

Cyclopentadienyl System: Solving the Secular Determinant, π Energy, Delocalization Energy, Wave Functions, Electron Density and Charge Density

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ABSTRACT

In this study, characteristics of Hückel strategy, were abused to acquire some significant outcomes, through a theoretical technique with which it is conceivable to get secular equations, π energy, wave functions, electron density and charge density, as an account of cyclopentadienyl system i.e. $C_5H_5^+$ (cation), $C_5H_5^-$ (anion), and $C_5H_5^\cdot$ (radical) and permitting the expression of delocalization energy of conjugated cyclopentadienyl ring framework. Here, it was presented the secular determinant of the Hückel technique and applied to cyclopentadienyl system framework so as to communicate their orbital energies of cyclopentadienyl system, also to communicate its electron and charge density in terms of stable configuration of a system. It is settled by the Hückel strategy and applied by the assumptions for nearby comparability such as coulomb integrals, exchange integrals and overlap integrals. This simple way hypothetical strategy will allow to graduate and post graduate understudies to understanding the investigation of stable configuration, electron and charge density and also other parameters.

1. Introduction

The conjugated aromatic cyclic molecules such as benzene, cyclobutene, cyclopentadiene, naphthalene, etc. were investigated by Hückel in 1931 (Puri, Sharma, Pathania & Kaur, 2009). This method further extended by C. Coulson, H. C. Longuet Higgins and R. Hoffmann (Puri, Sharma, Pathania & Kaur, 2009). In the fully conjugated system, there is present of alternate double bonds, the molecule considers as planer. In the n^{th} number of carbon atoms in a molecule, shows sp^2 hybridization (planer), $2p_z$ orbital involved in the hybridization, sigma bond is formed when an axial overlapping between the half-filled atomic orbitals and pi bond is formed by the lateral or side wise overlapping of a half-filled atomic orbitals. Here each $2p_z$ orbital is perpendicular to the molecular plane. According to the linear combination of molecular orbital approximation (Puri, Sharma, Pathania & Kaur, 2009) (LCAO), the wave function of molecular orbital is written as

$$\Psi_i = \sum_{j=1}^n C_{ij} \Phi_j$$

Where, $\Phi_j = 2p_z$ orbital of j^{th} carbon atoms.

n = number of molecular orbitals.

C_{ij} = coefficients of i and j values

$i = 1, 2, 3, \dots, n$

The Hückel molecular orbital theory of conjugate cyclic molecules is similar to the molecular orbital theory of homonuclear diatomic (Freeman, Tilley, Liable-Sands & Rheingold, 1996). In the Hückel molecular orbital theory (Freeman, 1980; Yates, 2012), the basic functions are $2p_z$ atomic orbitals, whereas in the H_2 the basic functions are of the $1s$ atomic orbitals. Hückel made the following assumptions as, Coulomb integral, exchange integral and overlap integral (Puri, Sharma, Pathania & Kaur, 2009). All overlap integrals are zero, coulomb integral (α), refers to the energy of an electron in the $2p_z$ orbital on the i^{th} carbon atom. The exchange or resonance integral represents the energy of interaction of two atomic orbitals. Additional information regarding the Hückel molecular orbital theory is given in an elsewhere (Puri, Sharma, Pathania & Kaur, 2009). To be aromatic, a molecule must be cyclic and planer and it must have cyclic electron cloud π , it must satisfy

Hückel rule ($4n+2$) π electrons. However, the number of p orbitals participating in the pi system does not necessarily have to be equal to the number of pi electrons (Slee & Macdougall, 2019). Therefore, anions, cations, and radicals can also be aromatic and the Hückel rule can also be applied accordingly.

Cyclopentadienyl cation is formed from cyclopentadiene as shown in Figure 5, when the hydride anion is removed from sp^3 hybridised carbon atom (Jadhav, 2018) in the ring framework, to achieved sp^2 carbon atom, so the cyclic cyclopentadienyl cation (Chalyavi *et al.*, 2013) is planar and a cyclic π electron cloud as shown in Figure 2. However, it does not obey Hückel rule (4π) electrons. Therefore, it is antiaromatic.

