

Topological analysis and quantum mechanical structure of H_3^+

Abdolreza Sadjadi^{a*}, Maryam Abdzadeh^a and Hassan Behnejad^b

^aNo.18, 29th West Alley, Shahrara Ave, Tehran14457, Iran.

^bDepartment of Chemistry, Faculty of Science, Tehran University, Tehran, Iran

Ab initio calculations have been performed for H_3^+ at the Restricted–Hartree–Fock, RHF/cc-pVQZ, level of calculations. The electron density function [$\rho(r)$] of this simple classical ring system was analysed using AIM theory. Our results showed the nature of the bonds and the quantum mechanical structure of H_3^+ . This analysis resulted in a thoroughly different bond scheme and structure in comparison to what is deduced from the classical view and the previous AIM analysis. The $\rho(r)$ of the H_2 molecule was also analysed by the same manner for comparison.

Keywords: H_3^+ , AIM theory, molecular graph, chemical bond, AIL, IAS, NNA, atomic charges, catastrophe point

By the efforts of such workers as Feynman, Schwinger and Bader, a theoretical bridge between *ab initio* results and chemical concepts has been constructed. This theory, which is known as AIM, introduces the quantum mechanical meaning of bond, molecular structure and geometry.¹ The geometry of a molecule is defined as a list of nuclear coordinates,¹ but the structure is defined on the basis of a molecular graph. The molecular graph (MG) of a molecule consist of bond critical points (BCP) and their corresponding atomic interaction lines (AIL) in the equilibrium geometry.¹ AIL is a gradient path in $\rho(r)$, that originates at the BCP and terminates at the nucleus.¹

Many *ab initio* calculations have been performed on closed shell H_n^+ clusters since 1978 and the latest one was the work of M. Barbatti *et al.*^{2,3} As the starting point for AIM analysis of this kind of hydrogen cluster, H_3^+ was chosen.

Topological analysis of H_3^+ has been also performed by Bader *et al.*^{4,5,20} but we could not find a clear chemical scheme from their calculations.

Method and levels of calculation

Restricted–Hartree–Fock (RHF) calculations have been performed on H_2 and H_3^+ , using Dunning's cc-pVQZ correlation consistent basis set,⁶ therefore, the calculations were performed at near the HF limit. After determining the equilibrium geometry, the RHF wave functions for both species were analyzed by AIM theory to determine their full chemical features. The *ab initio* calculations were performed using PC-GAMESS software^{7,8} and AIM calculations with MORPHY99⁹⁻¹⁴ and AIM2000 (Demo version) programs.¹⁵⁻¹⁸

Results and discussion

Topological analysis of H_3^+ was started by searching the critical points (CP) on $\rho(r)$, using the MORPHY99 program. Only three (3,-1) CPs or BCPs were found on $\rho(r)$.¹⁹ At this stage the Poincare–Hopf rule was not satisfied.¹⁹

$$N-b+r-c = 3-3+0+0 = 0.$$

The MG of the molecule was searched for AILs and IASs (interatomic surface). As Fig. 1 shows, all the AILs pass through the BCPs and intersect with each other at the centre of the molecule, the gap between IASs can be also detected.

Termination of AILs at the centre of the molecule implies the existence of CP at the point of intersection. Use of AIM2000 (Demo version) revealed that a (3,-3) CP existed at the centre of the molecule (Fig. 2).

This is a non-nuclear attractor (NNA). By including this NNA the Poincare–Hopf rule is satisfied:

