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Conformational and Bonding Analysis of $C_2H_4^{2+}$

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ABSTRACT

In this report, different models of bonding and structure such as Lewis, VSEPR, Ligand close packing (LCP), VB, qualitative MO and QTAIM have been applied to analyze the Bonds and structures of two equilibrium geometries (planar D_{2h} and perpendicular D_{2d}) of $C_2H_4^{2+}$. The geometries were optimized at near RHF and MP2 limit using cc-pVTZ basis set. While the above bonding models are successfully applied for predicting the low energy isomers of molecules, prior to solving the Schrödinger equation, it is shown that the cited models fail in predicting the existence of perpendicular, D_{2d} form of $C_2H_4^{2+}$. In this regard the interpretations of significant energetic stabilization of D_{2d} form over planar isomer has also been revisited. This is attributed to the hidden effect of the Pauli Exclusion principle.

Keywords: $C_2H_4^{2+}$; LCP; Hyperconjugation; QTAIM; Pauli Exclusion Principle

1. Introduction

The earliest work on the potential energy surface (PES) of $C_2H_4^{2+}$ has shown the existence of twisted (D_{2d}) $H_2CCH_2^{2+}$ minimum and planar (D_{2h}) transition state geometries [1]. The remarkably large rotational barrier energy, 28.1 kcal/mol has been described by the Hyperconjugation between two formally vacant orbitals and corresponding vicinal CH_2 group [1]. The substituted ethylene dications have also been extensively studied [2,3] and the results were explained using descriptive tools such as π donation/conjugation, orbital diagrams, lone pairs, steric repulsion and Hyperconjugation. The energy lowering in twisted geometry of ethylene radical cation [4,5] has also been described by the attractive interaction of a p orbital of C atom with the p-like group orbital of adjacent σ bonds [6,7]. We believe that the proposed explanations about the energy lowering in twisted geometry of $C_2H_4^{2+}$ are based on the mixed effects of overlapping, charge separation, Hyperconjugation models. It is the goal of this work to reinvestigate the effect of each of these models on the final geometry of $C_2H_4^{2+}$ individually. In this work the previous computations with small size Pople type basis sets [1,2] have been extended to larger correlation-consistent basis sets.

2. Computational Details

Ab initio computations were performed at both RHF and MP2 methods using cc-pVTZ basis set [8]. PC GAMESS 7.1.5 package [9] running on parallel mode on 5 PCs cluster was used for optimization and frequency calculations. The total electron densities (Rho functions) constructed from wave functions were analyzed, using AIM2000 and MORPHY99 softwares [10-13]. The useful utilities implemented in the ChemCraft program [14] were optimized for handling the outputs of PC GAMESS.

3. Results and Discussion

The resulted *ab initio* geometries and energies of C_2H_4 and $C_2H_4^{2+}$ are gathered in **Figure 1**. Some differences between the results of present computations at MP2 level and those of 6-31G* and 6-31G** [1,2] are discussed first. C-C distances which have been reported previously as 1.317 and 1.587 Å in C_2H_4 and $C_2H_4^{2+}$ (D_{2h}) respectively [1], are 1.332 and 1.603 Å, each are 0.015 Å longer at MP2 level. In contrast, the C-C distance in $C_2H_4^{2+}$ (D_{2d}) shrinks from 1.432 [1] to 1.393 Å, the significant shortening of 0.039 Å. The difference between C-C distances between two $C_2H_4^{2+}$ isomers is reported as 0.21 Å, 0.055 Å longer than previously computed value, *i.e.* 0.155 Å [1]. The energy difference between two isomers is reported as 30.9 kcal/mol at MP2 level, in agreement with previously reported value of 28.1 kcal/mol [1,2]. As depicted in **Figure 1**, two major geometrical changes occur from D_{2h} to D_{2d} form.

1) The perpendicular arrangement of Hydrogen atoms in D_{2d} form,

2) The significant shortening of C-C distances in D_{2d} C-H distances are almost equal between two $C_2H_4^{2+}$ isomers.

