

Report1: Hückel Model Hamiltonian

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Abstract

Understanding the electronic properties of conjugated systems is fundamental to advancements in organic electronics and photonics. In this study, we employ the Hückel model to investigate the π -electron structures of various conjugated molecules, serving as a foundational approach before progressing to more complex models. By implementing the Hückel Hamiltonian, we calculate the orbital energies, including the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) levels, which are critical for predicting electronic transitions and reactivity.

Our computational analysis utilizes the Restricted Hartree-Fock (RHF) method, providing a more accurate description of electronic interactions compared to the purely qualitative Hückel model. This approach enables us to derive precise energy levels and molecular orbital characteristics for the studied molecules. The findings indicate a significant correlation between the Hückel and RHF models in predicting electronic properties of simple conjugated systems, validating the utility of the Hückel approach as an initial step in electronic structure analysis.

Future work will extend this study to the Pariser-Parr-Pople (PPP) model Hamiltonian, aiming to achieve a more comprehensive understanding of electron correlation effects in conjugated molecules. This research provides valuable insights into the electronic behavior of conjugated systems, with implications for the design and development of new organic materials for electronic applications.

1 Introduction

Quantum chemistry serves as a cornerstone in elucidating the behavior of atoms and molecules at a fundamental level. Central to the study of molecular systems are theoretical models that aim to predict electronic structure properties amidst quantum mechanical complexities. Among these models, the Hückel model stands out as a foundational tool for approximating molecular orbital energies in conjugated systems. The simplicity of the Hückel model lies in its ability to capture essential electronic interactions by incorporating π -electrons within a molecular framework [3]. Building upon this concept, the PPP model refines our understanding by accounting for additional atomic interactions and molecular distortions [4].

In investigating these models, one must consider the language of quantum mechanics, particularly the transition from first quantization to second quantization. The former focuses on describing particles in terms of wavefunctions and operators, while the latter offers a more efficient representation by treating particles as excitations in a quantum field theory. By leveraging powerful software tools capable of performing orbital energy computations, this study aims to dissect the intricacies of the Hückel and PPP model Hamiltonians. Through a holistic analysis of these theoretical frameworks, we endeavor to unlock new insights into electronic structure predictions and expand the frontiers of quantum chemical studies.

This revised version incorporates references to the works of Hückel [1], Parr, and Pearson [2] to provide credibility and context to your abstract and introduction. Let me know if you need further assistance or if you would like more references included.

1.1 Molecular Orbital

A chemical bond occurs when the net attractive forces between an electron and two nuclei exceed the electrostatic repulsion between the two nuclei. For this to happen, the electron must be in a region called the "binding region". Conversely, if an electron is located on the other side and in the anti bonding region, it creates repulsion between two nuclei and pushes them away from each other. Finally, the nuclei of two atoms reach a distance that is equal to the distance between the two nuclei of the desired molecule. Finally, the orbital that is formed is known as a molecular orbital.

1.2 Bonding and anti bonding molecular orbitals

The two molecular orbitals of the H^+ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the j th molecular orbital can be expressed as a linear combination of many atomic orbitals ϕ_i :

$$|\psi_J\rangle = \sum_i^N c_{J,i} \phi_i \quad (1)$$

A molecule will have the same number of molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 1). When two atomic orbitals combine, it is analogous to the constructive interference of two waves, which enhances their intensity. This results in an increase in the internuclear electron probability density. The molecular orbital formed from the constructive combination of two H 1s orbitals is referred to as a σ 1s combination.

