JOURNAL OF CHEMICAL RESEARCH 2004 DECEMBER, 797–801 **RESEARCH PAPER** 797

Topological analysis and quantum mechanical structure of H_n^+ clusters II. H_5^+ and H_7^+

Abdolreza Sadjadi[a]* and Maryam Abdzadeh[a]

[a] *PO Box: 14515 /964, Tehran, Iran*

Full typologocal and chemical features of H_5^+ and H_7^+ have been calculated at RHF/6-311G(3P) using AIM theory. The results have been compared with previous work on H_3^+.

Keywords: H_5^+, H_7^+, AIM theory, core atoms, charge distribution, atomic properties, bond natures, chemical view

AIM analysis has been performed for the next two members of the H_n^+ closed shell clusters beyond H_3^+. These are $H_5^+$and H_7^+ with C_{2v} symmetries. Using the benefit of the 6-311G(3P) basis set to recover about 99.94% of the near HF limit energy calculated with a large cc-pVQZ basis set; RHF/6-311G(3P) wave functions of the two cited species were fully analysed by atoms in molecules theory after optimising their structures at the same level of calculations. In addition to quantum mechanical structures and bond natures, full atomic properties in these species were calculated, based on partitioning theorems of Rho(r) which construct the corner stone of AIM theory. Comparison of the topological properties of core atoms of H_5^+ and H_7^+ with H_3^+, revealed great topological and chemical differences.

Introduction

About 90% of our world is composed of hydrogen. This simple element is the main source of energy in our solar system as well as in other galaxies. The cationic and anionic clusters of hydrogen atoms are the subject of broad investigations in physics, chemistry and astronomy. For example the statement : "Spectroscopic studies of the upper atmospheres of the giant planets using infrared wavelengths sensitive to the H_3^+ molecular ion showed that this species plays a critical role in determining the physical conditions there".[1,2] The oldest paper which we can refer to it is the work of Shull and Christoffersen[3] on the nature of bonds in H_3^+. Herschbach *et al.* reported the electronic structure of H_n^+ and HeH_n^+ clusters using CI methods. [4] Wright and DiLabio reported theoretical calculations on the structure and stability of various hydrogen clusters such as: H_3^+, H_5^+, H_5^- and H_6 using SCF–CI methods.[5] The concept of aromaticity was investigated in H_x^q clusters such as $H_3^+(D_{3h})$, $H_5^+(C_{2v})$, H_5^- (D_{5h}, D_{4h}) and $H_9^+(D_{3h})$ by Schleyer *et al*.[6] Jensen investigated the effects of basis function angular momentum on estimating the HF limit energy of H_3^+ and estimated the value of –1.300372125 a.u for this energy.[7] Isomeric structures and energies of H_n^+ clusters were completely investigated by the theoretical work of M. Barbatti *et al*. [8,9] They also investigated the nature of bonds and charge distribution around each H atom using a MO approach.[8] It is also apparent from their works that they tried to derive a simple chemical model from their *ab initio* calculations to predict the structures of H_n^+ clusters of various size.[9] Parallel to these *ab intio* calculations, AIM theory began to grow.[10] Only a few references about the topological properties of H_n^+ clusters exist. The oldest references are the works of Bader *et al.*[10–12] on H_3^+. We have reported on the topological behaviour of H_3^+ at RHF limit,[13] and H_3^+ was the starting point for our investigations on H_n^+ clusters. In this report, we will proceed further to investigate the chemical features of H_5^+ and H_7^+ in the light of AIM theory.

Method and levels of calculations

Restricted–Hartree–Fock (RHF) calculations have been performed on $H_7^+(C_{2V})$, $H_5^+(C_{2V})$, $H_3^+(D_{3h})$ and H_2; using 6-311G (3P) basis set. (P exponents: 3. 0, 0. 75, 0. 1875 and Scale factor: 1. 000);[8] this basis set recovers about 99.94% of HF energy calculated with a large basis set like cc-pVQZ for H_5^+ to H_9^+ clusters. Using this basis set allowed us to perform both *ab initio* and AIM calculations with desired computational time, near the HF limit. After determining the equilibrium geometries, the RHF wave functions for all species were analysed by AIM theory to determine their full chemical features. All *ab initio* calculations were performed using PC-GAMESS (version 6. 4) software[14,15] and AIM analysis with MORPHY99[16-21] and AIM2000[22-25] (Demo version) packages.

