

PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA
MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH



University of Batna 1
Faculty of Material Sciences,
Department of Chemistry



Course Handout

STRUCTURE AND SPECTROSCOPY OF **POLYATOMIC MOLECULES**

3rd Year Physical Chemistry

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Academic year 2024-2025

République Algérienne Démocratique et Populaire
MINISTRE DE L'ENSEIGNEMENT SUPERIEUR ET DE LA RECHERCHE
SCIENTIFIQUE
UNIVERSITE BATNA 1
FACULTE DES SCIENCES DE LA MATIERE

Extrait du PV N° 04/2025 de la session ordinaire de la réunion du conseil scientifique tenue le 16 Octobre 2025.

Restitution de rapports d'expertise de polycopié de cours

Le CSF a reçu les rapports d'expertise du polycopié de cours du Dr. ZIADI Kamal. Les membres du CSF ont émis un avis favorable quant à l'utilisation du polycopié comme support pédagogique.

En effet, les trois rapports de chaque expertise sont positifs et portent la mention avis favorable.

Intitulé du polycopié : Structure and Spectroscopy of Polyatomic Molecules ;
Spécialité : Troisième année Licence Chimie physique (Semestre 5) ;

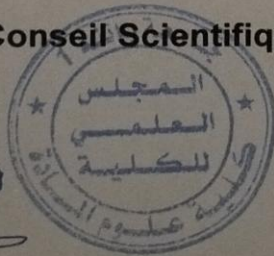
Les experts désignés (CSF N°3/2025 du 10/07/2025), Pr. HAFIED Meriem (Université Batna 2), Pr. MESSAOUDI Abdelatif (Université Batna 1) et Dr. MESMOUDI Rida (Université Batna 1).

Fait à Batna le 26/01/2026

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Foreword

This course booklet is intended for third-year undergraduate students in Physical Chemistry. It is specifically aimed at those who wish to deepen their understanding of the electronic structure of polyatomic molecules and the associated spectroscopic techniques. The course adopts a modern and integrated approach, linking concepts from quantum chemistry to experimental tools used in spectral analysis.

The main objective is to provide a rigorous theoretical foundation for the study of molecular orbitals, symmetry properties, and electronic, vibrational, and rotational transitions. Particular emphasis is placed on the computational implementation of key quantum methods. To this end, Python code examples are included to illustrate the practical application of the Hückel method and the Hartree-Fock method, allowing students to simulate and visualize the electronic structures of simple molecules.

This document has been carefully designed to ensure a coherent pedagogical progression, combining clarity of explanation, scientific accuracy, and contextual relevance of the concepts. Nevertheless, any comments or suggestions for improvement are welcome and encouraged as part of an ongoing effort to enhance this educational resource.

The course is organized into five chapters, each covering essential aspects of the subject:

- ❖ Chapter I – Mean-Field Framework: Introduction to the simple and extended Hückel methods, used to model π and (σ, π) systems in conjugated organic molecules.
- ❖ Chapter II – Self-Consistent Field Framework: Hartree-Fock Method: Presentation of the Hartree-Fock theory, including the Fock operator, the SCF procedure, and the Roothaan equations, along with an introduction to atomic orbital basis sets, ab initio and semi-empirical methods, and population analysis.
- ❖ Chapter III – Qualitative Approach to Electronic Structure: Study of molecular orbital formation based on fragment orbitals, molecular symmetry, orbital interactions, and correlation diagrams. Applied examples include AB_n -type molecules and simple organic compounds.
- ❖ Chapter IV – Electronic Spectra of Polyatomic Molecules: Analysis of general types of electronic transitions, quantum selection rules, and low-resolution electronic spectra, particularly for conjugated organic molecules.
- ❖ Chapter V – IR and Raman Spectra of Polyatomic Molecules: Examination of rotational and vibrational motions in polyatomic molecules, and interpretation of IR and Raman spectra from both theoretical and qualitative perspectives.

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Abbreviations

H: Hamiltonian

HMO: Hückel Molecular Orbital

LCAO: Combination Of Atomic Orbitals

α : Coulomb Integral

β : Resonance Integral

S: Overlap Integral

AO: Atomic Orbital

MO: Molecular Orbital

q_r : Charge Density

P_{rs} : Bond Order

K: Empirical Constant

EHT: Extended Hückel Theory

EHMO: Extended Hückel Molecular Orbital Theory

VOIE: Atomic Orbital Ionization Energies

HF: Hartree-Fock

SCF: Self-Consistent Field

\hbar : Reduced Planck Constant

M_e : Mass Of An Electron

M_A : Mass Of Nucleus A

∇_k^2 : Laplacian Operators

Au: Atom Unit

$\langle 12|12 \rangle$: Coulomb Integral

$\langle 12|21 \rangle$: Exchange Integral

P: Density Matrix

$M_v/\Lambda\sigma$: Two-Electron Integrals

\hat{f} : Fock Operator

F: Fock Matrix

STO: Slater-Type Orbital

GTO: Gaussian-Type Orbital

CGTO: Contracted Gaussian-Type Orbitals

PGTO: Primitive Gaussian-Type Orbitals

CNDO: Complete Neglect Of Differential Overlap

IP: The Ionization Potential Of The Atom

EA: The Electron Affinity Of The Atom

IRREP: Irreducible Representation

CIS: Configuration Interaction Singles

M: Electric Dipole Moment Operator

f_{if} : Oscillator Strength

q : Normal Coordinate

k : Force Constant

ψ_{vib} : Vibrational Wavefunction

$H_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$: Hessian Matrix

x_i Normal Cartesian Coordinates

\tilde{x}_i Mass-Weighted Coordinates

General Introduction

The course entitled Structure and Spectroscopy of Polyatomic Molecules is a fundamental component of the Physical Chemistry curriculum in the “L3 Physical Chemistry”. Its primary objective is to provide students with a deep understanding of the relationship between molecular electronic structure, symmetry, and spectroscopic properties. Grounded in the principles of molecular quantum chemistry, this course equips students with both theoretical and computational tools to model, analyze, and interpret the structural and spectral characteristics of complex molecules. Practical aspects are also included, notably through the use of Python code to simulate and visualize the computational methods covered, such as the Hückel and Hartree-Fock approaches.

The first part of the course focuses on the mean-field framework, beginning with a detailed introduction to the simple Hückel method, which allows for the modeling of π orbitals in conjugated systems such as ethylene, butadiene, and benzene. This is followed by an extension to the extended Hückel method, which considers both π and σ orbitals, offering a more realistic description of certain organic molecules. These methods provide an essential foundation for understanding electron delocalization and the stability of conjugated structures.

The second chapter introduces the self-consistent field (SCF) framework through the Hartree-Fock (HF) method, a cornerstone of *ab initio* quantum chemistry. This chapter covers the construction of the Fock operator, the SCF procedure, and the Roothaan equations used for matrix-based solutions. Special emphasis is placed on the use of atomic basis sets, such as STO-3G or 6-31G, which play a crucial role in the accuracy of quantum chemical calculations. The chapter also addresses semi-empirical methods, along with population analysis tools like Mulliken’s method, to bridge numerical results with chemical interpretation.

The third chapter develops a qualitative approach to molecular electronic structure. It introduces the fragment orbital method, which constructs molecular orbitals from simpler atomic or molecular subunits. This analysis is enriched by the study of symmetry properties (point groups, symmetry operations) and interactions between fragment orbitals. Correlation diagrams are also presented, allowing students to trace the evolution of orbitals during molecular transformations or geometry changes. Practical examples are provided for AB_n -type molecules and simple organic systems.

The fourth chapter is dedicated to electronic spectroscopy, which examines electronic transitions in molecules exposed to UV-visible radiation. It presents the types of transitions ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc.), quantum selection rules, and the characteristics of low-resolution electronic spectra in polyatomic molecules. Particular attention is given to conjugated organic compounds, in which electronic structure directly influences observed absorption bands. This chapter emphasizes the link between theoretical energy levels and experimental spectroscopic features.

The fifth and final chapter addresses vibrational and rotational spectroscopy, based on the analysis of infrared (IR) and Raman spectra. After introducing molecular rotational and vibrational motions, the chapter explains the associated selection rules and how to interpret spectra in terms of normal modes. A significant section is devoted to the Hessian matrix, a fundamental mathematical tool used to compute vibrational frequencies from second derivatives of the energy. Once mass-weighted and diagonalized, this matrix provides both frequencies and normal modes, which are essential for predicting IR and Raman spectra.

Through the exploration of these five major topics, this course offers an integrated and coherent view of molecular structure and spectroscopy. It prepares students to use quantum chemistry not only as a theoretical tool but also as a practical means of understanding and interpreting experimentally observed physicochemical phenomena.

Chapter 1: Mean Field Framework

1. Hückel Molecular Orbital Theory

1.1. Introduction:

The Hückel method is a semi-empirical quantum mechanical approach used primarily to describe the electronic structure of conjugated π -systems in organic molecules, such as benzene and polyenes. Developed by Erich Hückel in 1931, this method simplifies the complex problem of molecular orbitals by making several approximations, making it particularly useful for π -electron systems in planar conjugated molecules.

Historically, the Hückel method was one of the first quantum mechanical models applied successfully to organic chemistry. It emerged in the early 20th century as scientists sought to understand the stability and electronic properties of aromatic compounds. At a time when computational resources were limited, Hückel's approach provided an analytical framework that could predict molecular orbitals, bonding patterns, and delocalization energies with relatively simple mathematical techniques. This was particularly important in explaining why benzene and other aromatic molecules exhibit exceptional stability, leading to the development of Hückel's rule, which states that a conjugated system is aromatic if it contains $(4n + 2)$ π -electrons.

The Hückel method finds wide applications in organic and theoretical chemistry, especially in the study of aromaticity, molecular orbital theory, and spectroscopic properties of conjugated systems. It helps predict the energy levels and electron densities of π -systems, providing insight into UV-Vis absorption spectra of organic compounds. Additionally, it has been used to understand reactivity patterns in pericyclic reactions, where molecular orbitals play a crucial role. Even though it is a simple model that does not account for σ -bonding, electron correlation, or three-dimensional molecular effects, it serves as a foundational tool for more advanced methods like Density Functional Theory (DFT) and Hartree-Fock theory.

Despite its approximations, the Hückel method remains a valuable teaching tool and a first step in quantum chemical analysis of conjugated systems. It allows chemists to gain qualitative insights into bonding, electronic transitions, and aromatic stability without requiring intensive computational resources, making it a cornerstone in the development of molecular orbital theory in organic chemistry.

1.2. Fundamentals and Conjugation Effects

In chemistry, the structure and reactivity of molecules depend significantly on the type of bonding between atoms. The fundamental types of covalent bonds are sigma (σ) bonds and pi (π) bonds. These bonds play a crucial role in determining molecular geometry, stability, and chemical behavior. Additionally, conjugation is an important concept that influences the electronic properties of molecules.

A sigma bond (σ) is the strongest type of covalent bond, formed by the head-on (axial) overlap of atomic orbitals. It allows free rotation around the bond axis and is present in all single bonds. Examples of orbitals involved in σ -bond formation include:

s-s orbital overlap (e.g., H-H bond in H_2)

s-p orbital overlap (e.g., C-H bond in methane, CH_4)

p-p orbital overlap (e.g., C-C single bond in ethane, C_2H_6)

A pi bond (π) is formed by the sideways (lateral) overlap of p orbitals. Unlike sigma bonds, π bonds do not allow free rotation, making molecules more rigid. A double bond consists of one σ bond and one π bond, while a triple bond consists of one σ bond and two π bonds.

Example: In ethene (C_2H_4), the carbon-carbon double bond consists of:

One σ bond (sp^2 - sp^2 overlap)

One π bond (p-p sideways overlap)

Since π bonds are weaker than σ bonds, they are more reactive in chemical reactions.

Conjugation occurs when a molecule has alternating single and multiple bonds, allowing delocalization of electrons across multiple atoms. This delocalization stabilizes the molecule by spreading out electron density. Conjugation is common in systems such as:

Benzene (C_6H_6): A fully conjugated system with alternating single and double bonds, leading to aromatic stability.

Polyenes (e.g., Butadiene, C_4H_6): Extended conjugation increases stability and alters the molecule's electronic properties.

Chromophores: Conjugated systems in dyes and pigments absorb light at specific wavelengths.

Sigma (σ) bonds provide strong structural stability, while pi (π) bonds influence reactivity and rigidity. Conjugation enhances molecular stability by delocalizing electrons, leading to unique chemical and physical properties. Understanding these bonding interactions is fundamental in organic chemistry, materials science, and molecular electronics.

1.3. Approximations of HMO

The Hückel Molecular Orbital (HMO) theory is a simplified quantum mechanical approach to studying conjugated hydrocarbons. This method enables chemists to predict molecular orbital energies, electronic distributions, and the overall stability of π -electron systems. The theory is based on a series of well-defined approximations that simplify calculations while preserving the essential physics of molecular bonding. Below, we explore the core principles and applications of the Hückel method, enriched with details for a better understanding.

The Hückel method provides valuable insights into the electronic properties of conjugated molecules:

1. **Energy Levels and Stability:** By solving the secular determinant, the energies of the π -molecular orbitals can be calculated. This allows chemists to evaluate the relative stability of conjugated systems. For instance, molecules with completely filled bonding orbitals are more stable.
2. **Delocalization and Aromaticity:** The Hückel method is particularly effective for studying aromatic compounds like benzene. It predicts the delocalization of π -electrons, which leads to exceptional stability. The method also validates Hückel's rule, stating that planar, cyclic systems with $4n+2$ π -electrons exhibit aromaticity.
3. **Molecular Orbitals and Reactivity:** The calculated molecular orbitals provide a detailed understanding of the distribution of π -electrons. This information is crucial for predicting chemical reactivity, such as electrophilic aromatic substitution reactions.
4. **Electronic Transitions:** The energy differences between molecular orbitals are used to predict electronic transitions in UV-Vis spectroscopy. Conjugated systems with extended π -networks absorb at longer wavelengths due to smaller energy gaps.

1.4. Principles of the Hückel Method

Separation of the Hamiltonian: The total Hamiltonian of the system is divided into one-electron Hamiltonians, each operating independently on a single electron. This simplification reduces the complexity of solving multi-electron wavefunctions:

$$H_{tot} = \sum_i H_{uni\text{ele}}(i) \quad 1$$

Variational Method: The wavefunctions (ψ) for molecular orbitals are determined by minimizing the total energy E . This minimization is carried out by varying the coefficients of the linear combination of atomic orbitals (LCAO):

$$E = \int \frac{\psi H \psi d\tau}{\int \psi \psi d\tau} \quad 2$$

Here, H is the Hamiltonian operator, and ψ represents the trial molecular orbital.

Linear Combination of Atomic Orbitals (LCAO): Molecular orbitals are constructed as a linear combination of atomic orbitals:

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n \quad 3$$

The coefficients c_i describe the contribution of each atomic orbital to the molecular orbital.

1.5 Worked Example: The Allyl Radical ($\text{CH}_2=\text{CH}-\text{CH}_2$)

Consider the allyl radical, a simple conjugated system with three carbon atoms. Using the Hückel method:

1. Atomic Orbitals: Each carbon atom contributes one 2pz (ϕ_1, ϕ_2, ϕ_3)
2. Molecular Orbitals: The molecular orbitals are constructed as:

$$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 \quad 4$$

$$\psi_2 = c_{21}\phi_1 + c_{22}\phi_2 + c_{23}\phi_3$$

$$\psi_3 = c_{31}\phi_1 + c_{32}\phi_2 + c_{33}\phi_3$$

3. Energy Levels: Solving the determinant yields three energy levels, corresponding to bonding, non-bonding, and anti-bonding orbitals.

$$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3$$

$$E = \int \frac{\psi H \psi d\tau}{\int \psi \psi d\tau} = \frac{\langle c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 | H_1 + H_2 + H_3 | c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 \rangle}{\langle c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 | c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 \rangle}$$

$$E = \frac{C_1^2 H_{11} + C_2^2 H_{22} + C_3^2 H_{33} + 2C_1 C_2 H_{12} + 2C_1 C_3 H_{13} + 2C_2 C_3 H_{23}}{C_1^2 + C_2^2 + C_3^2 + 2C_1 C_2 S_{12} + 2C_1 C_3 S_{13} + 2C_2 C_3 S_{23}} \quad 5$$

The condition for obtaining the equilibrium coefficients is written as $\frac{\partial E}{\partial C_i} = 0$. We obtain three expressions by differentiating E with respect to C_1, C_2 and C_3 . Let D be the denominator of E and N the numerator, $E = \frac{N}{D}$.

$$\frac{\partial E}{\partial C_1} = \frac{(2C_1H_{11}+2C_2H_{12}+2C_3H_{13})*D-(2C_1+2C_2S_{12}+2C_3S_{13})*N}{D^2}$$

$$\frac{\partial E}{\partial C_2} = \frac{(2C_1H_{21}+2C_2H_{22}+2C_3H_{23})*D-(2C_1S_{12}+2C_2+2C_3S_{23})*N}{D^2}$$

$$\frac{\partial E}{\partial C_3} = \frac{(2C_1H_{31}+2C_2H_{32}+2C_3H_{33})*D-(2C_1S_{13}+2C_2S_{23}+2C_3)*N}{D^2} \quad 6$$

Now, we will solve for C_1, C_2 and C_3 by expressing them in a matrix system:

$$\begin{pmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{12} - ES_{12} & H_{22} - E & H_{23} - ES_{23} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = 0 \quad 7$$

For a non-trivial solution (i.e., C_1, C_2 and C_3 not all zero), the determinant of the coefficient matrix must be zero:

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{12} - ES_{12} & H_{22} - E & H_{23} - ES_{23} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - E \end{vmatrix} = 0 \quad 8$$

1.6. Approximations of the Hückel Method

The Hückel method introduces several assumptions to make calculations feasible for π -conjugated systems:

1. Coulomb Integral ($H_{ii} = \alpha$): For each atom in the conjugated system, the Coulomb integral α accounts for the energy of a π -electron localized on that atom. This value is constant for all atoms in the system.
2. Resonance Integral ($H_{ij} = \beta$): The resonance integral β represents the energy stabilization due to the overlap of π -electrons between adjacent atoms. For non-adjacent atoms, $H_{ij} = 0$, simplifying the computations. The magnitude of β reflects the strength of the π -bonding interaction.
3. Overlap Integral ($S_{ij} = 0$): The overlap integral between different atomic orbitals is assumed to be zero for non-adjacent atoms. This eliminates the need to account for complex wavefunction overlaps in the calculation.

1.7. Applications of the allyl radical

The energy levels of the molecular orbitals of 3 atoms are determined by solving the secular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

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Expanding this determinant yields a polynomial equation for the molecular orbital energies.

Expanding the determinant gives:

$$(\alpha - E)[(\alpha - E)^2 - \beta^2] = 0$$

This simplifies to:

$$(\alpha - E)^3 - 2\beta^2(\alpha - E) = 0$$

Factoring out $(\alpha - E)$, we get:

$$(\alpha - E)[(\alpha - E)^2 - 2\beta^2] = 0$$

Energy Levels (E)

The equation splits into two parts:

1. $\alpha - E = 0$, giving: $E_2 = \alpha$
2. $(\alpha - E)^2 - 2\beta^2 = 0$, giving:

So:

$$E_1 = \alpha + \sqrt{2}\beta \text{ and } E_3 = \alpha - \sqrt{2}\beta$$

Coefficients calculate (C_1, C_2 and C_3)

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix} = 0$$

For $E_1 = \alpha + \sqrt{2}\beta$, substituting E_1 into matrix

$$\begin{vmatrix} -\sqrt{2}\beta & \beta & 0 \\ \beta & -\sqrt{2}\beta & \beta \\ 0 & \beta & -\sqrt{2}\beta \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix} = 0$$

From symmetry and normalization:

$$C_1 = C_3 \text{ and } C_2 = \sqrt{2}$$

Normalized coefficients:

$$C_1 = \frac{1}{2}, C_2 = \frac{\sqrt{2}}{2} \text{ and } C_3 = \frac{1}{2}$$

The wave function Ψ can be expressed as a linear combination of basis functions ϕ_i weighted by the normalized coefficients C_i :

$$\Psi_{OMi} = \Psi_1 = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$

The same method, for $E_2 = \alpha$

$$C_1 = \frac{1}{\sqrt{2}}, C_2 = 0 \text{ and } C_3 = -\frac{1}{\sqrt{2}}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$$

And, for $E_3 = \alpha - \sqrt{2}\beta$

$$C_1 = \frac{1}{2}, C_2 = \frac{-\sqrt{2}}{2} \text{ and } C_3 = \frac{1}{2}$$

$$\Psi_3 = \frac{1}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$$

Here is the plot of figure-1 of the molecular orbital coefficients visualized as wave functions for the allyl radical. Each line corresponds to a molecular orbital (E_i) with the coefficients at each atom (C_i) plotted as points.

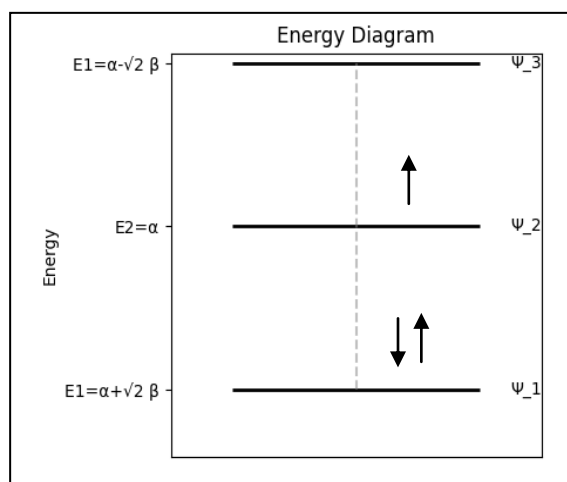


Figure 1. Energy diagram

This enhanced plot provides a clear and detailed visualization of the molecular orbitals for the allyl radical. Each subplot represents one molecular orbital:

1. Ψ_1 (Bonding Orbital):

All coefficients are positive, showing a completely bonding interaction.

Peaks at C_2 , indicating the strongest contribution from this atom.

2. Ψ_2 (Non-bonding Orbital):

Includes a node (zero coefficient) at C_2 , highlighted with a vertical dashed line.

The alternating signs indicate non-bonding behavior.

3. Ψ_3 (Anti-bonding Orbital):

Opposite signs between C_1 , C_3 and C_2 , typical of anti-bonding interactions.

A node exists between C_1 and C_2 , as well as between C_2 and C_3 , both highlighted with vertical dashed lines.

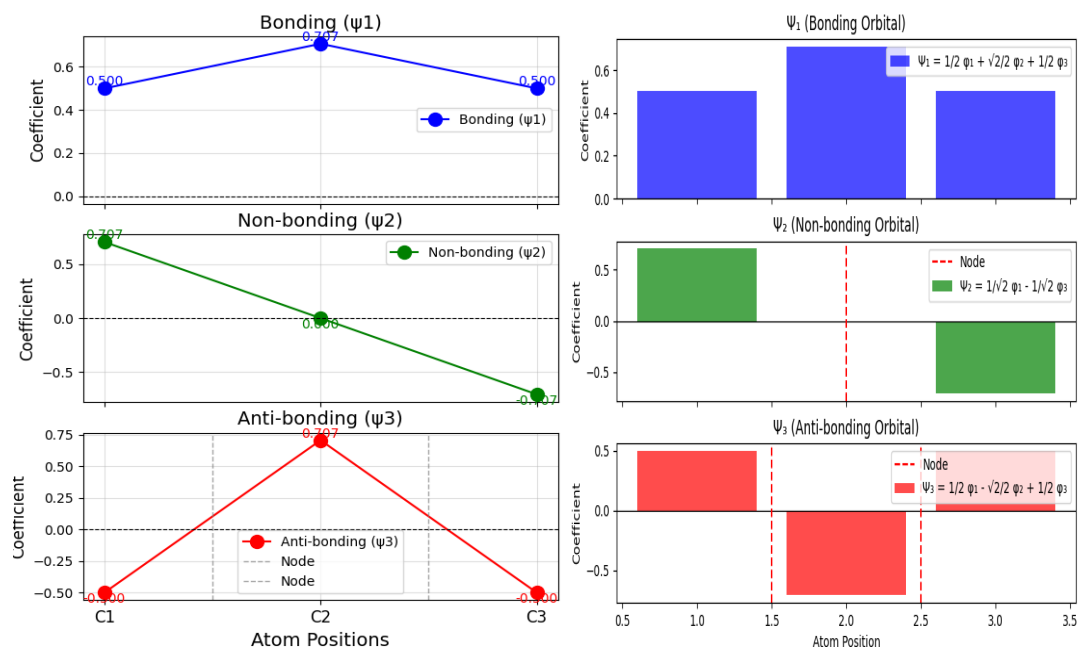


Figure 2. Molecular orbital coefficients of ψ_1 , ψ_2 , and ψ_3 .

Charge and Bond Order:

To calculate the charge density q_r on each atom and the bond order P_{rs} between atoms using the Hückel molecular orbital (HMO) method, we use the following equations:

Charge Density Calculation

The charge density q_r on atom r is given by:

$$q_r = \sum_j n_j C_{jr}^2$$

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Where:

- r is the atom number,
- j is the molecular orbital index,
- n_j is the number of electrons in the j -th molecular orbital,
- C_{jr} is the coefficient of the atomic orbital on atom r in the j -th molecular orbital.

Thus, the charge on each atom can be computed as:

$$q_r = 2c_{1r}^2 + 1c_{2r}^2 + 0c_{3r}^2$$

For atom1 $r = 1$

$$q_1 = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

For atom2 $r = 2$

$$q_2 = 2\left(\frac{\sqrt{2}}{2}\right)^2 + 1(0)^2 = 1$$

For atom3 $r = 3$

$$q_3 = 2\left(\frac{1}{2}\right)^2 + 1\left(-\frac{1}{\sqrt{2}}\right)^2 = 1$$

So, we obtain: $q_1 = q_2 = q_3$

Bond Order Calculation

The bond order P_{rs} between atoms r and s is calculated as:

$$P_{rs} = \sum_j n_j C_{jr} C_{js} \quad 11$$

Where:

- C_{jr} and C_{js} are the coefficients of the atomic orbitals on atoms r and s in the j -th molecular orbital.

These equations are used to determine electron distribution and bonding characteristics in conjugated systems like the allyl radical

Assuming that the allyl radical has three π -electrons, they fill the lowest-energy orbitals according to the Aufbau principle:

- Ψ_1 has 2 electrons (fully occupied),
- Ψ_2 has 1 electron (half-occupied),
- Ψ_3 has 0 electrons (unoccupied).

We compute the bond order P_{rs} for each pair of atoms:

$$P_{12} = 2 * C_{11}C_{12} + 1 * C_{21}C_{22} + 0 * C_{31}C_{32}$$

$$P_{12} = 2 * \frac{1}{2} * \frac{\sqrt{2}}{2} + 1 * \frac{\sqrt{2}}{2} * 0 = \frac{\sqrt{2}}{2}$$

$$P_{23} = \frac{\sqrt{2}}{2}, P_{13} = 0$$

- $P_{12} = P_{23} = 0.707 \rightarrow$ Indicates delocalization over C1-C2 and C2-C3.
- $P_{13} = 0 \rightarrow$ No direct bonding interaction between C1 and C3.

This suggests a resonance structure where π -electrons are delocalized over C_1 , C_2 , and C_3 , as expected for an allylic system.

Bond Order vs. Bond Length Relationship

To estimate the bond length using the bond order, we typically use empirical relationships between bond order and bond length.

Step 1: Understanding the Bond Order vs. Bond Length Relationship

For conjugated systems like $\text{CH}_2=\text{CH}-\text{CH}_2$ (the allyl system), bond lengths decrease as bond order increases. A common empirical formula for carbon-carbon bonds is:

$$d_{rs} = d_0 - k(P_{rs}) \quad 12$$

where:

- d_{rs} is bond length (in Å),
- d_0 is reference single bond length (~ 1.54 Å for C–C),
- k is empirical constant (typically ~ 0.3 Å per bond order increase),
- P_{rs} is bond order.

For C=C, the typical bond length is about 1.34 Å, while for C–C, it is about 1.54 Å.

1- for $C_1 - C_2$ and $C_2 - C_3$:

$$d_{12} = d_{23} = 1.54 - 0.3 * 0.707$$

$$d_{12} = d_{23} = 1.33 \text{ Å}$$

This means that both $C_1 - C_2$ and $C_2 - C_3$ have nearly the same length, intermediate between C–C and C=C.

2- for $C_1 - C_3$:

Since $P_{13} = 0$, there is no direct bond between $C_1 - C_3$, so no bond length applies.

$C_1 - C_2$ and $C_2 - C_3$ are shorter than a pure single bond (1.54 Å) but longer than a pure double bond (1.34 Å), confirming π -electron delocalization. The bond length 1.33 Å is close to a C=C bond due to resonance.