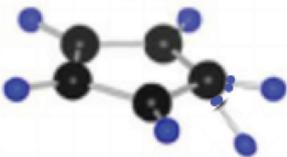


Figure 1: Cyclopentadiene.

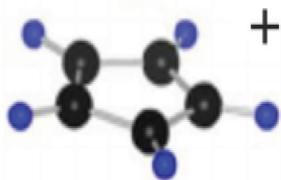


Figure 2: Cyclopentadienyl cation $[C_5H_5]^+$.

The abstraction of a hydrogen atom from the carbon of the sp^3 hybrid ring produces the cyclopentadienyl radical as shown in Figure 5. The carbon hybridisation is transformed into sp^2 . Like the cyclopentadienyl cation, the cyclopentadienyl radical does not conform to Hückel rule, since it has five π electrons. Therefore, it is not aromatic.

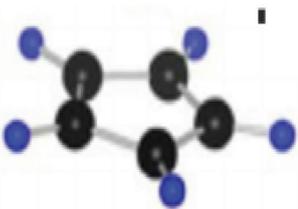


Figure 3: Cyclopentadienyl radical $[C_5H_5]$.

The abstraction of a proton from the sp^3 hybrid carbon (Jadhav, 2018) ring produces the cyclopentadienyl anion (Breton, 1997) as shown as Figure 5. The carbon hybridisation also changed in sp^2 . The cyclic cyclopentadienyl anion is planer, has cyclic π electron cloud and complies with Hückel rule. Therefore, cyclopentadienyl anion is a relatively stable aromatic species³. Consequently, unlike the cyclopentadienyl and radical cation, it can be easily obtained through the basis treatment. The cyclopentadienyl cation and the radical are remarkably unstable and reactive species.

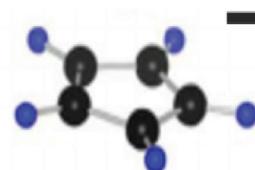


Figure 4. Cyclopentadienyl anion $[C_5H_5]^-$.

In modern computation (Litofsky & Viswanathan, 2015; Slee & Macdougall, 1988) all the resonance integrals and overlap would be included but an indication of the molecule parameters can be obtained with the help of Hückel approximation. The difficulties arising from the severe assumptions of Hückel method have been overcome for more sophisticated theories that helpful to understanding the systems parameters (Jadhav *et al.*, 2020) as shapes or geometries, π energies (Atkins & Paula, 2006), delocalization energy electron (Atkins & Paula, 2006; Jadhav *et al.*, 2020) and charge density (Atkins & Paula, 2006) and consequently, to predict the stability of a cyclic molecular system (Puri, Sharma, Pathania & Kaur, 2009; Jadhav *et al.*, 2020).

2. Theoretical Method

2.1. Formation of Cyclopentadiene System

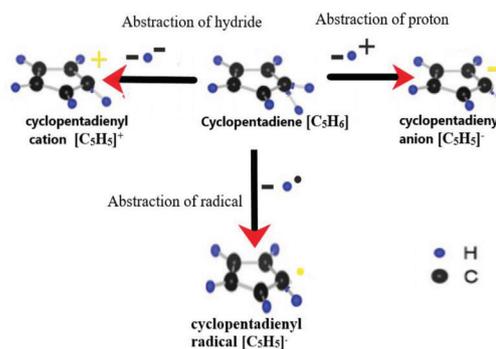


Figure 5. Cyclopentadienyl system i.e. formation of cation, anion and radical species.