Results and discussion

Ab initio calculations have predicted that H_n^+ clusters are composed of core H atoms coordinated with H_2 molecules.[4,5,8,9] (laying on the corners of a triangle as in H_3^+). To investigate the correctness of this chemical view as well as other chemical properties of H_5^+ and H_7^+, the results for H_3^+ and H_2 will also be presented for comparison. Topological analyses for all species were started by searching the critical points (CP) in Rho(r).[10,27] The results were all gathered in Table 1. The Poincare–Hopf rule[10,27] was also tested for each set of CPs of each molecule to ensure the completeness of analysis. This rule was satisfied in all cases. We first tested the change of topological properties from the RHF/cc-pVQZ level[13] to RHF/6-311G(3P). For H_2 and H_3^+ the same types of CPs were detected in both levels of calculations. This reassured us that our results for H_5^+ and H_7^+ are in near HF limit. Without referring to molecular graphs (MG)[10,27], the results in Table 1 show

Table 1 Mathematical characters of CPs in the rho(r) functions at RHF/6-311G(3P)

CP's number	Type of CP	ρ_b a.u	$\nabla^2 \rho_b$	ε
H_2				
1	BCP	0. 27412	–1. 25779	0. 0000
$H_3^+(D_{3h})$				
1	BCP	0. 24069	–0. 8355	3. 4933
2	BCP	0. 24069	–0. 8355	3. 4933
3	BCP	0. 24069	–0. 8355	3. 4933
4	NNA	0. 24075	–0. 8314	12. 3397
$H_5^+(C_{2v})$				
1	BCP	0. 21849	–0. 8222	0. 5957
2	BCP	0. 24361	–0. 8804	0. 8429
3	BCP	0. 0349	0. 0502	0. 1411
4	BCP	0. 26459	–1. 1746	0. 0164
$H_7^+(C_{2v})$				
1	BCP	0. 235181	–0. 8433	0. 9891
2	BCP	0. 235181	–0. 8433	0. 9891
3	BCP	0. 02291	0. 05299	0. 1170
4	BCP	0. 02291	0. 05299	0. 1170
5	BCP	0. 2675	–1. 1997	0.00988
6	BCP	0. 2675	–1. 1997	0.00988

---

* Correspondence. E-mail: abdi_1374@yahoo.com

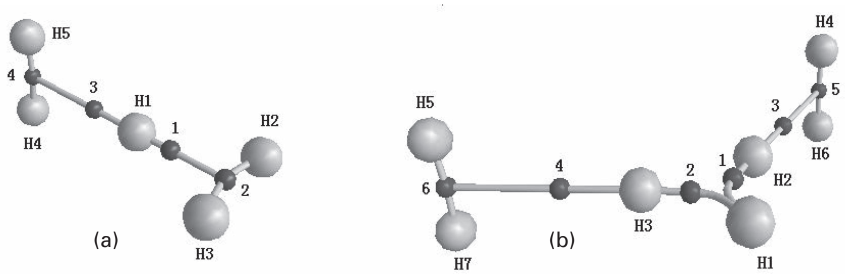

Fig. 1 Complete molecular graphs (MG) for (a)H_5^+; (b) H_7^+ at RHF/6-311G(3P). Small circles are BCPs and large circles are H atoms nuclei.

