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Theoretical Approach to Understanding an Electron Density, Charge Density and Most Stable Configuration of H_3 System

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ABSTRACT

Secular determinant for the Hydrogen system i.e. H_3^+ (Cation), $H_3^{\cdot}$ (Radical) And H_3^- (Anion) are reported, as mentioned by the quantum theory particularly in the Hückel theory approximations of atoms in molecules. An interesting feature of the electron density and charge density is that they differ considerably from expectations based on simple orbital models. This paper has mentioned theoretical concept to understanding the secular equation, energy equations, total ∏ energy, delocalization energy, wave functions, electron density, charge density and most stable configuration of the triatomic hydrogen systems such as H_3^+ (Cation), $H_3^{\cdot}$ (Radical) And H_3^- (Anion). Specifically, graduate and post graduate students has been faced difficulties, it will be helpful to quick understanding the systems parameters.

Keywords: Charge density, Electron density, Hückel theory, Secular equation, Triatomic hydrogen.

INTRODUCTION

Hückel theory is completely based on variation principle; an important assumption is based on ∏ electron system i.e. conjugated molecules[3], in which there is an alternation of single and double bonds or delocalization of electrons along a chain of atoms. The ∏ molecular orbital energy level diagrams of conjugated molecules can be constructed using a set of approximations which is suggested by Erich Hückel in 1931[6, 8.] The ∏ orbitals treated separately sigma orbitals can form a rigid framework that determine the geometries of the molecule[5]. All the hydrogen atoms treated identically in the triatomic hydrogen system, so all coulomb integrals α for the atomic orbitals that contribute to the ∏ orbitals are set equal. In modern computation 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[1] i.e. all overlap integrals are set equal to zero, all resonance integrals between non-neighbours are set equal to zero and all remaining resonance integrals are set equal (β). The assumptions result in the following structure of the secular determinant[8] i.e. all diagonal elements (α – E), off-diagonal elements between neighbouring atoms (β) and all other element (0), the secular determinant[2,7], secular equation[7], roots (X) values and energy values as shown as in the table-1 which is obtained by using Hückel approximation assumptions. The difficulties arising from the severe assumptions of Hückel method have been overcome for more sophisticated theories that not only calculate the shapes or geometries and energies of molecular orbitals but also predict with reasonable accuracy in the structure and reactivity of a molecules. The development of computational techniques such as the Hartree-Fock method[8], Semi - empirical[8] and ab initio methods[10] and Density functional theory[10] for the elucidation of molecular structure and reactivity[8].

THEORETICAL METHODS

Using Hückel Molecular Orbital theory[4] we can calculate the charge density as well as electron density of an atom and also the most stable structure or geometry of the H_3 system. The H_3 system consists of H_3^+ (Cation), $H_3^{\cdot}$ (Radical) and H_3^- (Anion), the cation, radical and anion contains two, three and four electrons respectively. Strictly speaking, we can not solve the problems with the Hückel approximation[9] since the electrons which hold the three molecular species together are not ∏ electrons. However, if we assume that the electrons are delocalized over the entire nuclear framework in the triatomic hydrogen system, which is reasonable assumptions then the system is amenable to Hückel treatment[10]. The most stable geometrical structure[11] can be triangular (Cation), triangular (radical) and linear (anion) of the H_3 system as shown in figure-1.

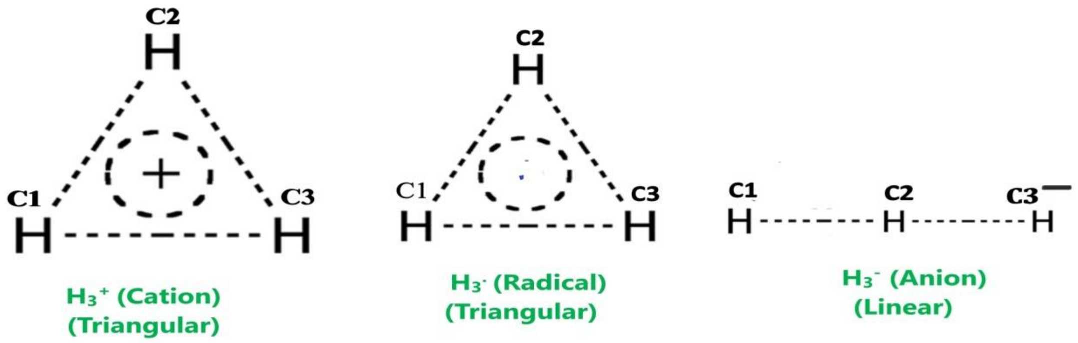


Fig. 1: H_3 system such as H_3^+ (Cation), $H_3^{\cdot}$ (Radical) And H_3^- (Anion) and their most stable structure and geometries

The secular determinant, secular equation, roots (X) values and energy levels of the H_3 system has shown in the given table -1.