2.2. Secular determinant for cyclopentadienyl system

$C_5H_5^+$ (cation), $C_5H_5^-$ (anion), and $C_5H_5^\cdot$ (radical). The number of carbon atoms is the same in three system, so the secular determinant is unchanged.

$$\begin{vmatrix} x & 1 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

2.3. Secular Equation: (unchanged for the system)

Consider, the carbon atom (C_1), It is next to atoms C_5 and C_2 , then the corresponding secular equation is:

$$XC_1 + C_2 + C_5 = 0$$

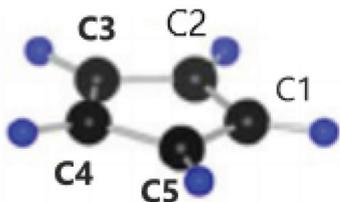


Figure 6. cyclopentadienyl system (Indicated the position of carbon atoms).

- Each secular equation includes 3 non-zero terms.
- All the five secular equations have the same molecular structure, and they can be obtained from each other by permuting the indices.
- It can be solved by using trigonometric functions.
- The trigonometric solutions can be represented by a simple geometric construction i.e. Circle method.

Similarly, for C_2 , C_3 , C_4 and C_5 the secular equation as follows,

$$C_1 + XC_2 + C_3 = 0, C_2 + XC_3 + C_4 = 0,$$

$$C_3 + XC_4 + C_5 = 0, C_1 + C_4 + XC_5 = 0$$

2.4. X values: (Unchanged for the system)

The X values can be obtained by solving the secular determinant, $X_1 = -2.000$, $X_2 = -0.618$, $X_3 = -0.618$, $X_4 = 1.618$, $X_5 = 1.618$. Energy levels, $X = \frac{\alpha - E}{\beta}$

2.5. Total π energy

$$E_\pi = \sum n_i E_i = n_1 E_1 + n_2 E_2 + n_3 E_3 + n_4 E_4 + n_5 E_5$$

Where, n_i = number of electrons in the i^{th} energy state. E_i = i^{th} energy equation or value.

2.6. Delocalization energy (DE)

D.E = (π electron energy of the system) – (π electron energy of an equivalent number of isolated double bonds).

An odd number of carbon atoms in a conjugated system then the comparison energy is taken to be that of an equivalent number of isolated double bonds plus alpha for the energy of the odd electron.

2.7. Wave functions

The general wave function equation as,

$$\Psi_i = a_1 P_1 + a_2 P_2 + a_3 P_3 + a_4 P_4 + a_5 P_5$$

Solving the wave functions for the cyclopentadienyl system in terms of coefficients (a) by using the normalized and orthogonalized condition as

$$\int \psi_i \Psi_j dX = 1 \text{ ----- (i = j, normalized condition)}$$

$$\int \psi_i \Psi_j dX = 0 \text{ ----- (i \neq j, orthogonalized condition)}$$

The wave function for the system as,

$$\Psi_1 = \frac{1}{\sqrt{5}} (P_1 + P_2 + P_3 + P_4 + P_5)$$

$$\Psi_2 = -0.51 P_1 + 0.63 P_2 - 0.51 P_3 + 0.20 P_4 + 0.20 P_5$$

$$\Psi_3 = -0.3717 P_1 + 0.3717 P_3 + 0.6015 P_4 + 0.6015 P_5$$

$$\Psi_4 = -0.21 P_1 - 0.63 P_2 - 0.20 P_3 + 0.51 P_4 + 0.51 P_5$$

$$\Psi_5 = 0.6015 P_1 - 0.6015 P_3 + 0.3717 P_4 + 0.3717 P_5$$

2.8. Electron Density

The total electron density at an atom r is defined as the sum of electron densities contributed by different electrons in each HMO as,

$$\text{Electron Density } (q_r) = \sum n_i a_i^2$$

Where, a_i is the coefficients of the atom r in the i^{th} HMO and n_i is the number of electrons in that HMO. (values of $n = 0, 1, \text{ or } 2$).