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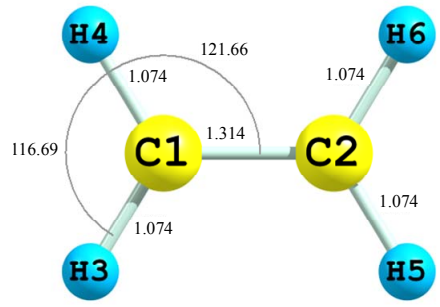
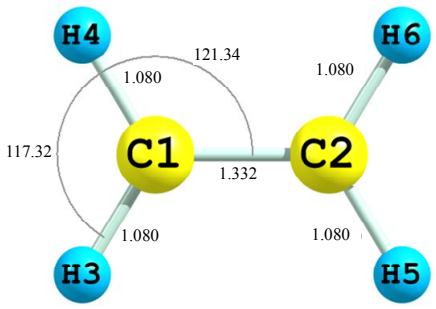
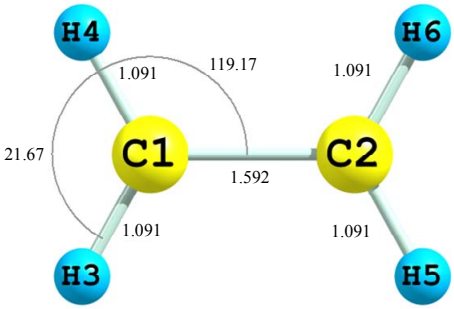


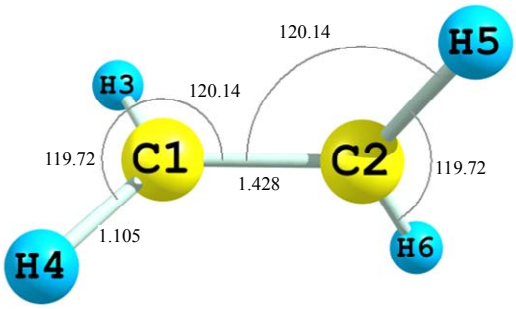
C_2H_4 (D_{2h})
E(RHF): –78.0647728914 *a.u*
H4-H6 = 2.442 Å



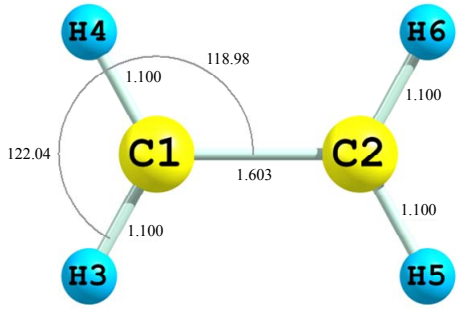
C_2H_4 (D_{2h})
E(MP2): –78.4014122454 *a.u*
H4-H6 = 2.456 Å, H3-H4 = 1.846 Å



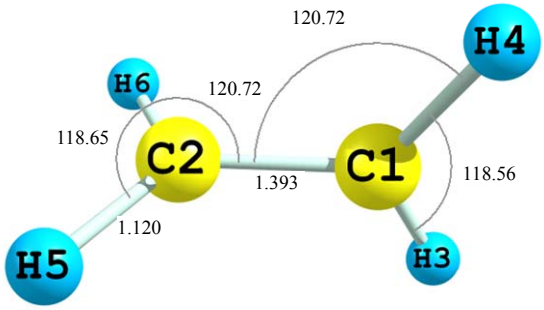
$C_2H_4^{2+}$, Min (D_{2d})
E(RHF): –77.0770048672 *a.u*
H4-H6 = 2.655 Å



$C_2H_4^{2+}$, TS (D_{2d})
E(RHF): –77.1165234897 *a.u*
H4-H6 = 2.537 Å (In Planar Form)



$C_2H_4^{2+}$, Min (D_{2d})
E(MP2): –77.3117689261 *a.u*
H4-H6 = 2.669 Å, H3-H4 = 1.924 Å, H3-H6 = 3.290 Å
U(H6) = a^2(1/2.669 + 1/3.290 + 1/1.924)
U(H6) = 1.198 a^2, V_{NN} = 30.11963 *a.u*



$C_2H_4^{2+}$, TS (D_{2d})
E(MP2): –77.3609539882 *a.u*
H4-H6 = 2.537 Å (In Planar Form), H3-H4 = 1.926 Å, H3-H6 = 2.879 Å
U(H6) = b^2(1/2.879 + 1/2.879 + 1/1.924)
U(H6) = 1.210 b^2, V_{NN} = 32.10244 *a.u*

Figure 1. Geomertical parameters, total energie, germinal and vicinal HH distances in C_2H_4 and $C_2H_4^{2+}$ at RHF/cc-pVTZ and MP2(FC)/cc-pVTZ models. "TS" stands for transition state and "Min" stands for local minimum geometry on PES. U is the electrostatic repulsive potential energy. (a) and (b) are the charges of H atoms in two molecules.