$$N-b+r-c = 4-3+0-0 = 1$$

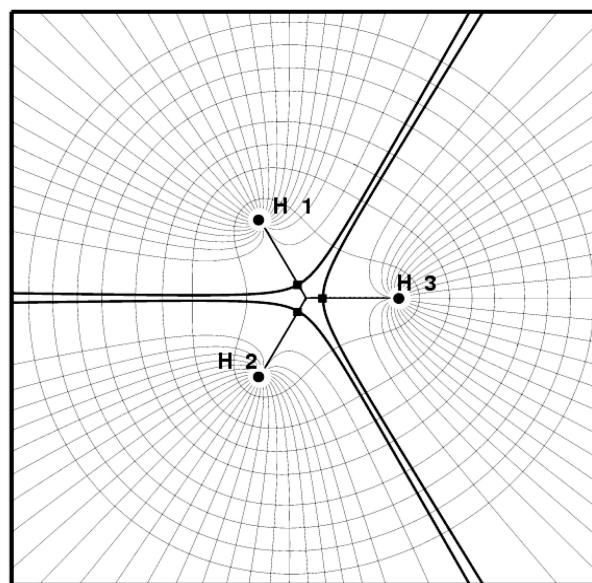


Fig. 1 Gradient vector field and contour map of $\rho(r)$ in H_3^+ at RHF/cc-pVQZ.

(a) Three BCPs (black squares) and six AILs or bond paths (black straight lines) are shown. (b) Intersection of three IASs with the plane of the molecule are shown (black curved lines).

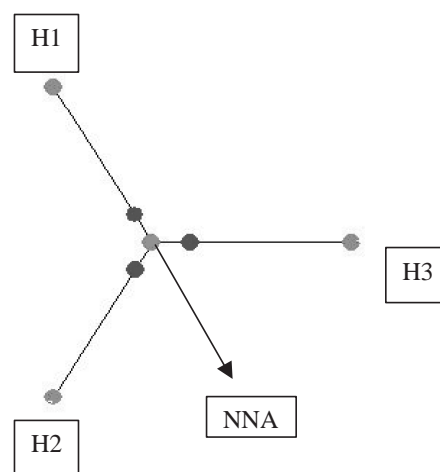


Fig. 2 Complete molecular graph (MG) of H_3^+ . The non-nuclear attractor (NNA) was detected in the centre of molecule.

and the topological analysis is complete. The same topological analysis was performed for the H_2 molecule. The mathematical characters of CPs are all gathered in Table 1 and Table 2 for both H_3^+ and H_2 . On the basis of machine accuracy the gradient of $\rho(r)$ was zero at CPs. We must mention here

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

Table 1 Mathematical characters of CPs in the Rho(r) function of (H₃)⁺

CP's number	(r, s)	ρ_b a.u	$\nabla^2 \rho_b$	ϵ	Type of CP	ALLs' length (BCP to NNA) Å
1	(3,-1)	0.25560	-1.0463	1.6651	BCP	0.1612
2	(3,-1)	0.25561	-1.0461	1.6716	BCP	0.1598
3	(3,-1)	0.25550	-1.0522	1.5838	BCP	0.1754
4	(3,-3)	0.25596	-0.9808	7.2131	NNA	-

Table 2 Mathematical characters of CPs in the Rho(r) function of H₂

CP's number	(r, s)	ρ_b a.u	$\nabla^2 \rho_b$	ϵ	Type of CP
1	(3,-1)	0.2789	-1.5454	0.000028	BCP

that the results of MORPHY99 and AIM2000 are exactly the same, as we have compared them, except for detecting NNA.

In comparison to the ϵ values near each H nucleus (0.0098) the large value of this quantity at NNA reveals that Rho(r) has become flat in the direction of eigenvector \mathbf{u}_2 .¹⁹ The calculated atomic charges which were derived from AIM2000 software were also gathered in Tables 3 and 4. The $L(\Omega)$ values are integration accuracy over atomic basins⁵ for calculating atomic properties (for more details see AIM2000 and MORPHY99 user's manuals). For good results, they should be zero.

As Figs 1 and 2 show, no bond paths exist between H atoms but the bond paths exist between each H atom and NNA. This is totally different from the classical bonding scheme (triangle bond path). The gap between IASs is the result of existence of this NNA, therefore the AIM2000 was used for calculating the atomic charges instead of MORPHY99. If we sum over all atomic charges in Table 3, we will reach the amount of +1.18197 a.u instead of +1.0000. Because of the existence of NNA, the amount of electronic charge is enclosed by IASs, outside the basins of any H atoms, it belongs to the NNA's basin. The amount of this electronic charge is

$$1.0000 - 1.18197 = -0.18197 \text{ a.u.}$$

Further interesting chemical features maybe found from our tables, which will be further discussed in later papers. The results for the H₂ molecule were also shown in parallel to the results for H₃⁺, which makes the chemical comparison between these two species easier for readers.