1.8. Applications of the Butadiene molecule

1,3-Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) is a conjugated molecule consisting of 4 carbon atoms forming a π -electron system. Each carbon atom contributes one π -electron, resulting in a system with 4 delocalized π -electrons. These electrons interact via the atomic p_z orbitals that are perpendicular to the molecular plane.

The Hückel Molecular Orbital (HMO) method is a semi-empirical approach used to determine the energy levels and the distribution of electrons in molecular orbitals. The goal is to approximate the solutions of the Schrödinger equation for the π -electrons.

We will analyze the problem using two methods:

1. Direct Method: Solving the full Hückel determinant.
2. Symmetry and Anti-Symmetry Method: Exploiting the molecule's symmetry to simplify the problem.

1-Solving the full Hückel determinant:

For a system with four conjugated carbon atoms, the Huckel matrix is given by:

$$H = \begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix}$$

Dividing the entire determinant by β and defining $x = (\alpha - E)/\beta$, we rewrite the matrix as:

$$\begin{bmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{bmatrix}, \text{ The determinant equation is } \det\left(\frac{H}{\beta}\right) = 0:$$

Solving this determinant results in the characteristic polynomial:

$$x^4 - 3x^2 + 1 = 0, \text{ Substituting } y = x^2, \text{ we find:}$$

$$x = \pm \sqrt{\frac{3+\sqrt{5}}{2}}, \quad x = \pm \sqrt{\frac{3-\sqrt{5}}{2}}$$

Using $E = \alpha - x\beta$, we get the energy levels where the energy levels are ordered as follows:

$$E_1 = \alpha + 1.618\beta, \quad E_2 = \alpha + 0.618\beta, \quad E_3 = \alpha - 0.618\beta, \quad E_4 = \alpha - 1.618\beta$$

Molecular orbital coefficients:

For $x=1.618$

$$\begin{bmatrix} 1.618 & 1 & 0 & 0 \\ 1 & 1.618 & 1 & 0 \\ 0 & 1 & 1.618 & 1 \\ 0 & 0 & 1 & 1.618 \end{bmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = 0$$

Solve determinant and use normalization condition to find coefficient C_i

$$C_1 = 0.3717, C_2 = 0.6015, C_3 = 0.6015, C_4 = 0.3717$$

The same method for remain energy level

Molecular Orbitals with Energy Levels:

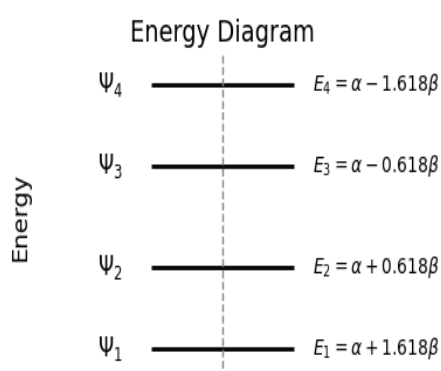


Figure 3. Energy diagram of Butadiene molecule

The molecular orbitals ($\Psi_1, \Psi_2, \Psi_3, \Psi_4$) of 1,3-butadiene illustrate the bonding and anti-bonding interactions between the atomic p_z orbitals of the four carbon atoms. Ψ_1 is the most stable orbital, fully bonding with 0 nodes, while Ψ_2 is a partially bonding and non-bonding orbital with 1 node between C_2 and C_3 . On the anti-bonding side, Ψ_3 has the highest energy and exhibits 3 nodes, representing the most destructive interference. Ψ_4 with 2 nodes, is also anti-bonding but less destabilized than Ψ_3 . This progression of nodes from 0 to 3 correlates directly with the increase in orbital energy levels.

The energy ordering is $E_1 < E_2 < E_3 < E_4$, reflecting the stability of the orbitals. Bonding orbitals like Ψ_1 contribute to molecular stability, while anti-bonding orbitals like Ψ_3 and Ψ_4 reduce stability. Symmetry also plays a role: Ψ_1 and Ψ_4 are symmetric, while Ψ_2 and Ψ_3 are anti-symmetric. The molecular orbitals and their coefficients align with the principles of Hückel theory, where the number of nodes directly determines the bonding or anti-bonding nature of each orbital and its corresponding energy.

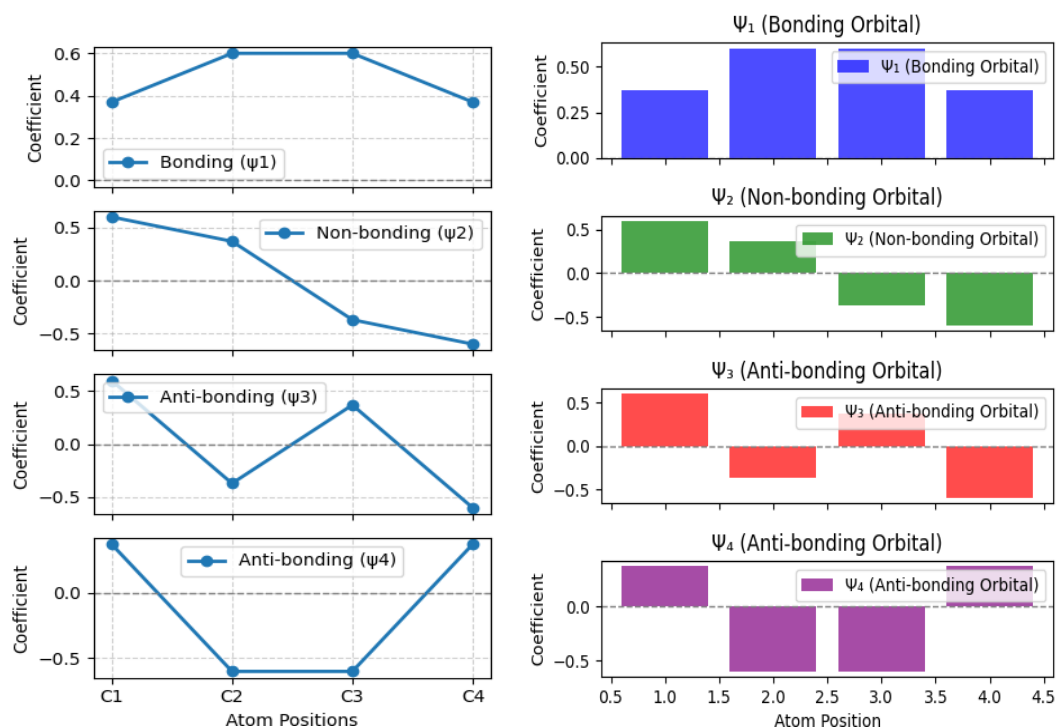


Figure 4. Molecular orbital coefficients of ψ_1 , ψ_2 , ψ_3 and ψ_4 .

2-Symmetry and Anti-Symmetry Assumptions

This method simplifies the problem by leveraging the symmetry of the molecule.

Symmetry: assume $C_1 = C_4$ and $C_2 = C_3$

Anti-Symmetry: Assume $C_1 = -C_4$ and $C_2 = -C_3$

This reduces the problem to smaller 2×2 determinants.

Case 1: symmetric orbitals ($C_1 = C_4$ and $C_2 = C_3$)

The Hückel equations become:

$$\begin{cases} xc_1 + c_2 = 0 \\ c_1 + (x+1)c_2 = 0 \end{cases} \Rightarrow \begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0$$

Solves are : $x = -1.61, x = 0.61$

$$E = \alpha + 1.618\beta, E = \alpha - 0.618\beta$$

Case 1: anti-symmetric orbitals ($C_1 = -C_4$ and $C_2 = -C_3$)

The Hückel equations become:

$$\begin{cases} xc_1 + c_2 = 0 \\ c_1(x-1)c_2 = 0 \end{cases} \Rightarrow \begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0$$

Solves are : $x = +1.61$, $x = -0.61$

$$E = \alpha - 1.618\beta, E = \alpha + 0.618\beta$$

the energy levels are ordered as follows:

$$E_1 = \alpha + 1.618\beta, E_2 = \alpha + 0.618\beta, E_3 = \alpha - 0.618\beta, E_4 = \alpha - 1.618\beta$$

1.9. Python script

This Python script computes molecular orbital properties using the Hückel method.

It determines energy levels, molecular orbital coefficients, atomic charges, and bond orders

for conjugated systems like butadiene.

The script follows these steps:

1. Construct the Hückel Hamiltonian matrix.
2. Solve for eigenvalues (energy levels) and eigenvectors (coefficients).
3. Compute atomic π -charges and bond orders using molecular orbital coefficients.
4. Display results in tabular format.

Adjustable parameters allow extending the model to other conjugated systems.

```
import numpy as np
import pandas as pd
import sympy as sp

# Function to construct the Hückel matrix
def construct_huckel_matrix(size, alpha_values, beta_values):
    H = np.zeros((size, size))
    np.fill_diagonal(H, alpha_values)
    for i in range(size - 1):
        H[i, i + 1] = beta_values[i]
        H[i + 1, i] = beta_values[i]
    return H

# Function to solve the Hückel matrix
def solve_huckel(H, alpha, beta):
    eigenvalues, eigenvectors = np.linalg.eig(H)
    sorted_indices = np.argsort(eigenvalues)
    sorted_eigenvalues = eigenvalues[sorted_indices]
    sorted_eigenvectors = eigenvectors[:, sorted_indices]
    normalized_eigenvectors = sorted_eigenvectors /
np.linalg.norm(sorted_eigenvectors, axis=0)
```

```

energies = [f"E{i + 1} = {alpha} + ({x:.3f}) * {beta}" for i, x in
enumerate(sorted_eigenvalues)]
return energies, sorted_eigenvalues, normalized_eigenvectors

# Function to calculate charges and bond indices
def calculate_charges_and_bond_indices(coefficients, occupation_numbers):
    size, num_orbitals = coefficients.shape
    charges = np.zeros(size)
    for r in range(size):
        for j in range(num_orbitals):
            charges[r] += occupation_numbers[j] * coefficients[r, j] ** 2
    bond_indices = np.zeros((size, size))
    for i in range(size):
        for j in range(size):
            if abs(i - j) == 1:
                for k in range(num_orbitals):
                    bond_indices[i, j] += occupation_numbers[k] *
coefficients[i, k] * coefficients[j, k]
    return charges, bond_indices

# Define system parameters for butadiene
# # CH2=CH-CH=CH2

size = 4
alpha = 0
beta = -1
alpha_values = [alpha] * size
beta_values = [beta] * (size - 1)

# Construct and solve Hückel matrix
H = construct_huckel_matrix(size, alpha_values, beta_values)
energies, eigenvalues, coefficients = solve_huckel(H, alpha, beta)

# Define occupation numbers (4 π-electrons, 2 per bonding orbital)
occupation_numbers = [2, 2, 0, 0]

# Calculate charges and bond indices
charges, bond_indices = calculate_charges_and_bond_indices(coefficients,
occupation_numbers)

# Create DataFrames for display
df_energy = pd.DataFrame({
    "Energy Level": [f"E{i + 1}" for i in range(len(energies))],
    "Energy (E = alpha + x * beta)": energies,
    "Eigenvalues (x)": eigenvalues
})

df_coefficients = pd.DataFrame(
    coefficients,
    columns=[f"MO {i + 1}" for i in range(size)],
    index=[f"C{i + 1}" for i in range(size)]
)

df_charges = pd.DataFrame({

```

```

    "Atom": [f"C{i + 1}" for i in range(size)],
    "Charge": charges
})

df_bond_indices = pd.DataFrame(
    bond_indices,
    index=[f"C{i + 1}" for i in range(size)],
    columns=[f"C{i + 1}" for i in range(size)]
)

# Print results
print("Hückel Energy Levels:")
print(df_energy.to_string(index=False))
print("\nMolecular Orbital Coefficients:")
print(df_coefficients.to_string())
print("\nAtomic Charges:")
print(df_charges.to_string(index=False))
print("\nBond Indices:")
print(df_bond_indices.to_string())

```

Results of code of butadiene are:

Hückel Energy Levels:

Energy Level Energy ($E = \alpha + x * \beta$)

$$E1 \quad E1 = \alpha + (-1.618) * \beta$$

$$E2 \quad E2 = \alpha + (-0.618) * \beta$$

$$E3 \quad E3 = \alpha + (0.618) * \beta$$

$$E4 \quad E4 = \alpha + (1.618) * \beta$$

Molecular Orbital Coefficients:

	MO 1	MO 2	MO 3	MO 4
C1	0.371748	-0.601501	0.601501	-0.371748
C2	0.601501	-0.371748	-0.371748	0.601501
C3	0.601501	0.371748	-0.371748	-0.601501
C4	0.371748	0.601501	0.601501	0.371748

Atomic Charges:

Atom Charge

C1 1.0

C2 1.0

C3 1.0

C4 1.0

Bond Indices:

	C1	C2	C3	C4
C1	0.000000	0.894427	0.000000	0.000000
C2	0.894427	0.000000	0.447214	0.000000
C3	0.000000	0.447214	0.000000	0.894427
C4	0.000000	0.000000	0.894427	0.000000

1.10. Heteroatomic Hückel Model

The Heteroatomic Hückel Model extends the Hückel Molecular Orbital (HMO) Theory to systems containing heteroatoms (atoms other than carbon, such as nitrogen, oxygen, or sulfur). This extension is essential for studying heterocyclic compounds and understanding their electronic properties.

1. Fundamental Modifications in the Heteroatomic Hückel Model

The standard Hückel method assumes that all atoms in the conjugated π -system are carbon atoms with the same properties. When introducing heteroatoms, the following modifications are applied:

a) Coulomb Integral (α)

Represents the energy of an electron in a p_z orbital of an atom. In hydrocarbons, all carbons have the same energy $\alpha_c = \alpha$. When heteroatoms are introduced, their energy levels differ due to electronegativity effects

$$\alpha_X = \alpha + k\beta \quad 13$$

where: X is the heteroatom.

k is an empirical parameter that accounts for the change in energy due to the heteroatom.

b) Resonance Integral (β)

Represents the π -electron interaction (overlap) between two adjacent atoms. In hydrocarbons, resonance between adjacent carbon atoms is $\beta_{CC} = \beta$. When heteroatoms are introduced, the resonance interaction is modified $\beta_{CX} = h\beta$

Where h is an empirical factor that depends on the heteroatom's size, electronegativity, and bonding.

2. Empirical Parameters for Different Atoms

The table below shows empirical values for α and β in the heteroatomic Hückel model:

Application to Heterocyclic Compounds

Example 1: Pyridine (C₅H₅N)

Pyridine is a six-membered aromatic ring where one carbon is replaced by nitrogen.

- The nitrogen atom introduces a different Coulomb integral: $\alpha_N = \alpha + 1.5\beta$.
- The resonance interaction between C and N is weaker than between C and C:

$$\beta_{CN} = 0.8\beta$$

This results in a shift in energy levels and electron density, making pyridine less reactive than benzene.

Example 2: Furan (C₄H₄O)

Furan is a five-membered heterocyclic compound with oxygen contributing two lone pairs.

- The oxygen atom modifies its Coulomb integral: $\alpha_O = \alpha + 2\beta$.
- The resonance interaction is reduced: $\beta_{CO} = 0.8\beta$.

This leads to a lower electron density on oxygen, affecting its reactivity and aromaticity.

1.12.Code python

```
# CH2=CH-CH2=O
alpha = 0
beta = -1
alpha_values = [alpha, alpha, alpha, alpha + beta] #  $\alpha_O = \alpha + \beta$ 
beta_values = [beta, beta, beta]
```

```
H = construct_hetero_huckel_matrix(alpha_values, beta_values)
energies, eigenvalues, coefficients = solve_huckel(H, alpha, beta)
```

```

occupation_numbers = [2, 2, 0, 0]

charges, bond_indices = calculate_charges_and_bond_indices(coefficients,
occupation_numbers)

df_energy = pd.DataFrame({
    "Energy Level": [f"E{i + 1}" for i in range(len(energies))],
    "Energy (E = alpha + x * beta)": energies,
    "Eigenvalues (x)": eigenvalues
})

df_coefficients = pd.DataFrame(
    coefficients,
    columns=[f"MO {i + 1}" for i in range(len(coefficients))],
    index=["C1", "C2", "C3", "O4"]
)

df_charges = pd.DataFrame({
    "Atom": ["C1", "C2", "C3", "O4"],
    "Charge": charges
})

df_bond_indices = pd.DataFrame(
    bond_indices,
    index=["C1", "C2", "C3", "O4"],
    columns=["C1", "C2", "C3", "O4"]
)

# Output
print("Hückel Energy Levels (CH2=CH-CH2=O):")

```

Results

Hückel Energy Levels (CH₂=CH-CH₂=O):

Energy Level (E = alpha + x * beta)

$$E_1 = \alpha + (-1.879) * \beta, E_2 = \alpha + (-1.000) * \beta, E_3 = \alpha + (0.347) * \beta, E_4 = \alpha + (1.532) * \beta$$

Molecular Orbital Coefficients:

	MO 1	MO 2	MO 3	MO 4
C1	0.228013	-5.773503e-01	0.656539	0.428525
C2	0.428525	-5.773503e-01	-0.228013	-0.656539
C3	0.577350	1.652222e-16	-0.577350	0.577350
O4	0.656539	5.773503e-01	0.428525	-0.228013

π -Electron Charges on Atoms:

Atom Charge

C1 0.770647

C2 1.033934

C3 0.666667

O4 1.528752

Bond Indices:

C1 C2 C3 O4

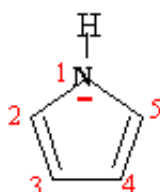
C1 0.000000 0.862086 0.000000 0.000000

C2 0.862086 0.000000 0.494818 0.000000

C3 0.000000 0.494818 0.000000 0.758105

O4 0.000000 0.000000 0.758105 0.000000

Study of the delocalized orbitals of Furan



$$\begin{vmatrix}
 \alpha+1,5\beta-E & 0,8\beta & 0 & 0 & 0,8\beta \\
 0,8\beta & \alpha-E & \beta & 0 & 0 \\
 0 & \beta & \alpha-E & \beta & 0 \\
 0 & 0 & \beta & \alpha-E & \beta \\
 0,8\beta & 0 & 0 & \beta & \alpha-E
 \end{vmatrix}
 =
 \begin{vmatrix}
 x+1,5 & 0,8 & 0 & 0 & 0,8 \\
 0,8 & x & 1 & 0 & 0 \\
 0 & 1 & x & 1 & 0 \\
 0 & 0 & 1 & x & 0 \\
 0,8 & 0 & 0 & 1 & x
 \end{vmatrix}
 = 0$$

Furan: N-C1=C2-C3=C4 (5-membered ring)

alpha = 0

beta = -1

alpha_values = [alpha + 2 * beta] + [alpha] * 4 # Oxygen: alpha + 2beta

beta_CN = 0.8 * beta

beta_CC = beta

Define beta matrix with ring connections

beta_matrix = np.zeros((5, 5))

beta_matrix[0][1] = beta_matrix[4][0] = beta_CN # N-C1 and C4-N

beta_matrix[1][2] = beta_matrix[2][3] = beta_matrix[3][4] = beta_CC

```

# Build and solve
H = construct_furan_huckel_matrix(alpha_values, beta_matrix)
energies, eigenvalues, coefficients = solve_huckel(H, alpha, beta)
occupation_numbers = [2, 2, 2, 0, 0] # 6 π-electrons

# Charges and bond orders
charges, bond_indices = calculate_charges_and_bond_indices(coefficients,
occupation_numbers)

# Display
df_energy = pd.DataFrame({
    "Energy Level": [f"E{i + 1}" for i in range(len(energies))],
    "Energy (E = α + xβ)": energies,
    "Eigenvalue x": eigenvalues
})

df_coefficients = pd.DataFrame(
    coefficients,
    columns=[f"M0 {i + 1}" for i in range(5)],
    index=["N", "C1", "C2", "C3", "C4"]
)

df_charges = pd.DataFrame({
    "Atom": ["N", "C1", "C2", "C3", "C4"],
    "π-Electron Charge": charges
})

df_bond_indices = pd.DataFrame(
    bond_indices,
    index=["N", "C1", "C2", "C3", "C4"],
    columns=["N", "C1", "C2", "C3", "C4"]
)

# Output
print("Hückel Energy Levels (Furan):")

```

Results

Hückel Energy Levels (**Furan**):

Energy Level	Energy (E = α + xβ)	Eigenvalue x
E1	0 + (-2.354) * -1	-2.353796
E2	0 + (-1.517) * -1	-1.517183
E3	0 + (-0.481) * -1	-0.481314
E4	0 + (0.707) * -1	0.707376
E5	0 + (1.645) * -1	1.644917

Molecular Orbital Coefficients:

	MO 1	MO 2	MO 3	MO 4	MO 5
N	-0.886637	0.315563	-0.270490	-0.181776	0.089928
C1	-0.392111	-0.190449	0.513487	0.615169	-0.409726
C2	-0.213640	-0.541395	0.463541	-0.289736	0.602023
C3	-0.110755	-0.630948	-0.290379	-0.410217	-0.580552
C4	-0.047054	-0.415868	-0.603304	0.579913	0.352937

π -Electron Charges on Atoms:

Atom π -Electron Charge

N	1.917741
C1	0.907382
C2	1.107243
C3	0.989362
C4	1.078272

Bond Indices:

	N	C1	C2	C3	C4
N	0.000000	0.297338	0.000000	0.000000	0.147350
C1	0.297338	0.000000	0.849802	0.000000	0.000000
C2	0.000000	0.849802	0.000000	0.461303	0.000000
C3	0.000000	0.000000	0.461303	0.000000	0.885577
C4	0.000000	0.000000	0.000000	0.885577	0.000000

2. Extended Hückel Molecular Orbital Theory (EHMO)

2.1. Foundations of Extended Hückel Theory

From Basic Hückel to Extended Hückel The Hückel Molecular Orbital (HMO) method was initially developed to describe the behavior of π -electrons in planar conjugated hydrocarbons such as ethylene, butadiene, and benzene. It is a semi-empirical approach grounded in the Linear Combination of Atomic Orbitals (LCAO) method. In the Hückel model, simplifications are made: σ -bonds are treated

as a fixed framework, only π -electrons are considered, and all carbon atoms are assumed to be equivalent with identical Coulomb (α) and resonance (β) integrals. Furthermore, the overlap between atomic orbitals is neglected (i.e., the overlap matrix S is taken as the identity matrix). These assumptions limit the model's applicability, although it provides insight into aromaticity, electron densities, and relative reactivities of π -systems.

In contrast, the Extended Hückel Molecular Orbital (EHMO) method significantly improves upon the original by incorporating σ - and π -orbitals, real atomic orbital ionization energies, and explicit consideration of the overlap between orbitals. Originally proposed by Roald Hoffmann, the EHMO model allows for qualitative and semi-quantitative evaluation of molecular electronic structures in both organic and inorganic systems. It is particularly effective for systems with heteroatoms and transition metals, which are not handled well in the basic Hückel method.

2.2. Key Concepts of EHMO

In EHMO, the matrix elements of the Hamiltonian H and the overlap matrix S are no longer idealized. The diagonal elements H_{ii} of the Hamiltonian correspond to the negative of the Valence Orbital Ionization Energies (VOIEs) of atomic orbitals, reflecting the realistic energy of electrons localized on atoms. For off-diagonal elements H_{ij} , which describe the interactions between different orbitals, EHMO uses an empirical expression:

$$H_{ij} = K \cdot S_{ij} \cdot \frac{H_{ii} + H_{jj}}{2} \quad 14$$

where:

- H_{ii} are the diagonal matrix elements (ionization potentials),
- S_{ij} is the overlap integral between orbitals i and j ,
- K is an empirical constant, typically 1.75.

The inclusion of overlap integrals introduces geometric and electronic sensitivity into the model, enabling the study of more complex systems.

2.3. The Generalized Secular Equation

Instead of solving the standard eigenvalue problem $HC = EC$, EHMO uses the more accurate generalized form:

$$H C = E S C \quad 15$$

This accounts for the non-orthogonality of atomic orbitals. Solving this equation gives eigenvalues E (molecular orbital energies) and eigenvectors C (coefficients of atomic orbitals in molecular orbitals).

This formulation accounts for the fact that atomic orbitals used as a basis are not orthogonal meaning the overlap matrix S is not the identity. Solving this directly is more complex than solving the standard eigenvalue problem, but we can simplify it through a matrix transformation.

To do so, we pre-multiply both sides by the inverse of the overlap matrix, S^{-1} . This yields:

$$S^{-1} \cdot HC = E C \quad 16$$

This transformed equation is now in standard eigenvalue form:

$$AC = E C \quad 17$$

Where we define $A = S^{-1} \cdot H$

Matrix A is often referred to as the effective Hamiltonian or the transformed Hamiltonian in an orthonormal basis. Diagonalizing A directly yields the molecular orbital energies (eigenvalues E) and their corresponding molecular orbital wavefunctions (eigenvectors C).

This approach is widely used in EHMO implementations because it bypasses the need for solving the generalized eigenvalue problem directly and allows the use of standard linear algebra tools. However, one must ensure that the overlap matrix S is invertible and well-conditioned, since poor numerical stability can affect the reliability of S^{-1} .

2.4. Application of EHMO and Theoretical Details

Atomic Orbital Ionization Energies (VOIEs) EHMO uses experimental ionization energies as diagonal elements in the Hamiltonian. These VOIEs represent the energy required to remove an electron from a given orbital. Below is a table of typical VOIEs:

Table1. Atomic Orbital Ionization Energies (VOIEs)

Atom	1s (eV)	2s (eV)	2p (eV)
H	13.60		
He	24.5		
Li		5.45	3.50
C		19.5	10.7
N		25.5	13.1
O		32.3	15.9
F		40.4	18.7

These values may be adjusted depending on the environment and molecular bonding.

Importance of Overlap Integrals Overlap integrals quantify the extent to which atomic orbitals from different atoms spatially intersect. In EHMO, they determine the magnitude of interaction between orbitals, thereby affecting bonding, antibonding, and nonbonding character in molecular orbitals. The inclusion of S_{ij} terms allows EHMO to capture angular dependencies, bond lengths, and orbital symmetry effects more realistically than HMO.

Matrix Form of the Secular Equation In a minimal basis of two atomic orbitals a and b, the secular determinant becomes:

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{vmatrix}$$

Solving this determinant yields two energy levels corresponding to bonding and antibonding combinations. For polyatomic systems, this expands to an $n \times n$ matrix, where n is the number of basis orbitals.

In practical computation, the generalized eigenvalue problem $HC = ESC$ is simplified by computing $A = S^{-1}H$ and solving the standard eigenvalue problem $AC = EC$.

2.5. Examples, Benefits, and Limitations of EHMO

1. Case Study: Lithium Hydride (LiH) To illustrate EHMO in practice, consider a simple system involving lithium and hydrogen. We consider three orbitals: Li 2s, Li 2px, and H 1s. The diagonal elements of the Hamiltonian correspond to their VOIEs:

- Li 2s = -13.6 eV
- Li 2px = -3.5 eV
- H 1s = -5.45 eV

The overlap integrals between these orbitals are:

- $S(\text{Li } 2s\text{-H } 1s) = 0.392$
- $S(\text{Li } 2px\text{-H } 1s) = 0.505$
- $S(\text{Li } 2s\text{-Li } 2px) = 0.000$ (orthogonal orbitals)

We construct H and S matrices and compute $A = S^{-1}H$. Diagonalization yields molecular orbital energies and coefficients. For this system, one finds three MOs with energies such as:

- MO1 = -13.77 eV (mostly bonding)
- MO2 = -4.73 eV (non-bonding or weak bonding)

- MO3 = +5.22 eV (antibonding)

The MO coefficients reveal the distribution of atomic orbital character in each MO. For example, the lowest energy MO is dominated by the H 1s orbital, indicating a strong hydrogen character.

