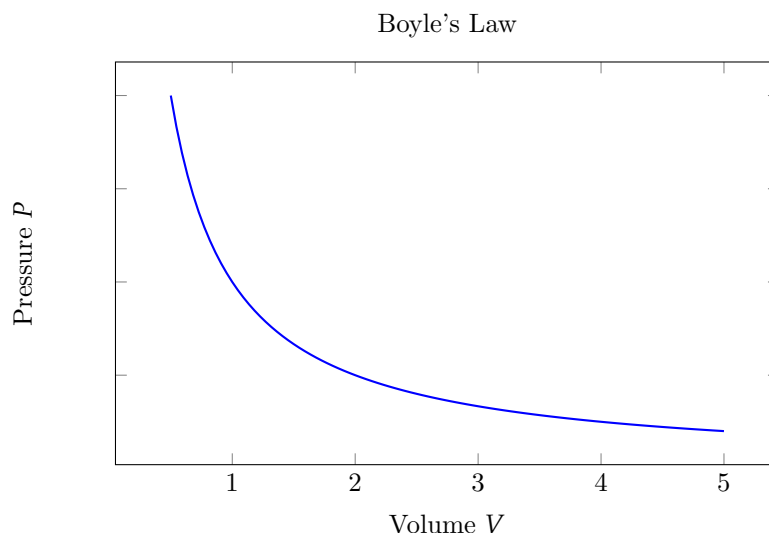


Figure 5.1: Graph of Boyle's Law showing the inverse relationship between pressure and volume.

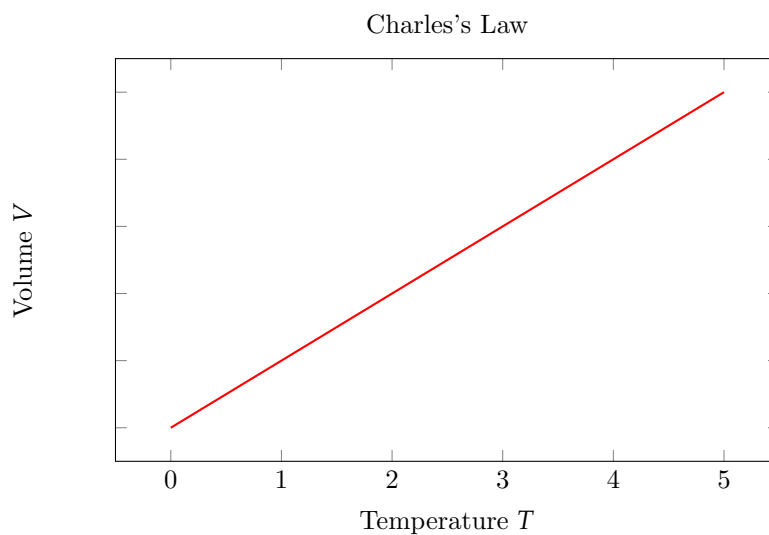


Figure 5.2: Graph of Charles's Law showing the direct relationship between volume and temperature (in Kelvin).

## 5.5 Absolute Zero and the Kelvin Scale

Absolute zero, defined as  $-273.15^{\circ}\text{C}$ , is the lowest possible temperature at which particles theoretically have no kinetic energy. This point serves as the foundation of the Kelvin temperature scale, where 0 K is absolute zero. The Kelvin scale is widely used in gas law calculations because it provides a direct measure of thermal energy.

## 5.6 Avogadro's Law

Avogadro's Law states that the volume  $V$  of a gas is directly proportional to the number of moles  $n$  of gas present, provided temperature and pressure are constant:

$$V \propto n \quad \text{or} \quad \frac{V}{n} = \text{constant}.$$

**Explanation:** Increasing the amount of gas (number of moles) at constant temperature and pressure will increase the volume, as there are more particles that need space to move.

