

Lecture 2 “Lecture 2: Model Representations of Atoms and Molecules in Physical Chemistry”

Goal of the lecture: To understand how atoms and molecules are represented in physical chemistry using theoretical and visual models, and to explain how these models help describe structure, bonding, and properties of matter.

Brief lecture notes: Physical chemistry connects microscopic atomic behavior with macroscopic physical properties. Since atoms and molecules are too small to be seen directly, scientists use models to represent their structure and predict their behavior. These models are not exact pictures but conceptual tools that help visualize and explain experimental results.

1. Atomic Models

Atomic models are scientific representations of an atom's structure that have evolved over time to incorporate new experimental data. Key models include Dalton's solid sphere, Thomson's "plum pudding" model, Rutherford's nuclear model with electrons orbiting a central nucleus, and Bohr's model where electrons orbit in specific energy shells. The modern model describes a dense nucleus of protons and neutrons surrounded by a cloud of electrons in energy levels or shells.

1.1 Dalton's Atomic Model (1803)

John Dalton proposed that matter is made up of small, indivisible particles called atoms. Each element consists of identical atoms, and chemical reactions involve rearrangement of these atoms. Although simple, Dalton's model laid the foundation for modern atomic theory.

1.2 Thomson's "Plum Pudding" Model (1898)

J.J. Thomson discovered the electron and proposed that atoms consist of a positively charged sphere with negatively charged electrons embedded in it, like "plums in a pudding." However, this model could not explain the scattering of alpha particles observed later.

1.3 Rutherford's Nuclear Model (1911)

Ernest Rutherford showed that atoms have a small, dense, positively charged nucleus surrounded by electrons. Most of the atom's volume is empty space. This model introduced the concept of the nucleus, but it could not explain the stability of atoms.

1.4 Bohr's Planetary Model (1913)

Niels Bohr proposed that electrons revolve around the nucleus in fixed orbits with specific energies. When electrons jump between orbits, they emit or absorb light of definite frequencies. This model successfully explained the hydrogen atom spectrum but failed for multi-electron atoms.

1.5 Quantum Mechanical Model (1926–present)

Developed by Schrödinger, Heisenberg, and others, this is the most accurate representation of atoms. Electrons are described by wave functions (ψ), which give the probability distribution of finding an electron in a particular region of space. The concept of atomic orbitals (s, p, d, f) arises from this model.

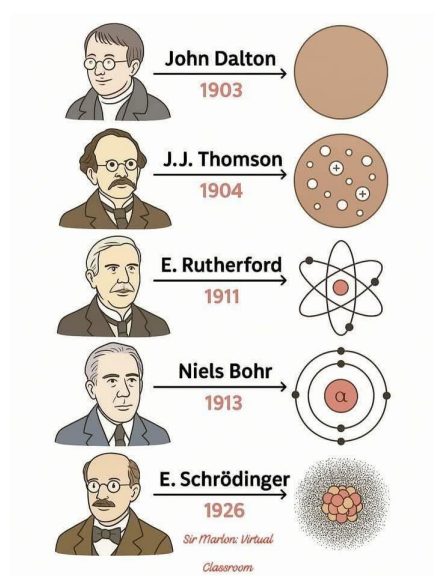


Figure 1. Evolution of atomic models

2. Molecular Models

2.1 Lewis Structure Model (1916)

A Lewis structure is a diagram that shows the arrangement of **valence electrons** around atoms in a molecule or ion. It uses dots for lone pairs of electrons and lines for shared pairs of electrons (covalent bonds) to represent covalent molecules. The main goal is to show how electrons are shared to satisfy the **octet rule**, where atoms aim for eight valence electrons for stability, although hydrogen only needs two. Figure 2:

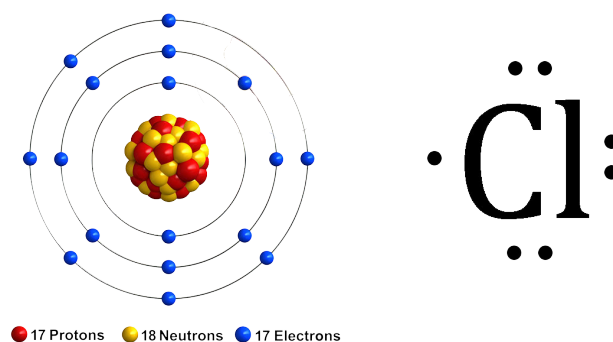


Figure – 2. Lewis Dot Diagram

2.2 Valence Bond (VB) Theory

Valence Bond (VB) Theory is a quantum mechanical model that describes covalent bonds as the result of atomic orbital overlap between atoms. It explains how bonds form when atomic orbitals containing unpaired electrons overlap to share a pair of electrons, creating a more

stable, lower-energy state. Key aspects include the formation of sigma (σ) bonds through head-on overlap and pi (π) bonds through parallel overlap, and the concept of hybridization, where atomic orbitals mix to form new hybrid orbitals that allow for bonding beyond what is possible with unhybridized orbitals. Figure 3:

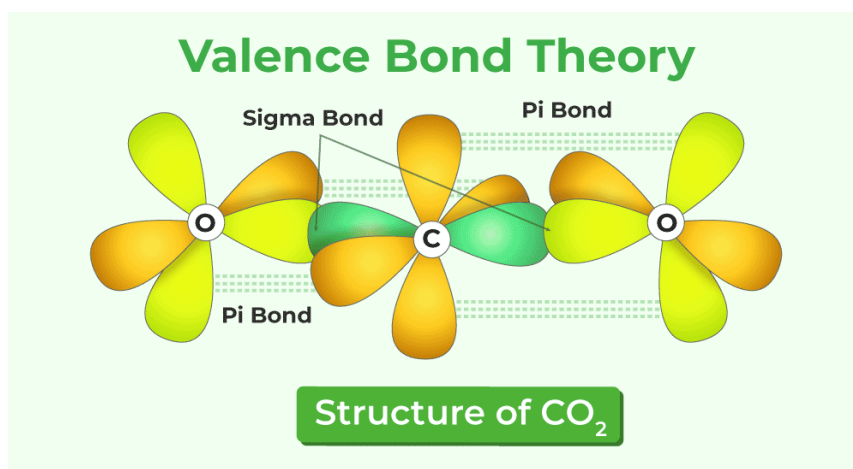


Figure – 3. Valence Bond Theory for the Structure of CO₂

2.3 Molecular Orbital (MO) Theory

MO theory considers that atomic orbitals combine to form molecular orbitals extending over the entire molecule. Electrons occupy these orbitals according to energy levels, providing insight into bond strength, magnetism, and molecular stability.

$\sigma, \pi, \sigma^*, \pi^*$

These represent bonding and antibonding orbitals.

The molecular orbital (MO) diagram of the diatomic carbon molecule (C₂) illustrates the combination of atomic orbitals from two carbon atoms to form bonding and antibonding molecular orbitals. Each carbon atom contributes six electrons, giving a total of twelve electrons in the molecule. The atomic orbitals combine according to their symmetry and energy levels to form molecular orbitals labeled as σ and π (bonding), and σ^* and π^* (antibonding).

For C₂ (Fig. 4), the energy ordering of molecular orbitals follows the typical pattern observed in lighter diatomic molecules (like B₂, C₂, and N₂), where the **$\pi 2p$ orbitals lie below the $\sigma 2p$ orbital**. The electron filling begins with the lowest energy orbitals: the $\sigma 2s$ bonding orbital, followed by the $\sigma^* 2s$ antibonding orbital. Next, electrons occupy the degenerate $\pi 2p$ orbitals, which are lower in energy than the $\sigma 2p$ orbital in C₂.

Thus, the electronic configuration of C₂ in molecular orbitals is written as:

$$(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$$

This configuration shows that all eight valence electrons occupy bonding orbitals (four from $\pi 2p$ and four from $\sigma 2s$), while four electrons occupy antibonding orbitals ($\sigma 2s$). *No electrons occupy the antibonding $\pi 2p$ or $\sigma^* 2p$ orbitals.*

From this configuration, the **bond order** can be calculated as:

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 4) = 2$$

This indicates that C_2 has a **double bond**, consistent with experimental evidence. Additionally, since all electrons are paired, the molecule is **diamagnetic** (it is not attracted to a magnetic field).

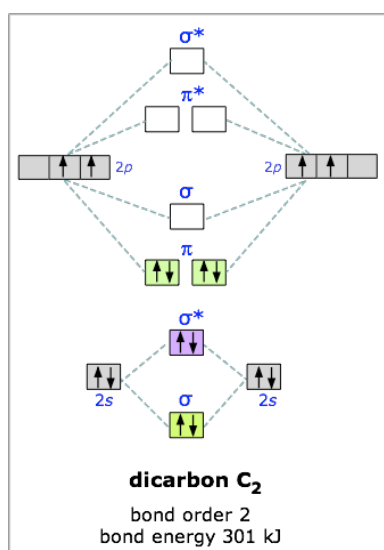


Figure – 4. Molecular Orbital for C_2

Table 1 – Comparison of VB and MO Theories

Feature	Valence Bond Theory	Molecular Orbital Theory
Concept	Bond forms by overlap of atomic orbitals	Bonding involves combination of orbitals forming new molecular orbitals
Electron location	Localized between atoms	Delocalized over the entire molecule
Explains	Bond strength, shape	Magnetism, stability, delocalization
Example	H_2 via overlap of 1s orbitals	H_2 with bonding ($\sigma 1s$) and antibonding ($\sigma^* 1s$) orbitals

In modern physical chemistry, atoms and molecules are represented through computational and visual models that help scientists better understand their structure and behavior. These representations include **electron density maps**, which show the regions where electrons are most likely to be found, **ball-and-stick** and **space-filling models**, which illustrate the geometric arrangement of atoms within molecules, and **quantum mechanical simulations**,

which are used to calculate bond lengths, bond angles, and potential energy surfaces. Such models provide valuable insight into the microscopic properties of matter and are extensively applied in fields such as spectroscopy, thermodynamics, reaction kinetics, and materials science.

Questions for self-control:

1. What is the difference between an atomic model and a molecular model?
2. Describe the main ideas of Bohr's and Rutherford's models.
3. What is the main principle of the quantum mechanical model?
4. How do VB and MO theories differ in explaining chemical bonding?
5. What modern tools are used to visualize molecules in physical chemistry?

Literature:

1. Atkins, P., de Paula, J. *Atkins' Physical Chemistry*, 11th Edition, Oxford University Press, 2018.
2. Moran, M.J. *Fundamentals of Engineering Thermodynamics*, 9th Edition, Wiley, p.156.
3. House, J.E. *Fundamentals of Quantum Chemistry*, 2nd Edition, Academic Press, 2004.
4. Hammes-Schiffer, S. et al. *Physical Chemistry for the Biological Sciences*, University Science Books, 2009.
5. Zhdanov, V.P. *Elementary Physicochemical Processes on Solid Surfaces*, Springer, 1991.