2.6. Code of example LiH

```
##### huchel etendue
import numpy as np
import pandas as pd
from numpy.linalg import inv, eig

# -----
# Step 1: Define constants
# -----
K = 1.75 # Empirical constant in Extended Hückel Theory

# Valence orbital ionization energies (VOIEs) in eV
# Orbital order: [Li 2s, Li 2px, H 1s]
H_diag = np.array([
    -13.6, # Li 2s
    -3.50, # Li 2px
    -5.45 # H 1s
])

# -----
# Step 2: Define overlap matrix (S)
# -----
S = np.array([
    [1.000, 0.000, 0.392], # Li 2s
    [0.000, 1.000, 0.505], # Li 2px
    [0.392, 0.505, 1.000] # H 1s
])

# -----
# Step 3: Construct Hamiltonian matrix (H)
# -----
size = len(H_diag)
H = np.zeros((size, size))
for i in range(size):
    for j in range(size):
        if i == j:
            H[i, j] = H_diag[i]
        else:
            H[i, j] = K * S[i, j] * (H_diag[i] + H_diag[j]) / 2

# -----
# Step 4: Construct A = S-1 · H and diagonalize
# -----
A = inv(S).dot(H)
eigenvalues, eigenvectors = eig(A)

# Sort results by energy
sorted_indices = np.argsort(eigenvalues)
eigenvalues = eigenvalues[sorted_indices]
eigenvectors = eigenvectors[:, sorted_indices]
```

```

# Normalize eigenvectors (MO coefficients)
eigenvectors_normalized = eigenvectors / np.linalg.norm(eigenvectors, axis=0)

# -----
# Step 5: Print matrices and results
# -----
labels = ["Li 2s", "Li 2px", "H 1s"]

# Convert to DataFrames for pretty printing
df_H = pd.DataFrame(H, columns=labels, index=labels)
df_S = pd.DataFrame(S, columns=labels, index=labels)
df_A = pd.DataFrame(A, columns=labels, index=labels)
df_E = pd.DataFrame(eigenvalues, columns=["Energy (eV)"])
df_C = pd.DataFrame(eigenvectors_normalized, columns=[f"MO {i+1}" for i in
range(size)], index=labels)

# -----
# Step 6: Output results
# -----
print("\nHamiltonian matrix H (eV):")
print(df_H.round(6))

print("\nOverlap matrix S:")
print(df_S.round(6))

print("\nMatrix A = S-1 · H:")
print(df_A.round(6))

print("\nMolecular Orbital Energies (eV):")
print(df_E.round(6))

print("\nMolecular Orbital Coefficients (normalized):")
print(df_C.round(6))

```

Results is

Hamiltonian matrix H (eV):

	Li 2s	Li 2px	H 1s
Li 2s	-13.60000	-0.000000	-6.534150
Li 2px	-0.00000	-3.500000	-3.954781
H 1s	-6.53415	-3.954781	-5.450000

Overlap matrix S:

	Li 2s	Li 2px	H 1s
Li 2s	1.000	0.000	0.392
Li 2px	0.000	1.000	0.505
H 1s	0.392	0.505	1.000

Matrix $A = S^{-1} \cdot H$:

Li 2s Li 2px H 1s

Li 2s -12.802524 1.450022 -5.943179

Li 2px 1.027361 -1.631986 -3.193453

H 1s -2.034378 -3.699037 -1.507580

Molecular Orbital Energies (eV):

Energy (eV)

0 -13.773032

1 -4.797891

2 2.628833

Molecular Orbital Coefficients (normalized):

MO 1 MO 2 MO 3

Li 2s 0.987624 -0.323387 -0.332936

Li 2px -0.043973 0.721969 -0.615613

H 1s 0.150548 0.611704 0.714265

Application to Methane (CH₄) Methane is more complex, involving a carbon atom with four valence orbitals (2s, 2p_x, 2p_y, 2p_z) interacting with four hydrogen 1s orbitals. The geometry of the molecule (tetrahedral) affects the overlap integrals. After constructing the appropriate matrices and solving for MOs, one can analyze electron densities and charges.

Benefits and Limitations of EHMO is valuable because of its computational simplicity and interpretability. It is especially effective for systems where full ab initio calculations would be too complex or computationally expensive. EHMO excels in predicting qualitative electronic features, trends across series, and in providing insight into bonding patterns. However, it is limited by its empirical nature. The accuracy of EHMO results depends heavily on the choice of VOIEs and overlap integrals. Furthermore, it neglects electron correlation, relativistic effects, and spin interactions, making it less suitable for precision spectroscopy or very high-accuracy energy calculations.

Extended Hückel Theory remains a cornerstone method in computational chemistry education and qualitative molecular analysis. It extends the usefulness of the Hückel model to a wider class of molecules, including heteroatomic and three-dimensional structures, while preserving an intuitive physical picture of molecular bonding.

Chapter 2: Self-Consistent Field Framework: Hartree-Fock Method

1. Introduction

The study of molecular systems with multiple electrons represents a fundamental challenge in quantum chemistry, as it is impossible to solve exactly the Schrödinger equation associated with their full Hamiltonian. This Hamiltonian includes not only the interactions between each electron and the nuclei, but also the repulsive interactions among electrons, which make the problem intrinsically complex and of many-body nature. Since the early days of quantum mechanics, physicists have sought approximate methods to approach the exact solution while respecting the fundamental principles of the theory, most notably, the antisymmetry of the electronic wavefunction as required by the Pauli exclusion principle.

It was in this context that Douglas Hartree introduced, in 1928, an initial method based on a mean-field approach: each electron was assumed to move independently of the others, in an effective potential that represents the average influence of the other electrons. Although innovative, this model did not yet account for the antisymmetry of the wavefunction. Shortly thereafter, Vladimir Fock refined the approach by introducing the formalism of the Slater determinant, which allows for the construction of an antisymmetric wavefunction from products of one-electron orbitals. This improvement gave rise to what is now known as the Hartree-Fock (HF) method.

At the core of the Hartree-Fock method lies the assumption that the electronic wavefunction of a system can be approximated by a single Slater determinant, built from a set of molecular orbitals. These orbitals are not imposed a priori but are determined self-consistently: they are solutions to a variational equation in which the total energy of the system is minimized under the constraint of orbital orthonormality. This minimization leads to a set of nonlinear eigenvalue equations—called the Hartree-Fock equations—in which each orbital depends on the average field created by all other occupied orbitals. The self-consistent nature of this approach necessitates an iterative process: starting from an initial guess for the orbitals, the mean field is calculated, the Fock equations are solved, a new set of orbitals is obtained, and the cycle is repeated until convergence is achieved.

This self-consistent field (SCF) framework forms a cornerstone of computational quantum chemistry. It not only provides a reasonable approximation to the ground state of an electronic system, but also

serves as the foundation for more advanced methods that can more accurately account for electron correlation. Indeed, while the Hartree-Fock method incorporates some exchange effects due to the antisymmetry of the wavefunction, it neglects dynamic correlation, which refers to the fine adjustments electrons make to avoid each other in space. This limitation has motivated the development of post-Hartree-Fock methods such as MP2, CI, and Coupled Cluster, all of which rely on Hartree-Fock orbitals as a computational starting point.

Today, despite its limitations, the Hartree-Fock method remains a fundamental tool for the theoretical study of molecules. It combines quantum mechanical rigor, mathematical clarity, and numerical efficiency. It allows the computation of important properties such as orbital energies, electron density, and optimized molecular structures, and serves as a benchmark for assessing the accuracy of more sophisticated techniques. Understanding the Hartree-Fock method, both in its theoretical foundations and its mathematical and computational formulations, is therefore essential for mastering the field of modern quantum chemistry.

2. Principle of the Hartree-Fock Methodology

The Hartree-Fock methodology is based on a fundamental principle of quantum mechanics: the variational principle. This principle states that, for a given quantum system, any normalized trial wavefunction provides an estimate of the total energy that is greater than or equal to the exact ground-state energy. The central idea of the Hartree-Fock method is thus to search, among all admissible wavefunctions belonging to a given class in this case, Slater determinants for the one that minimizes the total energy of the system.

The choice of the Slater determinant as the form of the wavefunction is motivated by the Pauli exclusion principle, which requires that the exchange of two electrons must result in a change of sign in the total wavefunction. The Slater determinant automatically satisfies this antisymmetry condition. Each row of the determinant represents an electron, and each column corresponds to an occupied one-electron molecular orbital.

In this approach, the N-electron system is described by a set of N molecular orbitals, which are eigenfunctions of an effective operator known as the Fock operator. This operator includes the effects of the one-electron Hamiltonian (kinetic energy and electron–nucleus attraction) as well as average electron–electron interactions, represented by Coulomb terms (mean-field repulsion) and exchange terms (arising from the antisymmetry of the wavefunction).

The total energy of the system is then expressed as a functional of these orbitals, and the method consists of minimizing this energy under the constraint that the orbitals remain orthonormal. This

procedure leads to a set of coupled nonlinear eigenvalue equations, known as the Hartree-Fock equations. These equations can only be solved analytically in very simple cases (e.g., the helium atom under certain approximations), and in practice, they require an iterative process known as the Self-Consistent Field (SCF) procedure.

Thus, the principle of the Hartree-Fock methodology is both conceptually simple and mathematically rigorous: it transforms a many-body N -electron problem too complex to be treated directly into a set of N one-electron equations whose solution is obtained self-consistently. This strategy provides a systematic way to approximate the ground state of an electronic system and serves as a reliable foundation for more refined post-Hartree-Fock treatments.

2.1 The Schrödinger Equation

It is well established that the state and all observable properties of a quantum system be it an atom, a molecule, a molecular assembly, a macromolecule, or a solid are, in principle, entirely determined by its wavefunction, denoted by Ψ . This wavefunction depends on the spatial coordinates and the spin of each particle, resulting in four variables per particle (three spatial and one spin coordinate). The wavefunction must satisfy the time-independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi \quad 1$$

Here, E represents the total energy of the system, and \hat{H} is the Hamiltonian operator, which encapsulates the full energy contributions kinetic and potential of all particles in the system. The function Ψ , known as the wavefunction, is a function of the coordinates of both the electrons and the nuclei, and it contains the complete quantum information of the system. The eigenvalues of the Hamiltonian (E) correspond to the observable energy levels, while the associated wavefunctions are the eigenfunctions of the system.

However, this equation can be solved exactly only for the hydrogen atom and the molecular hydrogen cation (H_2^+). For all other systems, especially those with multiple electrons, the equation becomes analytically unsolvable due to the complexity of electron–electron interactions. As a result, approximate methods must be employed to find usable solutions. These approximations may concern either the form of the Hamiltonian itself (e.g., via the Born-Oppenheimer approximation, effective potentials) or the functional form of the wavefunction, which must still satisfy key physical and mathematical constraints such as normalization, antisymmetry (for fermions), and correct asymptotic behavior.

To obtain optimal approximate solutions within these constraints, quantum chemistry relies primarily on two major mathematical approaches: the variational method and perturbation theory. These techniques allow the construction of energy-minimizing or systematically improved wavefunctions. The general framework for applying such methods is presented in this chapter.

Assuming the problem has been solved within this framework, we will also provide an overview of the main physicochemical properties that can be readily accessed using standard quantum chemistry software packages, such as total energies, optimized geometries, electronic densities, orbital energies, vibrational frequencies, and spectroscopic constants.

2.2 Molecular Hamiltonian

In quantum chemistry, when treating a molecular system as composed of point charges that is, $2n$ electrons and N nuclei under the non-relativistic approximation, the Hamiltonian operator \hat{H} for a closed-shell system (all electrons paired) is given by the sum of kinetic and potential energy contributions of both electrons and nuclei:

$$\hat{H} = -\sum_{k=1}^{2n} \frac{\hbar^2}{2m_e} \nabla_k^2 - \sum_{A=1}^N \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{k=1}^{2n} \sum_{A=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 r_{kA}} + \sum_{k<l}^{2n} \frac{e^2}{4\pi\epsilon_0 r_{kl}} + \sum_{A<B}^N \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \quad 2$$

where:

- \hbar is the reduced Planck constant,
- m_e is the mass of an electron,
- M_A is the mass of nucleus A,
- ∇_k^2 are the Laplacian operators acting respectively on electron k and nucleus A,
- r_{kA} is the distance between electron k and nucleus A,
- r_{kl} is the distance between electrons k and l,
- R_{AB} is the distance between nuclei A and B,
- Z_A and Z_B are the nuclear charges of atoms A and B,
- e is the elementary charge,
- ϵ_0 is the vacuum permittivity (in SI units).

We will henceforth adopt the atomic unit (a.u.) system for all expressions. In this system of units, the following fundamental constants are set to 1 for convenience and simplification:

Atom units: $m_e = 1$, $\hbar = 1$, $e = 1$, $4\pi\epsilon_0 = 1$

These choices eliminate the need to explicitly carry physical constants in quantum mechanical equations. Furthermore, we will assume that the system under study is closed-shell, meaning all molecular orbitals are doubly occupied.

Under these assumptions and using atomic units, the full non-relativistic molecular Hamiltonian for a system of $2n$ electrons and N nuclei simplifies to the following form:

$$\hat{H} = -\sum_{k=1}^{2n} \frac{1}{2} \nabla_k^2 - \sum_{A=1}^N \frac{1}{2M_A} \nabla_A^2 - \sum_{k=1}^{2n} \sum_{A=1}^N \frac{Z_A}{r_{kA}} + \sum_{k<l}^{2n} \frac{1}{r_{kl}} + \sum_{A<B}^N \frac{Z_A Z_B}{R_{AB}} \quad 3$$

2.3 The Born–Oppenheimer Approximation

In the general case of a polyatomic, multi-electron system, the full molecular Schrödinger equation does not admit an exact analytical solution. However, through a series of successive approximations, it becomes possible to obtain wavefunctions Ψ and energies E that closely approximate the true solutions.

In 1927, Max Born and J. Robert Oppenheimer introduced a foundational approximation aimed at simplifying the resolution of the full molecular Hamiltonian by separating the electronic and nuclear contributions in the total wavefunction Ψ . This approximation relies on the fact that electrons move much faster than nuclei, due to their much smaller mass approximately 1836 times less than that of a proton. As a result, electrons can be considered to respond almost instantaneously to changes in the positions of the nuclei.

In practical terms, this means that for a fixed nuclear configuration \mathbf{R} , only the electronic energy contribution $\epsilon(\mathbf{R})$ is needed to describe most properties of the system. The total molecular problem is thus decomposed into two separate Schrödinger equations: one for the electronic part, and one for the nuclear motion. The total wavefunction of the molecule, within the Born–Oppenheimer approximation, can therefore be expressed as a product of two functions:

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \cdot \chi_{\text{nuc}}(\mathbf{R}) \quad 4$$

where:

- $\psi_{\text{el}}(\mathbf{r}; \mathbf{R})$ is the electronic wavefunction, depending on the electronic coordinates \mathbf{r} , and parametrically on the fixed nuclear positions \mathbf{R} ,

- $\chi_{\text{nuc}}(\mathbf{R})$ is the nuclear (vibrational and rotational) wavefunction,

- $\Psi(\mathbf{r}, \mathbf{R})$ is the total molecular wavefunction,

- $\varepsilon(\mathbf{R})$ is the electronic energy for configuration \mathbf{R} , which serves as the potential energy surface for the motion of the nuclei.

This approximation significantly reduces the complexity of molecular quantum mechanical calculations by decoupling fast and slow degrees of freedom. It forms the theoretical basis of almost all modern quantum chemistry calculations, enabling the study of molecular structures, electronic transitions, vibrational spectra, and reaction pathways.

By expressing the total Hamiltonian H in the following form:

$$\hat{H} = \hat{T}_n(\mathbf{R}) + \hat{H}_e(\mathbf{r}; \mathbf{R}) \quad 5$$

where $V(\mathbf{r}, \mathbf{R})$ is the total potential energy depending on both electronic (\mathbf{r}) and nuclear (\mathbf{R}) coordinates, we isolate the electronic Hamiltonian H_e , which is defined as:

$$\hat{H}_e(\mathbf{r}; \mathbf{R}) = \hat{T}_e(\mathbf{r}) + V(\mathbf{r}, \mathbf{R}) \quad 6$$

This operator includes all electronic kinetic energy terms and potential energy contributions due to electron–nucleus attraction, electron–electron repulsion, and nucleus–nucleus repulsion, where the nuclear positions \mathbf{R} are treated as fixed parameters.

By substituting the Born–Oppenheimer wavefunction ansatz:

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \cdot \chi_{\text{nuc}}(\mathbf{R})$$

into the full time-independent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})$$

and applying reasonable approximations (notably neglecting the non-adiabatic coupling terms between electronic and nuclear motions), one can show that this leads to the following coupled system of equations:

1. Electronic Schrödinger equation (for fixed nuclei):

$$\hat{H}_e(\mathbf{r}; \mathbf{R})\psi_{el}(\mathbf{r}; \mathbf{R}) = \varepsilon(\mathbf{R})\psi_{el}(\mathbf{r}; \mathbf{R})$$

2. Nuclear Schrödinger equation, with $\varepsilon(\mathbf{R})$ acting as the potential energy surface:

$$\left[\hat{T}_n(\mathbf{R}) + \varepsilon(\mathbf{R}) \right] \chi_{nuc}(\mathbf{R}) = E \chi_{nuc}(\mathbf{R})$$

Thus, the Born–Oppenheimer approximation reduces the full molecular problem into two more tractable steps: solving the electronic problem to obtain $\varepsilon(\mathbf{R})$, and then solving the nuclear motion problem using this potential energy surface.

$$H_e(\mathbf{r}, \mathbf{R})\Psi_e(\mathbf{r}, \mathbf{R}) = \varepsilon(\mathbf{R})\Psi_e(\mathbf{r}, \mathbf{R})$$

The wavefunction $\Psi_e(\mathbf{r})$ is an eigenfunction of the electronic Hamiltonian H_e , with eigenvalue $\varepsilon(\mathbf{R})$, for a fixed configuration \mathbf{R} of the nuclei. To solve the electronic part of the Schrödinger equation, we assume that the behavior of the electrons is only weakly affected by the small displacements of the nuclei, which are treated as frozen in their instantaneous positions. As a result, under the Born–Oppenheimer approximation, the molecular Hamiltonian reduces to the electronic Hamiltonian only:

$$\hat{H}_e = -\sum_{k=1}^{2n} \frac{1}{2} \nabla_k^2 - \sum_{k=1}^{2n} \sum_{A=1}^N \frac{Z_A}{r_{kA}} + \sum_{k=1}^{2n} \sum_{l>k}^{2n} \frac{1}{r_{kl}}$$

We observe that:

- The first two terms are one-electron operators: they act on each electron individually. These include the kinetic energy of the electrons and their attraction to the nuclei.
- The third term is a two-electron operator, involving pairwise electron–electron repulsion: it depends simultaneously on the positions of two different electrons.

This two-electron term introduces a fundamental complication in the mathematical treatment of the electronic wavefunction Ψ_e . Unlike the one-electron terms, which are additive over individual electrons, the electron–electron repulsion couples the motions of electrons together, making the wavefunction a function of all electron coordinates simultaneously. This non-separability is what makes the exact solution of the electronic Schrödinger equation impossible for many-electron systems, and it is the reason why approximate methods, such as the Hartree-Fock method and post-Hartree-Fock theories, must be used to find tractable solutions.

2.4 Hartree product:

In 1927, Douglas Hartree proposed a computational method in theoretical chemistry that laid the foundation for modern quantum chemistry. His technique consists of expressing the many-electron wavefunction as a product of single-electron wavefunctions (orbitals):

$$\Psi(x_1, x_2, \dots, x_N) = \psi_1(x_1)\psi_2(x_2) \cdots \psi_N(x_N)$$

Here, the functions $\psi(x_i)$ are called one-electron functions or orbitals, and each depends on the spatial and spin coordinates of a single electron.

In this framework, the total Hamiltonian operator \hat{H} is approximated as the sum of one-electron Hamiltonians:

$$\hat{H} = \sum_{i=1}^N \hat{h}_i$$

Each operator \hat{h}_i corresponds to the kinetic energy and the electron–nucleus attraction potential for electron i , and is given in atomic units as:

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}}$$

Within this approximation, the total energy of the system associated with the wavefunction Φ is simply the sum of individual orbital energies:

$$E = \sum_{i=1}^N \varepsilon_i = \varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_n$$

However, Hartree's original method does not respect the Pauli Exclusion Principle, which states that no two electrons can occupy the same quantum state. This principle requires that the total electronic wavefunction be antisymmetric with respect to the exchange of any two electrons.

To enforce this fundamental requirement of quantum mechanics, the Hartree-Fock method replaces the simple product of orbitals by a Slater determinant, which automatically satisfies the antisymmetry condition. This formulation leads to the Hartree-Fock equations, which are

solved self-consistently to determine the optimal set of spin-orbitals that minimize the total energy of the system under the constraint of antisymmetry.

2.5 Classical Approximation of Independent Electrons:

The term V_{ee} (electron–electron repulsion) is very difficult to compute exactly. We will therefore apply an approximation aimed at neglecting this term by assuming that electrons behave as if they were independent from one another, which effectively removes the electron–electron interaction from the treatment.

We can then define an approximate electronic Hamiltonian as:

$$\hat{H}_{e,\text{approx}} = \hat{H}_{\text{el}}^{(1)} + \hat{H}_{\text{el}}^{(2)} + \dots + \hat{H}_{\text{el}}^{(n)}$$

This approximation leads to the consequence that the total wavefunction can be written as a product of one-electron solutions of this equation:

$$\Psi_{\text{total}} = \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n)$$

Exercise

Using the approximate Hamiltonian and the wavefunction defined above, show that the total energy corresponds to the sum of the individual one-electron energies:

$$\begin{aligned} \hat{H}_{e,\text{approx}} | \Psi_{\text{total}} \rangle &= \hat{H}_{e,\text{approx}} | \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n) \rangle \\ &= \left[\hat{H}_{\text{el}}^{(1)} + \hat{H}_{\text{el}}^{(2)} + \dots + \hat{H}_{\text{el}}^{(n)} \right] | \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n) \rangle \\ &= \hat{H}_{\text{el}}^{(1)} | \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n) \rangle + \hat{H}_{\text{el}}^{(2)} | \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n) \rangle + \dots \\ &\quad + \hat{H}_{\text{el}}^{(n)} | \Psi(1) \cdot \Psi(2) \cdot \dots \cdot \Psi(n) \rangle \\ &= \Psi(2) \cdot \dots \cdot \Psi(n) \cdot \varepsilon_{\text{el}}(1) \cdot \Psi(1) + \Psi(1) \Psi(3) \cdot \dots \cdot \Psi(n) \cdot \varepsilon_{\text{el}}(2) \cdot \Psi(2) \\ &\quad + \Psi(1) \cdot \dots \cdot \Psi(n-1) \cdot \varepsilon_{\text{el}}(n) \cdot \Psi(n) \\ &= \left[\varepsilon(1) + \varepsilon(2) + \dots + \varepsilon(n) \right] \Psi(1) \Psi(2) \cdot \dots \cdot \Psi(n) \end{aligned}$$

2.6 Study of the Helium Atom Using the Independent-Electron Approximation

To obtain an approximate solution for the helium atom, we apply the method of separation of variables and assume that the total wavefunction can be written as the product of two one-electron wavefunctions:

$$\psi(1,2) = \psi_1(1) \cdot \psi_2(2), \quad E = E_1 + E_2$$

Here, $\psi_1(1)$ and $\psi_2(2)$ represent functions of the spatial coordinates of electrons 1 and 2, respectively. These are atomic orbitals. The time-independent Schrödinger equation for the two-electron system becomes:

$$\left[-\frac{1}{2}(\Delta_1 + \Delta_2) - \frac{Z}{r_1} - \frac{Z}{r_2} \right] \psi_1(1) \cdot \psi_2(2) = (E_1 + E_2) \psi_1(1) \cdot \psi_2(2)$$

By dividing both sides of this equation by $\psi_1(1) \cdot \psi_2(2)$, we obtain:

$$\psi_1 \left(-\frac{1}{2} \Delta_1 - \frac{Z}{r_1} \right) \psi_1 + \psi_2 \left(-\frac{1}{2} \Delta_2 - \frac{Z}{r_2} \right) \psi_2 = E_1 + E_2$$

Each term in this equation depends on only one electron. The first term concerns electron 1 and the second term, electron 2. Therefore, this is a sum of two independent one-electron Schrödinger equations:

$$\psi_1 \left(-\frac{1}{2} \Delta_1 - \frac{Z}{r_1} \right) \psi_1 = E_1, \quad \psi_2 \left(-\frac{1}{2} \Delta_2 - \frac{Z}{r_2} \right) \psi_2 = E_2$$

In reality, each of these equations describes the motion of a single electron in the Coulomb field of a nucleus, similar to the hydrogen atom problem. The approximate solution is given by hydrogen-like orbitals:

$$\psi(1,2) = \psi_{n_1 \ell_1 m_1}(1) \cdot \psi_{n_2 \ell_2 m_2}(2)$$

The energy is then approximated as:

$$E = E_1 + E_2 = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$$

Assuming both electrons occupy the ground state ($n_1=n_2=1$), we get:

$$E = 2 \cdot E_1 = 2 \cdot \left(-\frac{Z^2}{2n^2} \right) = -2 \text{ hartree} = -54.5 \text{ eV} \Rightarrow E_{\text{He}} = -108.8 \text{ eV}$$

However, the experimental value of the helium atom ground state energy is $E_{\text{exp}} = -78.6$

The discrepancy of about 30 eV arises from the fact that this model neglects the electron–electron repulsion $\frac{1}{r}$, which introduces significant destabilization due to Coulomb repulsion between the two electrons. Ignoring this two-electron interaction leads to a gross overestimation of the binding energy.

2.7 Principle of the Hartree-Fock Method (HF)

In quantum chemistry, the behavior of many-electron systems is governed by the time-independent Schrödinger equation, but solving it exactly becomes impossible for systems with more than one electron due to the complexity of electron–electron interactions. As a first approximation, Hartree (1927) proposed to simplify the problem by assuming that the total wavefunction of an N-electron system could be expressed as a simple product of one-electron wavefunctions (orbitals), each describing the state of an individual electron.

This is known as the Hartree product. While this formulation makes the mathematical treatment more manageable, it has a fundamental flaw: it does not satisfy the Pauli Exclusion Principle, which requires that the total wavefunction of a system of fermions (electrons) must be antisymmetric with respect to the exchange of any two particles.

To correct this, Fock introduced an improved model where the total wavefunction is written not as a product, but as a Slater determinant, which ensures the required antisymmetry:

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \cdots & \varphi_1(x_n) \\ \varphi_2(x_1) & \varphi_2(x_2) & \cdots & \varphi_2(x_n) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_n(x_1) & \varphi_n(x_2) & \cdots & \varphi_n(x_n) \end{vmatrix}$$

Here, the $\varphi_i(x_i)$ are spin-orbitals, functions of both spatial and spin coordinates. The Slater determinant automatically imposes antisymmetry: exchanging two rows (i.e., two electrons) changes the sign of the wavefunction, as required for fermions.

This formulation marks the transition from the Hartree model to the Hartree-Fock method, which respects the physical and quantum mechanical reality of electrons. The central goal of the Hartree-

Fock method is to find the best possible set of spin-orbitals that minimizes the total electronic energy, under the constraint that the wavefunction remains antisymmetric and the orbitals are orthonormal.

Because each electron moves in a potential generated by all other electrons, the Hartree-Fock equations are coupled and non-linear. They must be solved iteratively, leading to the development of the Self-Consistent Field (SCF) procedure. In this approach, one starts with an initial guess for the orbitals, computes the Fock operator, solves the resulting equations for new orbitals, and repeats the process until self-consistency is achieved.

Thus, the Hartree-Fock method, through the use of the Slater determinant and the SCF cycle, provides a more accurate and physically consistent foundation for describing the electronic structure of atoms and molecules, compared to the original Hartree model.