Conclusions

Total chemical features of H₃⁺ were investigated using AIM theory. Three BCPs and one NNA were detected in the Rho(r) function of H₃⁺. The molecular graph of H₃⁺ showed that the bonds are thoroughly different from their classical view and no bond exists between H atoms, these bonds exist between each H atom and NNA. In comparison to the Bader *et al.* calculations, we found six bond paths (Fig. 2) instead of three, three BCPs and one NNA instead of a single catastrophe point.^{4,5,20} H₃⁺ is one example of molecules whose quantum mechanical molecular graph are thoroughly different from their classical bond scheme. Therefore this molecule cannot be classified as a ring system on the basis of our results. We also believe that the topology of electron density distribution is highly dependent on the method of calculations and the basis sets.²¹ Convergence criteria, similar to what Dunning's group have used in *ab initio* calculations using correlation consistent basis sets, are needed to find the ultimate behaviour of Rho(r) at the limit of each *ab initio* method. AIM calculations must be extended beyond f functions.

Table 3 Atomic charges for H₃⁺

Atom	q(AIM) a.u	L(Ω)	q(Mulliken)
H1	0.38982	-0.00017	0.33333
H2	0.39443	-0.00017	0.33333
H3	0.39772	-0.00017	0.33333

Table 4 Atomic charges for H₂

Atom	q(AIM) a.u	L(Ω)	q(Mulliken)
H1	0.00114	0.000014	0.00000
H2	0.00105	0.000014	0.00000

We thank Professor Kirk A. Peterson from Washington State University for his very useful comments and Dr. Paul Lode Albert Popelier from UMIST.UK, for helping us to Access MORPHY99 software and sending the related papers.

Received 1 December 2003; accepted 25 March 2004
Paper 03/2246

References

- R.F.W. Bader, *Acc. Chem. Res.*, 1985, **18**, 9.
- M. Barbatti, G. Jalbert and M.A.C. Nascimento, *J. Chem. Phys.*, 2000, **113**, 4230.
- M. Barbatti, G. Jalbert and M.A.C. Nascimento, *J. Chem. Phys.*, 2001, **114**, 7066.
- R.F.W. Bader, S.G. Anderson and A.J. Duke, *J. Am. Chem. Soc.*, 1979, **101**, 1389.
- R.F.W. Bader, *Atoms in Molecules*, Clarendon, Oxford, 1990.
- T.H. Dunning, Jr., *J. Chem. Phys.*, 1989, **90**, 1007.
- A.A. Granovsky, <http://classic.chem.msu.su/gran/gamess/index.html>
- M.W. Schmidt, K.K. Baldrige, 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.
- "MORPHY99, a topological analysis program written by PLA Popelier with a contribution from RGA Bone (UMIST, Engl,EU)".
- PLA Popelier, *Comp. Phys. Comm.*, 1996, **93**, 212.
- PLA Popelier, *Theor. Chim. Acta*, 1994, **87**, 465.
- PLA Popelier, *Mol. Phys.*, 1996, **87**, 169.
- PLA Popelier, *Comp. Phys. Comm.*, 1998, **108**, 180.
- PLA Popelier, *Can. J. Chem.*, 1996, **74**, 829.
- AIM2000 homepage: <http://www.aim2000.de>.
- F. Biegler-König, *J. Comp. Chem.*, 2000, **21**, 1040.
- F. Biegler-König, J. Schönbohm and D. Bayles, *J. Comp. Chem.*, 2001, **22**, 545.
- F. Biegler-König and J. Schönbohm, *J. Comp. Chem.*, 2002.
- P. Lode Albert Popelier, *Atoms in Molecules*, Prentice Hall, UMIST, 2000
- R.F.W. Bader, *et al.*, *J. Chem. Phys.*, 1979, **70**, 4316.
- O.A. Zhikol, *et al.*, *Chem. Phys.*, 2003, **288**, 159.