that no sets of CPs for H_5^+ and H_7^+ resemble the CPs of H_3^+. No NNAs or RCPs[10,27] were found in Rho(r) functions of these species. One BCP(4) in H_5^+ and two BCPs(5, 6) in H_7^+resemble the mathematical characters of the BCP in H_2. Next, the MGs of H_5^+ and H_7^+ were searched for BPs (bond paths).[10,27] As has been pointed out; "The importance of BP is that it is a universal indicator of bonded interactions, which is mirrored by a virial path, a line linking the same neighbouring nuclei, along which the potential energy density is maximally negative, *i.e.*, maximally stabilising with respect to any neighbouring line".[26] The MG of H_3^+ is the same as what we have reported previously,[13] therefore we did not represent it here. The 3D pictures of MGs, derived from AIM2000 are shown in Fig. 1, including the H atoms numbering. The numbering of BCPs are the same as in Table 1. Figure 1 shows that the interactions between core atoms (H1, H2, H3)in both species are completely different from H_3^+. The other interesting feature of these MGs is their conflicting natures.[10,27,28] In H_5^+ a BP links BCP(3) to BCP(4) instead of terminating at each nucleus (H4, H5) separately. This means that both nuclei are in competition to be linked to BCP(3) or they have equal tendency to link to H1.[27] The same is true for (H1 and H2, H3). H_7^+ is also a conflict structure; H7 and H5 have same tendency to link to H3 and on the other side of molecule H4 and H6 have the same tendency to link to H2. Before discussing the bond natures in these ion-molecules it is better to look at their gradient vector fields and contour maps (GRVF)[10,27] of Rho(r)s, searching the shapes of atomic basins,[10,27] and compare them with that of H_3^+ [13] and H_2. These maps were gathered in Fig. 2. Figures 2a and 2c are the maps of core atoms. They no longer resemble those of H_3^+. In H_5^+, the H1 basin is completely different in shape and size to that of H2 and H3 (Fig. 2a). H4 and H5 resemble the H_2 map [Fig 2(b, f)]. H1 is a unique quantum atom in H_5^+. In H_7^+, (H4, H6) and (H7, H5) maps resemble H_2 [Fig. 2 d, e]. H1 has a different topology from that of H2 and H3. Here again H1 is a unique quantum atom in H_7^+. Comparison between the GRVF maps of H_5^+ and H_7^+ also revealed that when an atomic basin of the core atom and the H_2 resemblance part get close to each other the result is the large deformation of the atomic basin of the core H atom in comparison to others (H1 in H_5^+ and H2, H3 in H_7^+). On the basis of signs of ($\nabla^2\rho_b$)s; (Laplacian with negative sign corresponds to the existence of shared interaction and with positive sign corresponds to closed shell interaction[27]), H_5^+ has three shared interactions and one closed shell interaction. Shared interactions exist between H4–H5 and H2–H3 pairs, because of the conflict nature it is safe to say that the shared