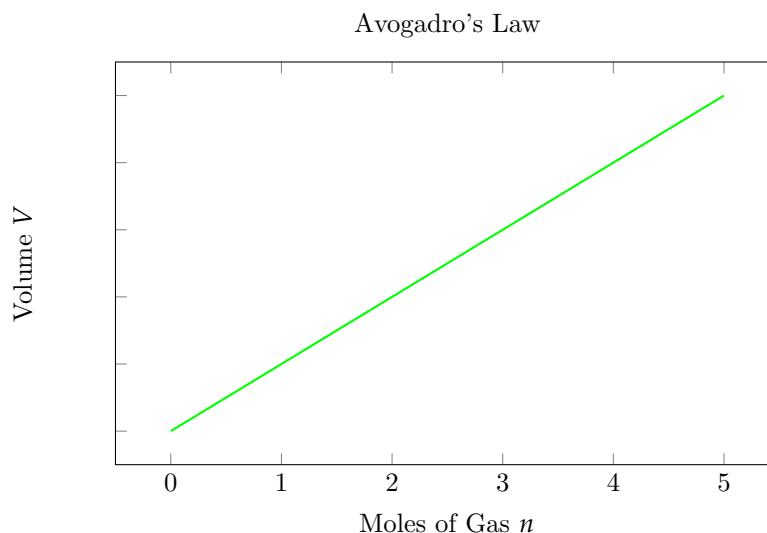


Figure 5.3: Graph of Avogadro's Law showing the direct relationship between volume and the amount of gas in moles.

## 5.7 Summary of Gas Laws

### Definition 5.7.1: Ideal Gas Law

The behavior of gases can be summarized by the Ideal Gas Law, which combines Boyle's, Charles's, and Avogadro's laws:

$$PV = nRT,$$

where

- $P$  is the pressure of the gas,
- $V$  is the volume of the gas,
- $n$  is the amount of substance (in moles),
- $R$  is the ideal gas constant,
- $T$  is the temperature (in Kelvin).

### 5.7.1 Units for Each Variable

To use the Ideal Gas Law correctly, we need to ensure all variables are in consistent units:

- $P$  (Pressure): Measured in atmospheres (atm), pascals (Pa), or torr. For simplicity, we'll use atmospheres, where  $1 \text{ atm} = 101,325 \text{ Pa}$ .
- $V$  (Volume): Measured in liters (L) or cubic meters ( $\text{m}^3$ ), where  $1 \text{ L} = 0.001 \text{ m}^3$ .
- $n$  (Moles): Measured in moles (mol).
- $R$  (Ideal Gas Constant): Varies depending on the pressure and volume units. Common values are:
  - $R = 0.0821 \text{ L atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,
  - $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .
- $T$  (Temperature): Measured in Kelvin (K). To convert from Celsius to Kelvin, use  $T(\text{K}) = T(\text{C}) + 273.15$ .



### 5.7.2 General Gas Equation

For conditions where gases do not behave ideally, we may use the General Gas Equation, also known as the Combined Gas Law, which combines Boyle's, Charles's, and Gay-Lussac's laws:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}.$$

This equation describes the relationship between pressure, volume, and temperature of a gas when transitioning between two states, where:

- $P_1$  and  $P_2$  are the initial and final pressures,
- $V_1$  and  $V_2$  are the initial and final volumes,
- $T_1$  and  $T_2$  are the initial and final temperatures (in Kelvin).

#### Example 5.7.1 (Ideal Gas Law Example)

Suppose we want to find the volume of 1.5 moles of an ideal gas at a pressure of 2.0 atm and a temperature of 300 K.

Given:

$$P = 2.0 \text{ atm}, \quad n = 1.5 \text{ mol}, \quad T = 300 \text{ K}, \quad R = 0.0821 \text{ L atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

Using the Ideal Gas Law:

$$PV = nRT.$$

Solving for  $V$ :

$$V = \frac{nRT}{P}.$$

Substitute the values:

$$V = \frac{(1.5 \text{ mol})(0.0821 \text{ L atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(300 \text{ K})}{2.0 \text{ atm}}.$$

Calculating each part:

$$V = \frac{1.5 \times 0.0821 \times 300}{2.0} = \frac{36.945}{2.0} = 18.4725 \text{ L}.$$

Thus, the volume of the gas is approximately 18.47 L. This example illustrates the importance of using consistent units to ensure accurate calculations when applying the Ideal Gas Law.