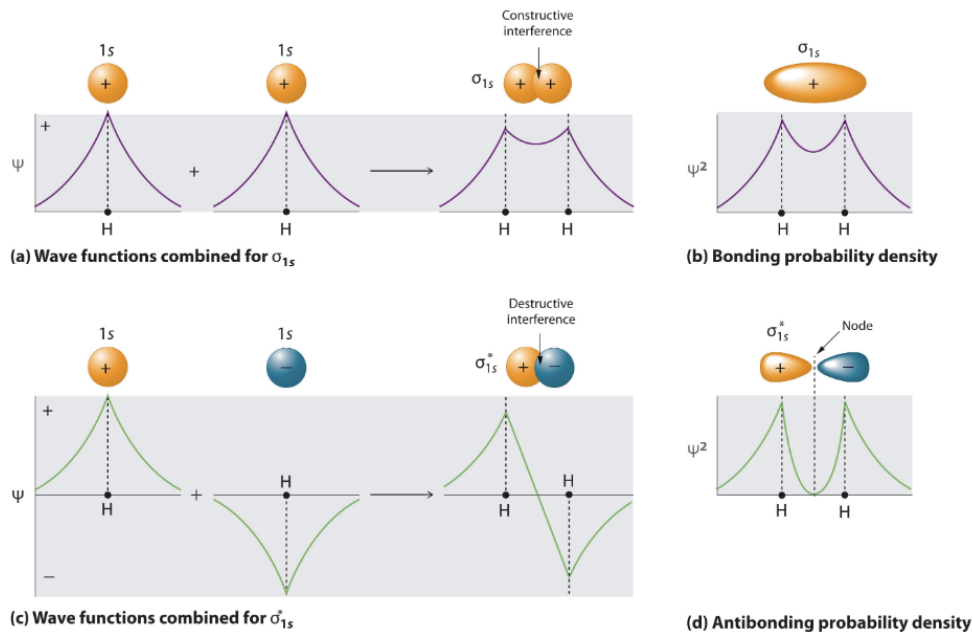


Figure 1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wavefunction.) (c) This diagram shows the formation of an antibonding σ_{1s}^* molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wavefunction (Ψ^2) for the σ_{1s}^* antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

In a sigma (σ) orbital, the electron density is highest along the axis between the nuclei, and it

has cylindrical symmetry, meaning that cross-sections perpendicular to this axis are circular. The subscript "1s" indicates that the molecular orbital is formed from 1s atomic orbitals.

The equation

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}}(|1s_A\rangle + |1s_B\rangle)$$

describes how the sigma orbital is a combination of two 1s atomic orbitals from atoms A and B, resulting in constructive interference that increases electron density between the nuclei.

On the other hand, when one atomic orbital is subtracted from another, it leads to destructive interference, reducing the electron density between the nuclei. This is described by the equation

$$|\sigma_{1s}^*\rangle = \frac{1}{\sqrt{2(1-S)}}(|1s_A\rangle - |1s_B\rangle) \quad (2)$$

creating an antibonding molecular orbital (σ^*1s) with a nodal plane where the electron density is zero.

Electrons in the σ_{1s} orbital have lower energy because they interact with both nuclei, stabilizing the molecule by reducing nuclear repulsions. Conversely, electrons in the σ^*1s orbital have higher energy, as they interact with only one nucleus at a time and are located farther from the nucleus, destabilizing the molecule.

The energy-level diagram in Figure 9.5.2 shows that the σ_{1s} orbital (bonding) is lower in energy compared to the 1s atomic orbitals, while the σ^*1s orbital (antibonding) is higher in energy.

2 The Total Energy of an Electronic State

Neglecting spin-orbit, spin-spin and relativistic effects the Hamiltonian for n electrons in a molecule is defined in the Born-Oppenheimer approximation as

$$H = H_{core} + \frac{1}{2} \sum_{i,j}^n \frac{1}{r_{ij}} \quad (3)$$

where H_{core} is the sum of the kinetic and potential energies of all electrons in the field of the core

$$H_{core} = \sum_i^n [T(i) + U_{core}(i)] \quad (4)$$

In order to get the electronic energy of the system, we have to find a solution of the relevant eigenvalue equation

$$H\psi = E\psi \quad (5)$$

As in most cases the eigenvalue problem (1.3) is too complicated to yield directly analytical expressions as solutions, we have to restrict ourselves to approximations. Among those, one of the best-known is the ASMO CI (antisymmetric molecular orbital configuration interaction) approximation which represents the total wavefunction ψ as a finite linear combination of antisymmetrized product functions ϕ consisting of molecular orbitals ϕ . The ϕ 's may be taken in the form of determinants:

$$\psi = \sum_i^k A_i \phi_i \quad (6)$$

with $\phi_i = \det|\phi_{i1}\phi_{i2}\dots\phi_{in}|$. The coefficients A are regarded as variation parameters and determined by the application of the variation principle to the total energy expression