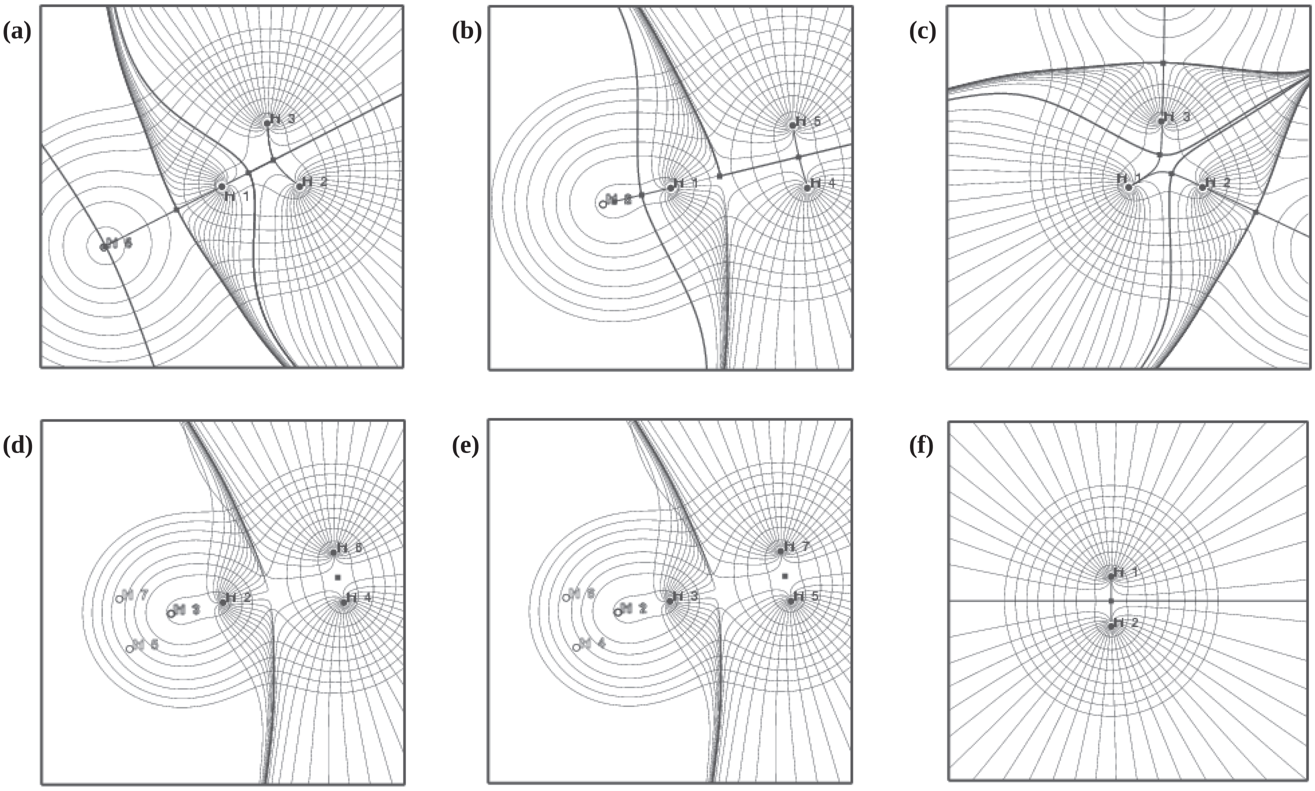

Fig. 2 Gradient vector fields and contour maps of Rho(r)s at RHF/6-311G(3P). (a) (H1, H2, H3) plane in H_5^+; (b) (H1, H4, H5) plane in H_5^+; (c) (H1, H2, H3) plane in H_7^+; (d) (H2, H4, H6) plane in H_7^+; (e) (H3, H5, H7) plane in H_7^+; (f) H_2 molecule.

interactions exist between H1–H3 and H1–H2 simultaneously. Closed shell interactions exist between H1–H5 and H1–H4. In H_7^+, shared interactions exist between H1–H2, H1–H3, H4–H6 and H5–H7 pairs while closed shell interactions exist between H3–H5, H3–H7 and H2–H4, H2–H6 simultaneously. Shared and closed shell interactions are divided to subgroups like : covalent, polar, ionic and Van der Waals bonds on the basis of ρ_b and charge transfer (atomic charges) values between a pair of atoms. Therefore the complete bonding nature can not be deduced without atomic properties.[27,31]

Atomic properties[29]

This was the most difficult and time consuming part of our calculations. As Fig. 2 shows, the basins of some H atoms have long spiky tails which makes it difficult to obtain a small integration error. The results we found most acceptable are gathered in Table 2. We have also calculated the differences between total *ab initio* charge and energy with that of AIM results for each molecule and put them in this table. The columns of Mulliken atomic charges were also inserted in Table 2. The results for H_2 were obtained from MORPHY99 and for other ion-molecules from the AIM2000 program. The largest difference between the AIM and *ab initio* results for H_3^+ is due to the existence of NNA and Gap between IASs[13]. In addition to L(Ω) values, the reliability of the calculated atomic properties (q and $E(\Omega)$) were tested on the basis of ranges of changes of these quantities due to Δ (AIM-*ab initio*). These ranges were collected in Table 3. Each value in this table was obtained by adding to and subtracting the Δ (AIM-*ab initio*) from each value of Table 2. Because of the effect of NNA and IASs gap on the integration results for H_3^+, the accuracy of results in this case were only deduced due to L(Ω) values. According to Table 3 the calculated atomic properties for each species are reliable. From the q values in Table 2, one can see that Mulliken analysis predicts the same charge for each core H atom in H_5^+ and H_7^+ in comparison to great differences obtained from AIM. The chemical pictures which Mulliken analysis brings to us from *ab initio* calculations will be $[H_3(H_2)]^+$ for H5$^+$ and $[H_3(H_2)_2]^+$ for H_7^+. Referring to MGs and atomic properties derived from AIM theory, the chemical view for H_5^+ will be predicted as $[H(H_2)(H_2)]^+$ and for H_7^+ will be $[H(H_2)(H_2)_2]^+$, in which the (H_2) parts are different from isolated H_2 molecule according to their atomic properties (Table 2). To investigate the charge distribution in each molecule and for easy comparison between the Mulliken and AIM analysis, bar line charts were drawn and depicted in Fig. 3. As it was predicted from Fig. 2, the unique H atoms in H_5^+ and H_7^+ have the unique atomic properties among other H atoms. Comparing the GRVF maps with the atomic properties revealed that the H atoms, neighbouring to the H_2 resemblance parts, (H_1 in H_5^+ and H_2, H_3 in H_7^+) bear the greatest positive charge and have the smallest atomic volumes. Core charge is 0. 9263 a.u in H_5^+ while for H_7^+ it is 0.9119 a.u. On the basis of the values in Table 3, it is hard to predict which core part bears the more positive charge. Referring to the ρ_b values in Table 1, clarified the situation. The difference between the values of BCP(4) in H_5^+ and BCP(5), BCP(6) in H_7^+ is only 0. 00291 a.u whereas this difference between