How different chemical models predict or provide the explanation about these geometrical changes is discussed below. Here we start with basic Lewis model.

3.1. Lewis Model

In Lewis model, a planar structure composed of single bonds for $C_2H_4^{2+}$ can be written [15]. The formal charge of each C is +1 and that of H is zero. Simple electrostatic rule predicts that the C-C distances in planar Lewis structure should be longer than 1.5 Å, the normal C-C single bond in saturated hydrocarbons, because of the repulsion between two C atoms; each bears a positive formal charge. In this model the existence of more stable perpendicular form cannot be predicted or described.

3.2. VSEPR

The VSEPR model predicts that the three single bonding pairs around each C atom should adapt the trigonal ar-

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rangement and thus the molecular geometry could be planar [15,16]. However the model is only reliable for predicting the relative geometry around any one central atom and not the relative arrangements of the bonds around two adjacent atoms [16]. Usually the bond-pair bond-pair repulsion and Ligand-Ligand interaction (steric repulsion) effects are added to VSEPR to account for geometrical changes. The internuclear distances depicted in **Figure 1**, show that the vicinal CH bonds repulsion in planar isomer is less than twisted, since they are separated from each other by longer C-C distances. **Figure 1** indicates that in both $C_2H_4^{2+}$ isomers the vecinal HH distances are significantly longer than 2.40 Å (sum of the Van der Waals radia) so steric repulsion between them is negligible and therefore is not responsible for twisting the geometry to D_{2d} form. Therefore VSEPR together with steric repulsion model cannot predict or explain the existence of twisted $C_2H_4^{2+}$.

3.3. Ligand Close-Paking

Empirical Ligand close-packing (LCP) model which is the extension of VSEPR [16], treats ligands as hard sphere objects packed around central atom, *i.e.*, C atom. "Each ligand can be considered to be touching its neighbors and can be assigned a nonbonded radious, which is given by the half the ligand-ligand distance" [16]. The 1,3 nonbonded radius of H atom is 0.92 Å [16]. For example the MP2 geometry of ethylene shows a near perfect close-packing of two H atoms and one CH_2 group around each C atom, since C-C distance is 1.339 and germinal HH distance is 1.846 Å (twice that of their 1,3 nonbonded radius). No steric repulsion exists between two vicinal H atoms too. Close inspection of MP2 geometries of $C_2H_4^{2+}$, **Figure 1**, reveals that the internuclear distances in perpendicular $C_2H_4^{2+}$ is approximately consistent with the LCP model. H3-H4 distance is 1.926 Å and C-C is 1.393 Å. The observed lengthening of Ligand-Ligand distances, in comparison to ethylene, can be assigned to the electrostatic repulsion between positively charged ligands. Still the preferred D_{2d} isomer of $C_2H_4^{2+}$ obtained at MP2 level can not be predicted by LCP model.

3.4. VB, Hyperconjugation and Steric Repulsion

The bond angles about 120.0° around C nuclei, **Figure 1**, in both forms are consistent with the SP^2 hybridization in VB model. Assuming that each C atoms loses one electron, the valence atomic orbitals in C^+ with the electronic configuration as $1s^2\ 2s^2\ 2p^1$, could participate in hybridization process and produce three SP^2 orbitals to overlap with 1s orbitals of H atoms and SP^2 orbital of adjacent Carbon. The existence of twisted isomer is explained by adding hyperconjugation concept to VB. While VB tends to localize electrons between the nuclei, the hyperconjugation tends to delocalize them. The vacant p orbitals, one on each C atom, interact with corresponding vicinal σ bonds in CH_2 [1,6] and therefore lowers the molecular energy. According to our MP2 results this effect (hyperconjugation) should be abnormally strong if it solely responsible for significant lowering in energy (30 kcal/mol) of D_{2d} isomer and corresponding geometrical changes (0.21 Å C-C shortening). This is surprising since the hyperconjugation is a weak effect.

We examined the strength of steric effect which was used to account for the perpendicular arrangement of positively charged Hydrogen atoms [1]. Simple calculation of the electrostatic repulsion energy (U) for each H atom (assuming them as point charges) has been done on MP2 geometries, **Figure 1.** The results demonstrate that if each H atom bears more positive charges on D_{2d} isomer, then each H atom will suffer greater repulsion in comparison to D_{2h} form. If the H atoms bear same charge in two isomers, then D_{2d} form will again suffer from greater repulsion between hydrogen atoms, or at least the same as D_{2h}. In agreement with our simple analysis the V_{NN} (nuclear-nuclear potential energy) value is also greater in D_{2d} form at MP2 level, **Figure 1**.