The average energy associated with a normalized Slater determinant (SD)

$$\Psi = \frac{1}{\sqrt{n!}} \varphi_1 \varphi_2 \cdots \varphi_n$$

is given by the following expression

Average Energy of a Normalized Slater Determinant

$$\left\langle \frac{1}{\sqrt{n!}} \varphi_1(1) \cdots \varphi_n(n) \mid \hat{H}_e \mid \frac{1}{\sqrt{n!}} \varphi_1(1) \cdots \varphi_n(n) \right\rangle$$

The computation in the general case appears quite complex, since both the bra and ket contain the $n!n!$ permutations of the coordinates of n electrons. Fortunately, the result is greatly simplified by the orthonormality of the spin-orbitals, which leads to the cancellation of many terms. We will develop the expression in the simple case of two electrons, and then present the result for the general case

1.2. Two-Electron System

The Hamiltonian simplifies, using the previous notation, to:

$$\hat{H} = \hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}}$$

The wavefunction is expressed in terms of two orthonormal spin-orbitals φ_1 and φ_2 as:

$$\Psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) \\ \varphi_2(1) & \varphi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)]$$

The energy is decomposed into one-electron and two-electron integrals:

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{H}(1) + \hat{H}(2) | \Psi \rangle + \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle$$

Development of the one-Electron Term

We analyze the one-electron terms first. Consider the first bracket involving $\hat{H}(1)$:

$$\begin{aligned} & \left\langle \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] | \hat{H}(1) | \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] \right\rangle \\ &= \frac{1}{2} \langle \varphi_1(1)\varphi_2(2) | \hat{H}(1) | \varphi_1(1)\varphi_2(2) \rangle \\ &+ \frac{1}{2} \langle \varphi_2(1)\varphi_1(2) | \hat{H}(1) | \varphi_2(1)\varphi_1(2) \rangle \\ &- \frac{1}{2} \langle \varphi_1(1)\varphi_2(2) | \hat{H}(1) | \varphi_2(1)\varphi_1(2) \rangle \\ &- \frac{1}{2} \langle \varphi_2(1)\varphi_1(2) | \hat{H}(1) | \varphi_1(1)\varphi_2(2) \rangle \end{aligned}$$

This can be simplified using the product structure of the two-electron functions:

$$\begin{aligned} &= \frac{1}{2} \langle \varphi_1(1) | \hat{H}(1) | \varphi_1(1) \rangle \cdot \langle \varphi_2(2) | \varphi_2(2) \rangle \\ &+ \frac{1}{2} \langle \varphi_2(1) | \hat{H}(1) | \varphi_2(1) \rangle \cdot \langle \varphi_1(2) | \varphi_1(2) \rangle \\ &- \frac{1}{2} \langle \varphi_1(1) | \hat{H}(1) | \varphi_2(1) \rangle \cdot \langle \varphi_2(2) | \varphi_1(2) \rangle \\ &- \frac{1}{2} \langle \varphi_2(1) | \hat{H}(1) | \varphi_1(1) \rangle \cdot \langle \varphi_1(2) | \varphi_2(2) \rangle \end{aligned}$$

Since the spin-orbitals φ_i are orthonormal:

$$\langle \varphi_i(x) | \varphi_j(x) \rangle = \delta_{ij}$$

Thus:

$$\begin{aligned} \langle \varphi_2(2) | \varphi_2(2) \rangle &= \langle \varphi_1(2) | \varphi_1(2) \rangle = 1 \\ \langle \varphi_2(2) | \varphi_1(2) \rangle &= \langle \varphi_1(2) | \varphi_2(2) \rangle = 0 \end{aligned}$$

Final result:

$$= \frac{1}{2} \langle \varphi_1(1) | \hat{H}(1) | \varphi_1(1) \rangle + \frac{1}{2} \langle \varphi_2(1) | \hat{H}(1) | \varphi_2(1) \rangle$$

The term involving $\hat{H}(2)$ gives analogous contributions, with variable 2 replacing variable 1. Thus, the full one-electron energy becomes:

$$\begin{aligned} \langle \Psi | \hat{H}(1) + \hat{H}(2) | \Psi \rangle &= \frac{1}{2} \langle \varphi_1(1) | \hat{H}(1) | \varphi_1(1) \rangle + \frac{1}{2} \langle \varphi_2(1) | \hat{H}(1) | \varphi_2(1) \rangle \\ &\quad + \frac{1}{2} \langle \varphi_1(2) | \hat{H}(2) | \varphi_1(2) \rangle + \frac{1}{2} \langle \varphi_2(2) | \hat{H}(2) | \varphi_2(2) \rangle \end{aligned}$$

It is important to recall that these integrals are definite values numbers depending on the nature of the function φ , not on the name of the integration variable. We define:

$$\begin{aligned} \langle \varphi_1(1) | \hat{H}(1) | \varphi_1(1) \rangle &= \langle \varphi_1(2) | \hat{H}(2) | \varphi_1(2) \rangle = H_1 \\ \langle \varphi_2(1) | \hat{H}(1) | \varphi_2(1) \rangle &= \langle \varphi_2(2) | \hat{H}(2) | \varphi_2(2) \rangle = H_2 \end{aligned}$$

The index i of H_i refers to the spin-orbital φ_i . Thus, the one-electron energy becomes:

$$\langle \Psi | \hat{H}(1) + \hat{H}(2) | \Psi \rangle = H_1 + H_2$$

Development of the Two-Electron Term $\frac{1}{r_{12}}$

The two-electron term expands as:

$$\left\langle \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] \middle| \frac{1}{r_{12}} \middle| \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] \right\rangle$$

Which gives:

$$\begin{aligned} &= \frac{1}{2} \langle \varphi_1(1)\varphi_2(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_2(2) \rangle + \frac{1}{2} \langle \varphi_2(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_1(2) \rangle \\ &\quad - \frac{1}{2} \langle \varphi_1(1)\varphi_2(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_1(2) \rangle - \frac{1}{2} \langle \varphi_2(1)\varphi_1(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_2(2) \rangle \end{aligned}$$

Now observe:

The first two terms are equal: they only differ by exchange of dummy variables $1 \leftrightarrow 2$, and integration over $d\tau_1 d\tau_2$ is symmetric.

The last two terms are also equal, for the same reason.

We can then define:

$$\langle \varphi_1(1)\varphi_2(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_2(2) \rangle = \langle 12 | \frac{1}{r_{12}} | 12 \rangle = \langle 12 | 12 \rangle$$

$$\langle \varphi_1(1)\varphi_2(2) | \frac{1}{r_{12}} | \varphi_2(1)\varphi_1(2) \rangle = \langle 12 | \frac{1}{r_{12}} | 21 \rangle = \langle 12 | 21 \rangle$$

Using standard notation:

i-Coulomb integral: $\langle 12|12 \rangle = J_{12}$

ii-Exchange integral: $\langle 12|21 \rangle = K_{12}$

Coulomb and Exchange Integrals in Hartree-Fock Theory:

Let us now explicitly evaluate the two-electron terms in the energy expression of a system consisting of two electrons, each described by spin-orbitals $\varphi_1 = \phi_1 \sigma_1$ and $\varphi_2 = \phi_2 \sigma_2$, where:

1- ϕ_i is the spatial part of the spin-orbital,

2- $\sigma_i \in \{\alpha, \beta\}$ is the spin function of electron i.

To evaluate the electron–electron repulsion energy, we compute two integrals involving the operator $\frac{1}{r_{12}}$, which represents the Coulomb interaction between the two electrons.

1. Coulomb Integral $\langle 12|12 \rangle$

We start with the direct (Coulomb) integral:

$$\langle 12 | 12 \rangle = \left\langle \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2) \left| \frac{1}{r_{12}} \right| \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2) \right\rangle$$

We now separate spin and spatial components, and use the fact that the integral over spin is normalized:

$$\langle 12 | 12 \rangle = \langle \varphi_1(1)\varphi_2(2) | \frac{1}{r_{12}} | \varphi_1(1)\varphi_2(2) \rangle \cdot \langle \sigma_1(1)\sigma_2(2) | \sigma_1(1)\sigma_2(2) \rangle$$

Since the spin product is unity:

$$\langle 12 | 12 \rangle = \iint \varphi_1^*(1)\varphi_2^*(2) \frac{1}{r_{12}} \varphi_1(1)\varphi_2(2) d\tau_1 d\tau_2 = J_{12}$$

This is the Coulomb integral J_{12} , which represents the classical electrostatic repulsion between two continuous charge clouds $|\varphi_1|^2$ and $|\varphi_2|^2$. It is always positive and has a clear physical interpretation.

2. Exchange Integral $\langle 12|21 \rangle$

Now consider the exchange term, which arises solely from the antisymmetrization of the wavefunction:

$$\langle 12|21 \rangle = \left\langle \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2) \left| \frac{1}{r_{12}} \right| \varphi_2(1)\sigma_2(1)\varphi_1(2)\sigma_1(2) \right\rangle$$

Again separating spatial and spin parts:

$$\langle 12|21 \rangle = \left\langle \varphi_1(1)\varphi_2(2) \left| \frac{1}{r_{12}} \right| \varphi_2(1)\varphi_1(2) \right\rangle \cdot \langle \sigma_1(1)\sigma_2(2) | \sigma_2(1)\sigma_1(2) \rangle$$

Note that the spin integral is zero if $\sigma_1 \neq \sigma_2$, because the spin functions are orthonormal. This implies that exchange only occurs between electrons with the same spin.

If $\sigma_1 = \sigma_2$, the spin scalar product equals 1, and we define:

$$K_{12} = \left\langle \varphi_1(1)\varphi_2(2) \left| \frac{1}{r_{12}} \right| \varphi_2(1)\varphi_1(2) \right\rangle$$

This is the exchange integral, which has no classical analogue. It represents a purely quantum-mechanical interference effect arising from the indistinguishability and fermionic nature of electrons. Its value is always positive, but it enters the total energy with a negative sign, effectively lowering the energy. The existence of K_{12} stems entirely from the requirement of antisymmetry under exchange of two electrons. If the total wavefunction were a simple product of orbitals (Hartree model), the exchange integral would not appear. The exchange energy thus reflects the quantum correlations imposed by the Pauli Exclusion Principle.

Combining one- and two-electron terms, the Hartree-Fock total energy of the system becomes:

$$E = H_1 + H_2 + J_{12} - K_{12}$$

2.8 General Case of an N-Electron System Closed-Shell Configuration

In the Hartree-Fock framework, the average electronic energy of an n-electron system is expressed using Slater's formula:

$$E = \sum_{i=1}^n H_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n (\langle ij|ij \rangle - \langle ij|ji \rangle)$$

Here:

1- H_i is the one-electron energy of the spin-orbital ϕ_i ,

2- $\langle ij|ij\rangle$ is the Coulomb integral,

3- $\langle ij|ji\rangle$ is the exchange integral.

To obtain the total energy, one must also add the nuclear repulsion term V_{NN} , which is considered constant in the Born–Oppenheimer approximation.

Closed-Shell Systems: Pairing by Spin

In a closed-shell system, the number of electrons n is even. The $n/2$ spatial orbitals ϕ_i are each occupied by two electrons of opposite spin α and β . The corresponding spin-orbitals are defined as:

$$\phi_1 = \varphi_1\alpha, \quad \phi_2 = \varphi_1\beta, \quad \phi_3 = \varphi_2\alpha, \quad \phi_4 = \varphi_2\beta, \quad \dots, \quad \phi_n = \varphi_{n/2}\beta$$

Each spatial orbital ϕ_i is thus doubly occupied: once by an α -spin electron and once by a β spin electron.

Simplification of the Hartree-Fock Energy Expression

The one-electron terms $H_i = \langle \phi_i | \hat{h} | \phi_i \rangle$ occur twice for each spatial orbital (once for each spin). For instance, ϕ_1 and ϕ_2 , which are associated with the same ϕ_1 , contribute the same H_1 .

The Coulomb integrals $\langle ij|ij\rangle$ are invariant under permutations of electron labels and spin states, so they appear four times for each spatial orbital pair. For example:

$$\langle 13|13\rangle = \langle 23|23\rangle = \langle 14|14\rangle = \langle 24|24\rangle = J_{12}$$

The exchange integrals $\langle ij|ji\rangle$ are non-zero only for same-spin pairs, and therefore appear only twice. For example:

$$\langle 13|31\rangle = \langle 24|42\rangle = K_{12}$$

But spin orthogonality implies:

$$\langle \alpha | \beta \rangle = 0 \quad \Rightarrow \quad \langle 23|32\rangle = \langle 14|41\rangle = 0$$

We can now simplify the total energy expression by grouping terms according to spatial orbitals ϕ_i . Since each spatial orbital contributes two spin-orbitals, we obtain:

This form is widely used in practice for restricted Hartree-Fock (RHF) calculations on closed-shell systems. It reflects:

$$E = 2 \sum_{i=1}^{n/2} H_i + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

- The double occupation of spatial orbital,
- The classical Coulomb repulsion between electron densities,
- The quantum-mechanical exchange correction due to anti-symmetry.

2.9 Variation principle

In quantum mechanics, the variational principle states that for any normalized trial wavefunction Ψ , the expectation value of the Hamiltonian provides an upper bound to the exact ground-state energy:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$$

To apply this to multi-electron systems, we approximate Ψ by a Slater determinant built from a set of orthonormal spin-orbitals $\{\chi_i(x)\}$, where x includes both spatial and spin coordinates.

The electronic Hamiltonian (within the Born–Oppenheimer approximation) is given by:

$$\hat{H} = \sum_{i=1}^N \hat{h}(i) + \sum_{i<j} \frac{1}{r_{ij}}$$

Where $\hat{h}(i)$ is the one-electron operator (kinetic energy + electron–nucleus attraction) and $\frac{1}{r_{ij}}$ is the electron–electron repulsion.

2.10 Hartree-Fock Energy Expression

Using the Slater determinant, the total energy can be written as a functional of the orbitals:

$$E[\{\chi_i\}] = \sum_{i=1}^N \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N \left[\langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_j \chi_i \rangle \right]$$

- 1-The first term is the sum of one-electron energies.
- 2-The second term contains Coulomb and exchange contributions from the two-electron repulsion.

Applying the Variational Principle

To minimize $E[\{\chi_i\}]$ with respect to the orbitals χ_i , under the constraint that they remain orthonormal ($\chi_i\chi_j = \delta_{ij}$), we introduce Lagrange multipliers and solve:

$$\delta \left(E[\{\chi_i\}] - \sum_{i,j} \varepsilon_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij}) \right) = 0$$

This leads to the Hartree-Fock equations:

$$\hat{f} \chi_i = \varepsilon_i \chi_i$$

where \hat{f} , the Fock operator, is defined as:

$$\hat{f}(\mathbf{1}) = \hat{h}(\mathbf{1}) + \sum_{j=1}^N [\hat{J}_j(\mathbf{1}) - \hat{K}_j(\mathbf{1})]$$

2.11.Exercise

The ground state of the helium atom with electron–electron interaction:

- (i) What orbitals are occupied in the ground state of the helium atom?
- (ii) Use these orbitals to construct the Slater determinant.
- (iii) Evaluate the determinant and separate the wavefunction into a product of a spatial part and a spin part.
- (iv) Provide the Hamiltonian operator of the helium atom.
- (v) List the contributions to the total energy, and demonstrate that the result for the ground-state energy obtained in the lecture is correct.

Solution:

- i) The helium atom has two electrons. In its ground state, both electrons occupy the two 1s spin-orbitals.

- ii)
$$\Phi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1S(1)\alpha(1) & 1S(2)\alpha(2) \\ 1S(1)\beta(1) & 1S(2)\beta(2) \end{vmatrix}$$

$$\Phi = \frac{1}{\sqrt{2}}(1S(1)\alpha(1)1S(2)\beta(2) - 1S(2)\alpha(2)1S(1)\beta(1))$$

iii)

$$\Phi = \frac{1}{\sqrt{2}}(1S(1)1S(2))(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

iv)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

v) Let us begin by eliminating the spin contributions. Since the Hamiltonian operator HHH does not depend on spin, we can integrate the spin part separately:

$$\langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} \langle (1S(1)1S(2))(\alpha(1)\beta(2) - \alpha(2)\beta(1)) | \hat{H} | (1S(1)1S(2))(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} \langle (\alpha(1)\beta(2) - \alpha(2)\beta(1)) | (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \rangle \langle 1S(1)1S(2) | \hat{H} | 1S(1)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} \left[\langle \alpha(1)\beta(2) | \alpha(1)\beta(2) \rangle - \langle \alpha(1)\beta(2) | \alpha(2)\beta(1) \rangle \right. \\ \left. - \langle \alpha(2)\beta(1) | \alpha(1)\beta(2) \rangle + \langle \alpha(2)\beta(1) | \alpha(2)\beta(1) \rangle \right] \langle 1S(1)1S(2) | \hat{H} | 1S(1)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} \left[\langle \alpha(1) | \alpha(1) \rangle \langle \beta(2) | \beta(2) \rangle - \langle \alpha(1) | \beta(1) \rangle \langle \alpha(2) | \beta(2) \rangle \right. \\ \left. - \langle \alpha(1) | \beta(1) \rangle \langle \alpha(2) | \beta(2) \rangle + \langle \alpha(2) | \alpha(2) \rangle \langle \beta(1) | \beta(1) \rangle \right] \langle 1S(1)1S(2) | \hat{H} | 1S(1)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \frac{1}{2} [1*1 - 0*0 - 0*0 + 1*1] \langle (1S(1)1S(2)) | \hat{H} | (1S(1)1S(2)) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle 1S(1)1S(2) | \hat{H} | 1S(1)1S(2) \rangle$$

We can now separate this integral into known contributions (as done in the lecture). Reminder:

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle 1S(1)1S(2) | \hat{H} | 1S(1)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle 1S(1)1S(2) | -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} | 1S(1)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle 1S(1)1S(2) | -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} | 1S(1)1S(2) \rangle + \langle 1S(1)1S(2) | -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} | 1S(1)1S(2) \rangle$$

$$+ \langle 1S(1)1S(2) | \frac{1}{r_{12}} | 1S(1)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle 1S(2) | 1S(2) \rangle \langle 1S(1) | -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} | 1S(1) \rangle + \langle 1S(1) | 1S(1) \rangle \langle 1S(2) | -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} | 1S(2) \rangle$$

$$+ \langle 1S(1)1S(1) | \frac{1}{r_{12}} | 1S(2)1S(2) \rangle$$

$$\langle \Phi | \hat{H} | \Phi \rangle = 1*E_1 + 1*E_1 + J_{1S1S}$$

$$\langle \Phi | \hat{H} | \Phi \rangle = 2E_1 + J_{1S1S}$$

Exercise 2

Given the following electronic configurations:

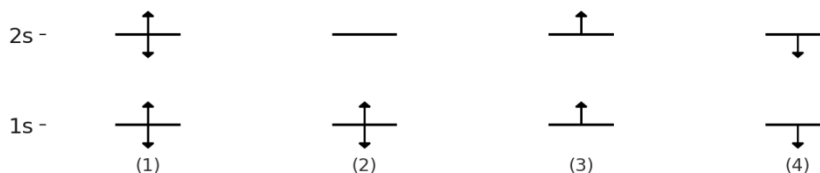


Figure 1

1) For Figure 1, give the Slater determinant and the Hartree energy E(HF) of the system in terms of the integrals h,J and K.

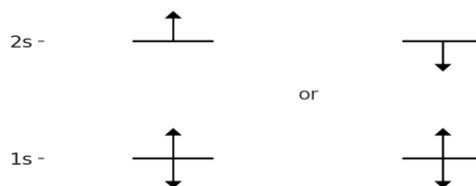


Figure 2

2) For Figure 2, write the Hartree energy E(HF) of the system as a function of the integrals h,J and K.

3. Roothaan Equations:

3.1 Matrix Form of the Hartree-Fock-SCF Method

In the Hartree-Fock method, the molecular orbitals ϕ_i are unknown and must be determined. In practice, they are expressed as linear combinations of known atomic basis functions χ_μ :

$$\phi_i(\mathbf{r}) = \sum_{\mu=1}^K c_{\mu i} \chi_\mu(\mathbf{r})$$

Where: $\chi_\mu(\mathbf{r})$:known atomic orbital basis functions (STO or GTO), $c_{\mu i}$: expansion coefficients to be determined, K : number of basis sets, i : molecular orbital index.

This approach is called the LCAO approximation.

Substituting LCAO into the Hartree-Fock Equations

The Hartree-Fock equation for molecular orbital ϕ_i is:

$$\hat{f} \phi_i = \epsilon_i \phi_i$$

Substituting the LCAO expansion gives:

$$\hat{f} \left(\sum_{\mu} c_{\mu i} \chi_{\mu} \right) = \varepsilon_i \sum_{\mu} c_{\mu i} \chi_{\mu}$$

Multiply both sides by $\chi_{\nu}^*(\mathbf{r})$ and integrate:

$$\sum_{\mu} c_{\mu i} \int \chi_{\nu}^*(\mathbf{r}) \hat{f} \chi_{\mu}(\mathbf{r}) d\mathbf{r} = \varepsilon_i \sum_{\mu} c_{\mu i} \int \chi_{\nu}^*(\mathbf{r}) \chi_{\mu}(\mathbf{r}) d\mathbf{r}$$

This gives a generalized eigenvalue equation:

$$\sum_{\mu=1}^K F_{\nu\mu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^K S_{\nu\mu} c_{\mu i}$$

Or in matrix form:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

3.2 Definition of Matrices in the Roothaan Formalism

To numerically solve the Hartree-Fock equations using basis functions, the continuous differential problem is transformed into a matrix eigenvalue problem. This requires defining a number of key matrices, each with a clear physical and mathematical role:

Overlap Matrix S

The overlap matrix accounts for the fact that the atomic orbitals $\chi_u(\mathbf{r})$ used in the LCAO approach are generally non-orthogonal. The element $S_{\mu\nu}$ measures the overlap between two basis functions $\chi_u(\mathbf{r})$ and $\chi_v(\mathbf{r})$:

$$S_{\mu\nu} = \int \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d\mathbf{r}$$

If the orbitals are orthonormal $S_{\mu\nu} = \delta_{\mu\nu}$. However, in most realistic atomic basis sets, orbitals overlap spatially, and so S must be explicitly computed and used to solve a generalized (not standard) eigenvalue problem.

Core Hamiltonian Matrix H

The core Hamiltonian contains all one-electron operators: the kinetic energy of each electron and the electron–nucleus attraction. Its matrix representation is given by:

$$H_{\mu\nu} = \int \chi_{\mu}(\mathbf{r}) \hat{h} \chi_{\nu}(\mathbf{r}) d\mathbf{r} = T_{\mu\nu} + V_{\mu\nu}^{\text{nuc}}$$

This term does not depend on the electron density or orbital occupation. It is fixed for a given molecular geometry and basis set.

Density Matrix P

The density matrix P plays a central role in building the electron–electron interaction. For closed-shell systems, each spatial molecular orbital is doubly occupied. The density matrix is defined as:

$$P_{\mu\nu} = 2 \sum_{i=1}^{n/2} c_{\mu i} c_{\nu i}$$

This represents the weighted contribution of orbital coefficients to the total electron density. Since the Fock matrix depends on the density matrix (which itself depends on the orbitals), this feedback loop is the basis of the self-consistent field process.

Two-Electron Integrals ($\mu\nu/\lambda\sigma$)

These integrals describe the Coulomb interaction between charge densities from basis functions:

$$(\mu\nu | \lambda\sigma) = \iint \frac{\chi_{\mu}(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) \chi_{\lambda}(\mathbf{r}_2) \chi_{\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

They are the most computationally expensive part of the Hartree-Fock calculation, because there are K^4 of them for a basis of size K. Efficient storage and evaluation strategies (e.g., symmetry exploitation, integral screening) are critical.

3.3 Fock Matrix F

The matrix elements of F are:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\sigma} P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

The first term in brackets is the Coulomb contribution J, and the second term is the exchange contribution K. These reflect how all electrons interact with each other in an averaged (mean-field) sense.

3.4 Roothaan Self-Consistent Field (SCF) Algorithm

Solving the Roothaan equations:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

requires an iterative algorithm, as the Fock matrix F depends on the orbitals we are trying to solve for. This leads to the Self-Consistent Field (SCF) procedure:

Step-by-Step Description:

1. Initial Guess

Start with an initial guess for the molecular orbitals. This is typically done by diagonalizing the core Hamiltonian H , assuming a minimal electron–electron interaction (or using superposition of atomic densities).

2. Compute Density Matrix P

Using the initial orbital coefficients C , build the electron density matrix, which reflects how electrons are distributed across space.

3. Build the Fock Matrix F

Use the current density matrix and the two-electron integrals to compute the Fock F , capturing the mean field felt by each electron.

4. Solve the Generalized Eigenvalue Problem

Diagonalize the matrix equation $\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$, to obtain updated molecular orbital coefficients C and orbital energies $\boldsymbol{\varepsilon}$. Since $S \neq I$, standard eigenvalue routines are not sufficient; orthogonalization techniques like Löwdin or canonical transformation are used.

5. Check for Convergence

Compare the new orbitals, energies, or density matrix with the previous iteration:

-If the changes are below a defined threshold, the procedure is considered converged.

-If not, update P with the new coefficients and return to step 3.

6. Final Results

Once convergence is achieved, compute:

- The total Hartree-Fock energy,
- The final electron density,
- molecular properties (dipole moment, charges, orbital diagrams, etc.).

4. Atomic Basis Functions

In the Hartree-Fock method, molecular orbitals (MOs) are constructed as linear combinations of atomic orbitals (AOs), following the Linear Combination of Atomic Orbitals (LCAO) approximation. To achieve this, it is essential to define a set of atomic basis functions that can best represent the molecular orbitals. If this basis set were complete, it would allow for an exact description of the molecular orbitals. However, in practice, it is necessary to adopt an approximate representation of the basis functions, as complete basis sets are unfeasible.

The size and nature of the basis set directly impact both the computational cost and the accuracy of the results. A smaller basis set reduces the resources required to evaluate integrals but compromises the accuracy with which molecular orbitals are described. Consequently, the quality of the computational results suffers. It becomes evident that the choice of the atomic basis set is critical in quantum chemistry calculations.

There are two primary types of atomic basis functions widely used in electronic structure calculations: Slater-Type Orbitals (STOs) and Gaussian-Type Orbitals (GTOs).

4.1 Slater-Type Orbitals (STOs):

At the dawn of quantum chemistry, Slater proposed the use of functions with the following form:

$$\chi_{\zeta,n,l,m}(r, \theta, \phi) = N Y_{l,m}(\theta, \phi) r^{n-1} e^{-\zeta r}$$

In this expression, N is a normalization constant, and $Y_{l,m}$ are spherical harmonics that define the angular part of the orbital. The exponential decay with respect to the radial distance r reflects the behavior of hydrogen-like atomic orbitals, making STOs physically realistic.

However, Slater orbitals present several limitations. Most notably, they lack radial nodes, which limit their flexibility in representing the electronic distribution. Furthermore, the computation of multi-center two-electron integrals (e.g., three- or four-center integrals) involving STOs cannot be carried out analytically and becomes computationally demanding.

4.2 Gaussian-Type Orbitals (GTOs):

Gaussian functions offer a more practical alternative for computational purposes. They are generally expressed as:

$$\chi(x, y, z) = N x^l y^m z^n e^{-\alpha r^2}$$

These functions exhibit a Gaussian decay with respect to the radial coordinate r , which simplifies mathematical manipulations. A key advantage is that the product of two Gaussian functions remains a Gaussian function, greatly facilitating the evaluation of integrals involved in electronic structure calculations. This property contrasts with STOs, where such simplifications do not apply.

Despite their computational advantages, Gaussian orbitals do not accurately model the sharp behavior of electronic wavefunctions near the nucleus or at long ranges. Nevertheless, they are preferred in practice due to their ease of use and the possibility of combining them in flexible ways to improve accuracy.

4.3 Strategies for Constructing Basis Sets

There are several strategies to build atomic orbitals using Gaussian functions:

1. **Minimal Basis Set:** In this simplest case, each atomic orbital is represented by a single Gaussian function (a GTO). For example, the hydrogen 1s orbital is modeled using only one s-type Gaussian. However, this approach is limited because it does not accurately capture the electron density near the nucleus or far from it.
2. **Double- or Triple-Zeta Basis Sets:** These involve duplicating or tripling the number of Gaussian functions used for each atomic orbital. In this way, the 1s orbital of hydrogen would be represented by two or three Gaussian functions with different exponents (ζ values). This provides a more flexible and accurate description of the electron distribution across different spatial regions.
3. **Contracted Gaussian-Type Orbitals (CGTOs):** A more sophisticated approach involves forming contracted functions by taking linear combinations of primitive Gaussian functions (PGTOs):

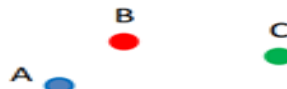
$$\phi_{\text{CGTO}} = \sum_i a_i \phi_i^{\text{PGTO}}$$

This allows a single contracted orbital to approximate the behavior of a Slater orbital more accurately while retaining the computational benefits of Gaussians.

4.4 Linear Combination of Atomic Orbitals (LCAO)

We express molecular orbitals (MOs) as a linear combination of atomic orbitals (AOs) using the LCAO approach. This method provides a powerful and general framework: it can be applied to any molecule, regardless of the number or types of atoms involved.

The strength of the LCAO approach lies in its generality and flexibility; molecular orbitals are constructed as weighted sums of atomic orbitals centered on different atoms:



$$\psi(\mathbf{r}) = c_1\chi_1(\mathbf{r}) + c_2\chi_2(\mathbf{r}) + c_3\chi_3(\mathbf{r}) + c_4\chi_4(\mathbf{r}) + c_5\chi_5(\mathbf{r}) + c_6\chi_6(\mathbf{r}) + c_7\chi_7(\mathbf{r}) \cdots$$

}
A

}
B

}
C

Each term $\chi_i(\mathbf{r})$ represents an atomic orbital located on a given atom (e.g., A, B, C), and each coefficient c_i is a weight determined through quantum chemical calculations. The molecular orbital thus spreads over multiple atoms, incorporating their atomic orbitals into a unified wavefunction.

We can extend the LCAO concept further by refining the choice of atomic orbitals:

- Use of multiple AOs per atom: For example, a hydrogen atom might be described by more than one atomic orbital (1s, possibly 2s, or diffuse s functions). Heavier atoms might have several s, p, or d orbitals. This flexibility allows us to better describe the molecular orbitals and improve the precision of quantum calculations.
- Use of mathematically convenient functions: Rather than using the exact atomic orbitals of isolated atoms (which are not analytically tractable in most molecules), we use approximate atomic orbitals chosen for their ease of integration and computational efficiency (e.g., Gaussians).
- Systematic basis set construction: These simplified AOs form the basis set used in calculations. The more functions included in the basis, the more accurately we can represent the MOs — especially in regions near the nucleus or far away from it.
- Focus on coefficients: Instead of solving for the full shape of molecular orbitals (which is practically impossible analytically or numerically), the problem reduces to solving for the LCAO coefficients c_i . These coefficients are optimized to yield the best approximation to the true molecular orbital within the chosen basis set.

