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Theoretical Study of the Structure of Protonated Ethane ($C_2H_7^+$)*

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The floating spherical gaussian orbital method is employed for predicting the shape of $C_2H_7^+$. The pentavalency of carbon may be explained by the presence of a two-electron three-centre bond in addition to the standard two-electron two-centre bonds in this ion.

The existence of ions like CH_5^+ and $C_2H_7^+$ has been proved experimentally by various workers [1–6]. In recent years much interest has been shown in the structure of these ions since they do not seem to fit into classical valence theory. Some theoretical works on the structures of these ions have been carried out [7–14]. Though an accurate *ab-initio* study has been made [14] for CH_5^+, no such study has yet been reported for $C_2H_7^+$. In this paper we report an *ab-initio* study of $C_2H_7^+$ using the spherical gaussian orbital model (FSGO) method [15]. For the sake of comparison we also report the results of study of CH_5^+ by the same method.

In the FSGO method each pair of electrons is assumed to occupy a normalized floating spherical gaussian, *i.e.*

$$\Phi_i = (2/\pi \varrho_i^2)^{3/4} \exp[-(r-R_i)^2/\varrho_i^2]$$

where ϱ_i is the radius of the orbital and R_i its position. The energy expression for the system with single determinantal wave function is given by

$$E = 2\sum_{j,k}(j|k)\,T_{jk} + \sum_{k,l,p,q}(kl|pq)\,[2T_{kl}T_{pq} - T_{kq}T_{lp}] + \sum_{u<v}(Z_u Z_v/r_{uv})$$

where

$$(j|k) = \int \Phi_j^* \left(-\frac{1}{2}\Delta^2 - \sum_v^N \frac{Z_v}{r_v}\right)\Phi_k\,dv\,,$$

$$(kl|pq) = \int \Phi_k^*(1)\,\Phi_l^*(2)\,r_{12}^{-1}\,\Phi_p(1)\,\Phi_q(2)\,dv_1\,dv_2$$

and

$$T_{kl} = (S^{-1})_{kl}\,.$$

The energy E depends on the positions of the gaussian orbitals, orbital radii and all nuclear positions. In the present study we obtain the best values for these

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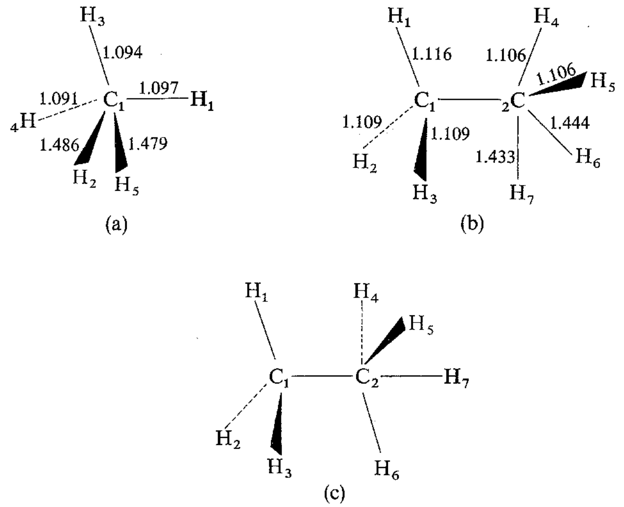


Fig. 1. Systems studied (lengths in Å)

quantities by minimizing E. The optimization was carried out by the subroutine VAO4A [16].

The results of our calculations for CH_5^+ and $C_2H_7^+$ are given in Tables 1 and 2 and Fig. 1. It may be noted from Table 1 that the gaussian representing the 1s orbital of C is more or less centered on the C nucleus and its radius is nearly equal to the value obtained earlier for CH_4 or C_2H_6 [17]. So to save computer time, the co-ordinates of C 1s orbitals were taken fixed while computing the energy of $C_2H_7^+$. The radii for these orbitals were also taken as 0.328 (the

Table 1. *Results for* CH_5^+ [a]