It is concluded that the energetic and geometric changes cannot be explained based on the weak hyperconjugation or even reduction of steric repulsion between H atoms in D_{2d} isomers.

3.5. Qualitative MO

Analyzing the orbital density [7,17] is other method for tracking the geometrical changes. The densities, of HOMO and HOMO-1 for each isomer of $C_2H_4^{2+}$ are depicted in **Figure 2**. The shape of MOs in D_{2h} form support the VB picture of bonding. The HOMO and HOMO-1 of D_{2d} are degenerate and they are more delocalized than HOMO of D_{2h}. Non of the MOs in D_{2d} show the orbital density between C nuclei, the density which is necessary for accounting the significant shortening of C-C distances in this isomer. More inspection revealed that The HOMO-2 of the D_{2d} shows orbital density between C nuclei. HOMO-2 shape of D_{2d} is the same in shape to HOMO-1 in D_{2h}.

Again we did not find any reasonable explanations for the two major geometrical changes which we mentioned earlier in this work. We suggest that more sophisticated orbital analysis such as Walsh diagrams [18] can be applied to predict the lowest isomer of $C_2H_4^{2+}$.

3.6. The QTAIM

In the framework of QTAIM theory, the total molecular electron density, Rho(ρ) [19], is the source of chemical information about the molecule. The integration of Rho over all space is exactly equal to the total number of electrons in the molecule [7,19].

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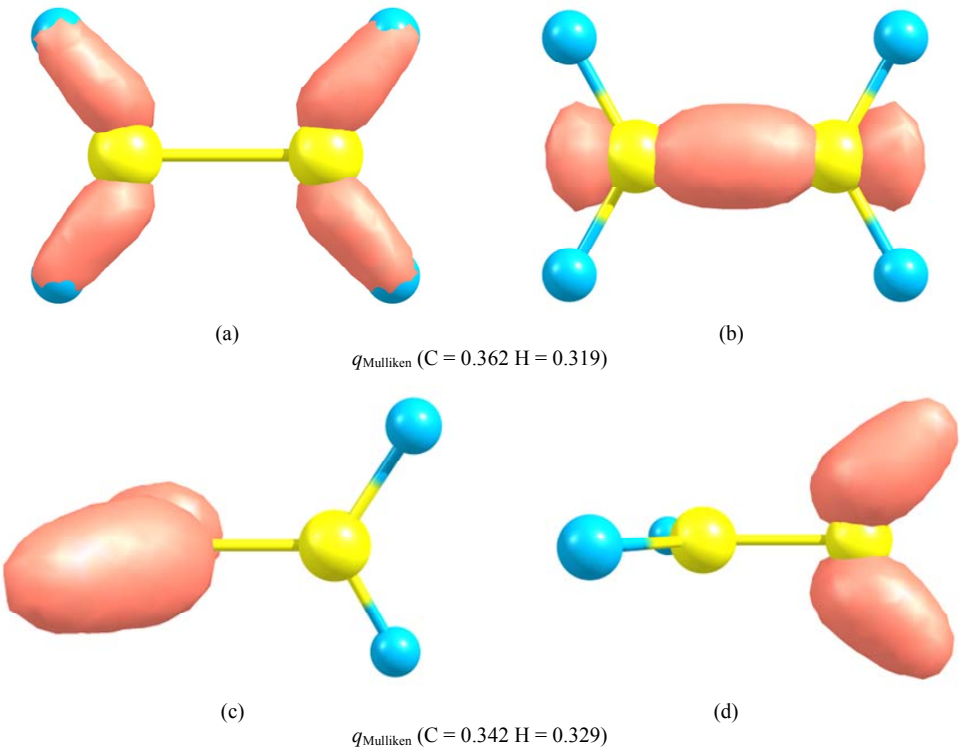

Figure 2. The RHF orbital density (Ψ^2_{MO}) of the HOMO (a, c), HOMO-1 (b, d) and Mulliken atomic charges in planar (a, b) and perpendicular (c, d) forms of $C_2H_4^{2+}$.