4.5 Interpretation of the Molecular Orbital Expansion

The molecular orbital $\psi_i(\mathbf{r})$ is expressed as a linear combination of basis functions G_α , each multiplied by a coefficient $C_{\alpha i}$:

$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{N_{\text{BF}}} G_\alpha(\mathbf{r}) C_{\alpha i}$$

$\psi_i(\mathbf{r})$ The i th molecular orbital (spatial wavefunction), describing the probability amplitude of finding an electron in space.

G_α The α th basis function, which is typically a Gaussian-Type Orbital (GTO) or Slater-Type Orbital (STO). These functions are fixed and known before the calculation begins.

C_{ai} The LCAO coefficient associated with basis function G_α in the construction of orbital ψ_i . These are determined by solving the Hartree-Fock or DFT equations using the Self-Consistent Field (SCF) procedure.

This representation highlights a key idea in quantum chemistry: molecular orbitals are built from fixed basis functions, but the way they are combined (i.e., the coefficients) is what we solve for.

4.6. Gaussian Basis Functions

Atomic orbitals that resemble those of the hydrogen atom; known as Slater-type orbitals (STOs); are theoretically ideal for expanding molecular orbitals (MOs), as they have the correct behavior:

1-Close to the nucleus: They accurately reproduce the sharp peak due to strong nuclear attraction.

2-Far from the nucleus: They exhibit the correct exponential decay, matching physical expectations.

However, in practice, Gaussian-type orbitals (GTOs) are widely preferred because they greatly simplify the evaluation of molecular integrals. The mathematical properties of Gaussians allow for efficient and analytic integration in quantum chemistry software, which is not possible with Slater orbitals.

The image below illustrates the difference between a Slater function and a Gaussian function:

The Slater function is written as:

$$s_\nu(\mathbf{r}) = e^{-\zeta_\nu |\mathbf{r}|} = e^{-\zeta_\nu \sqrt{x^2 + y^2 + z^2}}$$

The Gaussian function is given by:

$$g_\nu(\mathbf{r}) = e^{-\zeta_\nu r^2} = e^{-\zeta_\nu (x^2 + y^2 + z^2)}$$

While the Gaussian function does not capture the electron-nucleus cusp behavior as accurately as the Slater function, it provides a reasonable approximation and is computationally superior, especially when combined in linear combinations (contracted Gaussians) to better mimic Slater behavior.

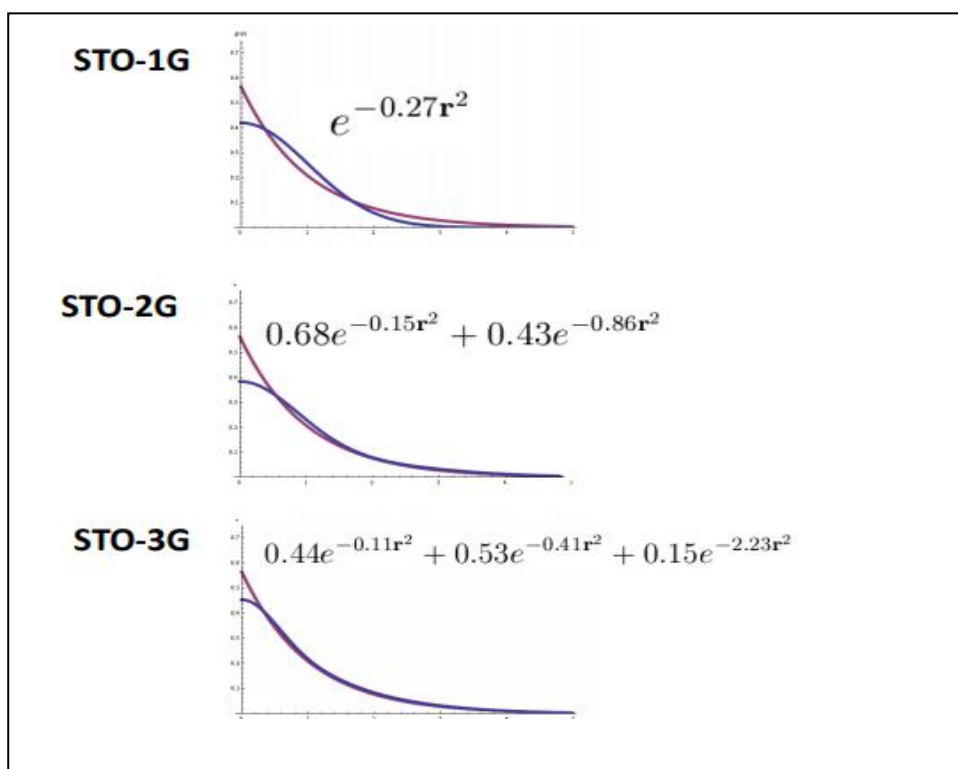


Figure 1. Approximation of Slater-type orbitals using Gaussian functions in STO-nG basis sets.

STO-1G (Single Gaussian Approximation)

In the STO-1G basis set, the 1s Slater-type orbital is approximated using a single primitive Gaussian function: $e^{-0.27r^2}$

This function decays too rapidly at short distances and too slowly at long distances compared to a true Slater function $e^{-0.27r^2}$. As a result, STO-1G poorly reproduces the cusp behavior near the nucleus and is not accurate for quantitative calculations. However, its simplicity makes it computationally efficient, and it's mainly used for pedagogical purposes or extremely fast qualitative modeling.

STO-2G (Two-Gaussian Approximation)

The STO-2G basis function combines two primitive Gaussians: $0.68e^{-0.23r^2} + 0.43e^{-1.3r^2}$

This linear combination significantly improves the fit to the Slater-type function. One Gaussian handles the long-range decay while the other adjusts for the short-range behavior near the nucleus. STO-2G offers a compromise between computational simplicity and improved physical accuracy compared to STO-1G.

STO-3G (Three-Gaussian Approximation)

STO-3G uses three primitive Gaussians: $0.44e^{-0.16r^2} + 0.53e^{-0.62r^2} + 0.15e^{-3.4r^2}$

This basis set provides a much closer approximation to the original Slater orbital across all radial distances. The combination of exponents allows better modeling of both nuclear cusp behavior and asymptotic decay. STO-3G is widely used as a minimal basis set in computational chemistry, offering a balance between efficiency and reasonable accuracy for small molecules and preliminary studies.

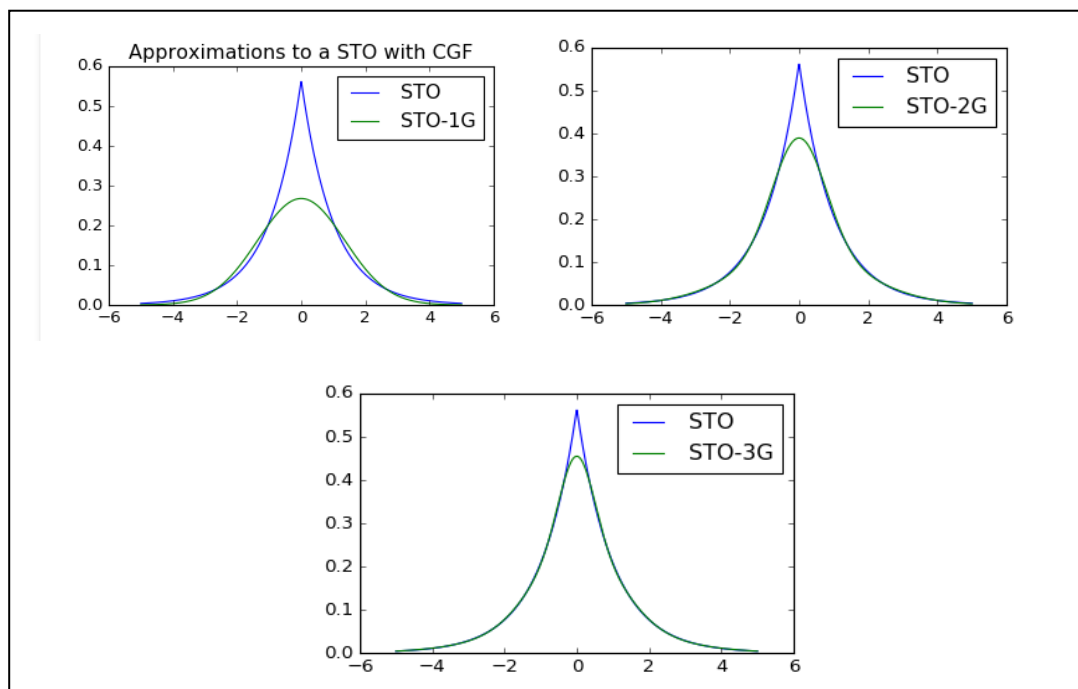


Figure 2. Comparison of STO-nG basis sets with Slater-type orbitals (STO).

Table 1. Characteristics and Applications of STO-nG Basis Sets

Basis Set	Number of Gaussians	Accuracy vs STO	Usage
STO-1G	1	Poor	Teaching, very rough estimates
STO-2G	2	Better fit, moderate improvement	Fast semi-quantitative work
STO-3G	3	Best approximation among the three	Standard for minimal basis SCF

4.7 Cartesian Primitive Gaussian Functions (GTOs)

In computational quantum chemistry, primitive Gaussian-type orbitals (GTOs) are the foundational mathematical functions used to approximate atomic orbitals in molecular systems. A primitive Gaussian function takes the general form:

$$g_v(\mathbf{r}) = x^k y^m z^n e^{-\zeta r^2} = x^k y^m z^n e^{-\zeta(x^2+y^2+z^2)}$$

Where:

- 1- x, y, z Cartesian coordinates,
- 2- k, m, n : Non-negative integers that define the angular momentum components along the x , y , and z axes, respectively.
- 3- ζ : The orbital exponent, which controls the spatial extent of the orbital — smaller ζ values yield more diffuse functions.
- 4- $k+m+n=l$: The total angular momentum quantum number l (e.g., 0 for s, 1 for p, 2 for d...).

Examples of Cartesian GTOs by Angular Momentum:

- s orbital ($l=0$): $g(\mathbf{r}) = e^{-\zeta r^2}$
- p orbital ($l=1$): $x e^{-\zeta r^2}$, $y e^{-\zeta r^2}$, $z e^{-\zeta r^2}$
- d orbital ($l=2$): $x^2 e^{-\zeta r^2}$, $y^2 e^{-\zeta r^2}$, $z^2 e^{-\zeta r^2}$, $xy e^{-\zeta r^2}$, $xz e^{-\zeta r^2}$, $yz e^{-\zeta r^2}$

These functions are not normalized yet in practical software, normalization constants are applied to ensure orthonormality in the basis set.

Why Cartesian GTOs Are Useful:

- **Simplicity in Computation:** The product of two Cartesian Gaussians is another Gaussian centered between the two original centers. This makes integral evaluation (overlap, Coulomb, and exchange integrals) very efficient and fully analytical.
- **Compatibility with Multicenter Systems:** Cartesian GTOs are particularly suitable for representing orbitals in molecules with multiple nuclei, as their form allows easy manipulation under translation and rotation.

4.8 Split-Valence Gaussian Basis Sets: 3-21G, 4-31G, and 6-31G

In quantum chemistry, split-valence basis sets provide a more flexible and accurate description of valence electrons compared to minimal basis sets. Common examples include 3-21G, 4-31G, and 6-31G, all of which are categorized under the Pople-style basis sets. The key idea of a split-valence basis is to represent core and valence orbitals differently, allocating more functions to the chemically reactive valence region.

In these notations:

- The first digit (e.g., 3, 4, or 6) refers to the number of primitive Gaussian functions used to describe the core orbitals of heavy atoms (atoms other than hydrogen). These core functions are kept fixed and relatively compact.
- The second part (e.g., 21 or 31) refers to how the valence orbitals are split:

- In 3-21G, the valence shell is represented by two basis functions: one composed of two primitives, the other of one primitive.
- In 4-31G, the core orbital is built from four primitives, and the valence is split into two contracted functions—three and one primitive respectively.
- In 6-31G, the core orbital is made of six primitives, and the valence shell is again described by a split pair of functions: three and one primitive each.

This approach is referred to as double-zeta (two components per valence orbital). If a basis set includes three groups of functions to describe the valence orbitals, such as in 6-311G, it is called a triple-zeta basis. The inclusion of multiple functions for valence electrons enhances flexibility, especially in capturing polarization and charge distribution changes during bonding or excitation.

Split-valence basis sets strike a balance between computational cost and accuracy, making them widely used in practical molecular quantum chemical calculations.

- Used in Many Programs: Quantum chemistry software like Gaussian, GAMESS, and ORCA often use Cartesian GTOs, especially in older basis sets like STO-3G or Pople basis sets (6-31G, etc.).

Example: 3-21G Basis Set for H atom

This code is recognized by the GAUSSIAN program:

	α	$d_i (s)$	Code
H	S		
	0.5447178000E+01	0.1562849787E+00	2
	0.8245472400E+00	0.9046908767E+00	
H	S		
	0.1831915800E+00	1.0000000	1
END			

There are two contracted functions and three primitive functions used to represent the hydrogen 1s orbital. The first contracted function is made of two primitives with respective coefficients (code 2).

The second function is a single primitive Gaussian (code 1). This structure corresponds to the 3-21G split-valence basis, where the valence shell is described using two different scales for improved flexibility.

Example: 6-31G Basis Set for C atom

	α	$d_i (s)$	$d_i (p)$	Code	
C	S	0.3047524880E+04	0.1834737132E-02	6	
		0.4573695180E+03	0.1403732281E-01		
		0.1039486850E+03	0.6884262226E-01		
		0.2921015530E+02	0.2321844432E+00		
		0.9286662960E+01	0.4679413484E+00		
		0.3163926960E+01	0.3623119853E+00		
C	SP	0.7868272350E+01	-0.1193324198E+00	0.6899906659E-01	3
		0.1881288540E+01	-0.1608541517E+00	0.3164239610E+00	
		0.5442492580E+00	0.1143456438E+01	0.7443082909E+00	
C	SP	0.1687144782E+00	0.1000000000E+01	0.1000000000E+01	1
END					

This basis set consists of three contracted shells:

Core shell (code 6-): made up of 6 primitive Gaussians combined to form one s-type contracted function.

Valence shell (code 3): composed of three primitives, forming one contracted s-function and one p-function each.

Diffuse/valence flexibility shell (code 1): a single primitive used separately for s and p orbitals.

This structure follows the split-valence 6-31G basis philosophy, providing improved flexibility for bonding and electron distribution modeling, especially for valence electrons.

Table 2. Basis Set Composition for NH₃ Using the 3-21G Basis

Atom	N # of Atoms	Atomic Orbital (AO)	Degeneracy	Basis Functions	Primitives	Total Basis Functions	Total Primitives
N	1	1s (core)	1	1	3	1	3
		2s (valence)	1	2	2 + 1 = 3	2	3
		2p (valence)	3	2	2 + 1 = 3	6	9
H	3	1s (valence)	1	2	2 + 1 = 3	6	9
						Total = 15	Total = 24

5. Integral Evaluation Using 1s Primitive Gaussians

In the context of Hartree–Fock calculations, the use of 1s primitive Gaussian-type orbitals (GTOs) significantly simplifies the evaluation of multicenter integrals. A primitive Gaussian function centered on atom A is given by:

$$1s(\mathbf{r} - \mathbf{R}_A) = e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2}$$

For two such Gaussian functions centered on distinct atoms A and B with exponents α and β , respectively, their product can be expressed as a single Gaussian function centered at an intermediate point \mathbf{R}_P along the axis connecting A and B. The product is mathematically equivalent to:

$$\tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_A) \cdot \tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_B) = \tilde{K} \cdot \tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_P)$$

Here, the scaling factor \tilde{K} accounts for the exponential decay due to spatial separation between centers:

$$\tilde{K} = \exp\left[-\frac{\alpha\beta}{\alpha + \beta} |\mathbf{R}_A - \mathbf{R}_B|^2\right]$$

The new center \mathbf{R}_P is the weighted average of the centers:

$$\mathbf{R}_P = \frac{\alpha\mathbf{R}_A + \beta\mathbf{R}_B}{\alpha + \beta}$$

The combined exponent of the resulting Gaussian is $p = \alpha + \beta$

This property, known as the Gaussian product theorem, allows the transformation of any two-center integral involving 1s primitives into a one-center form, thereby making analytical integration tractable. This principle underlies the efficiency of Hartree–Fock and other ab initio methods when using Gaussian-type basis sets.

5.1 Evaluation of Two-Center Integrals with Primitive 1s Gaussians

To simplify the evaluation of molecular integrals in quantum chemical calculations, we frequently use unnormalized primitive 1s Gaussian functions. These functions offer analytical simplicity, especially when dealing with products of orbitals on different atomic centers.

We first consider the two-center overlap integral between two primitive Gaussians centered on atoms A and B:

$$(A|B) = \int d\mathbf{r}_1 \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A) \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B)$$

Using the Gaussian product theorem, this product becomes a single Gaussian centered at an intermediate point \mathbf{R}_P , allowing the integral to be rewritten as:

$$(A|B) = \tilde{K} \int d\mathbf{r}_1 e^{-p|\mathbf{r}_1 - \mathbf{R}_P|^2}$$

Changing variables to $\mathbf{r} = \mathbf{r}_1 - \mathbf{R}_P$, the integral becomes:

$$(A|B) = \tilde{K} \int d\mathbf{r} e^{-pr^2} = \tilde{K} \cdot 4\pi \int_0^\infty dr r^2 e^{-pr^2}$$

This last integral is a known Gaussian integral $\int_0^\infty dr r^2 e^{-pr^2} = \frac{4\pi}{p^{3/2}}$

Thus, the final result for the overlap integral is:

$$(A|B) = \left(\frac{p}{\pi}\right)^{3/2} \exp\left[-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2\right]$$

This formula is central to computing overlap matrices in Hartree–Fock methods.

5.2 Kinetic Energy Integral

We now examine the kinetic energy integral of the form:

$$\left(A \left| -\frac{1}{2} \nabla^2 \right| B\right) = \int d\mathbf{r}_1 \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A) \left(-\frac{1}{2} \nabla^2\right) \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B)$$

Following a procedure similar to the overlap integral and applying the Laplacian operator to the Gaussian function, we obtain:

$$\left(A \left| -\frac{1}{2} \nabla^2 \right| B\right) = \alpha\beta \left(\frac{3}{\alpha+\beta} - \frac{2\alpha\beta}{(\alpha+\beta)^2} |\mathbf{R}_A - \mathbf{R}_B|^2\right) \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} \exp\left[-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2\right]$$

5.3 Nuclear Attraction and Two-Electron Integrals with Primitive Gaussians:

In Hartree–Fock calculations based on primitive 1s Gaussian-type orbitals, all required integrals including overlap, kinetic, nuclear attraction, and electron–electron repulsion can be evaluated analytically using the Gaussian product theorem and the Boys function.

The attraction of an electron located in an orbital centered at point A to a nucleus at point \mathbf{R}_C can be written, in the Gaussian basis, as:

$$\left(A \left| -\frac{Z_C}{r_{1C}} \right| B\right) = -\frac{2\pi Z_C}{\alpha+\beta} \cdot \exp\left[-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2\right] \cdot F_0\left[(\alpha+\beta) |\mathbf{R}_P - \mathbf{R}_C|^2\right]$$

- Where:
- $F_0(t)$ is the Boys function of order 0,
- \mathbf{R}_P is the Gaussian product center between A and B,
- α and β are the Gaussian exponents on centers A and B,
- This expression permits rapid evaluation of the Coulomb attraction term analytically.

5.4 Two-Electron Repulsion Integral

The integral representing the Coulomb repulsion between two electrons, each in different orbital pairs (A,B) and (C,D), is given by the compact formula:

$$(AB|CD) = 2\pi^{5/2} \left[\frac{1}{(\alpha + \beta)(\gamma + \delta)\sqrt{\alpha + \beta + \gamma + \delta}} \right] \cdot \exp \left[-\frac{\alpha\beta}{\alpha + \beta} |\mathbf{R}_A - \mathbf{R}_B|^2 - \frac{\gamma\delta}{\gamma + \delta} |\mathbf{R}_C - \mathbf{R}_D|^2 \right] \\ \cdot F_0 \left[\frac{(\alpha + \beta)(\gamma + \delta)}{\alpha + \beta + \gamma + \delta} |\mathbf{R}_P - \mathbf{R}_Q|^2 \right]$$

here:

- \mathbf{R}_P and \mathbf{R}_Q are the effective centers for the pairs AB and CD,
- The exponential terms account for the electron localization,
- F_0 again is the Boys function handling the radial integration component.

These explicit forms allow all the electron-nucleus and electron–electron interaction terms in Hartree–Fock to be calculated exactly when using 1s primitive Gaussians, and they form the mathematical foundation for efficient integral routines in quantum chemistry software.

6. Semi-Empirical Implementations of Molecular Orbital Theory

How can we make Hartree-Fock theory less computationally expensive without sacrificing too much accuracy? The most demanding step the calculation of two-electron integrals (with four indices) (J and K), which appear in the elements of the Fock matrix $F_{\mu\nu}$ (where N is the number of basis functions) takes the most time. One way to save time is to estimate their value accurately in advance, thus avoiding numerical integration.

Coulomb integrals measure the repulsion between electrons in regions of space defined by basis functions. When the basis functions in the integral for one electron are very far from those for the other, the value of the integral tends toward zero. In a large molecule, one could avoid calculating a very large number of integrals simply by assuming they are negligible.

HF theory is intrinsically imprecise because it does not include correlation energy. Therefore, modifications made to the theory to simplify the formalism can actually improve it, provided that the new approximations introduce, in some way, the treatment of correlation effects. Most of the time, these approximations involve adopting a parametric form for part of the calculation where the parameters are chosen to best reproduce experimental data, this is what we call a semi-empirical method.

Another motivation for introducing a semi-empirical approximation into HF theory was to facilitate the calculation of derivatives (gradients, Hessians) so that geometries can be optimized more efficiently.

Extended Hückel Theory

Before discussing semi-empirical methods, let us revisit Hückel theory:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

The size of the secular determinant depends on the choice of the basis set.

The Extended Hückel Theory (EHT) is based on two critical conventions:

- 1- All core electrons are ignored (this approximation is adopted by all modern semi-empirical methods).
- 2- If an atom has occupied d orbitals, the highest occupied level among these orbitals is considered part of the set of valence orbitals.

Each remaining valence orbital is represented by a Slater-Type Orbital (STO):

$$\varphi(r, \theta, \phi; \zeta, n, l, m) = \left(\frac{(2n)!}{2\zeta} \right)^{n+1/2} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi)$$

Where:

ζ : an exponent, depends on the atomic number.

n : principal quantum number for the valence orbital.

$Y_{lm}(\theta, \phi)$: spherical harmonics functions, depending on the angular momentum quantum numbers l , m

Size of the Secular Determinant

It is dictated by the total number of valence orbitals in the molecule.

Example – MnO_4^- anion: 25 STO basis functions:

One 2s orbital and three 2p orbitals for each oxygen atom (16 orbitals total),

One 4s orbital, three 4p orbitals, and five 3d orbitals for the manganese atom.

6.1 Characteristics of STOs (Slater-Type Orbitals)

- 1-Proper exponential decay as the distance r increases.
- 2-The angular component is hydrogen-like.
- 3-The 1s orbital has a cusp at the nucleus (as it should), unlike Gaussian-type orbitals, which are smooth.

From a practical standpoint, overlap integrals between two STOs as a function of interatomic distance can be easily computed. The elements of the overlap matrix in extended Hückel theory (EHT) are not assumed to be 0 or 1, but are actually calculated.

6.2 Resonance Integrals H

The diagonal term $H_{\mu\mu}$ is taken as the negative of the average ionization potential of an electron in the corresponding valence orbital.

Example: $H_{\mu\mu} = -13.6$ eV for a 1s orbital of hydrogen.

In multi-electron atoms, the valence shell ionization potential (VSIP) for the ground state may not be the best choice to describe the atom within a molecule. This term is therefore generally treated as an adjustable parameter.

VSIP values have been tabulated for most atoms in the periodic table.

In molecular environments, atoms can develop significant partial charges. Methods for adjusting the neutral atomic VSIP based on the partial atomic charge have been proposed, for example, the Fenske-Hall effective Hamiltonian calculations, which are still used for inorganic and organometallic systems where atoms exhibit very different electronegativities.

Off-diagonal resonance integrals:

$$H_{\mu\nu} = \frac{1}{2} C_{\mu\nu} (H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu}$$

C: is an empirical constant,

S: is the overlap integral.

The energy associated with the matrix element is therefore proportional to the average of the VSIP values (Valence Shell Ionization Potentials) of the two orbitals μ and ν , multiplied by the spatial overlap between the two orbitals. By symmetry, the overlap between two STOs located on the same atom is zero.

Using standard linear algebra methods, the molecular orbital (MO) energies and wavefunctions can be obtained by solving the secular equation.

The matrix elements do not depend on the molecular orbitals (unlike in Hartree-Fock theory), so the calculation is non-iterative and computationally very fast, even for large molecules.

The Extended Hückel Theory (EHT) is not accurate enough to reliably predict molecular geometries; therefore, its use is generally limited to systems with known experimental geometries. Nevertheless, EHT remains useful for qualitative prediction of molecular orbitals and is still applied to very large systems, including molecules, solids, band structures, and more.

6.3 Complete Neglect of Differential Overlap (CNDO)

In returning to the Self-Consistent Field (SCF) formalism of Hartree-Fock theory, one can adopt the philosophy of the effective Hamiltonian method (as discussed earlier) by developing a simplified procedure to replace the matrix elements in the Hartree-Fock secular equation.

The CNDO method — Complete Neglect of Differential Overlap — represents one of the earliest and most influential semi-empirical quantum chemical models. It was introduced by John Pople and collaborators in 1965, with the aim of significantly reducing the computational cost of ab initio methods while retaining essential physical accuracy.

The main approximations and assumptions in the CNDO model include:

1-Minimal basis set of Slater-Type Orbitals (STO):

Only valence atomic orbitals are included in the basis set, and each valence orbital is represented by a single STO.

In the original CNDO formulation (CNDO/2), only atoms with valence s and p orbitals (i.e., elements from the first and second periods of the periodic table) were supported. This simplification drastically reduces the number of basis functions and integrals to be evaluated.

2-Neglect of differential overlap:

All overlap integrals involving different atomic orbitals (i.e., $S_{\mu\nu}$ where $\mu \neq \nu$) are set to zero.

This approximation assumes that the product of two different atomic orbitals centered on the same or different atoms contributes negligibly to the total electron density.

$$S_{\mu\nu} = \int \varphi_{\mu}(\mathbf{r})\varphi_{\nu}(\mathbf{r})d\mathbf{r} \approx 0 \quad \text{for } \mu \neq \nu$$

As a result, differential overlap effects are completely ignored, leading to a dramatic simplification of.

3. Two-Electron Integrals Are Parametrized Using the Following Scheme:

$$\langle \mu\nu | \lambda\sigma \rangle = \delta_{\mu\nu} \delta_{\lambda\sigma} \langle \mu\mu | \lambda\lambda \rangle$$

The only non-zero two-electron integrals are those where $\mu=\nu$ and $\lambda=\sigma$, and both pairs of orbitals are on the same atom. The second atom (λ) may differ from the first one.

Any integrals involving overlap between different basis functions are completely neglected, this is the core approximation of the CNDO method.

4. For the Remaining Two-Electron Integrals:

$$\langle \mu\mu | \lambda\lambda \rangle = \gamma_{AB}$$

Where:

- A and B are the atoms on which the basis functions μ and λ reside, respectively.
- The parameter γ can be explicitly calculated from Slater-type orbitals (STOs), or simply treated as a fitted parameter.

Pariser-Parr Approximation:

$$\gamma_{AA} = IP_A - E_{AA}$$

Where:

IP is the ionization potential of the atom,

EA is the electron affinity of the atom.

For Two-Center Terms, the Mataga–Nishimoto Formula Is Used:

$$\gamma_{AB} = \frac{\gamma_{AA} + \gamma_{BB}}{2 + r_{AB}(\gamma_{AA} + \gamma_{BB})}$$

This equation interpolates between r_{AB} at large distances, and the average of the two one-center values at short distances.

5. One-Electron Integrals for Diagonal Matrix Elements:

$$\langle \mu | -\frac{1}{2}\Delta - \sum_k \frac{Z_k}{r_k} | \mu \rangle = -IP_\mu - \sum_k (Z_k - \delta_{Z_A Z_k}) \gamma_{Ak}$$

This expression includes:

The kinetic energy term, the electron–nucleus interaction, a correction term depending on the nuclear type Z_k and the empirical parameter γ .