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (7)$$

This yields a set of linear equations for the A_i

$$\sum_m^k A_m (H_{mn} - S_{mn}E) = 0, \quad n = 1, \dots, K \quad (8)$$

and a secular equation for E

$$\det|H_{mn} - S_{mn}E| = 0 \quad (9)$$

where S_{mn} and H_{mn} are integrals over ϕ functions:

$$S_{mn} = \int \phi_m^* \phi_n d\tau, \quad (10)$$

$$H_{mn} = \int \phi_m^* H \phi_n d\tau. \quad (11)$$

3 Closed and Open Shell Systems

In molecules with an even number of electrons ($2n$), the ground state wavefunction is often dominated by a single determinant, where electrons are paired in molecular orbitals with the same spatial part and differing only by spin[?].

$$\begin{aligned} \phi_1 &= \psi_1 \alpha, & \phi_2 &= \psi_1 \beta, \\ \phi_{2n-1} &= \psi_n \alpha, & \phi_{2n} &= \psi_n \alpha. \end{aligned} \quad (12)$$

This scenario, known as a "closed-shell" case, occurs when the electrons fill the lowest energy levels in pairs, with each level accommodating a maximum of two electrons due to the Pauli exclusion principle. However, in molecules with an odd number of electrons, the resulting spin is non-zero, and the electrons cannot be fully paired. These cases, known as "open-shell" systems, involve at least one "singly occupied" orbital and are more complex to describe, often requiring consideration of effective Hamiltonian operators and spin restrictions.

4 Hückel model

The Hückel model, also known as the Hückel molecular orbital (HMO) theory, is a simple and effective method used in quantum chemistry to determine the electronic structure of conjugated systems, particularly unsaturated hydrocarbons like alkenes and aromatic compounds. The model was introduced by the German physicist Erich Hückel in the 1930s.

Key Features of the Hückel Model:

- **Application to π -Electrons:** The Hückel model focuses on the π -electrons in conjugated systems, assuming the σ -electrons form a stable framework that doesn't affect the π -electron system.
- **Hamiltonian Matrix:** The model involves setting up a Hamiltonian matrix that describes the energy interactions between π -electrons in the molecule. This matrix is constructed using two parameters:
 - α (alpha): The Coulomb integral, representing the energy of an electron in a p-orbital (on a carbon atom).
 - β (beta): The resonance or exchange integral, representing the interaction energy between two p-orbitals on adjacent carbon atoms.
- **Hückel Determinant:** The energy levels of the π -electrons are found by solving the secular determinant, which is a determinant of the Hamiltonian matrix minus an energy term (E) times the identity matrix. This is set equal to zero to find the allowed energy levels (E) of the system

- **Construction of the Matrix:** For a molecule with n carbon atoms, the Hamiltonian matrix is $n \times n$, where diagonal elements are α , and off-diagonal elements are β for atoms that are directly bonded and zero otherwise.
- **Eigenvalues and Eigenvectors:** Solving the determinant provides eigenvalues, which correspond to the energy levels of the π -electrons. The eigenvectors correspond to the molecular orbitals.
- **Simplifying Assumptions:** The model assumes all carbon atoms and bonds are equivalent (same α and β), neglects electron-electron repulsion beyond the π -electrons, and assumes the π -electrons only interact with nearest neighbors.
- **Bond Order and Charge Density:** The Hückel model allows for the calculation of bond order (indicative of bond strength) and charge density (electron distribution) in the molecule, providing insights into chemical reactivity and stability.
- **Limitations:** While the Hückel model provides qualitative insights and is useful for simple conjugated systems, it does not account for more complex interactions and is less accurate for large or highly substituted systems. It also doesn't consider 3D molecular conformations or effects beyond π -electron interactions.