Table-1: H_3 system parameters

System	*Secular Determinant*	*Secular Equation*	*'X' Values*	*Energy levels,* $X = \frac{\alpha - E}{\beta}$
H_3^+ (Cation) (Triangular)	$\begin{bmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{bmatrix}=0$	$XC_1 + C_2 + C_3 = 0$ $C_1 + XC_2 + C_3 = 0$ $C_1 + C_2 + XC_3 = 0$	X = -2 X= 1, 1	$E_1 = \alpha + 2\beta$ $E_2 = \alpha - \beta$ $E_3 = \alpha - \beta$
$H_3^{\cdot}$ (Radical) (Triangular)	$\begin{bmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{bmatrix}=0$	$XC_1 + C_2 + C_3 = 0$ $C_1 + XC_2 + C_3 = 0$ $C_1 + C_2 + XC_3 = 0$	X = -2 X = 1, 1	$E_1 = \alpha + 2\beta$ $E_2 = \alpha - \beta$ $E_3 = \alpha - \beta$
H_3^- (Anion) (Linear)	$\begin{bmatrix} x & 1 & o \\ 1 & x & 1 \\ 0 & 1 & x \end{bmatrix}=0$	$C_1X + C_2 = o$ $C_1 + C_2X + C_3 = o$ $C_2 + C_3X = o$	$X = \sqrt{2}$ X = 0 $X = -\sqrt{2}$	$E_1 = \alpha + \sqrt{2}\beta$ $E_2 = \alpha$ $E_3 = \alpha - \sqrt{2}\beta$

❖ *H_3^+ (Cation): Triangular configuration*

- Total Hückel energy = $E_{\prod +} = 2\alpha + 4\beta$
- Delocalization energy = 2β
- Wave functions:

$\Psi_1 = \frac{1}{\sqrt{3}} P_1 + \frac{1}{\sqrt{3}} P_2 + \frac{1}{\sqrt{3}} P_3$

$\Psi_2 = \frac{1}{\sqrt{2}} P_1 - \frac{1}{\sqrt{2}} P_3$

$\Psi_3 = \frac{1}{\sqrt{6}} P_1 - 2 \text{ x } \frac{1}{\sqrt{6}} P_2 + \frac{1}{\sqrt{6}} P_3$

❖ *$H_3^{\cdot}$ (Radical): Triangular configuration*

- Total Hückel energy = $E_{\prod \cdot} = 3\alpha + 3\beta$
- Delocalization energy = β
- Wave functions:

$\Psi_1 = \frac{1}{\sqrt{3}} P_1 + \frac{1}{\sqrt{3}} P_2 + \frac{1}{\sqrt{3}} P_3$

$\Psi_2 = \frac{1}{\sqrt{2}} P_1 - \frac{1}{\sqrt{2}} P_3$

$\Psi_3 = \frac{1}{\sqrt{6}} P_1 - 2 \text{ x } \frac{1}{\sqrt{6}} P_2 + \frac{1}{\sqrt{6}} P_3$

❖ *H_3^- (Anion): Linear configuration*

- Total Hückel energy = $E_{\prod}^{-} = 4\alpha + 2\sqrt{2}\beta$
- Delocalization energy = $2\beta(\sqrt{2} - 1)$
- Wave functions:

$\Psi_1 = \frac{1}{2}P_1 + \frac{1}{\sqrt{2}}P_2 + \frac{1}{2}P_3$

$\Psi_2 = \frac{1}{\sqrt{2}}P_1 - \frac{1}{\sqrt{2}}P_3$

$\Psi_3 = \frac{1}{2}P_1 - \frac{1}{\sqrt{2}}P_2 + \frac{1}{2}P_3$

RESULT AND DISCUSSION

In a conjugated system the $\prod$ electrons are delocalized over the entire molecule and even the single bonds part take of the double bond character, even at only presence of delocalized electrons in a system, the electron density at a given atom, the bond order between a pair of atoms and the residual valence at each atom, such concept has introduced in the Hückel molecular orbital theory. The most stable Huckel energy equations of the H_3 system as $E_{\prod+} = 2\alpha + 4\beta$ (cation), $E_{\prod}^{\cdot} = 3\alpha + 3\beta$ (radical), $E_{\prod}^{-} = 4\alpha + 2\sqrt{2}\beta$ (anion) shows triangular in both H_3^+ (Cation) and $H_3^{\cdot}$ (Radical) And linear in H_3^- (Anion) cases are the most stable configuration.

Here shown in below the electron density as well as charge density of each atom in the H_3 system.