Table 2 Atomic properties(in atomic units) from AIM analyses at RHF/6-311G(3P)

	Vol[0.001][a]	q[b]	$q_{mulliken}$	$E(\Omega)$[c]	$L(\Omega)$[d]
H_2					
H1	59.74	0.0000	0.0000	–0.566537	0.3×10^{-4}
H2	59.74	0.0000	0.0000	–0.566537	0.3×10^{-4}
Total		0.0000		–1.133074	
Total *(ab initio)*		0.0000		–1.133057	
Δ (AIM–*ab initio*)		0.0000		–0.000017	
$H_3^+(D_{3h})$					
H1	30.406	0.3621	0.3333	–0.421266	-0.94×10^{-5}
H2	30.336	0.3631	0.3333	–0.420809	-0.99×10^{-5}
H3	30.422	0.3626	0.3333	–0.421022	0.38×10^{-3}
Total		1.0878		–1.263097	
Total *(ab initio)*		1.0000		–1.299405	
Δ (AIM–*ab initio*)		0.0878		0.036308	
$H_5^+(C_{2v})$					
H1	21.03	0.5020	0.2780	–0.343848	-0.60×10^{-4}
H2	35.93	0.2123	0.2769	–0.494441	-0.30×10^{-4}
H3	35.92	0.2120	0.2769	–0.494589	-0.35×10^{-4}
H4	51.52	0.0321	0.0841	–0.556559	-0.24×10^{-4}
H5	51.51	0.0319	0.0841	–0.556618	-0.23×10^{-4}
Total		0.9903		–2.446055	
Total *(ab initio)*		1.0000		–2.441514	
Δ (AIM–*ab initio*)		–0.0097		–0.004541	
$H_7^+(C_{2v})$					
H1	39.47	0.1057	0.2544	–0.543813	0.65×10^{-4}
H2	26.03	0.4032	0.2669	–0.400273	0.53×10^{-4}
H3	26.03	0.4030	0.2669	–0.400362	0.53×10^{-4}
H4	53.89	0.0212	0.0530	–0.559562	0.79×10^{-4}
H5	53.86	0.0211	0.0530	–0.559612	0.79×10^{-4}
H6	53.85	0.0212	0.0530	–0.559580	0.79×10^{-4}
H7	53.86	0.0212	0.0530	–0.559573	0.79×10^{-4}
Total		0.9966		–3.582775	
Total *(ab initio)*		1.0000		–3.580836	
Δ (AIM–*ab initio*)		–0.0034		–0.001939	

[a] Atomic volume is integrated over atomic basin(Ω) to the contour surface of 0. 001 a.u.

[b] Total atomic charge.

[c] Total atomic energy which is calculated by integrating over atomic basin(Ω).

[d] Total integration error over atomic basin (Ω) for calculating atomic properties.