2.9. Charge Density

In the π system, a neutral carbon is associated with an electron density of 1.0 and so the net charge density is defined by the equation, Charge density = $1 - q_r$

3. Results and Discussion

In a conjugated cyclic system, the π electrons are delocalized over the entire cyclic system and even the single bonds part takes of the double bond character, even at only presence of delocalized electrons in a system. The molecular parameters as follows which is solved by using Hückel approximation theory,

3.1. Total π energy

- **[C₅H₅]⁺ cation:**

$$E_{\pi} = 2(\alpha + 2\beta) + 2(\alpha + 0.618\beta) \\ = 4\alpha + 5.296\beta$$

- **[C₅H₅] Radical:**

$$E_{\pi} = 2(\alpha + 2\beta) + 3(\alpha + 0.618\beta) \\ = 5\alpha + 5.854\beta$$

- **[C₅H₅]⁻ anion:**

$$E_{\pi} = 2(\alpha + 2\beta) + 4(\alpha + 0.618\beta) \\ = 6\alpha + 6.472\beta$$

According to the value of total π energy of a system in which anion species shows high energy indicates more stability.

3.2. Delocalization energy (DE)

- **[C₅H₅]⁺ cation:**

$$E_{DE} = 4\alpha + 5.296\beta - \{2(\alpha + \beta) + 2(\alpha + 0.618\beta)\} \\ = 2\beta$$

- **[C₅H₅] Radical:**

$$E_{DE} = 4\alpha + 5.854\beta - \{2(\alpha + \beta) + 3(\alpha + 0.618\beta)\} = 2\beta$$

- **[C₅H₅]⁻ anion:**

$$E_{DE} = 6\alpha + 6.472\beta - \{2(\alpha + \beta) + 4(\alpha + 0.618\beta)\} = 2\beta$$

The delocalization energy of a cyclopentadienyl system remains unchanged.

3.3. Electron and charge density

- **[C₅H₅]⁺ cation:**

Electron Density (q_r),

$$\text{at } C_1, q_r = n_1 a_1^2 + n_2 a_2^2$$

$$= 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 + 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 = 0.800$$

$$\text{at } C_2, q_r = n_1 a_1^2 + n_2 a_2^2$$

$$= 2 \times (-0.51)^2 + 2 \times (0.63)^2 = 1.314$$

$$\text{at } C_3, q_r = n_1 a_1^2 + n_2 a_2^2$$

$$= 2 \times (-0.3717)^2 + 2 \times (0.3717)^2 = 0.552$$

$$\text{at } C_4, q_r = n_1 a_1^2 + n_2 a_2^2$$

$$= 2 \times (-0.21)^2 + 2 \times (-0.63)^2 = 0.8820$$

$$\text{at } C_5, q_r = n_1 a_1^2 + n_2 a_2^2$$

$$= 2 \times (0.6015)^2 + 2 \times (-0.6015)^2 = 1.447$$

$$\text{Charge density} = 1 - q_r$$

$$\text{At, } C_1 = 0.200, C_2 = -0.314, C_3 = 0.4474,$$

$$C_4 = 0.118, C_5 = -0.4472$$

- **[C₅H₅] Radical:**

Electron Density (q_r),

$$\text{at } C_1, q_r = n_1 a_1^2 + n_2 a_2^2$$

$$= 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 + 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 + 1 \times \left(\frac{1}{\sqrt{5}}\right)^2$$