5 Hückel model Hamiltonian in second quantization notation

The Hückel model Hamiltonian for a conjugated system can be expressed in second quantization notation. It includes on-site energy terms and hopping terms, which describe the interaction between neighboring atomic orbitals. The Hamiltonian is given by:

$$\hat{H} = \sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i - \sum_{\langle i,j \rangle} t \left(\hat{c}_i^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{c}_i \right) \quad (13)$$

In this expression: - ϵ_i is the on-site energy for the π -electron at site i . - \hat{c}_i^\dagger and \hat{c}_i are the creation and annihilation operators, respectively, for an electron at site i . - t is the hopping integral (resonance integral) between neighboring sites i and j . - $\langle i,j \rangle$ indicates that the sum is over nearest-neighbor pairs.

The first term $\sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i$ represents the on-site energy of the electrons, while the second term $\sum_{\langle i,j \rangle} t \left(\hat{c}_i^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{c}_i \right)$ accounts for the hopping of electrons between adjacent sites, reflecting the delocalization of π -electrons in the conjugated system.

This Hamiltonian captures the essential physics of the π -electron systems within the Hückel approximation and serves as a foundational model for more complex electronic structure calculations.

5.1 On-site term

This term accounts for the energy contribution from each individual π -electron localized at its respective atomic orbital. It represents the potential energy associated with the presence of electrons at specific sites within the conjugated system.

5.2 Hopping term

In a molecule or atom, electrons occupy discrete energy levels, analogous to shelves on a bookcase. According to quantum mechanics, electrons possess both particle and wave-like properties, allowing their wave functions to extend beyond the confines of individual atoms. This means that electron density can overlap between neighboring atoms within a molecule. When atoms are in close proximity, the electron wave functions can intermingle, enabling electrons to effectively move or "hop" between atoms. This phenomenon, often referred to as electron delocalization, occurs due to a delicate balance of attractive and repulsive forces within the molecule or atom. The attractive force arises from the electrostatic attraction between the negatively charged electrons and the positively charged nuclei of

the atoms. Conversely, there is also repulsion between electrons due to their like charges. This interplay of attractive and repulsive forces dictates the possibility of electron movement within the molecule or atom. If the energy levels of neighboring atoms align favorably, an electron on one atom can transition to a neighboring atom, effectively "hopping" between them. This process, known as electron tunneling, is a manifestation of quantum mechanical principles at the atomic and molecular scale. Understanding electron hopping or tunneling is crucial in quantum chemistry as it underpins the behavior and properties of molecules and atoms. It influences phenomena such as chemical bonding, molecular structure, and electronic properties. The ability of electrons to move within a molecule or atom greatly impacts its reactivity, stability, and overall behavior. Thus, electron hopping is a fundamental concept in quantum chemistry, reflecting the intricate interplay of atomic interactions within molecules and atoms.

6 Results:

All calculation are done for ϵ (the α parameter) with a value of 1 and the t parameter (β) with a value of -1. Also, we consider periodic boundary condition in ring shape structure molecules like benzene. pbc = periodic boundary condition.