Table 3 Estimated limits of changing the values of atomic properties(q and E(Ω)) due to integration errors for $H_5^+(C_{2v})$ and $H_7^+(C_{2v})$ at RHF/6-311G(3P)

	q		*E*(Ω)	
	+Δ	-Δ	+Δ	-Δ
$H_5^+(C_{2v})$				
H1	0.4923	0.5117	-0.3484	-0.3393
H2	0.2026	0.2220	-0.4990	-0.4899
H3	0.2023	0.2217	-0.4991	-0.4901
H4	0.0224	0.0418	-0.5611	-0.5520
H5	0.0222	0.0416	-0.5612	-0.5521
$H_7^+(C_{2v})$				
H1	0.1023	0.1091	-0.5458	-0.5419
H2	0.3998	0.4066	-0.4022	-0.3983
H3	0.3996	0.4064	-0.4023	-0.3984
H4	0.0178	0.0246	-0.5615	-0.5576
H5	0.0177	0.0245	-0.5616	-0.5577
H6	0.0178	0.0246	-0.5615	-0.5576
H7	0.0178	0.0246	-0.5615	-0.5576

BCP(3) in H_5^+ and; BCP(4), BCP(3) in H_7^+ is 0. 01199 a.u, which is 4 times greater. Therefore we conclude that the charge accumulations in BCP(3) in H_5^+ and; BCP(4), BCP(3) in H_7^+ are mainly caused by withdrawing electron density from core parts, which largely affects the atomic properties in these parts of molecules as mentioned before. On the basis of these results we predict that the core part of H_5^+ must be slightly the more positive. The atomic properties of (H4, H5) pair in H_5^+ and; (H5, H7), (H4–H6) pairs in H_7^+ are comparable to that of isolated H_2, but because of the total positive charge of each ion-molecule, each H atom bears positive charge and has smaller volume. This lowers the ρ_b between each pair (in comparison to that of H2) as is obvious from Table 1. Also the mathematical characters of BCPs which connect these pairs are similar to (but do not exactly match) that of isolated H_2. With the aid of E(Ω) values the contribution of each H atom to the total energy of molecule can be investigated. Here we introduce the simple concept named as energy density, defined by the ratio: $\frac{E(\Omega)}{\text{volume}[0.001]} = E_d(\Omega)$ for