Remember that the full Fock matrix element $F_{\mu\mu}$ is the sum of one-electron and two-electron contributions.

If the number of valence electrons on each atom equals the nuclear charge, then repulsive interactions between valence electrons and attractive nucleus–electron interactions cancel out, simplifying the final result:

$$F_{\mu\mu} = h_{\mu\mu} - \sum_{B \neq A} V_{AB} = -IP_\mu - \sum_k (Z_k - \delta_{Z_A Z_k}) \gamma_{Ak} + (P_{AA} - \frac{1}{2} P_{\mu\mu}) \gamma_{AA} + \sum_{B \neq A} P_{BB} \gamma_{AB}$$

Where:

$P_{\lambda\sigma} = 2 \sum_{i \in \text{occ}} c_{\lambda i} c_{\sigma i}$ is the density matrix element constructed from the occupied MOs.

6. One-Electron Integrals for the Off-Diagonal Elements of the Matrix:

$$\left\langle \mu \left| -\frac{1}{2} \nabla^2 - \sum_k \frac{Z_k}{r_k} \right| \nu \right\rangle = \frac{2}{\beta_A + \beta_B} S_{\mu\nu} = \beta_{AB} S_{\mu\nu}$$

Where:

- μ are basis functions centered on atoms A and B, respectively.
- β : semi-empirical parameters
- $S_{\mu\nu}$: overlap matrix element, calculated using the STO basis set.

The parameters β provide a measure of the interaction strength across space between atoms. They were originally adjusted to reproduce specific experimental quantities (e.g., ionization energies, bond lengths).

CNDO Method Summary

The CNDO method represents a major simplification of Hartree-Fock theory.

- The number of two-electron integrals scales as N^2 , but they are computed using simple algebraic expressions.
- The direct evaluation of one-electron integrals is also completely avoided, thanks to the approximations described earlier.

By discarding differential overlaps and limiting the basis set, CNDO significantly simplifies the Fock matrix construction, avoiding expensive four-index electron repulsion integrals that dominate Hartree-Fock methods. This makes it possible to perform fast quantum chemical calculations on molecules with dozens or even hundreds of atoms, a significant achievement in the 1960s.

However, this simplicity comes at the cost of accuracy. The method is not suitable for quantitative predictions of energies or molecular geometries, but is useful for qualitative electronic structure analysis, chemical intuition, and as a pedagogical tool.

The CNDO approach laid the foundation for further developments such as INDO (Intermediate Neglect of Differential Overlap) and MNDO, which introduced refined approximations and better treatment of d orbitals and polarization.

6.4 Limitations of the CNDO Method

As with any simplification, the CNDO method comes at a chemical cost.

Although it offers computational efficiency and conceptual clarity, the CNDO approximation fails to accurately predict molecular structures. Because it neglects key elements of electronic correlation and directional orbital character, CNDO has limited ability to represent chemically important features.

For example:

- The CNDO method cannot distinguish between different types of atomic orbitals, such as singlet vs. triplet states in molecules like methylene (CH_2). These electronic configurations

differ significantly in energy and spatial electron distribution, but CNDO treats them identically due to its neglect of orbital-specific interactions.

- Similarly, CNDO cannot distinguish between different orientations of orbitals. Directional effects, such as the alignment of lone pairs or the spatial overlap of p orbitals, are not properly modeled.

Another illustrative case is the internal rotation about the N–N bond in hydrazine (N₂H₄):

- In reality, the repulsion between the non-bonding lone pairs on the two nitrogen atoms significantly affects the molecule's energy profile as the N–N bond rotates.
- However, in the CNDO approximation, this repulsion is represented by the two-center electron repulsion parameter γ_{NN} , which is a scalar value depending only on the N–N distance, not on the relative spatial orientation of the lone pairs.

In short, CNDO ignores angular dependency in electron–electron repulsion, which limits its ability to model conformational effects, spin states, and anisotropic electron density distributions — features that are often critical in molecular chemistry.

6.5. CNDO Exercise: H₂ Molecule

We consider the hydrogen molecule H₂ with an interatomic distance of $R=0.74 \text{ \AA}$.

Using the CNDO method, you are asked to:

1. Calculate the one-center electron repulsion parameter γ_{AA} using the ionization potential (IP) and electron affinity (EA) of hydrogen.
2. Deduce the two-center electron repulsion integral γ_{AB} using the Mataga–Nishimoto formula.
3. Compute the elements of the Fock matrix $F_{\mu\nu}$ for the minimal basis set {1sH, 1sH}.
4. Diagonalize the Fock matrix to find the molecular orbital energies.
5. Calculate the electronic energy and the total energy of the H₂ molecule.

Data

Quantity	value
IP _H	13.6 eV (exp.)
EA _H	0.8 eV (approx.)
S ₁₂	0.35
R _{HH}	0.74 Å
β	-9 eV

CNDO/2 Exercise Solution – H₂ Molecule

1-Calculation of γ_{AA} (Pariser–Parr)

$$\gamma_{HH} = IPA - EAA = 13.6 - 0.8 = 12.8 \text{ eV}$$

2-Calculation of γ_{AB} (Mataga–Nishimoto)

$$\gamma_{AB} = \frac{\gamma_{AA} + \gamma_{BB}}{2 + R_{AB}(\gamma_{AA} + \gamma_{BB})}$$

For H₂:

$$\gamma_{AB} = \frac{2 + 0.74(12.8 + 12.8)}{12.8 + 12.8} = \frac{2 + 18.944}{25.6} = \frac{20.944}{25.6} \approx 1.22 \text{ eV}$$

3-Molecular orbital and density matrix

Bonding MO:

$$\Psi = \frac{1}{\sqrt{2}} \chi_1 + \frac{1}{\sqrt{2}} \chi_2$$

Density matrix element:

$$P_{\mu\nu} = 2 \sum_{i \in \text{occ}} c_{\mu i} c_{\nu i}$$

$$P_{11} = P_{22} = 2 \left(\frac{1}{\sqrt{2}} \right)^2 = 1, \quad P_{12} = 2 \times \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2}} = 1$$

4-One-electron matrix element $H_{\mu\mu}$

$$H_{\mu\mu} = h_{\mu\mu} + V_{AB}$$

$$\text{Où } h_{\mu\mu} = -IP_{\mu} - \sum_{k \neq A} (Z_k - \delta_{Z_A, Z_k}) \gamma_{Ak}$$

$$\text{For H}_2: (Z_2 - \delta_{Z_2, Z_2}) \gamma_{12} = (1 - 0) \cdot 1.22 = 1.22 \text{ eV}$$

$$H_{\mu\mu} = -13.6 - (1 - 0) \times 1.22 = -14.82 \text{ eV}$$

5-Fock matrix elements

Given

$$P_{AA} = 1, \quad P_{\mu\mu} = 1, \quad P_{BB} = 2$$

$$F_{11} = H_{11} + \left(P_{AA} - \frac{1}{2} P_{\mu\mu} \right) \gamma_{AA} + P_{BB} \gamma_{AB} = -14.82 + (1 - 0.5) \times 12.8 + 1 \times 1.22 = -14.82 + 6.4 + 2.44 = -7.2 \text{ eV}$$

Off-diagonal term F_{12} :

$$F_{12} = \beta \cdot S_{12} + \frac{1}{2} P_{12} \cdot \gamma_{AB}$$

$$F_{12} = -8 \cdot 0.35 + 0.5 \cdot 1.22 = -2.8 - 0.61 = -3.41 \text{ eV}$$

6- Fock matrix

$$\mathbf{F} = \begin{pmatrix} -7.2 & -3.41 \\ -3.41 & -7.2 \end{pmatrix}$$

7-Diagonalization, molecular orbital energies

Solve:

$$\det(\mathbf{F} - \varepsilon \mathbf{I}) = 0 \Rightarrow \varepsilon_{1,2} = -7.2 \pm 3.41$$

$$\varepsilon_1 = -7.2 - 3.41 = -10.61 \text{ eV} \quad (\text{bonding})$$

$$\varepsilon_2 = -7.2 + 3.41 = -3.79 \text{ eV} \quad (\text{antibonding})$$

8-Electronic energy:

$$E_e = 2 \cdot \varepsilon_1 = 2 \cdot (-10.61) = -21.22 \text{ eV}$$

9-Nuclear repulsion

$$R_{12} = 0.74 \text{ \AA} = \frac{0.74}{0.529} \approx 1.351 \text{ bohr}^{-1} E_{\text{nuc}} = \frac{1}{R_{12}} = 1.351 \text{ a.u.}$$

$$E_{\text{nuc}} \text{ (eV)} = 1.351 \times 27.21 \approx 36.79 \text{ eV}$$

10-Total energy

$$E_T = E_e + E_{\text{nuc}} = -21.22 + 36.79 = 15.57 \text{ eV}$$

Chapter 3: Qualitative Approach in the Study of the Electronic Structure of Simple Polyatomic Molecules

1. Fragment Orbital Method: A Detailed Explanation

In quantum chemistry, the fragment orbital method provides a powerful framework for understanding the electronic structure of molecules more complex than diatomic hydrogen. When we deal with polyatomic molecules, direct construction of molecular orbitals (MOs) from atomic orbitals becomes cumbersome due to the increasing number of interactions. The fragment approach simplifies this process by conceptually decomposing a molecule into smaller, simpler fragments whose molecular or atomic orbitals are known or easier to analyze. This allows chemists to rebuild the electronic structure of the whole molecule by combining orbitals from different fragments that have compatible symmetry properties and significant spatial overlap.

The process begins with the division of a molecule into two fragments, typically chosen based on chemical intuition or symmetry considerations. For example, in a molecule like AH_2 , one could consider the fragments A and H_2 . The H_2 unit, being diatomic, has well-known bonding (σ_{H_2}) and antibonding ($\sigma^*_{H_2}$) molecular orbitals. The atom A contributes its valence atomic orbitals, such as s and p orbitals, which can then interact with those of H_2 . Only orbitals with matching symmetry and non-zero spatial overlap are allowed to interact. As a result, some combinations produce bonding orbitals, others lead to antibonding orbitals, and some orbitals remain nonbonding due to symmetry incompatibility or lack of spatial overlap.

Taking a linear AH_2 molecule as a concrete example, the H_2 fragment offers σ_{H_2} (bonding) and $\sigma^*_{H_2}$ (antibonding) orbitals. The atom A provides valence orbitals such as s , p_x , p_y , and p_z . Among these, only the s and p_z orbitals can effectively interact with the σ_{H_2} and $\sigma^*_{H_2}$ orbitals respectively. This is because the interactions must respect symmetry with respect to the molecular axis and nodal planes. The p_x and p_y orbitals, due to their antisymmetric behavior in certain planes, are unable to overlap constructively with the orbitals from the H_2 fragment. Consequently, they remain nonbonding.

In non-linear or bent molecules, such as water (H_2O), the interaction scheme becomes more complex. Here, a single orbital on the central atom may interact with two different orbitals on a fragment composed of the hydrogen atoms. This results in three-orbital interactions, producing three molecular

orbitals: one bonding, one antibonding, and one of intermediate character. The relative energy of these new orbitals depends on the bonding or antibonding nature of the interactions and the original energy levels of the fragment orbitals.

The method is especially insightful when applied to molecules such as LiH and HF. In lithium hydride (LiH), lithium is electropositive, and its valence orbitals (2s and 2p) are high in energy. The 1σ molecular orbital, formed primarily from hydrogen's 1s orbital, becomes a strongly bonding orbital. The second σ orbital, 2σ , arises from interaction between Li's 2s and 2p_z orbitals with H's 1s orbital, but the interaction is mixed: 2p_z contributes constructively, while 2s contributes destructively. Higher in energy, the 3σ orbital is antibonding and is mostly localized on lithium. Additionally, the p_x and p_y orbitals of lithium form nonbonding π -type orbitals. The net result is a polar bond, as the bonding orbital (1σ) is mostly localized near hydrogen, indicating an electron-rich H and electron-deficient Li. In contrast, hydrogen fluoride (HF) presents a very different picture due to fluorine's high electronegativity. The 2s orbital of fluorine is very low in energy, and due to a large energy mismatch with hydrogen's 1s orbital, it does not interact significantly, thus forming a nonbonding 1σ orbital. The bonding interaction mainly comes from fluorine's 2p_z and hydrogen's 1s orbital, resulting in the 2σ bonding orbital. The π orbitals (2p_x and 2p_y) on fluorine remain nonbonding. The 3σ orbital is antibonding, with electron density favoring the hydrogen end. The overall bond is again polar, with electron density primarily located on fluorine.

The case of the water molecule (H₂O) is a rich example of fragment orbital analysis in bent molecules. Water is often treated as the combination of an oxygen atom and a hydrogen pair. The H₂ unit offers bonding (σ_{H_2}) and antibonding ($\sigma_{H_2}^*$) orbitals. Oxygen contributes its valence orbitals: 2s and 2p (including p_x, p_y, and p_z). Symmetry analysis shows that only certain orbitals from oxygen can interact with σ_{H_2} and $\sigma_{H_2}^*$. Specifically, 2s and 2p_z can interact with σ_{H_2} , forming bonding ($1a_1$) and antibonding ($3a_1$) combinations. The 2p_y orbital interacts with $\sigma_{H_2}^*$ to give bonding ($1b_2$) and antibonding ($2b_2$) MOs. The 2p_x orbital does not interact due to incompatible symmetry and remains a nonbonding orbital ($1b_1$).

Water's molecular orbital configuration can thus be summarized as $(1a_1)^2 (1b_2)^2 (2a_1)^2 (1b_1)^2$. The two bonding orbitals ($1a_1$ and $1b_2$) represent the O–H bonding interactions. The lone pairs reside in the nonbonding orbitals $2a_1$ and $1b_1$, which are not energetically equivalent, this asymmetry is confirmed by photoelectron spectroscopy, which shows a 2.1 eV difference in their ionization energies. This highlights a key strength of MO theory: it reveals subtleties (like nonequivalent lone pairs) that are not captured by Lewis structures.

In summary, the fragment orbital method is a versatile and intuitive approach to understanding the electronic structure of molecules, especially when quantitative calculations are unavailable. By leveraging symmetry considerations and known orbital energies, chemists can qualitatively predict bonding patterns, nonbonding behavior, and electron density distributions. This method serves as a

foundational tool in both teaching and conceptual analysis of chemical bonding, particularly for systems where full molecular orbital calculations would be complex or computationally intensive.

1.2. Example: Linear AH₂ molecules

- **Fragment H₂** provides:
 - σ_{H_2} (bonding)
 - $\sigma^*_{H_2}$ (antibonding)
- **Fragment A** provides:
 - Valence orbitals: s, p_x, p_y, p_z
- **Interactions:**
 - Only s and p_z of A can interact with σ_{H_2} or $\sigma^*_{H_2}$ due to symmetry.
 - p_x and p_y are non-bonding (zero overlap).
- **Resulting MOs:**
 - From interaction of s with σ_{H_2} → bonding orbital
 - From interaction of p_z with $\sigma^*_{H_2}$ → bonding orbital
 - The rest are either antibonding or nonbonding

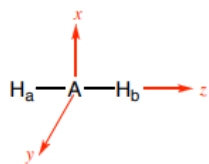
1.3. Case of Three-Orbital Interaction

In bent molecules (e.g., H₂O or AH₂ with a non-linear geometry), an orbital from one fragment (say χ_1) can interact with two orbitals from another fragment (χ_2 and χ_3).

- This leads to 3 MOs:
 - ϕ_1 : all interactions bonding → lowest energy
 - ϕ_2 : one bonding, one antibonding → intermediate
 - ϕ_3 : all antibonding → highest energy
- The relative energy levels and signs of coefficients in MOs depend on the nature of bonding and orbital energies.

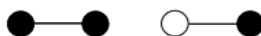
H₂O (Water)

- Bent geometry → 3 fragment interactions
- Orbitals involved:
 - σ_{H_2} (bonding)
 - $\sigma^*_{H_2}$ (antibonding)
 - O 2s, 2p_x, 2p_y, 2p_z
- OM labeling: 1a₁, 2a₁, 1b₁, 1b₂, etc.
 - 1a₁ and 1b₂ → bonding O-H
 - 2a₁ and 1b₁ → lone pairs (not energetically equivalent)



The molecule is divided into two fragments

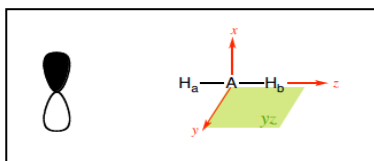
The H_a-H_b fragment, which carries the σ_{H_2} (bonding) and $\sigma^*_{H_2}$ (antibonding) orbitals



The central atom A, for which only the valence atomic orbitals s, p_x , p_y , and p_z are considered

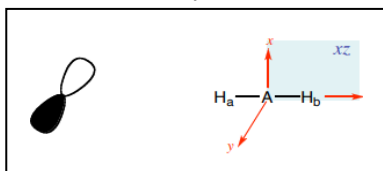
Case of p orbitals:

• p_x orbital:



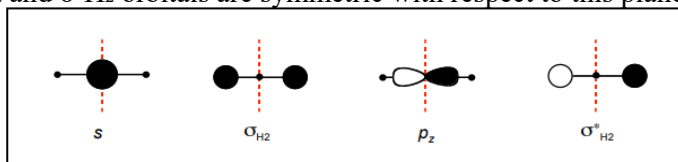
- Antisymmetric orbital with respect to the nodal yz plane
- The σ_{H_2} and $\sigma^*_{H_2}$ orbitals are symmetric with respect to this plane → **Zero overlaps**

orbitale p_y :



- Antisymmetric orbital with respect to the nodal xz plane
- The σ_{H_2} and $\sigma^*_{H_2}$ orbitals are symmetric with respect to this plane → **Zero overlaps**

orbitale p_z :



- s and σ_{H_2} are symmetric with respect to the xy plane
- p_z and $\sigma^*_{H_2}$ are antisymmetric with respect to the xy plane → **no interaction between s and $\sigma^*_{H_2}$, nor between p_z and σ_{H_2}**

- Overlap between s and σ_{H_2}
- Overlap between p_z and $\sigma^*_{H_2}$

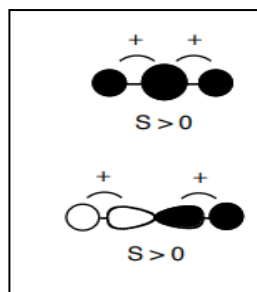


Figure 1. Fragmentation of the H_2-A-H_2 molecule and symmetry of atomic orbitals with respect to nodal planes.

2. Symmetry Properties of Molecular Orbitals

The symmetry properties of molecular orbitals are fundamental to understanding the electronic structure and behavior of molecules. In quantum chemistry, symmetry is more than a spatial concept; it is a formal mathematical property that determines how molecular orbitals transform under operations such as rotation, reflection, inversion, and identity; the core elements of point group theory.

Every molecule belongs to a specific point group that defines its symmetry elements. Atomic orbitals (AOs) and molecular orbitals (MOs) are said to "belong" to a given irreducible representation (IRREP) of that point group. This allows chemists to use group theory as a rigorous tool to classify orbitals, predict interactions, and determine selection rules.

When constructing molecular orbitals via the Linear Combination of Atomic Orbitals (LCAO) method, a key requirement is symmetry compatibility. Two atomic orbitals can only combine to form bonding or antibonding molecular orbitals if they transform according to the same irreducible representation within the molecule's point group. This ensures that the resulting molecular orbital respects the overall symmetry of the system. For instance, in a linear molecule such as H_2 or CO , an s orbital on one atom and a p_z orbital on another (assuming the bond lies along the z -axis) can combine because they both transform symmetrically under rotation and reflection in that axis. However, an s orbital and a p_x orbital cannot combine, as they belong to different symmetry species.

This principle extends to degeneracy in molecular orbitals. Orbitals that transform together as a set under the symmetry operations of the point group form degenerate representations. For example, in benzene (point group D_{6h}), the degenerate e_{1g} or e_{2u} π orbitals arise because the constituent p orbitals are symmetrically equivalent around the ring. Degeneracy is not just a mathematical convenience, it directly influences electronic transitions, magnetism, and reactivity.

From a quantum mechanical standpoint, symmetry considerations also dictate the ordering of molecular orbital energies. Symmetry-allowed combinations typically result in stronger orbital overlap and hence more stabilizing (lower-energy) bonding orbitals. Orbitals that are symmetry-forbidden or orthogonal due to differing IRREPs result in weaker interaction, preserving their original atomic character and energy.

Symmetry is particularly powerful in the analysis of electronic transitions, as it provides selection rules that govern which transitions are quantum mechanically allowed. According to quantum chemistry, a transition between an initial orbital ψ_i and a final orbital ψ_f is allowed if the product $\Gamma(\psi_i) \otimes \Gamma(\mu) \otimes \Gamma(\psi_f)$ contains the totally symmetric representation, where $\Gamma(\mu)$ corresponds to the symmetry of the dipole operator (x , y , or z). Transitions that do not satisfy this condition are symmetry-forbidden, even if they are energetically allowed. This explains, for example, why certain $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions may be weak or absent in UV-Vis spectra.

Moreover, symmetry is the organizing principle behind Molecular Orbital Correlation Diagrams, which track how molecular orbitals evolve as molecular geometry changes during chemical reactions. These diagrams are essential for understanding pericyclic reactions (e.g., electrocyclizations, sigmatropic shifts), and their behavior is governed by the conservation of orbital symmetry, as codified in the Woodward–Hoffmann rules. These rules assert that reactions proceed only if the symmetry of the occupied molecular orbitals is preserved along the reaction coordinate.

In summary, symmetry in quantum chemistry is a precise, predictive framework that governs:

- Which atomic orbitals can combine
- How molecular orbitals are classified and ordered
- Which transitions are allowed in spectroscopy
- How molecules behave during electronic excitation and chemical transformation

A deep understanding of symmetry, group theory, and orbital representations is thus indispensable for interpreting molecular structure, reactivity, and spectroscopic behavior in modern quantum chemistry

Common Point Groups and Irreducible Representations

Table 1. Common molecular point groups, symmetry elements, examples, and irreducible representations

Point Group	Symmetry Elements	Example Molecules	Irreducible Representations
C_{2v}	$E, C_2, \sigma_v(xz), \sigma_v'(yz)$	H_2O , formaldehyde	A_1, A_2, B_1, B_2
C_{3v}	$E, 2C_3, 3\sigma_v$	NH_3, BF_3 (non-planar)	A_1, A_2, E
$D_{\infty h}$	$E, \infty C_n, \infty \sigma_v, i, S_{\infty}, \infty C_2$	H_2, N_2, O_2	$\Sigma_g^+, \Sigma_g^-, \Sigma_u^+, \Sigma_u^-, \Pi_g, \Pi_u, \dots$

Example: Molecular Orbital Diagram of CO

Carbon monoxide (CO) is a heteronuclear diatomic molecule with ten valence electrons (4 from C and 6 from O). Its molecular orbital diagram is constructed by combining the 2s and 2p orbitals of carbon and oxygen according to their symmetry labels in the $C_{\infty v}$ point group. The orbitals are labeled as σ , σ^* , π , and π^* based on their symmetry and nodal structure.

- The 2s orbitals combine to form a σ (bonding) and a σ^* (antibonding) orbital.
- The 2p_z orbitals combine to form another σ and σ^* pair (along the internuclear axis).
- The 2p_x and 2p_y orbitals form two degenerate π and π^* orbitals.

Due to the difference in electronegativity, the oxygen atomic orbitals are lower in energy than those of carbon. This shifts the bonding MOs closer to oxygen in character and the antibonding MOs closer to carbon.

The HOMO in CO is a nonbonding orbital largely localized on carbon, which explains its role as a nucleophile in coordination chemistry. The LUMO is the π^* antibonding orbital, which is important for π back-donation in metal complexes.

This symmetry-based MO diagram not only predicts bond order and magnetic behavior but also explains CO's spectroscopic features and its strong affinity for metal centers in organometallic complexes.

3. Molecular Orbitals of AB_n Molecules

The construction of molecular orbitals in molecules of the general form AB_n , where a central atom A is bonded to n peripheral atoms B, follows principles similar to those in the fragment orbital method, but with an emphasis on symmetry-adapted linear combinations (SALCs) of the peripheral atoms' orbitals. This approach is particularly useful for triatomic (AB_2) and polyatomic (AB_3 , AB_4 , etc.) molecules, including those with high symmetry such as linear, trigonal planar, tetrahedral, and octahedral geometries.

In these systems, the first step is to identify the symmetry of the molecule (its point group). Then, one constructs SALCs of the B atom orbitals, typically using s or p orbitals depending on the element. These SALCs are then matched to the atomic orbitals of atom A based on symmetry compatibility, only SALCs that transform under the same irreducible representation as an AO of A can interact to form molecular orbitals.

For example, in a linear AB_2 molecule like CO_2 ($D_{\infty h}$ symmetry), the two O atoms each contribute an s orbital. These combine to form two SALCs: a symmetric (in-phase) combination and an antisymmetric (out-of-phase) combination. The symmetric SALC can interact with the 2s or $2p_z$ orbital of carbon (aligned along the molecular axis) to form bonding and antibonding MOs. The antisymmetric SALC may interact with a p orbital of carbon (if symmetry permits) or remain nonbonding.

In molecules like NH_3 (trigonal pyramidal) or CH_4 (tetrahedral), group theory is used to build SALCs from the hydrogen 1s orbitals. For CH_4 , the four hydrogen atoms form SALCs that transform according to A_1 and T_2 irreducible representations of the T_d point group. The A_1 SALC (totally symmetric) interacts with the 2s orbital of carbon, and the T_2 SALCs interact with the 2p orbitals to form bonding MOs. Antibonding combinations also arise and occupy higher energy levels.

Importantly, the AB_n approach provides a structured way to build the MO diagram, accounting for degeneracies, orbital energies, and bonding character. It also predicts the number of bonding, nonbonding, and antibonding orbitals, giving insight into molecular stability and reactivity.

4. Molecular Orbitals in Simple Organic Molecules

In simple organic molecules, molecular orbitals are typically constructed using the linear combination of atomic orbitals (LCAO) method, applied to π -systems and σ -frameworks separately. The MOs in these molecules explain bonding, lone pairs, conjugation, and aromaticity.

For σ -frameworks (such as in methane, ethane, or alcohols), bonding MOs are formed from the overlap of sp^3 hybrid orbitals on carbon with s orbitals on hydrogen or other atoms. These orbitals are typically localized and form single (σ) bonds. The electrons in these orbitals are strongly localized between atoms and define the molecular skeleton.

The more chemically interesting MOs often come from π -systems, which arise from the side-by-side overlap of unhybridized p orbitals. A classic example is ethylene (C_2H_4). Each carbon is sp^2 hybridized, forming a planar molecule. The remaining p orbitals on each carbon overlap to form a π bonding orbital (lower in energy) and a π^* antibonding orbital (higher in energy). The bonding π orbital is filled with two electrons and provides a delocalized π bond above and below the plane of the molecule.

In conjugated systems like 1,3-butadiene, four p orbitals combine to form four π MOs: two bonding (π_1, π_2) and two antibonding (π_3^*, π_4^*). The molecular orbital diagram shows increasing energy from bonding to antibonding levels. The delocalization of π electrons over multiple carbon atoms leads to conjugation, which stabilizes the molecule and lowers its total energy compared to isolated π bonds.

In aromatic molecules such as benzene (C_6H_6), the six p orbitals from each carbon atom combine to form six π MOs. Three are bonding (π_1, π_2, π_3), and three are antibonding ($\pi_4^*, \pi_5^*, \pi_6^*$). The three bonding π MOs are filled with six electrons, satisfying Hückel's $4n + 2$ rule ($n = 1$), and creating a highly stable aromatic system with delocalized electrons uniformly spread over the ring.

Molecular orbital theory in organic systems thus provides an explanation for:

- Bonding patterns and molecular shapes (σ MOs)
- Conjugation and stabilization (π MOs)
- Reactivity patterns, such as electrophilic attack at high-electron-density π orbitals
- UV-visible spectra ($\pi \rightarrow \pi^*$ transitions)

Overall, understanding the molecular orbitals of simple organic molecules gives deep insight into structure, stability, and chemical behavior beyond what is available from Lewis or valence bond models.

Chapter 4: Electronic Spectrum of Polyatomic Molecules

1. Introduction

The study of electronic spectra of polyatomic molecules lies at the heart of molecular spectroscopy and quantum chemistry. These spectra result from electronic transitions between different quantum states of a molecule and provide essential insights into its electronic structure, energy levels, and optical properties. Unlike atomic spectra, where electrons move in a central potential, molecular spectra are significantly more complex due to the interplay between nuclei and the collective behavior of electrons in delocalized molecular orbitals.

Historically, electronic spectroscopy developed in the early 20th century, following the foundational work on atomic line spectra by scientists like Balmer, Rydberg, and Ritz. However, it wasn't until the advent of quantum mechanics and the development of molecular orbital theory in the 1930s to 1950s that the understanding of molecular electronic spectra significantly advanced. Early theoretical models such as the Hückel method, followed by Hartree-Fock theory and later density functional theory (DFT), enabled the calculation of excited-state energies and helped predict the positions and intensities of absorption bands observed experimentally.