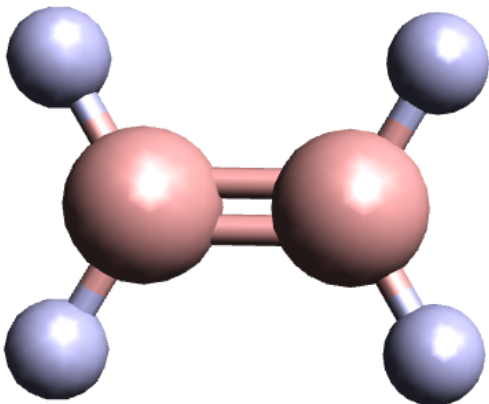


Figure 2: Etylen molecule

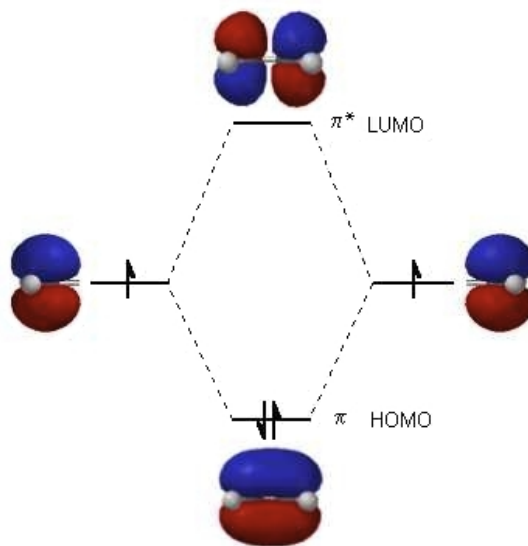


Figure 3: π molecular orbital for Etylen

Table 1: Orbital energy for Ethylene. $\alpha = 1$, $\beta = -1$. pbc = False

orb_index	Energy [E_h]	Energy [eV]
HOMO	0.0000000	0.000
LUMO	2.0000000	54.423

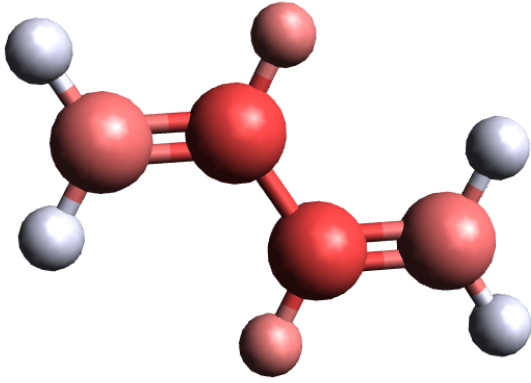


Figure 4: Butadien molecule

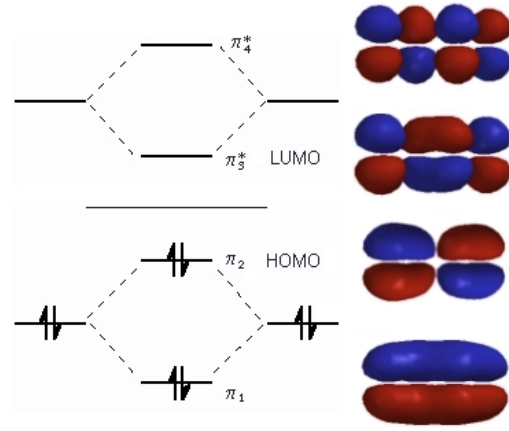


Figure 5: π molecular orbital for Butadien

Table 2: Orbital energy for Butadien. $\alpha = 1$, $\beta = -1$. pbc = False

orb_index	Energy [E_h]	Energy [eV]
1	-0.6180340	-16.818
HOMO	0.3819660	10.394
LUMO	1.6180340	44.029
4	2.6180340	71.240

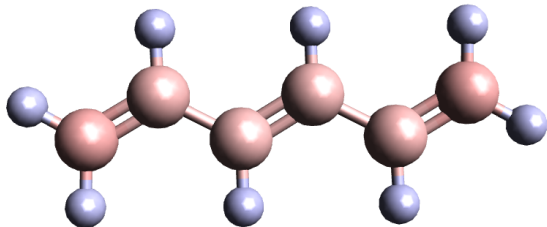


Figure 6: Hexatriene molecule

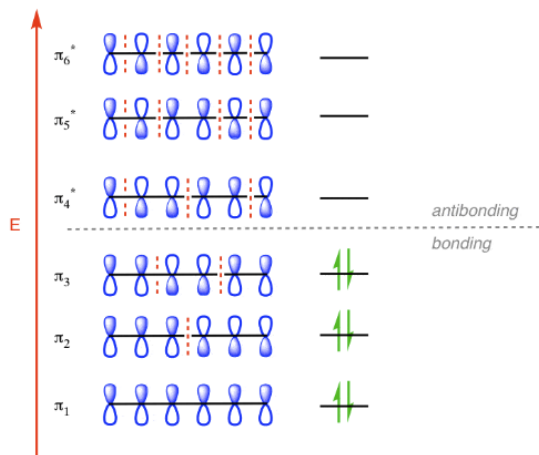


Figure 7: π molecular orbital for Hexatriene

Table 3: Orbital energy for Hexatriene $\alpha = 1$, $\beta = -1$. pbc = False

orb_index	Energy [E_h]	Energy [eV]
1	-0.8019377	-21.822
2	-0.2469796	-6.721
HOMO	0.5549581	15.101
LUMO	1.4450419	39.322
5	2.2469796	61.143
6	2.8019377	76.245