### 5.7.3 Conversion Between mmHg and Pa

To convert between millimeters of mercury (mmHg) and pascals (Pa), we use the following relationship:

$$1 \text{ mmHg} = 133.322 \text{ Pa}.$$

To convert a pressure  $P$  in mmHg to Pa, multiply by 133.322:

$$P(\text{Pa}) = P(\text{mmHg}) \times 133.322.$$

#### Example 5.7.2 (Example Conversion from mmHg to Pa)

Suppose we have a pressure of 760 mmHg. To convert to Pa:

$$P(\text{Pa}) = 760 \text{ mmHg} \times 133.322 = 101,325.72 \text{ Pa}.$$

Thus, 760 mmHg is approximately 101,325 Pa, which is close to standard atmospheric pressure.

## 5.8 Mixtures of Gases

When dealing with mixtures of gases, we can treat the system as if there were a single gas by using the total amount  $n = n_{\text{total}}$ .

### 5.8.1 Dalton's Law of Partial Pressures

Dalton's Law of Partial Pressures states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the individual gases. Mathematically, this can be expressed as:

$$P_{\text{tot}} = P_1 + P_2 + \dots$$

where  $P_{\text{tot}}$  is the total pressure and  $P_1, P_2, \dots$  are the partial pressures of each gas in the mixture.

Each partial pressure  $P_i$  is the pressure that each gas would exert if it were alone in the container at the same temperature and volume.

#### Example 5.8.1 (Calculating the Pressure of a Gas Mixture)

Suppose we have a mixture of 1 g of hydrogen ( $\text{H}_2$ ) and 5 g of helium ( $\text{He}$ ) in a container. We can calculate the partial pressures of each gas and the total pressure.

1. First, calculate the number of moles of each gas:

$$n_{\text{H}_2} = \frac{1}{2.02} = 0.495 \text{ mol}, \quad n_{\text{He}} = \frac{5}{4.003} = 1.25 \text{ mol}.$$

2. The total number of moles is:

$$n_{\text{total}} = n_{\text{H}_2} + n_{\text{He}} = 0.495 + 1.25 = 1.745 \text{ mol}.$$

3. Using the Ideal Gas Law, the total pressure  $P_{\text{tot}}$  is given by:

$$P_{\text{tot}} = \frac{n_{\text{total}}RT}{V}.$$

### 5.8.2 Mole Fraction and Partial Pressure

The mole fraction  $x_i$  of each gas in the mixture is the ratio of the number of moles of that gas to the total number of moles:

$$x_i = \frac{n_i}{n_{\text{total}}}.$$

The partial pressure  $P_i$  of each gas can then be calculated using the mole fraction and the total pressure:

$$P_i = x_i \cdot P_{\text{tot}}.$$

#### Example 5.8.2 (Calculating Mole Fractions and Partial Pressures)

Given the previous example with  $n_{\text{H}_2} = 0.495 \text{ mol}$  and  $n_{\text{He}} = 1.25 \text{ mol}$ :

1. The mole fraction of hydrogen is:

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{total}}} = \frac{0.495}{1.745} \approx 0.284.$$

2. The mole fraction of helium is:

$$x_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{total}}} = \frac{1.25}{1.745} \approx 0.716.$$

3. If the total pressure  $P_{\text{tot}}$  is known, the partial pressures can be calculated as:

$$P_{\text{H}_2} = x_{\text{H}_2} \cdot P_{\text{tot}}, \quad P_{\text{He}} = x_{\text{He}} \cdot P_{\text{tot}}.$$