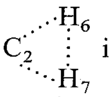
Atom	Nuclear co-ordinates			Energy
	X	Y	Z	
C_1	0.000	0.000	0.000	−34.239
H_1	2.074	0.000	0.000	
H_2	−0.410	−0.680	2.694	
H_3	−1.041	1.787	0.000	
H_4	−0.872	−1.451	−1.179	
H_5	−1.251	−1.660	1.871	
Orbital				
1 [0.327]	~0	~0	~0	
2 [1.612]	1.141	−0.008	0.041	
3 [1.615]	−0.580	0.986	0.033	
4 [1.620]	−0.508	−0.838	−0.648	
5 [1.748]	−0.728	−1.032	2.054	

[a] See Fig. 1(a). Numbers in the bracket are orbital radii. All numbers are in atomic units.

Table 2. *Results for* $C_2H_7^+$ [a]

Atom	Nuclear co-ordinates			Energy
	X	Y	Z	
C_1	0.000	0.000	0.000	−67.274
C_2	2.863	0.000	0.000	
H_1	−0.478	2.054	0.000	
H_2	−0.642	−0.965	−1.746	
H_3	−0.642	−0.965	1.746	
H_4	3.878	0.560	−1.740	
H_5	3.878	0.560	1.740	
H_6	4.433	−2.234	0.000	
H_7	2.970	−2.706	0.000	
Orbital				
1 [0.328]	0.000	0.000	0.000	
2 [0.328]	2.863	0.000	0.000	
3 [1.684]	−0.234	1.178	0.000	
4 [1.670]	−0.347	−0.567	−1.008	
5 [1.670]	−0.347	−0.567	1.008	
6 [1.636]	3.454	0.300	−0.994	
7 [1.636]	3.454	0.300	0.994	
8 [1.739]	3.579	−2.164	0.000	
9 [1.644]	1.621	−0.064	0.000	

[a] See Fig. 1(b). Numbers in brackets are orbital radii. All numbers are in atomic units.

value for 1*s* orbital of C in CH_4). Ethane was taken in the staggered form and the seventh proton was allowed to float on the plane bisecting the angle $H_2C_1H_3$ [see Fig. 1(b)]. Energy minimization was also specifically carried out for the structure in which the seventh proton approaches along the C–C bond axis [see Fig. 1(c)]. Since this gave a higher energy (−67.169 a.u.) results are given only for the structure shown in Fig. 1(b). It may be noted from Fig. 1(b) that the proton in protonated ethane is attached to only one of the carbon atoms (C_2) and the C_1–H_1, C_1–H_2, C_1–H_3, and C_1–C_2 bond lengths are very close to those in ethane. Though two of the C–H bonds, namely C_2–H_4 and C_2–H_5, have bond lengths quite close to those in ethane, the C_2–H_6 and C_2–H_7 distances are somewhat longer and very nearly equal to each other. It might be noted from our study (see Fig. 1) that the CH_5^+ ion has three short C–H bonds (values close to those in methane) and two long bonds. Though the short C–H bonds in $C_2H_7^+$ are comparable in length with those in CH_5^+, the long bonds in $C_2H_7^+$ are somewhat shorter than those in CH_5^+. Examination of Table 2 would indicate that in protonated ethane, C_2–H_4, C_2–H_5 and C_1–C_2 bond are each represented by a single gaussian as in ethane but the bond  $C_2\begin{matrix}\cdot\cdot H_6\\ \vdots\\ \cdot\cdot H_7\end{matrix}$ is represented by also only one gaussian as in H_3^+. In other words, in $C_2H_7^+$, at the C_2 end [see Fig. 1(b)], there are three standard two-electron two-centre bonds and one two-electron three-centre bond. Examination of Table 1 would also reveal the same pictorial model for CH_5^+. A recent *ab-initio* study by Dyczmons *et al.* [14] has also led to the same pictorial model of bonding in CH_5^+.

From the present study one might conclude that in protonated ethane ($C_2H_7^+$), the proton is attached to only one of the carbon atoms (C_2) and the bonding at that site is similar to that in CH_5^+. Further, the apparent exhibition of pentavalency of carbon in these molecules can be explained because of the presence of a two-electron three-centre bond in addition to standard two-electron two-centre bonds.

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