We skip the normal topological analysis of electron density at this stage and continue the discussion using the Rho(ρ) values at the geometric midpoint between C-C and C-H in two cited isomers of $C_2H_4^{2+}$.

At MP2 level the ρ values at the chosen points in D_{2h} are 0.232, 0.345 a.u., in D_{2d} are 0.343, 0.316 a.u. respectively. These numbers nicely represent the correct picture of distribution of electronic charge from C-H regions to C-C region when the geometry is changed from D_{2h} to D_{2d}.The accumulation of charge density between C nuclei in twisted form, result in the decrease of positive charge on C atoms and the marked decrease of C-C length [20]. Because of this transferring of negative charge, the H atoms bear more positive charge in D_{2d}. While the ρ between C-C changes by 0.111 a.u. from D_{2h} to D_{2d}, the corresponding value in each CH region is only 0.029 a.u. This explains why C-H distances remain almost the unchanged between two isomers.

Does the ρ provide the explanation for why the D_{2d} isomer is the lowest energy isomer? The quantum theory of atoms in molecules has provided the physical basis for the LCP and VSEPR models based on the arrangement of maxima in the Lapalcian map of ρ around the central atom [21]. Instead of electron pairs, the concept of electron domains is used when using LCP or VSEPR in their new forms [15]. It is expected that at least three maxima be found around each C atom. The maps of Laplacian of electron density for C_2H_4 and $C_2H_4^{2+}$ geometries are depicted in **Figure 3**. The number and the orientation of the maxima around C atoms are the same, 3 maxima in trigonal orientation in all cases, **Figures 3(a1)-(c1)**. The number of domains of charge concentration are also the same, **Figures 3(a3)-(c3)**. The comparison of contour maps of Laplacian among C_2H_4 and two isomers of $C_2H_4^{2+}$, **Figures 3(a)-(c)** show the existence of distinct regions of charge accumulation between C nuclei in C_2H_4. In both $C_2H_4^{2+}$ isomers this region disappears. This is due to the removal of two electrons from the parent molecule (C_2H_4). The Laplacian maps of the two $C_2H_4^{2+}$ isomers are essentially the same. It is not clear yet why $C_2H_4^{2+}$ preferred geometry is the D_{2d} isomer.

Finally we present the full QTAIM analysis [15,19-20, 22], Atomic basin charge and energy values in **Table 1**. The trends of basin charges are the same as what has been predicted by the ρ values at the midpoints of CH and C-Cs. The positive charge of each C basin in D_{2d} is half of the value in D_{2h}. The comparison of atomic charges (**Table 1**) indicates that 0.05 unit of charge is transferred from each H basin to C basins when the geometry is changed from D_{2h} to D_{2d}. The volumes of C basins increase and those of H basins decrease by this charge transfer. Energy analysis demonstrates that each C basin is stabilized by 68.15 kcal/mol but each H basin is destabilized by 26.36 kcal/mol, from D_{2h} to D_{2d} form.