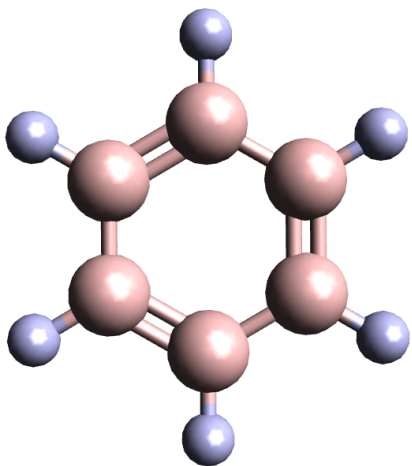


Figure 8: Benzene molecule

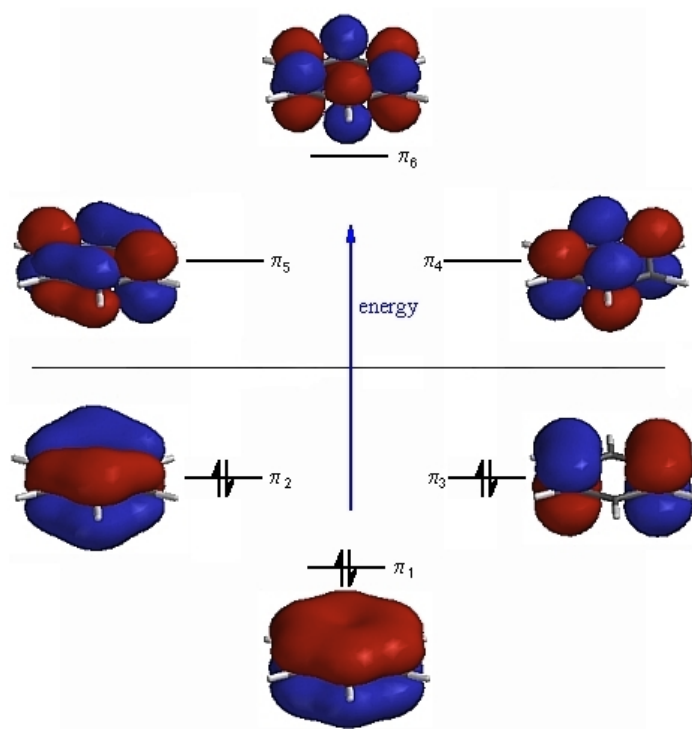


Figure 9: π molecular orbital for Benzene

Table 4: Orbital energy for Benzene. $\alpha = 1$, $\beta = -1$. pbc = True

orb_index	Energy [E_h]	Energy [eV]
1	-1.0000000	-27.211
2	0.0000000	0.000
HOMO	0.0000000	0.000
LUMO	2.0000000	54.423
5	2.0000000	54.423
6	3.0000000	81.634