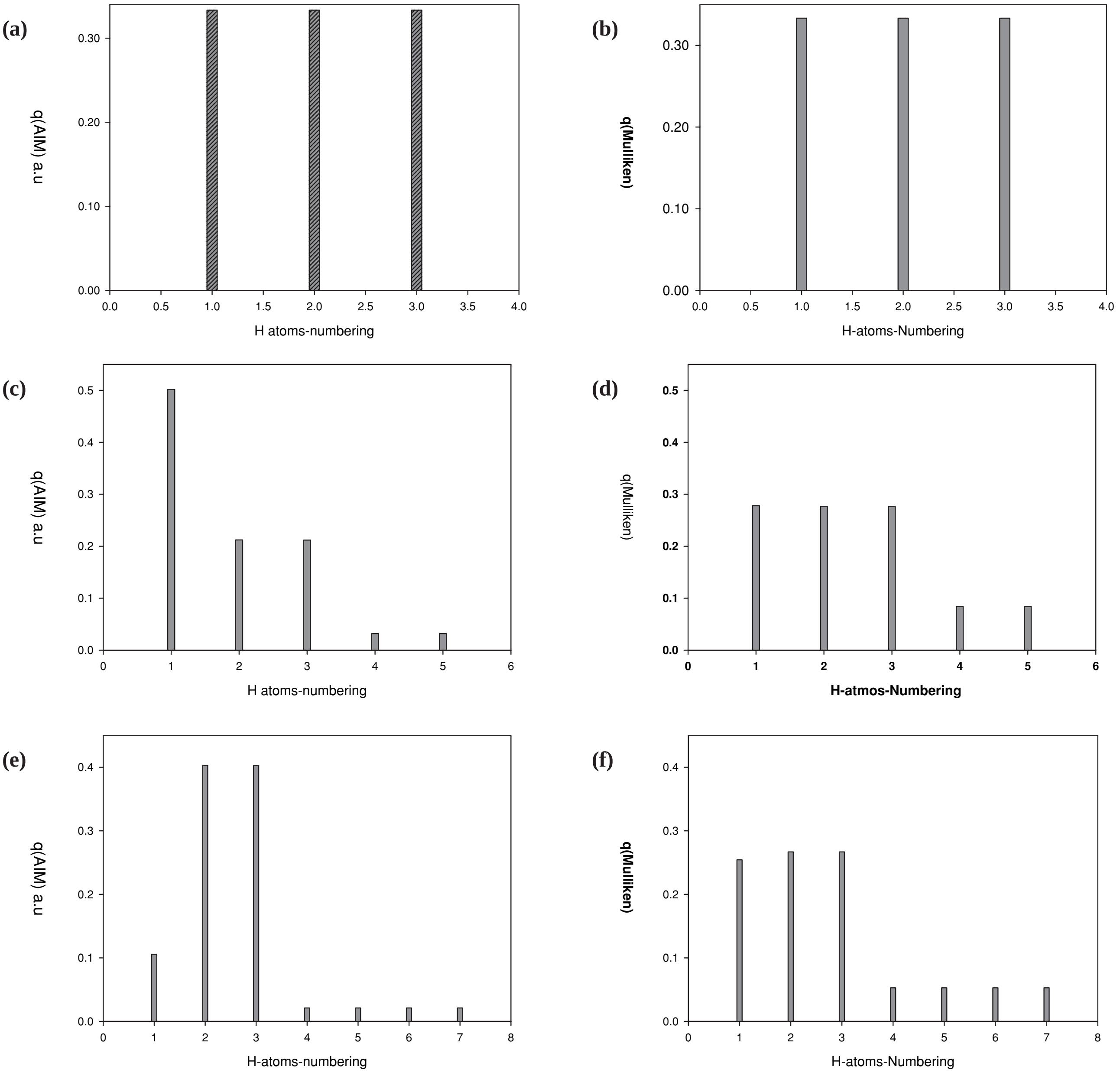

Fig. 3 Bar line charts of charge distributions, predicted by AIM(left) and Mulliken analysis (right) for H_3^+(a, b); H_5^+(c, d) and H_7^+ (e, f) at RHF/ 6-311G(3P).

each H-atom. This quantity brings us the spectrum of energy distribution through the whole molecule. We are looking for a chemical usage for this quantity, therefore we do not discuss it in this work. As Table 2 shows, the unique H atom (H1 in H_5^+) has the least contribution to the total energy, whereas in H_7^+ its contribution is comparable to H4, H5, H6 and H7. A general behaviour can be deduced among all molecules from Table 2. The more positive the AIM-charge on H atom, the smaller its volume[30] and the lesser contribution to total energy.

Bonding Scheme

Finally we proposed the complete bond natures in H_5^+ and H_7^+ on the basis of results in Tables 2 and 3.

In H_5^+: the H2–H3 bond is shared-covalent; the bond between the H1 and (H2, H3) pair is shared-polar because of their unequal atomic charges; the H4–H5 bond is shared-covalent; the bond between the H1 and (H4, H5) pair is closed-ionic due to $\nabla^2 \rho_b > 0$, ρ_b= 0. 0349 a.u (order 10^{-2} a.u)[27] and 0. 47 a.u difference in atomic charges. If the pure ionic bond is characterised by approximately 1e charge transfer between the atoms, the bond between the cited H atoms can be characterised as semi-ionic.

In H_7^+: the (H1–H2) and (H1–H3) bonds are shared-polar; the (H5–H7) and (H4–H6) bonds are shared-covalent; the bond between H3 and (H5, H7) pair is closed-ionic (38% ionic); the bond between the H2 and (H4, H6) pair is also closed-ionic (38% ionic)

Conclusions

Using the AIM theory; CPs in rho(r) functions, molecular graphs, gradient vector fields, atomic charges and energies were calculated for $H_5^+(C_{2v})$ and $H_7^+(C_{2v})$ at RHF/6-311G(3P). MGs revealed the conflict natures of these two species. These are rare examples of molecules which show the conflict shared interactions in their equilibrium (minimum) structures. Most of this kind of topological behavior was detected in transition state structures[27] and Van der Waals complexes (conflict closed shell interactions).[28] Comparing CPs, MGs and GRVF maps of the cited species with that of H_3^+ and H_2 at the same level of calculations showed that the core parts of H_5^+ and H_7^+ are greatly different from H_3^+, and the other parts did not exactly resemble the H_2 molecule. These differences were demonstrated quantitatively on the basis of calculated atomic properties. In comparison to what Mulliken analysis has predicted about the chemical natures of these molecules on the basis of atomic charges (core H atoms coordinated with the H_2 molecules), AIM theory proved that these pictures need significant modifications. If "core" means the unique parts with the uniform properties among its constituent atoms, then such a core will not exist for H_5^+ and H_7^+ on the basis of our results. The complete classification of chemical bonds for these two clusters were presented; covalent and semi-ionic bonds were detected. Finally we mention that our future researches will concentrate on the chemical usage of $E_d(\Omega)$ in these kind of clusters and prediction of geometry of them using the Laplacian of rho(r) functions of H_3^+ and H_2; our initial calculations have provided interesting evidences about the former subject.