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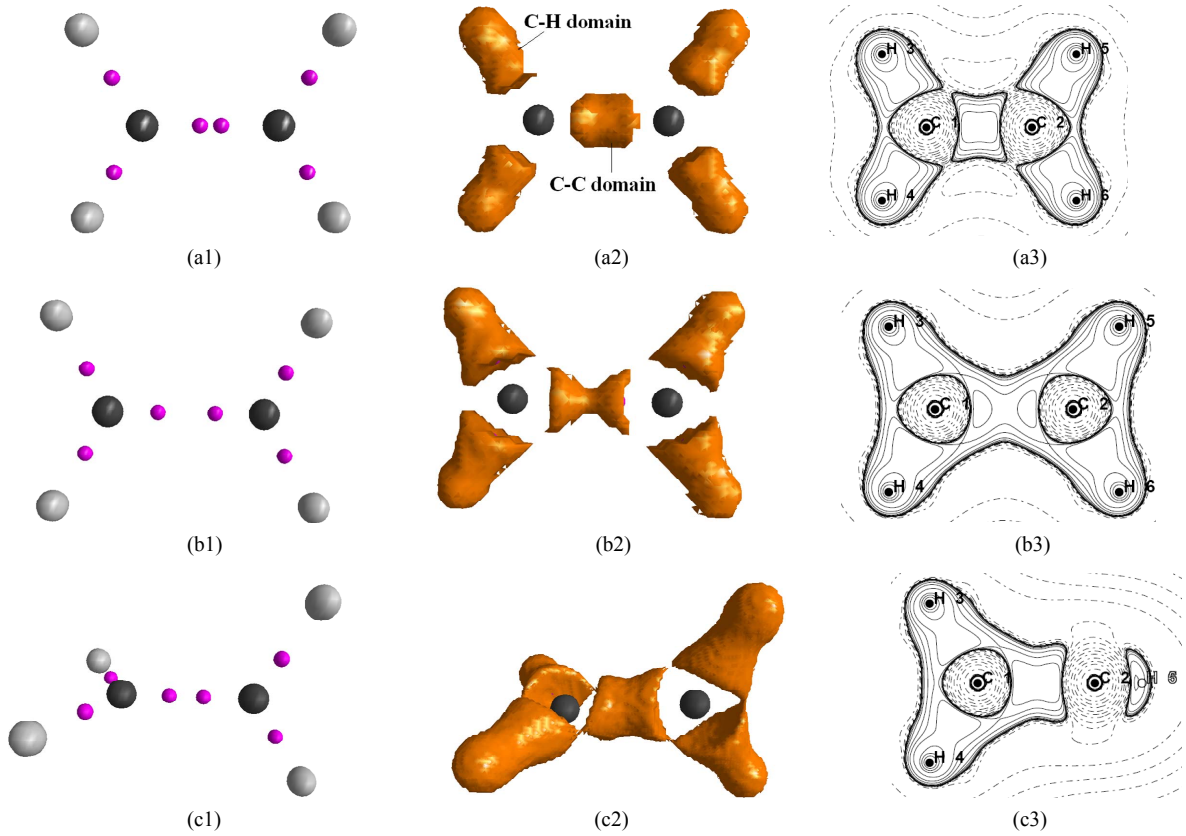

Figure 3. Laplacian maps of C_2H_4 (a), $C_2H_4^{2+}$ planar (b), $C_2H_4^{2+}$ perpendicular (c) at MP2/cc-pVTZ level.Maximum points (small circles) on Laplacian of Rho, (a1)-(c1). 3D pictures of isosurfaces), –0.1 a.u, of charge concentration *i.e.* negative value of Laplacian, (a2)-(c2). Contour plots of Laplacian maps (dash lines = charge depletion, solid line = charge concentration), (a3)-(c3).

Table 1. Atomic properties (in atomic units) from QTAIM analysis at MP2/cc-pVTZ.

	$Q^{\ddagger}$	$E(\Omega)^{**}$	$V(\Omega)^{*}$
$C_2H_4(D_{2h})$			
C1	–0.0650	–37.9776	98.69
C2	–0.0650	–37.9776	
H3	0.0327	–0.6116	48.75
H4	0.0327	–0.6116	
H5	0.0327	–0.6116	
H6	0.0327	–0.6116	
Δ|(*AIM-Ab initio*)|	0.0008	0.2 kcal/mol	
$C_2H_4^{2+}$ (D_{2d})			
C1	0.0954	–37.8837	89.97
C2	0.0954	–37.8837	
H3	0.4523	–0.3984	27.52
H4	0.4523	–0.3984	
H5	0.4523	–0.3984	
H6	0.4523	–0.3984	
Δ|(*AIM-Ab initio*)|	0.0000	0.002 kcal/mol	
$C_2H_4^{2+}$ (D_{2h})			
C1	0.2012	–37.7751	88.13
C2	0.2012	–37.7751	
H3	0.3994	–0.4404	29.01
H4	0.3994	–0.4404	
H5	0.3994	–0.4404	
H6	0.3994	–0.4404	
Δ|(*AIM-Ab initio*)|	0.0002	0.1 kcal/mol	

‡Total atomic charge (a.u); **Total atomic energy (a.u) which is calculated by integrating over atomic basin (Ω); *Atomic volume bounded by rho contour surface of 0.001 a.u.

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4. Conclusion

In 1954 Lennard-Jones published the paper, the distribution functions of neutral fermionic particles with same spin moving in the closed ring and Surface of sphere [23]. The orientation of maxima of probability of finding the particles on the ring or sphere, were demonstrated mathematically as 180˚ for two particles, 120˚ for three particles and tetrahedral arrangement for four particles moving on the surface of sphere. The paper has been written to show the net effect of PEP in distributing the electrons in confined region of space. Adding the presented discussion (Failure of different models) it seems that the molecular geometry is controlled by hidden effect of Pauli Exclusion Principle, PEP [21] which is imposed to the wave function.

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