In polyatomic molecules, electronic transitions typically involve the excitation of an electron from an occupied molecular orbital—often a non-bonding (n) or bonding π orbital—into a higher-energy antibonding orbital such as π^* , σ^* , or a Rydberg orbital. These transitions usually absorb radiation in the ultraviolet (UV) or visible (Vis) region of the electromagnetic spectrum. Due to coupling with vibrational and rotational degrees of freedom, the observed bands are often broad and structured, forming low-resolution spectra with smooth envelopes instead of sharp lines.

Electronic spectra are powerful tools for characterizing molecular orbital nature, determining the lowest allowed electronic transition energy (often interpreted as the HOMO–LUMO gap), and understanding conjugation, aromaticity, and photo-reactivity in organic and inorganic systems. Quantum mechanical selection rules based on spin, symmetry, and parity determine whether a particular transition is allowed or forbidden, and thus directly influence the spectral intensities.

With the advancement of both experimental techniques and theoretical models, electronic spectroscopy of polyatomic molecules has become a fundamental tool in a wide range of disciplines, including photochemistry, materials science, molecular biology, and atmospheric chemistry. Today, the prediction and interpretation of electronic spectra are routinely performed using computational methods such as Configuration Interaction Singles (CIS), Time-Dependent DFT (TD-DFT), or Multi-Reference approaches (CASSCF, EOM-CC), allowing chemists to bridge the gap between observed spectral features and underlying molecular electronic structure.

2. General Types of Electronic Transitions

An electronic transition occurs when a molecule absorbs a photon, causing one of its electrons to jump from an occupied molecular orbital (usually in the ground state) to an unoccupied one (in the excited state). This fundamental process underlies UV-Visible spectroscopy, where the energy of the absorbed photon corresponds exactly to the energy difference between the two orbitals:

$$\Delta E = E_{excited} - E_{ground} = h\nu = hc/\lambda$$

Electronic transitions are classified based on the nature of the starting and destination orbitals. These transitions vary in intensity and energy, and they provide valuable information about the structure and environment of the molecule.

The $\sigma \rightarrow \sigma^*$ transition involves an electron moving from a bonding σ orbital, such as those found in C–H or C–C single bonds, to an antibonding σ^* orbital. These transitions require high energy, typically below 150–200 nm, and are found in the far ultraviolet region. A common example is methane (CH₄), where the C–H bond undergoes such a transition around 125 nm.

In the $n \rightarrow \sigma^*$ transition, the electron originates from a non-bonding lone pair (designated as n) and is promoted to a σ^* antibonding orbital. These transitions require moderate energy, less than $\sigma \rightarrow \sigma^*$, and occur between 150–250 nm. They are observed in molecules such as water (H₂O), ammonia (NH₃), and ethers (R–O–R). For example, in water, the lone pair on oxygen can transition to σ^* at approximately 167 nm.

The $\pi \rightarrow \pi^*$ transition is one of the most intense and common transitions in conjugated and aromatic compounds. It involves an electron jumping from a bonding π orbital to an antibonding π^* orbital. These transitions generally occur in the UV region (180–300 nm), but in highly conjugated systems, they can extend into the visible region. Ethylene (C₂H₄) shows a $\pi \rightarrow \pi^*$ transition near 165 nm, butadiene around 217 nm, and benzene has a strong transition at about 180 nm.

Another important type is the $n \rightarrow \pi^*$ transition, where an electron from a non-bonding orbital (usually on oxygen or nitrogen) moves to a π^* orbital. These transitions are generally weak because they are symmetry-forbidden, although they can still be observed thanks to vibronic coupling. They typically appear between 250–350 nm and are characteristic of compounds such as carbonyls, nitriles, and amines. For instance, formaldehyde ($\text{H}_2\text{C}=\text{O}$) exhibits an $n \rightarrow \pi^*$ transition at around 280 nm.

Charge transfer (CT) transitions involve the movement of an electron from one part of the molecule to another — either from the ligand to the metal (LMCT) or from the metal to the ligand (MLCT). These transitions are extremely intense (very high molar absorptivity ϵ) and often occur in the visible region. LMCT is commonly observed with O^- or N^- donor ligands, while MLCT transitions typically involve electron transfer from a metal center to a π^* orbital of the ligand.

Finally, the extent of conjugation in a molecule greatly affects the energy of $\pi \rightarrow \pi^*$ transitions. As the length of the conjugated system increases, the HOMO–LUMO gap decreases, shifting the absorption toward longer wavelengths — a phenomenon known as the bathochromic effect. For example, butadiene (4 carbon atoms) absorbs around 217 nm, hexatriene (6 carbons) at about 258 nm, and β -carotene (11 conjugated double bonds) absorbs near 450 nm, giving it its characteristic orange color.

3. Electronic Molecular Transitions: The Case of Methanal

To illustrate how electronic states are labeled, we use the molecular orbital diagram of methanal (formaldehyde), which belongs to the C_{2v} point group (i.e., it has specific symmetry elements like a twofold rotation axis and two mirror planes).

Using the fragment molecular orbital approach, we model methanal as formed by combining a CH_2 carbene fragment with an oxygen ‘O’ atom. The oxygen contributes hybrid orbitals formed from s and pz atomic orbitals, which both belong to the a_1 symmetry species in the C_{2v} group. Its other p orbitals, px and py, correspond to the b_2 and b_1 symmetries, respectively.

The CH_2 group contributes both σ and σ^* orbitals, these are considered to be only slightly perturbed in the molecular structure as well as non-bonding orbitals.

1-The a_1 -type hybrid orbital on oxygen overlaps significantly with the corresponding orbital on carbon to form the σ bond of the carbon–oxygen ($\text{C}=\text{O}$) group.

2-The p_x orbital of oxygen, which also has b_1 symmetry, combines with the matching orbital on CH_2 to form the π bond of the carbonyl group.

3-The hybrid orbital composed of s + p_z on oxygen points away from CH₂ and does not participate significantly in bonding. It is referred to as a non-bonding orbital (n_{sp}) and lies energetically below the π orbital.

3-Lastly, the p_y orbital of oxygen creates another quasi non-bonding orbital (n_y). This one is found in energy between the π and π* molecular orbitals.

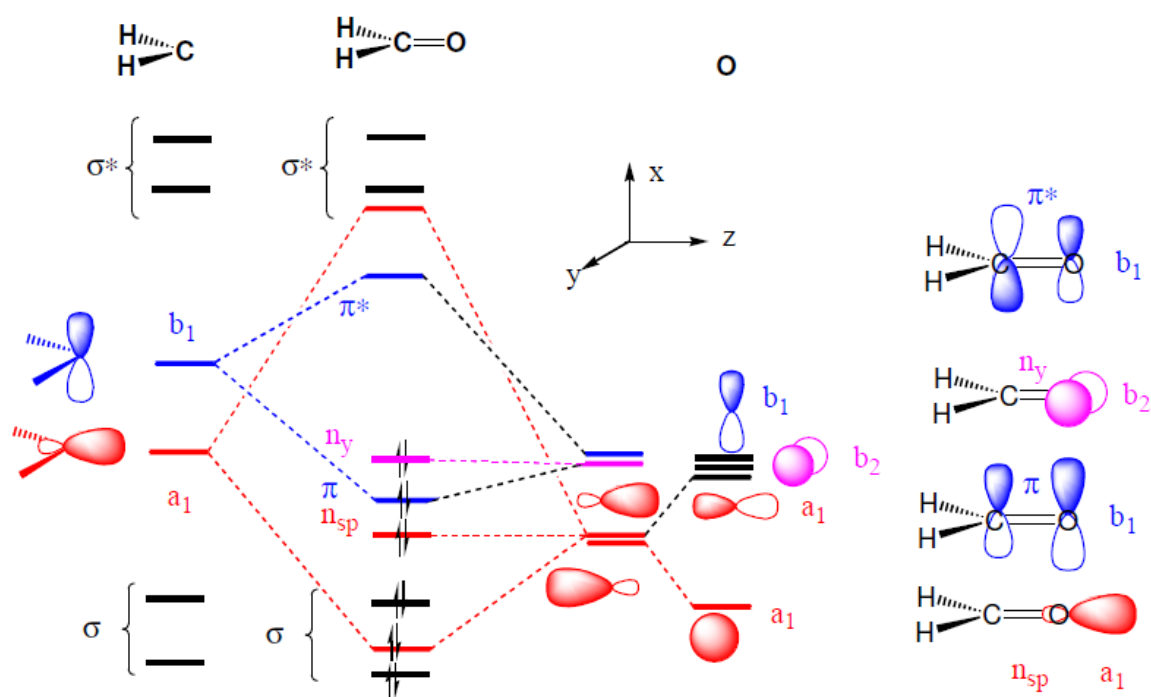


Figure 1. Orbital diagram of formaldehyde

Table 1. Main Types of Electronic Transitions in UV–Visible Spectroscopy

Transition	Type d'orbitale → cible	Domaine λ (approx.)	Intensité
$\sigma \rightarrow \sigma^*$	liaison forte	< 150 nm (UV)	Forte
$n \rightarrow \sigma^*$	doublets non liants	150–250 nm	Moyenne
$\pi \rightarrow \pi^*$	conjugaison	180–300 nm	Très forte
$n \rightarrow \pi^*$	doublets sur O, N	250–350 nm	Faible
d–d	métaux de transition	400–800 nm	Très faible
CT (LMCT, MLCT)	métal → ligand	300–600 nm	Très forte

4. Quantum Selection Rules for Electronic Transitions

In quantum chemistry, an electronic transition between two molecular states is only allowed if the transition dipole moment integral between the initial and final states is non-zero:

$$\mu_{if} = \langle \psi_f | \hat{\mu} | \psi_i \rangle \neq 0$$

Where:

- ψ_i is the wavefunction of the initial (ground) state
- ψ_f is the wavefunction of the final (excited) state
- $\hat{\mu}$ is the electric dipole moment operator

This integral must be non-zero for the transition to be allowed (i.e., observed in absorption/emission spectra).

4.1. Spin Selection Rule

Under the Born-Oppenheimer approximation and neglecting spin-orbit coupling, the total spin quantum number must be conserved:

$$\Delta S = 0$$

- Allowed transitions: between states of the same spin multiplicity (e.g., singlet \rightarrow singlet, triplet \rightarrow triplet)
- Forbidden transitions: between states of different spin (e.g., singlet \rightarrow triplet)

Note: In systems with heavy atoms or significant spin-orbit coupling, spin-forbidden transitions can become partially allowed.

4.2. Symmetry Selection Rule (Group Theory)

A transition is allowed by symmetry if the following condition is satisfied:

$$\Gamma(\psi_i) \otimes \Gamma(\hat{\mu}_x) \otimes \Gamma(\psi_f) \supset A_1$$

Where:

- $\Gamma(\cdot)$ represents the irreducible representation of a state or operator under the molecule's point group
- A_1 denotes the totally symmetric representation

If the product does not contain A_1 , the integral is zero \rightarrow symmetry-forbidden transition.

4.3. Oscillator Strength and Transition Intensity

The oscillator strength f_{if} measures the intensity of an electronic transition:

$$f_{if} = (2m_e / 3\hbar^2) \times (E_f - E_i) \times |\langle \psi_f | \mu | \psi_i \rangle|^2$$

Interpretation:

- $f_{if} = 0$: forbidden transition
- $f_{if} \approx 1$: strongly allowed (e.g., $\pi \rightarrow \pi^*$)
- $f_{if} \ll 0.01$: weakly allowed or forbidden (e.g., $n \rightarrow \pi^*$, d-d transitions)

Table 2. Summary Table of Selection Rules

Rule Type	Condition	Allowed Example	Forbidden Example
Spin Rule	$\Delta S = 0$	Singlet \rightarrow Singlet	Singlet \rightarrow Triplet
Symmetry Rule	Contains A_1 in product	$\pi \rightarrow \pi^*$ in ethylene	$\sigma \rightarrow \pi^*$ in planar ethylene
Laporte Rule	Change in parity	p \rightarrow s (u \rightarrow g)	d \rightarrow d (g \rightarrow g)

Advanced Notes

- Herzberg-Teller coupling: vibrational motion can relax symmetry rules.
- Magnetic dipole and quadrupole transitions: weaker but allow some forbidden transitions.
- Perturbation theory: used to estimate intensity of weakly allowed transitions due to mixing.

Absorption Spectrum of Methanal

The three lowest-energy transitions and their corresponding λ_{\max} for methanal are:

- $n \rightarrow \pi^*$ (${}^1A_1 \rightarrow {}^1A_2$) 270 nm
- $\pi \rightarrow \pi^*$ (${}^1A_1 \rightarrow {}^2A_1$) 185 nm
- $n \rightarrow \sigma^*$ 150 nm

Only the first two transitions are observable in the near-UV region. The selection rules are derived by analyzing the transition dipole moment:

$$M_f = \langle \Phi_i | \hat{\mu} | \Phi_f \rangle$$

The spatial part of the dipole moment is decomposed into three Cartesian projections:

$$P_x = \langle \Psi_i | \mu_x | \Psi_f \rangle$$

$$P_y = \langle \Psi_i | \mu_y | \Psi_f \rangle$$

$$P_z = \langle \Psi_i | \mu_z | \Psi_f \rangle$$

A transition is allowed if at least one of these projections is non-zero. This occurs if the integrand function (wavefunctions \times dipole operator) is totally symmetric, often with A_1 symmetry.

The symmetry of the total wavefunction product $\Psi_i^* \Psi_f$ is the same as that of the product of the molecular orbitals involved in the transition:

Initial MO: φ_i , Final MO: φ_f

For a closed-shell system in the ground state:

$$\Psi_i = (\dots)^2 \cdot \varphi_i^2$$

$$\Psi_f = (\dots)^2 \cdot \varphi_i^1 \varphi_f^1$$

Ψ_i is always symmetric. Ψ_f has the symmetry of the product $\varphi_i \varphi_f$. The same applies to an open-shell system (e.g., a radical):

$$\Psi_i = (\dots)^2 \cdot \varphi_i^1$$

$$\Psi_f = (\dots)^2 \cdot \varphi_f^1$$

The dipole moment components μ_x , μ_y , μ_z have the same symmetries as the spatial coordinates x, y, and z respectively.

5. Selection Rule for Electronic Transitions in Molecules

A molecular electronic transition is allowed by symmetry if the product of the molecular orbitals involved in the transition has the same symmetry as one of the Cartesian coordinates x, y, or z.

Applications:

(i) Transition $n\pi \rightarrow \pi^*$

$$- \varphi_i \cdot \varphi_f = b1 \otimes b2 = a2$$

- Dipole components μ_x , μ_y , μ_z have symmetries b1, b2, and a1 in the C2v point group

- No totally symmetric function is obtained, Transition is forbidden

(ii) Transition $\pi \rightarrow \pi^*$

$$- \varphi_i \cdot \varphi_f = b1 \otimes b2 = a1$$

- z-direction component P_z is non-zero (z has A1 symmetry), Transition is allowed

7. Low-Resolution Electronic Spectra of Conjugated Organic Molecules

Conjugated organic molecules, such as alkenes, aromatic compounds, and polyenes, exhibit characteristic electronic absorption spectra in the UV-visible region. These spectra arise from transitions between molecular orbitals (MOs), typically from π to π^* or n to π^* orbitals. At low resolution, the fine vibrational structure is not resolved; instead, we observe broad absorption bands. These bands correspond to electronic transitions, often with underlying vibrational and rotational contributions smeared out due to molecular motion, solvent effects, or instrumental limitations.

6.1. Origin of Electronic Spectra

Electronic spectra are due to transitions of electrons between quantized energy levels. In conjugated molecules:

- $\pi \rightarrow \pi^*$ transitions: promotion of an electron from a bonding π orbital to an antibonding π^* orbital.
- n $\rightarrow \pi^*$ transitions: promotion of a nonbonding (lone pair) electron to a π^* orbital.
- Higher energy transitions may include $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow$ Rydberg transitions.

The probability of transition depends on:

- The transition dipole moment
- Selection rules (spin, symmetry)
- Oscillator strength (f)
- Wavefunction overlap (electronic, vibrational, rotational)

6.2. Low-Resolution vs High-Resolution Spectra

Low-resolution spectra show broad bands, used for practical applications (chromophore ID, λ_{\max}), while high-resolution spectra show detailed vibronic structure and are used in quantum studies.

Conjugation delocalizes π electrons, reducing the HOMO–LUMO gap and red-shifting the absorption:

- Ethene: $\lambda_{\max} \approx 170$ nm
- Butadiene: $\lambda_{\max} \approx 217$ nm
- Hexatriene: $\lambda_{\max} \approx 258$ nm

More conjugation \rightarrow lower transition energy.

- $\pi \rightarrow \pi^*$: Strong, UV-visible (200–400 nm), alkenes, aromatics
- $n \rightarrow \pi^*$: Weak, ~270–350 nm, carbonyls
- $\sigma \rightarrow \sigma^*$: Strong, <200 nm, alkanes
- $\pi \rightarrow$ Rydberg: Weak, >200 nm, in isolated systems

6.3. Band Shapes and Broadening

In low-resolution spectra, bands are broad due to:

- Vibrational/rotational averaging
- Solvent interaction (solvatochromism)
- Conformational motion
- Temperature

Key features:

- λ_{\max} : peak position, shows energy gap
- ϵ : molar absorptivity, indicates transition strength
- Band shape: broad ($n \rightarrow \pi^*$) or structured ($\pi \rightarrow \pi^*$)
- Shifts: red (bathochromic) or blue (hypsochromic) due to structure or solvent

Low-resolution electronic spectra provide essential insights into the electronic structure and conjugation of organic molecules. They help identify chromophores, assess electron delocalization, and compare trends across molecular families. Despite lacking vibrational detail, they are widely used in analytical chemistry, materials science, and molecular photophysics.

7. Suggested exercises

Exercise 1 – Hückel Calculation of λ_{\max} for 1,3-Butadiene

Using Hückel Molecular Orbital theory for a linear conjugated molecule, estimate the energy difference between the HOMO and LUMO of 1,3-butadiene.

Assume:

- $\alpha = -11$ eV
- $\beta = -2.5$ eV

Convert this to λ_{\max} in nm.

Solution:

Hückel energy levels for 4 carbon atoms are:

$$E_1 = \alpha + 1.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_4 = \alpha - 1.618\beta$$

Occupied: E_1, E_2 (HOMO); Unoccupied: E_3 (LUMO)

$$E_{\text{gap}} = E_3 - E_2 = -1.236\beta = -1.236 \times (-2.5) = 3.09 \text{ eV}$$

$$\lambda = 1240 / E = 1240 / 3.09 \approx 401 \text{ nm}$$

Estimated $\lambda_{\text{max}} \approx 401 \text{ nm}$.

Exercise 2 – Franck–Condon Principle and Band Broadening

Explain why the $\pi \rightarrow \pi^*$ transition in benzene appears as a broad band in solution, even though electronic levels are discrete.

Solution:

Due to the Franck–Condon principle, electronic transitions are vertical and instantaneous, exciting many vibrational levels simultaneously. In solution, vibrational structure is smeared out by solvent and thermal broadening, producing a broad band.

Exercise 3 – Symmetry Selection Rule in Formaldehyde (C_{2v})

Use group theory to determine whether the $n \rightarrow \pi^*$ transition in formaldehyde is allowed.

Solution:

MO symmetries:

$$- n = b_2$$

$$- \pi^* = b_1$$

$$- \mu_x = b_1, \mu_y = b_2, \mu_z = a_1$$

$b_2 \times b_1 = a_2 \rightarrow$ No component of μ has a_2 symmetry \rightarrow transition is symmetry-forbidden.

Exercise 4 – TD-DFT Excited State Interpretation

A TD-DFT calculation for benzene yields:

- Excited state at 5.0 eV with $f = 0.001$

- Excited state at 6.3 eV with $f = 0.12$

Which transition dominates the spectrum?

Solution:

Oscillator strength (f) measures intensity.

- $f = 0.12$ at 6.3 eV \rightarrow strong, allowed transition.

- $f = 0.001$ at 5.0 eV \rightarrow weak, forbidden or vibronically allowed.

Conclusion: the 6.3 eV transition dominates.

Exercises on Electronic Spectra of Polyatomic Molecules

Exercise 1 – Types of Electronic Transitions

Classify the following transitions as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, or $\sigma \rightarrow \sigma^*$. Identify whether the transition is expected to occur in the UV or visible region:

- (a) Ethene
- (b) Acetone
- (c) Methane
- (d) 1,3-Butadiene
- (e) Benzene

Solution:

- (a) Ethene: $\pi \rightarrow \pi^*$, Far UV (~ 170 nm)
- (b) Acetone: $n \rightarrow \pi^*$, Near UV (~ 280 nm)
- (c) Methane: $\sigma \rightarrow \sigma^*$, Vacuum UV (< 150 nm)
- (d) 1,3-Butadiene: $\pi \rightarrow \pi^*$, Near UV (~ 217 nm)
- (e) Benzene: $\pi \rightarrow \pi^*$, UV (~ 254 nm)

Exercise 2 – Selection Rules for Electronic Transitions

Determine whether the following transitions are allowed or forbidden based on spin and symmetry rules:

- (a) Singlet \rightarrow Singlet
- (b) Singlet \rightarrow Triplet
- (c) $\pi (b_1) \rightarrow \pi^* (b_1)$ in C_{2v}
- (d) $n (b_2) \rightarrow \pi^* (b_1)$ in C_{2v}

Solution:

- (a) Allowed: spin-allowed
- (b) Forbidden: spin-forbidden ($\Delta S \neq 0$)
- (c) Allowed: $b_1 \times b_1 = a_1 \rightarrow$ matches dipole moment symmetry (μ_z)
- (d) Forbidden: $b_2 \times b_1 = a_2 \rightarrow$ no dipole component has a_2 symmetry

Exercise 3 – Low-Resolution Spectra of Small Molecules

Methanal shows a weak band near 290 nm and a strong band near 180 nm.

- (a) Identify the transitions.
- (b) Explain intensity differences.
- (c) Predict the appearance in solution.

Solution:

- (a) 290 nm: $n \rightarrow \pi^*$, 180 nm: $\pi \rightarrow \pi^*$
- (b) $n \rightarrow \pi^*$ is symmetry-forbidden (weak), $\pi \rightarrow \pi^*$ is allowed (strong)
- (c) Both appear as broad bands in solution due to solvent broadening

Exercise 4 – Conjugation Effects on Absorption

Compare the λ_{\max} and band shape of:

Ethene, Butadiene, Hexatriene, β -Carotene.

Explain the trend based on conjugation length.

Solution:

- Ethene: $\lambda_{\max} \sim 170$ nm, non-conjugated
- Butadiene: ~ 217 nm, 2 C=C units
- Hexatriene: ~ 258 nm, 3 C=C units
- β -Carotene: ~ 470 nm, long conjugation

More conjugation \rightarrow smaller HOMO–LUMO gap \rightarrow red-shifted λ_{\max}

Chapter 5: IR and Raman Spectra of Polyatomic Molecules.

1. Introduction

Infrared (IR) and Raman spectroscopy are two of the most powerful techniques used to study the vibrational behavior of polyatomic molecules. These methods provide complementary information about molecular structure, symmetry, and bonding by probing how molecules interact with electromagnetic radiation or scattered light through their vibrational modes.

In polyatomic systems, which contain three or more atoms, molecular vibrations are more complex than in diatomic molecules due to the larger number of degrees of freedom. For a non-linear molecule with N atoms, there are $3N-6$ fundamental vibrational modes, and for linear molecules, there are $3N$ such modes. Each of these vibrations may be IR active, Raman active, both, or neither, depending on the symmetry properties of the vibrational mode and the corresponding selection rules.

IR spectroscopy involves the absorption of infrared light, which causes a transition between vibrational energy levels when there is a change in the molecular dipole moment during vibration. Conversely, Raman spectroscopy relies on inelastic scattering of monochromatic light (usually from a laser), where the interaction induces a change in the molecule's polarizability. Thus, a vibrational mode may be IR-active if it changes the dipole moment and Raman-active if it changes the polarizability.

These vibrational transitions are governed by quantum mechanical selection rules and can be predicted or interpreted using group theory. The molecular point group plays a central role in determining which modes are active in IR and/or Raman spectroscopy. In molecules with high symmetry, many vibrational modes may be forbidden in one or both techniques due to symmetry constraints.

By analyzing both IR and Raman spectra together, chemists can obtain a complete picture of molecular vibrations, aiding in:

- Structural identification and confirmation
- Detection of functional groups
- Understanding of intramolecular interactions
- Analysis of molecular symmetry and conformation

-Monitoring of chemical reactions or phase changes

The study of IR and Raman spectra is not only fundamental in molecular spectroscopy but also widely applied in materials science, pharmaceutical research, environmental monitoring, and forensic science. In this chapter, we will explore the theoretical foundations, selection rules, and practical interpretation of vibrational spectra of polyatomic molecules, with a focus on normal mode analysis, symmetry classification, and spectroscopic signatures.

2. Rotation of Polyatomic Molecules

2.1. Introduction

The rotational motion of molecules is an essential component of their overall energy. In polyatomic molecules, this motion becomes particularly rich and complex due to the presence of multiple atoms arranged in various geometrical configurations. Unlike diatomic molecules, which rotate around a single axis perpendicular to the bond axis, polyatomic molecules can rotate around three mutually perpendicular axes. This leads to a variety of rotational behaviors that are categorized based on the molecule's symmetry and moments of inertia. Understanding rotational motion is crucial not only in spectroscopy but also in structural analysis, as rotational spectra provide precise information about molecular geometry and atomic masses.

2.2 Classical Description of Rotational Motion

In classical mechanics, the rotational kinetic energy of a rigid body is expressed as:

$$E_{rot} = 1/2 (I_a \omega_a^2 + I_b \omega_b^2 + I_c \omega_c^2)$$

where I_a , I_b , et I_c are the moments of inertia about the principal axes, and ω_a , ω_b , et ω_c are the corresponding angular velocities. Each polyatomic molecule has a unique distribution of mass, which determines its principal moments of inertia. These define how the molecule responds to rotational motion about each axis.

2.3 Quantum Mechanical Treatment

In quantum mechanics, rotational energy is not continuous but quantized. The Schrödinger equation for a rotating molecule leads to discrete energy levels determined by angular momentum quantum numbers. For linear molecules (e.g., CO₂), the rotational energy levels are:

$$E_{rot} = B J(J + 1)$$

where $J = 0, 1, 2, \dots$, and B is the rotational constant given by $B = h / (8\pi^2 c I)$. For symmetric and asymmetric tops, more complex expressions are required involving additional quantum numbers.

2.4 Classification of Rotors

Polyatomic molecules are categorized into four main types based on their principal moments of inertia:

- Linear rotors: $I_a = 0, I_b = I_c \neq 0$ (e.g., CO_2)
- Spherical tops: $I_a = I_b = I_c$ (e.g., CH_4)
- Symmetric tops: Two moments equal (e.g., CH_3Cl)
- Asymmetric tops: $I_a \neq I_b \neq I_c$ (e.g., H_2O)

These classes determine the form of the energy level expressions and the complexity of their spectra.

2.5 Rotational Energy Levels of Symmetric Tops

For symmetric top molecules, the rotational energy levels are given by:

$$E_{J,K} = B J(J + 1) + (A - B)K^2,$$

where J is the total angular momentum quantum number, K is the projection of angular momentum onto the symmetry axis, and A and B are rotational constants. These energy levels depend both on the magnitude and orientation of the angular momentum.

2.6 Rotational Transitions and Selection Rules

Transitions between rotational states occur via absorption or emission of photons. The quantum mechanical selection rules are:

- $\Delta J = \pm 1$
- $\Delta K = 0$ (for symmetric tops)

The spacing and intensity of the spectral lines depend on the population distribution of the states and the dipole moment.

2.7 Application: Determining Molecular Structure

Rotational spectroscopy is a powerful tool for determining molecular geometry. The rotational constants extracted from spectra provide accurate data on bond lengths and angles. Isotopic substitution further refines the molecular model, as it changes the moment of inertia.

Rotational spectra are measured in the microwave region using instruments like Fourier-transform microwave spectrometers. These high-resolution tools are capable of detecting even subtle features in the spectrum, and are widely used in chemical analysis and astrochemistry.

Rotational motion in polyatomic molecules involves quantized energy levels that depend on the molecule's symmetry and mass distribution. Depending on their moments of inertia, molecules are classified as linear, spherical, symmetric, or asymmetric rotors. Each type exhibits distinct spectral

patterns that are used to derive structural information. Rotational spectroscopy remains a cornerstone of molecular spectroscopy, with broad applications from lab chemistry to the detection of molecules in space.