Electron Density (q_r) = $\varepsilon\, n_i a_i^2$

Where, n_i = number of electrons at i^{th} terms energy state,

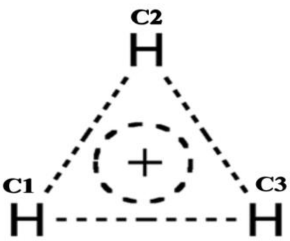
a_i = constant terms obtaining from wave functions, shown in the above wave function equations. $\{\Psi_i = a_1P_1 + a_2P_2 + a_3P_3\}$

Charge density = 1-q_r

Where, q_r = electron density

Calculate on each atom of the triatomic system

❖ *H_3^+ (Cation):*



H_3^+ (Cation)

Electron Density (q_r),

at C_1, $q_r = n_1a_1^2 + n_2a_2^2 + n_3a_3^2$

$= 2 \text{ x } (\frac{1}{\sqrt{3}})^2 + 0 \text{ x } (\frac{1}{\sqrt{3}})^2 + 0 \text{ x } (\frac{1}{\sqrt{3}})^2$

= 0.6666

at C_2, $q_r = n_1a_1^2 + n_2a_2^2$

$= 2 \text{ x } (\frac{1}{\sqrt{2}})^2 + 0 \text{ x } (-\frac{1}{\sqrt{2}})^2$

= 1.000

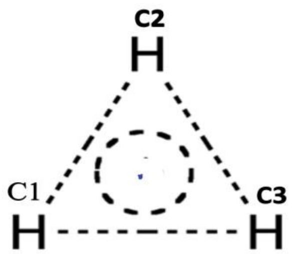
at C_3, $q_r = 2 \text{ x } (\frac{1}{\sqrt{6}})^2 + 0 \text{ x } (-2 \text{ x } \frac{1}{\sqrt{6}})^2 + 0 \text{ x } (\frac{1}{\sqrt{6}})^2$

= 0.3333

Charge density = 1- q_r

At C_1 = 0.3334, C_2 = 0 and C_3 = 0.6667

❖ *$H_3^{\cdot}$ (Radical):*



$H_3^{\cdot}$ (Radical)

Electron Density (q_r),

at C_1, $q_r = n_1a_1^2 + n_2a_2^2 + n_3a_3^2$

$= 2 \text{ x } (\frac{1}{\sqrt{3}})^2 + 1 \text{ x } (\frac{1}{\sqrt{3}})^2 + 0 \text{ x } (\frac{1}{\sqrt{3}})^2$

= 1.000

at C_2, $q_r = n_1a_1^2 + n_2a_2^2 + n_3a_3^2$

$= 2 \text{ x } (\frac{1}{\sqrt{2}})^2 + 1 \text{ x } (-\frac{1}{\sqrt{2}})^2$

= 1.500

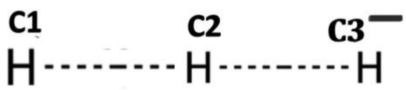
at C_3, $q_r = 2 \text{ x } (\frac{1}{\sqrt{6}})^2 + 1 \text{ x } (2 \text{ x } \frac{1}{\sqrt{6}})^2 + 0 \text{ x } (\frac{1}{\sqrt{6}})^2$

= 1.000

Charge density = 1- q_r

at C_1 = 0, C_2 = - 0.500, C_3 = 0

❖ *H_3^- (Anion):*



H_3^- (Anion)

Electron Density (q_r)

at C_1, $q_r = n_1a_1^2 + n_2a_2^2 + n_3a_3^2$

$= 2 \text{ x } (\frac{1}{2})^2 + 2 \text{ x } (\frac{1}{\sqrt{2}})^2 + 0 \text{ x } (\frac{1}{2})^2$

= 1.500

at C_2, $q_r = n_1a_1^2 + n_2a_2^2$

$= 2 \text{ x } (\frac{1}{\sqrt{2}})^2 + 2 \text{ x } (-\frac{1}{\sqrt{2}})^2$

$= 2.000$
at C_3, $q_r = n_1a_1^2 + n_2a_2^2 + n_3a_3^2$
$= 2 \times (\frac{1}{2})^2 + 2 \times (-\frac{1}{\sqrt{2}})^2 + 0 \times (\frac{1}{2})^2$
$= 1.500$
Charge density $= 1 - q_r$
at $C_1 = -0.500$, $C_2 = -1.00$, $C_3 = -0.500$

CONCLUSION

The criteria for the stability of the H_3 molecule in the given configuration, should be conclude that the lower energy in the ground state. As per in the ground state energy equations we conclude that both H_3^+ (Cation) and $H_3^{\cdot}$ (Radical) shows triangular configuration and H_3^- (Anion) shows linear configuration are most stable. The electron density in terms of cation (0.666, 1.000 and 0.330), radical (1.000, 1.500 and 1.000), and anion (1.500, 2.000 and 1.500) and the charge density of cation (0.3334, 0.000 and 0.6667), radical (0.000, -0.500 and 0.000), and anion (-0.500, -1.000 and -0.500) have different in the H_3 system.

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