$$= 1.000$$

$$\text{at } C_2, q_r = n_1 a_1^2 + n_2 a_2^2 + n_3 a_3^2$$

$$= 2 \times (-0.51)^2 + 2 \times (0.63)^2 + 1 \times (-0.51)^2$$

$$= 1.5741$$

$$\text{at } C_3, q_r = n_1 a_1^2 + n_2 a_2^2 + n_3 a_3^2$$

$$= 2 \times (-0.3717)^2 + 2 \times (0.3717)^2 + (0.6015)^2$$

$$= 0.9144$$

$$\text{at } C_4, q_r = n_1 a_1^2 + n_2 a_2^2 + n_3 a_3^2$$

$$= 2 \times (-0.21)^2 + 2 \times (-0.63)^2 + 1 \times (-0.20)^2$$

$$= 0.922$$

$$\text{at } C_5, q_r = n_1 a_1^2 + n_2 a_2^2 + n_3 a_3^2$$

$$= 2 \times (0.6015)^2 + 2 \times (0.6015)^2 + (0.3717)^2$$

$$= 1.585$$

$$\text{Charge density} = 1 - q_r$$

$$\text{At, } C_1 = 0.00, C_2 = -0.5741, C_3 = 0.0856,$$

$$C_4 = 0.078, C_5 = -0.5853$$

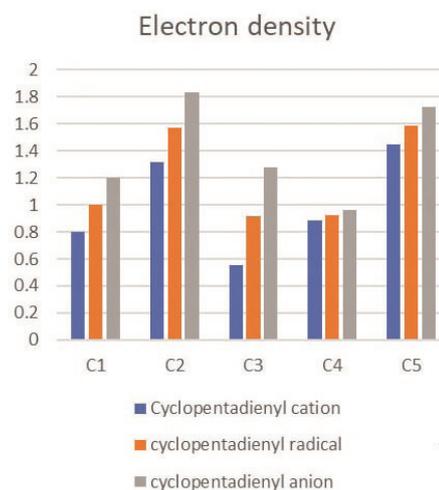


Figure 7: Graphical method of electron density for cyclopentadienyl system.

• $[C_5H_5]^-$ (Anion):

Electron Density (q_r)

$$\begin{aligned} \text{at } C_1, q_r &= n_1a_1^2 + n_2a_2^2 \\ &= 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 + 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 + 2 \times \left(\frac{1}{\sqrt{5}}\right)^2 \\ &= 1.200 \end{aligned}$$

$$\begin{aligned} \text{at } C_2, q_r &= n_1a_1^2 + n_2a_2^2 + n_3a_3^2 \\ &= 2(-0.51)^2 + 2(0.63)^2 + 2(-0.51)^2 \\ &= 1.834 \end{aligned}$$

$$\begin{aligned} \text{at } C_3, q_r &= n_1a_1^2 + n_2a_2^2 + n_3a_3^2 \\ &= 2(-0.3717)^2 + 2(0.3717)^2 + 2(0.601)^2 \\ &= 1.276 \end{aligned}$$

$$\begin{aligned} \text{at } C_4, q_r &= n_1a_1^2 + n_2a_2^2 + n_3a_3^2 \\ &= 2(-0.21)^2 + 2(-0.63)^2 + 2(-0.20)^2 \\ &= 0.962 \end{aligned}$$

$$\begin{aligned} \text{at } C_5, q_r &= n_1a_1^2 + n_2a_2^2 + n_3a_3^2 \\ &= 2(0.6015)^2 + 2(0.6015)^2 + 2(0.3717)^2 \\ &= 1.723 \end{aligned}$$

Charge density = $1 - q_r$

$$\text{At, } C_1 = -0.200, C_2 = -0.8342, C_3 = -0.2762,$$

$$C_4 = 0.038, C_5 = -0.7235$$

Conclusion

This study has obtained theoretical results on the cyclopentadienyl system i.e. $C_5H_5^+$, $C_5H_5^-$ and $C_5H_5^\cdot$. Which gives the same delocalization energy (2β) in terms of a system, the pi energy of a system is different, its shows that cyclopentadienyl anion is more stable, the stability trend as, $C_5H_5^+$ (cation, antiaromatic) < $C_5H_5^\cdot$ (radical, nonaromatic) < $C_5H_5^-$ (anion, aromatic). It also shows that the electron and charge density can yield electronic properties, the graphical method as shown in Figure 7, indicates that high electron density of cyclopentadienyl anion at each carbon atom, it is representation of the probability of finding electron more around the carbon atoms. Consequently, students easily get idea about the molecular parameters of the cyclopentadienyl system.

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