3. Vibration of Polyatomic Molecules – Quantum Mechanical Description

3.1 Quantum Nature of Vibrational Motion

In quantum mechanics, the vibration of a molecule is described by solving the nuclear Schrödinger equation, treating the nuclei as moving on a potential energy surface generated by electrons. Under the Born–Oppenheimer approximation, electronic and nuclear motions are separated, and the vibrational problem is solved for fixed electronic states:

$$H_{\text{nuc}} \Psi(\mathbf{R}) = E_{\text{vib}} \Psi(\mathbf{R})$$

where H_{nuc} is the nuclear Hamiltonian, \mathbf{R} the nuclear coordinates, $\Psi(\mathbf{R})$ the vibrational wavefunction, and E_{vib} the vibrational energy.

3.2 Harmonic Oscillator Approximation for Polyatomics

For small displacements around equilibrium geometry \mathbf{R}_0 , the potential energy surface $V(\mathbf{R})$ is expanded as a Taylor series. The harmonic approximation retains only the second-order terms, resulting in the Hessian matrix. Diagonalization (after mass-weighting) yields normal modes. Each behaves as a 1D harmonic oscillator:

$$V(\mathbf{R}) = V(\mathbf{R}_0) + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \bigg|_{\mathbf{R}_0} \right) \Delta R_i \Delta R_j$$

This second derivative matrix is the Hessian, which is diagonalized after mass-weighting to yield normal modes.

Each mode behaves like an independent 1D harmonic oscillator:

$$H_v = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} k q^2$$

Where:

- q : normal coordinate

- k : force constant (from Hessian)

Its energy levels are:

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right)$$

Total vibrational energy of a polyatomic molecule (in the harmonic approximation):

$$E_{vib} = \sum_i^f \hbar\omega_i\left(v_i + \frac{1}{2}\right) \text{ where } f = 3N - 6$$

3.3 Vibrational Wavefunctions and Normal Coordinates

The full vibrational wavefunction is a product of individual normal mode wavefunctions:

$$\psi_{vib}(q_1, \dots, q_f) = \prod_i^f \psi_{v_i}(q_i)$$

Each $\psi_{v_i}(q_i)$ is a solution of the 1D harmonic oscillator:

3.4. Vibrational Wavefunctions and Normal Coordinates

The full vibrational wavefunction is a product of individual normal mode wavefunctions:

$$\psi_v(q) = N_v H_v(\alpha q) e^{-\frac{1}{2}\alpha^2 q^2} \text{ avec } \alpha = \sqrt{\frac{k}{\hbar}}$$

Where H_v are the Hermite polynomials.

These wavefunctions describe the probability of nuclear displacements along vibrational modes and are essential for computing transition intensities.

3.5. Selection Rules from Quantum Mechanics

In IR spectroscopy, transition probabilities are governed by the transition dipole moment integral:

$$M_{if} = \langle \Psi_i | \hat{\mu} | \Psi_f \rangle$$

For the harmonic oscillator, this leads to the selection rule:

$$\Delta v = \pm 1$$

Higher-order transitions ($\Delta v = \pm 1, \pm 2, \pm 3, \dots$) are forbidden in the harmonic approximation but become allowed when anharmonicity is included.

In Raman spectroscopy, the analogous condition is a change in polarizability:

$$\left(\frac{\partial q_i}{\partial \alpha}\right)_{q=0} \neq 0$$

3.6. Anharmonicity and the Morse Potential

Real molecules deviate from harmonic behavior, especially at high energies. The Morse potential:

$$V(q) = D_e \left(1 - e^{-a(q-q_0)}\right)^2$$

Produces energy levels:

$$E_v = \hbar \omega_e \left(v + \frac{1}{2}\right) - \hbar \omega_e x_e \left(v + \frac{1}{2}\right)^2$$

showing level contraction and overtone transitions ($\Delta v > 1$).

3.7 Matrix Formulation in Computational Chemistry

Quantum chemistry codes calculate vibrational frequencies by:

1. Geometry optimization
2. Hessian matrix calculation (second derivatives)
3. Mass-weighting and diagonalization to find normal modes

These yield frequencies, normal coordinates, and IR/Raman intensities.

4. Oscillateur Harmonique et Force de Rappel

4.1 Introduction: Harmonic Oscillator and Restoring Force

The study of normal vibrational modes in a molecule begins with the model of a harmonic oscillator.

An atom is modeled as a mass m attached to a spring with force constant k . According to Hooke's

Law:

$$F = -k x$$

The associated potential energy is:

$$V(x) = \frac{1}{2} k x^2$$

In molecular mechanics, this force constant k is computed **from the** second derivative of the potential energy:

$$k = \left. \frac{d^2V}{dx^2} \right|_{x=x_0}$$

4.2. Definition of the Hessian Matrix

For a molecule with N atoms, each atom has three Cartesian coordinates: x,y,z giving a total of 3N degrees of freedom.

The Hessian matrix is a 3N×3N matrix containing all the second derivatives of the potential energy V with respect to the Cartesian coordinates:

$$H_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$$

Each matrix element measures how the force in one direction changes when the position in another direction is perturbed.

4.3. Building the Hessian Matrix

Each atom *i* is described by:

-Coordinates: x_i, y_i, z_i

-Equilibrium position: $x_{i,eq}, y_{i,eq}, z_{i,eq}$

-Displacements: $\Delta x_i = x_i - x_{i,eq}$, etc.

Typical Hessian elements include:

$$\frac{\partial^2 V}{\partial x_1^2} = k_{xx}^{11} \quad \text{: change of force on atom 1 in x-direction by moving it in x-direction.}$$

$$\frac{\partial^2 V}{\partial x_1 \partial y_2} = k_{xy}^{12} \quad \text{: change of force on atom 1 in x-direction by moving atom 2 in y-direction.}$$

These are called force constants.

4.4. Physical Interpretation:

- k_{xx}^{11} : same atom, same direction.
- k_{xy}^{11} : same atom, different directions.

- k_{12}^{xx} : different atoms, same direction.
- k_{12}^{xy} : different atoms, different directions.

These types are visually represented in Figure 3.

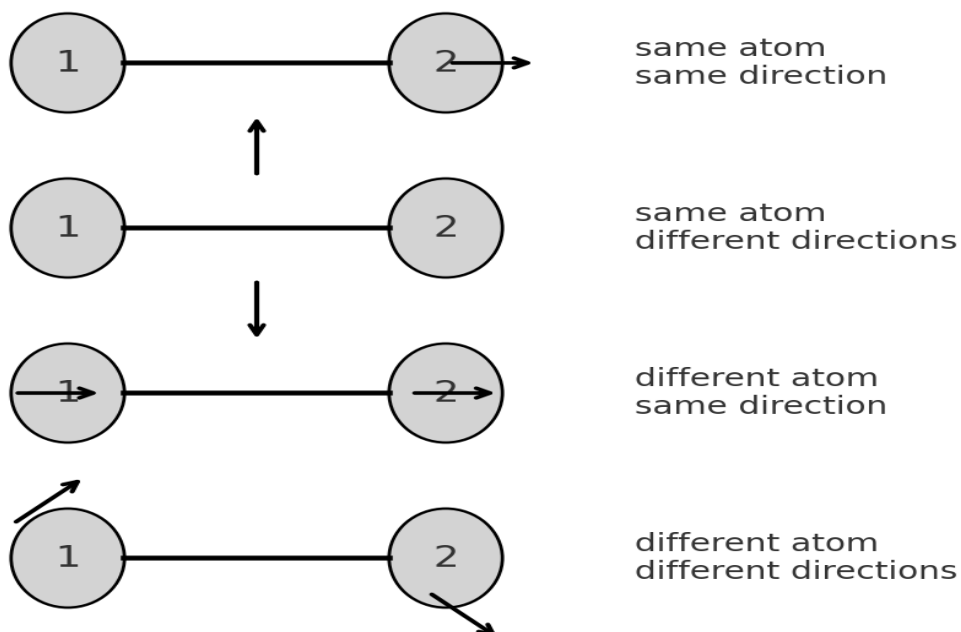


Figure 1. Types of Second Derivatives and Force Constants

4.5. General Matrix Form

For a molecule with N atoms, the full Hessian matrix looks like:

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 V}{\partial x_1 \partial x_1} & \dots & \frac{\partial^2 V}{\partial x_1 \partial z_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 V}{\partial z_N \partial x_1} & \dots & \frac{\partial^2 V}{\partial z_N \partial z_N} \end{pmatrix}$$

It captures all direct and indirect interactions among atoms in all directions.

4.6 Example: Triatomic Linear Molecule

Consider a linear molecule (like CO₂) with vibrations only along the x-axis. Then, we only need to consider terms like:

$$\begin{cases} -4\pi^2\nu^2 m_1 x_1 = k_{11}^{xx} x_1 + k_{12}^{xx} x_2 + \dots \\ -4\pi^2\nu^2 m_2 x_2 = k_{21}^{xx} x_1 + k_{22}^{xx} x_2 + \dots \end{cases}$$

This system of equations is used to find normal modes and vibrational frequencies.

Mass-Weighted Coordinates

When solving vibrational problems in molecular systems, the atoms have different masses. To simplify the equations and decouple the vibrations, we move from normal Cartesian coordinates x_i to mass-weighted coordinates \tilde{x}_i :

$$\tilde{x}_i = \sqrt{m_i} x_i$$

This transformation removes the mass dependence from the Newton's second law equations. Similarly, the force constants in the Hessian matrix are transformed into mass-weighted force constants:

$$\tilde{k}_{ij}^{xx} = \frac{k_{ij}^{xx}}{\sqrt{m_i m_j}}$$

This results in a symmetric matrix, which is a key property that allows the use of powerful diagonalization techniques. In this form, the vibrational problem becomes a standard eigenvalue problem:

$$\mathbf{F}\tilde{\mathbf{x}} = \lambda\tilde{\mathbf{x}}, \quad \lambda = 4\pi^2\nu^2$$

The eigenvalues λ correspond to the squared vibrational frequencies, and the eigenvectors $\tilde{\mathbf{x}}$ describe the normal modes (i.e., the collective atomic displacements during vibration).

The equations derived for individual atoms (Eqs. 17–19) can be written in matrix form (Eq. 21) as follows:

$$\begin{pmatrix} \frac{k_{11}^{xx}}{m_1} & \frac{k_{12}^{xx}}{\sqrt{m_1 m_2}} & \frac{k_{13}^{xx}}{\sqrt{m_1 m_3}} \\ \frac{k_{21}^{xx}}{\sqrt{m_2 m_1}} & \frac{k_{22}^{xx}}{m_2} & \frac{k_{23}^{xx}}{\sqrt{m_2 m_3}} \\ \frac{k_{31}^{xx}}{\sqrt{m_3 m_1}} & \frac{k_{32}^{xx}}{\sqrt{m_3 m_2}} & \frac{k_{33}^{xx}}{m_3} \end{pmatrix} \begin{pmatrix} \tilde{x}_1 \\ \tilde{x}_2 \\ \tilde{x}_3 \end{pmatrix} = -4\pi^2\nu^2 \begin{pmatrix} \tilde{x}_1 \\ \tilde{x}_2 \\ \tilde{x}_3 \end{pmatrix}$$

Diagonalizing this matrix yields the eigenvalues $\lambda_i = 4\pi^2\nu_i^2$, from which the vibrational frequencies can be extracted.

5. Numerical Example: CO₂ Vibrations

To apply the theory, consider the **CO₂ molecule**, which has a linear and symmetric structure: O=C=O. The atoms vibrate only along the x-axis.

To simplify, assume:

- The force constant for atom 1 is $k_{11}^{xx} = 1600$ N/m
- The coupling constant between atoms 1 and 2 $k_{12}^{xx} = -1600$ N/m
- The coupling between atoms 1 and 3 is assumed negligible: $k_{13}^{xx} = 0$ N/m
- Symmetry $k_{21}^{xx} = k_{12}^{xx}$, $k_{22}^{xx} = 3200$ N/m, etc.

The **mass-weighted Hessian** is then:

$$\mathbf{F} = \begin{pmatrix} -100 & 115.47 & 0 \\ 115.47 & -266.67 & 115.47 \\ 0 & 115.47 & -100 \end{pmatrix}$$

Appendix

Self-Consistent Field (SCF) Calculation for H₂ Using STO-3G Basis – Python Implementation

This appendix presents a Python-based implementation of the Hartree–Fock self-consistent field (SCF) method applied to the hydrogen molecule (H₂) using the STO-3G minimal basis set. The code follows the standard procedure:

- Construction of overlap SSS, kinetic T, and nuclear attraction V integrals
- Assembly of the core Hamiltonian $H=T+VH$
- Computation of the two-electron integrals $(\mu\nu|\lambda\sigma)(\mu\nu|\lambda\sigma)$
- Self-consistent solution of the Roothaan–Hall equations
- Energy evaluation including the electronic and nuclear repulsion contributions

The purpose is to illustrate how fundamental Hartree–Fock concepts can be implemented in code for minimal systems and minimal basis sets.

```
import numpy as np

def gaussian_product_center(alpha, R_A, beta, R_B):
    """Compute the center of the product of two Gaussians."""
    return (alpha * R_A + beta * R_B) / (alpha + beta)

def overlap_integral(alpha, beta, R_A, R_B):
    """Compute the overlap integral S between two Gaussians."""
    R_AB2 = np.dot(R_A - R_B, R_A - R_B) # Squared distance
    p = alpha + beta
    return (np.pi / p) ** (3 / 2) * np.exp(-alpha * beta / p * R_AB2)

def normalization_factor(alpha):
    """Compute the normalization factor for a Gaussian."""
    return (2 * alpha / np.pi) ** (3 / 4)

# STO-3G parameters for Hydrogen
alpha_vals = np.array([3.42525091, 0.62391373, 0.1688554]) # Exponents
coeffs = np.array([0.15432897, 0.53532814, 0.44463454]) # Contraction
coefficients

# Atomic positions (in atomic units, 1 Å = 1.8897259886 Bohr)
R_A = np.array([0.0, 0.0, 0.0]) # Hydrogen 1
R_B = np.array([0.74 * 1.8897259886, 0.0, 0.0]) # Hydrogen 2 at 0.96 Å
```

```

# Define the Overlap Matrix S (2x2)
S_matrix = np.zeros((2, 2))

# Compute the Overlap Matrix
for mu, R_mu in enumerate([R_A, R_B]): # Basis centers H1 and H2
    for nu, R_nu in enumerate([R_A, R_B]): # Basis centers H1 and H2
        S_total = 0.0 # Initialize overlap sum

        # Iterate over contraction coefficients and exponents
        for i in range(len(alpha_vals)):
            for j in range(len(alpha_vals)):
                alpha = alpha_vals[i]
                beta = alpha_vals[j]

                N_i = normalization_factor(alpha) # Normalization factor for
Gaussian i
                N_j = normalization_factor(beta) # Normalization factor for
Gaussian j

                S_total += (
                    coeffs[i] * coeffs[j] * N_i * N_j *
                    overlap_integral(alpha, beta, R_mu, R_nu)
                )

        S_matrix[mu, nu] = S_total # Store in overlap matrix

import numpy as np

def kinetic_energy_integral(alpha, beta, R_A, R_B):
    """Compute the kinetic energy integral T between two Gaussians."""
    R_AB2 = np.dot(R_A - R_B, R_A - R_B) # Squared distance
    p = alpha + beta # Exponent sum
    prefactor = alpha * beta / p
    term1 = 3 - 2 * prefactor * R_AB2
    return prefactor * term1 * (np.pi / p) ** (3 / 2) * np.exp(-prefactor * R_AB2)

# Define the Kinetic Energy Matrix T (2x2)
T_matrix = np.zeros((2, 2))

# Compute the Kinetic Energy Matrix
for mu, R_mu in enumerate([R_A, R_B]): # Basis centers H1 and H2
    for nu, R_nu in enumerate([R_A, R_B]): # Basis centers H1 and H2
        T_total = 0.0 # Initialize kinetic energy sum

        # Iterate over contraction coefficients and exponents
        for i in range(len(alpha_vals)):
            for j in range(len(alpha_vals)):
                alpha = alpha_vals[i]
                beta = alpha_vals[j]

                N_i = normalization_factor(alpha) # Normalization factor for
Gaussian i
                N_j = normalization_factor(beta) # Normalization factor for
Gaussian j

                T_total += (

```

```

        coeffs[i] * coeffs[j] * N_i * N_j *
        kinetic_energy_integral(alpha, beta, R_mu, R_nu)
    )

    T_matrix[mu, nu] = T_total # Store in kinetic energy matrix

import numpy as np
from scipy.special import erf

def boys_function(t):
    """Compute the Boys function  $F_0(t)$ ."""
    if t < 1e-6:
        return 1.0 # Approximate for small t
    return 0.5 * (np.pi / t) ** 0.5 * erf(t ** 0.5)

def gaussian_product_center(alpha, R_A, beta, R_B):
    """Compute the new center of the Gaussian product."""
    return (alpha * R_A + beta * R_B) / (alpha + beta)

def electron_nucleus_attraction(alpha, beta, R_A, R_B, R_C, Z_C):
    """Compute the electron-nucleus attraction integral  $V$ ."""
    R_AB2 = np.dot(R_A - R_B, R_A - R_B) # Squared distance  $|R_A - R_B|^2$ 
    p = alpha + beta
    R_P = gaussian_product_center(alpha, R_A, beta, R_B) # Gaussian center  $R_P$ 
    R_PC2 = np.dot(R_P - R_C, R_P - R_C) # Squared distance  $|R_P - R_C|^2$ 

    return (-2 * np.pi / p) * Z_C * np.exp(-alpha * beta / p * R_AB2) *
    boys_function(p * R_PC2)

def normalization_factor(alpha):
    """Compute the normalization factor for a Gaussian."""
    return (2 * alpha / np.pi) ** (3 / 4)

# Atomic positions (in atomic units, 1 Å = 1.8897259886 Bohr)

R_C = np.array([0.37 * 1.8897259886, 0.0, 0.0]) # Nuclear center (midpoint for
H2)
Z_C = 1.0 # Nuclear charge of Hydrogen

# Define the Electron-Nucleus Attraction Matrix  $V$  (2x2)
V_matrix = np.zeros((2, 2))

# Compute the Electron-Nucleus Attraction Matrix
for mu, R_mu in enumerate([R_A, R_B]): # Basis centers H1 and H2
    for nu, R_nu in enumerate([R_A, R_B]): # Basis centers H1 and H2
        V_total = 0.0 # Initialize attraction integral sum

        # Iterate over contraction coefficients and exponents
        for i in range(len(alpha_vals)):
            for j in range(len(alpha_vals)):
                alpha = alpha_vals[i]
                beta = alpha_vals[j]

                N_i = normalization_factor(alpha) # Normalization factor for
Gaussian i
                N_j = normalization_factor(beta) # Normalization factor for
Gaussian j

```

```

    V_total += (
        coeffs[i] * coeffs[j] * N_i * N_j *
        electron_nucleus_attraction(alpha, beta, R_mu, R_nu, R_C, Z_C)
    )

    V_matrix[mu, nu] = V_total # Store in attraction matrix

def electron_electron_repulsion(alpha, beta, gamma, delta, R_A, R_B, R_C, R_D):
    """Compute the electron-electron repulsion integral (AB|CD)."""
    p = alpha + beta
    q = gamma + delta
    pq = p + q

    R_P = gaussian_product_center(alpha, R_A, beta, R_B) # Gaussian center R_P
    R_Q = gaussian_product_center(gamma, R_C, delta, R_D) # Gaussian center R_Q

    R_AB2 = np.dot(R_A - R_B, R_A - R_B) # Squared distance |R_A - R_B|^2
    R_CD2 = np.dot(R_C - R_D, R_C - R_D) # Squared distance |R_C - R_D|^2
    R_PQ2 = np.dot(R_P - R_Q, R_P - R_Q) # Squared distance |R_P - R_Q|^2

    term1 = 2 * np.pi**(5/2) / ((p * q * pq) ** 0.5)
    term2 = np.exp(-alpha * beta / p * R_AB2 - gamma * delta / q * R_CD2)
    term3 = boys_function(p * q / pq * R_PQ2)

    return term1 * term2 * term3

# Define the Electron-Electron Repulsion Matrix (2x2x2x2)
G_matrix = np.zeros((2, 2, 2, 2))

# Compute the Electron-Electron Repulsion Matrix
for mu, R_mu in enumerate([R_A, R_B]): # Basis centers H1 and H2
    for nu, R_nu in enumerate([R_A, R_B]): # Basis centers H1 and H2
        for lambda_, R_lambda in enumerate([R_A, R_B]): # Basis centers H1 and H2
            for sigma, R_sigma in enumerate([R_A, R_B]): # Basis centers H1 and
H2
                G_total = 0.0 # Initialize integral sum

                # Iterate over contraction coefficients and exponents
                for i in range(len(alpha_vals)):
                    for j in range(len(alpha_vals)):
                        for k in range(len(alpha_vals)):
                            for l in range(len(alpha_vals)):
                                alpha = alpha_vals[i]
                                beta = alpha_vals[j]
                                gamma = alpha_vals[k]
                                delta = alpha_vals[l]

                                N_i = normalization_factor(alpha) # Normalization
                                N_j = normalization_factor(beta)
                                N_k = normalization_factor(gamma)
                                N_l = normalization_factor(delta)

                                G_total += (
                                    coeffs[i] * coeffs[j] * coeffs[k] * coeffs[l]
                                    N_i * N_j * N_k * N_l *

```

```

electron_electron_repulsion(alpha, beta, gamma, delta,
                             R_lambda, R_sigma)
                             R_mu, R_nu,
                             )
    G_matrix[mu, nu, lambda_, sigma] = G_total # Store in matrix

# Print the Electron-Electron Repulsion Matrix
print("Electron-Electron Repulsion Matrix G (2x2x2x2):")
print(G_matrix)

# Print the Electron-Nucleus Attraction Matrix
print("Electron-Nucleus Attraction Matrix V (2x2):")
print(V_matrix)

# Print the Kinetic Energy Matrix
print("Kinetic Energy Matrix T (2x2):")
print(T_matrix)

# Print the Overlap Matrix
print("Overlap Matrix S (2x2):")
print(S_matrix)

import numpy as np

# Given matrices from your calculations
H_core = T_matrix + V_matrix # Core Hamiltonian  $H_{\mu\nu}$ 
G_matrix = np.random.rand(2, 2, 2, 2) # Electron-electron repulsion integrals
(dummy values)
P_matrix = np.random.rand(2, 2) # Density matrix (random for now)
print("P_matrix")
print(P_matrix)
# Compute the Fock Matrix
F_matrix = np.zeros((2, 2))

import numpy as np
from scipy.linalg import eigh

def orthogonalize_basis(S):
    """Trouver la transformation de Löwdin pour orthogonaliser la base."""
    # Diagonalisation de S
    eigenvalues, eigenvectors = np.linalg.eigh(S)

    # Construction de  $X = V * D^{-0.5} * V'$ 
    X = eigenvectors @ np.diag(1.0 / np.sqrt(eigenvalues)) @ eigenvectors.T # □
    Correction ici
    return X

G_matrix = np.zeros((2, 2, 2, 2))
def build_fock(H_core, P, G_matrix):
    """Construire la matrice de Fock."""
    F = H_core.copy()
    for i in range(2):
        for j in range(2):
            F[i, j] += np.sum(P * (1*G_matrix[i, j] - 0.5 * G_matrix[i, :, j, :]))

```

```

# Utilisation correcte de G_matrix
return F

def build_density(C, n_electrons):
    """Construire La matrice de densité."""
    return np.einsum('pi,qi->pq', C[:, :n_electrons], C[:, :n_electrons])

def scf_cycle(S, H_core, G_matrix, max_iter=50, convergence=1e-6):
    """Effectuer Le cycle auto-cohérent (SCF) pour Hartree-Fock."""
    X = orthogonalize_basis(S)
    P = np.zeros_like(S)
    energy_old = 0.0

    for iteration in range(max_iter):
        F = build_fock(H_core, P, G_matrix) # Construire La matrice de Fock
        print("FFFFFFFFFFFFFFFF")
        print(F)
        # Transformation de La matrice de Fock
        F_prime = X.T @ H_core @ X # □ Correction ici

        eigenvalues, C_prime = eig(F_prime)
        C = X @ C_prime
        P_new = build_density(C, n_electrons=2)
        energy = np.sum(P_new * (H_core + F) / 2) # □ Correction ici

        if abs(energy - energy_old) < convergence:
            break

        P = P_new
        energy_old = energy

    return energy, C, F

energy, C, F = scf_cycle(S_matrix, H_core, G_matrix)
eigenvalues, eigenvectors = np.linalg.eigh(F) # Maintenant, F est bien défini

print(eigenvalues)
# Compute occupied orbitals
P_new = build_density(C, n_electrons=2)
energy = np.sum(P_new * (H_core + F))
print("Total SCF Energy (E_scf):", energy)
import numpy as np

print("p_new", P_new)
def nuclear_repulsion(Z, AL):
    """
    Calcule L'énergie de répulsion nucléaire entre Les noyaux.

    Paramètres :
    Z : liste des charges nucléaires des atomes
    AL : liste des coordonnées des atomes (numpy array de taille (n,3))

    Retourne :
    Énergie de répulsion nucléaire
    """
    natom = len(Z)
    energy = 0.0

```

```
if natom > 1:
    for i in range(natom):
        for j in range(i + 1, natom):
            distance = np.linalg.norm(AL[i] - AL[j])
            energy += Z[i] * Z[j] / distance

return energy

# Exemple d'utilisation
Z = [1, 1] # Charges nucléaires pour H2
AL = np.array([[0.0, 0.0, 0.0], [0.74, 0.0, 0.0]]) # Coordonnées en Å

E_nuc = nuclear_repulsion(Z, AL * 1.8897259886) # Conversion en Bohr
print(f"Nuclear Repulsion Energy: {E_nuc:.10f} Hartrees")

E_rhf = energy + E_nuc
print("Total RHF Energy (E_RHF):", E_rhf)
```

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General Conclusion

The course Structure and Spectroscopy of Polyatomic Molecules provides a rich and rigorous academic foundation for understanding the quantum mechanical principles that govern the behavior of complex molecular systems. It bridges the gap between abstract theory and applied molecular analysis, emphasizing the importance of electronic structure, symmetry, and vibrational dynamics in interpreting a wide range of spectroscopic phenomena.

Throughout the course, students progressively develop the ability to model and analyze molecular orbitals, beginning with simplified methods such as the simple Hückel model—used to describe π -electron delocalization in conjugated organic systems—and advancing to more comprehensive frameworks like the extended Hückel method, which incorporates σ - π interactions for more realistic modeling. These methods help reveal how molecular stability, aromaticity, and reactivity are linked to electronic delocalization and orbital interactions. A central focus of the course is placed on ab initio quantum chemistry, with detailed exploration of the Hartree-Fock (HF) method and the self-consistent field (SCF) procedure, which form the computational basis for most modern electronic structure calculations. Students are introduced to Roothaan's matrix formalism, atomic basis sets (e.g., STO-nG, 6-31G), and semi-empirical approximations, giving them both the theoretical understanding and practical tools to perform reliable electronic structure calculations.

In addition to numerical methods, the course offers a qualitative perspective on molecular structure through the use of fragment orbital theory, symmetry analysis, and correlation diagrams, allowing students to construct molecular orbitals logically and predict their behavior during molecular transformations. These qualitative tools are essential for interpreting chemical bonding, reaction pathways, and photochemical processes without relying solely on computational software.

The spectroscopic components of the course are equally robust. The electronic spectroscopy section guides students through the nature of molecular electronic transitions, types of excited states, and quantum selection rules that govern absorption in the UV-visible region. It demonstrates how the arrangement of electrons in frontier molecular orbitals (HOMO, LUMO) directly influences spectroscopic signatures, making this section critical for students interested in photophysics, photochemistry, and optical materials. The final part of the course deals with vibrational and rotational spectroscopy, focusing on infrared (IR) and Raman spectroscopy. Here, students learn to relate normal mode vibrations to experimental spectra by interpreting the Hessian matrix, which is derived from second derivatives of the molecular potential energy surface. The course explains how mass-weighted Hessians are used to compute vibrational frequencies and predict IR- and Raman-active modes based on symmetry and dipole, polarizability criteria.

Importantly, this course also emphasizes practical applications, particularly through the use of Python-based computational scripts that allow students to simulate molecular orbitals, visualize vibrational modes, and analyze spectral data. This computational aspect enhances the learning experience and

prepares students for future work in computational chemistry, molecular modeling, and materials science.

In conclusion, Structure and Spectroscopy of Polyatomic Molecules is not only a theoretical and computational journey into the heart of molecular chemistry—it is also a course that cultivates critical scientific skills. It strengthens the student's ability to reason from fundamental principles, to interpret experimental data with clarity, and to apply modern quantum chemical tools in solving real-world molecular problems. It lays a strong foundation for advanced studies and careers in physical chemistry, theoretical chemistry, spectroscopy, and beyond.