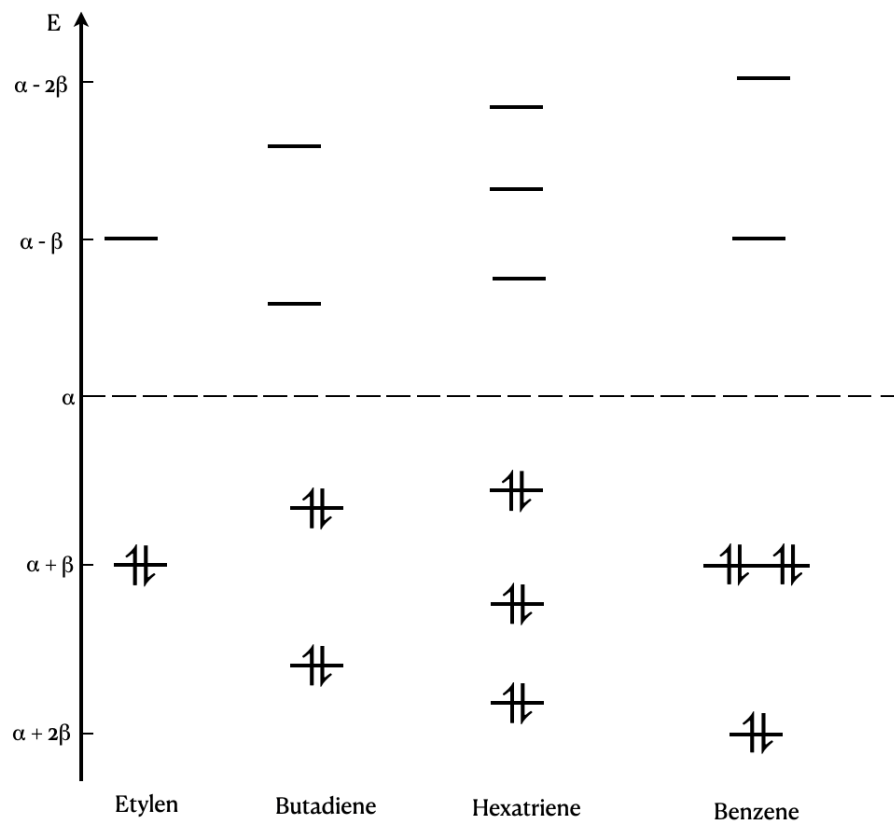


Figure 10: This is a caption for the figure.

6.1 cheking the results for Hartree-Fock (HF) with cc-pvdz basis

Benzene

Table 5: Orbital energy for Hartree-Fock (HF) with cc-pvdz basis. $\alpha = 1$, $\beta = -1$. pbc = True

orb_index	Energy [E_h]	Energy [eV]
17	-0.5010284	-13.634
20	-0.3346697	-9.107
HOMO	-0.3346458	-9.106
LUMO	0.1379622	3.754
23	0.1379962	3.755
30	0.3525805	9.594

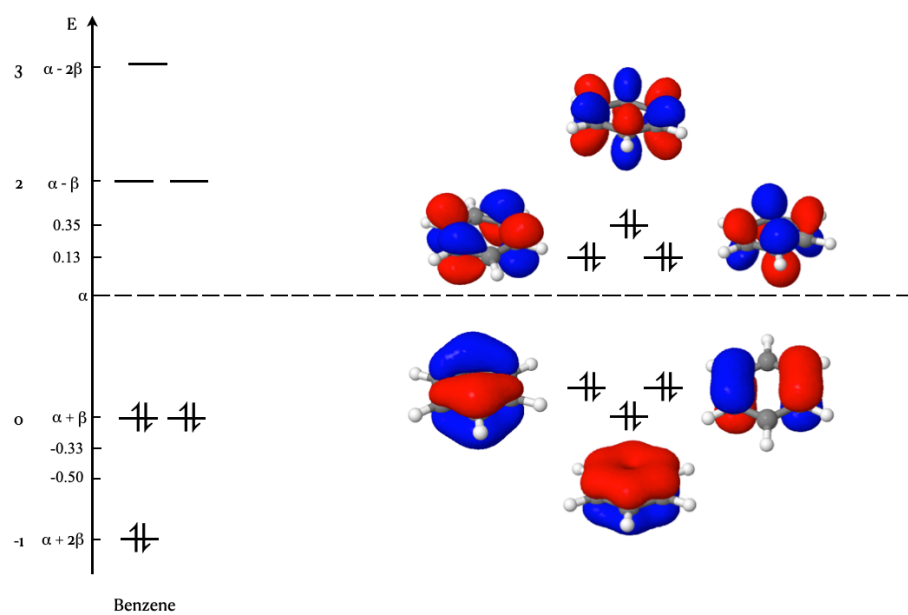


Figure 11: The result obtained by jmol