Special thanks to Professor Kirk A. Peterson from Washington State University for his useful comments and Dr Paul Lode Albert Popelier from UMIST, UK, for helping us to access MORPHY99 software and sending the related papers. We are grateful to Professor R. F. W Bader useful comments. We also thank Mr Hassan Deylami and Mr Moghimi for providing us suitable and efficient computer hardware and Mr Hossein Abdzadeh for typing this manuscript.

Received 5 August 2004; accepted 7 November 2004
Paper 04/2700

References

1 S. Miller. *et al*., *Phil. Trans. R. Soc. Lond. A*, 2000, **358**, 2485.
2 B.J. McCall and T. Oka, *Science*, 2000, **287**, 1941.
3 R.E. Christoffersen and H. Shull, *The. J. Chem. Phys.*, 1968, **48**, 1790.
4 S. Raynor and D.R. Herschbach, *J. Phys. Chem*, 1983, **87**, 289.
5 J.S. Wright and G.A. DiLabio, *J. Phys. Chem.*, 1992, **69**, 10793.
6 P. Von Schleyer. *et al*., *J. Phys. Chem.*, 1996, **100**, 12299.
7 F. Jensen, *Theor. Chem. Acc.*, 2000, **104**, 484.
8 M. Barbatti, G. Jalbert and M.A.C. Nascimento, *J. Chem. Phys.*, 2000, **113**, 4230.
9 M. Barbatti, G. Jalbert and M.A.C. Nascimento, *J. Chem. Phys.*, 2001, **114,** 7066.
10 R.F.W. Bader, *Atoms in Molecules*, Clarendon, Oxford, 1990.
11 R.F.W. Bader, S.G. Anderson and A.J. Duke, *J. Am. Chem. Soc*, 1979, **101**, 1389.
12 R.F.W. Bader. *et al*, *J. Chem. Phys*, 1979, **70**, 4316.
13 A. Sadjadi, M. Abdzadeh and H. Behnejad, *J. Chem. Res*, 2004, **5**, 358.
14 A.A. Granovsky, *http://classic. chem. msu. su/gran/gamess/index.html*
15 M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14,** 1347.
16 "MORPHY99, a topological analysis program written by PLA Popelier with a contribution from RGA Bone (UMIST, Engl, EU)".
17 P.L.A. Popelier, *Comp. Phys. Commun.*, 1996, **93**, 212.
18 P.L.A. Popelier, *Theor. Chim. Acta*, 1994, **87**, 465.
19 P.L.A. Popelier, *Molec. Phys.*, 1996, **87**, 169.
20 P.L.A. Popelier, *Comp. Phys. Commun.*, 1998, **108**, 180.
21 P.L.A. Popelier, *Can. J. Chem.*, 1996, **74,** 829.
22 AIM2000 homepage: *http://www. aim2000. de*.
23 F. Biegler-König, *J. Comp. Chem.*, 2000, **21**, 1040.
24 F. Biegler-König, J. Schönbohm and D. Bayles, *J. Comp. Chem.*, 2001, **22**, 545.
25 F. Biegler-König and J. Schönbohm, *J. Comp. Chem.*, 2002, **23**, 1489.
26 R.F.W. Bader, *J. Phys. Chem. A.*, 1998, **102**, 7314.
27 P.L.A. Popelier, *Atoms in Molecules*, Prentice Hall, UMIST, 2000
28 R.G.A. Bone, R.F.W. Bader, *J. Phys. Chem.*, 1996, **100**, 10892.
29 R.F.W. Bader, *Acc. Chem. Res.*, 1975, **8**, 34.
30 R.F.W. Bader. *et al*., *J. Am. Chem. Soc.*, 1987, **109**, 7968.
31 R.J. Gillespie and P.L.A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, 2001.