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Near-Hartree–Fock Energies and Geometries of the Hydrogen Clusters H_n^+ (n(odd) $\leq$ 13) Obtained with Floating Basis Sets

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The H_n^+ clusters, $n\,(\text{odd}) \leq 13$, are used to test the performance of an extreme approach with floating basis functions. Near-Hartree–Fock energies and structures are obtained by optimizing the positions of the nuclei and of nearly all basis functions independently with relatively small basis sets of *s*-type functions only. Advantages and disadvantages of this approach are discussed.

Key words: Hydrogen clusters – Floating basis sets.

1. Introduction

In recent years the H_n^+ clusters have been a favourite subject of quantum chemical investigations for several reasons. Their few electrons permit the application of relatively large basis sets but nevertheless they contain enough nuclei to test the efficiency of methods for geometry optimization. Also, some of their properties are known experimentally (e.g. reaction enthalpies) and allow one to check the quality of the calculations, whereas others are unknown or uncertain (e.g. geometries) and therefore allow predictions to be made.

The existence of the larger H_n^+ clusters with $n\,(\text{odd}) \leq 99$ was established in 1969 [1]. Equilibrium constants and dissociation enthalpies for the reaction

$$H_n^+ \rightarrow H_{n-2}^+ + H_2 \quad \Delta H^{\ominus}(T) \tag{1}$$

were measured in the early seventies for $n \leq 11$ [2]. In the late seventies and beginning of the eighties information on the structure of H_3^+ [3] was obtained and the infrared spectrum of H_3^+ was recorded [4]. Theoretical work on these clusters has been referenced in our previous study on this subject [5], when we used the analytical energy gradient and the Hellmann–Feynman force to optimize the geometry with floating orbitals. The H_n^+ clusters were then used to test the performance of floating orbitals in a geometry optimization procedure (see [6] and Ref. therein) instead of a basis set with polarization functions. The method allowed only all the basis functions of a nucleus to be floated together. Its successful application [5] caused us to make program changes in such a way that different basis functions can now be floated independently. In the meantime this program was used in many calculations to optimize geometries for relatively large molecules including polarization [7–9]. To keep the number of floating orbitals within limits we applied the method in these previous studies in such a way that only the most diffuse basis functions were allowed to float, whereas all others were fixed on the nuclei. This method corresponds to about a double zeta plus polarization basis set and is well suited for structure calculations.

Here we apply the method in a more rigorous way to obtain near-Hartree–Fock energies. A larger basis set of spherical gaussians only is applied. All of them, except the contracted function forming the cusp, are allowed to float independently. We expect to obtain near-Hartree–Fock energies in this way with relatively small basis sets but additional time will be needed for the geometry optimization of all the floating orbitals.

The expected results will permit an answer to questions such as the following
—will the Hartree–Fock-structure of H_5^+ converge in C_{2v} symmetry or will it, finally, change to D_{2d} symmetry as it did with CEPA [10]?
—will the structures, especially the long distance between the H_2 and the H_3^+ nucleating center in the larger systems, still change a lot compared to the previously best basis sets [5]?
—were the calculated D_e values for H_{11}^+ and H_{13}^+ accurate or will the more extended basis sets including even more diffuse functions change these values significantly?

2. Computational Method

To obtain near-Hartree–Fock energies with a basis set tractable also for the larger systems, one has to select the basis functions carefully. The 6*s* basis set by Huzinaga [11] deviates only 0.06 milli-hartree or 0.16 kJ/mol from the exact energy for the hydrogen atom. Taking its three functions with the largest exponents as the CGTO fixed on the nucleus to form the cusp we make sure that the deviation from the Hartree–Fock limit due to deviations at the cusp is smaller than one millihartree even for H_{13}^+. The additional basis functions were not contracted in order to keep the basis as flexible as possible also with respect to polarization. For them we decided to use an even-tempered set of exponents. In test calculations we used between 4 and 6 additional functions with exponents between 2.0 and 0.01. The goal was not to obtain energy optimized exponents for the hydrogen atom or the small clusters but rather to have functions included which are diffuse enough to account for long range effects in the larger clusters.

Table 1. Basis sets (only *s*-type functions)

Basis set I		Basis set II	
Exponent	Coefficient	Exponent	Coefficient
68.16	0.023654	293.5708	0.004916
10.2465	0.179767	43.93024	0.038606
2.34648	0.860803	9.891184	0.203102
		2.765179	0.821040
1.9	1	1.9	1
0.6435	1	0.79908	1
0.2179	1	0.33607	1
0.0738	1	0.14134	1
0.025	1	0.5944	1
		0.025	1
Energy of H: 0.499921 E_h		Energy of H: 0.499979 E_h	

Finally we decided to use the 8 lobes contracted to 6 basis functions given in Table 1 as basis set I. Applied to the hydrogen atom its deviation to the exact energy is 0.2 kJ/mol. This is slightly worse than Huzinaga's result [11] for H with a (6*s*) basis set. The reason is due to the inclusion of very diffuse functions as well as a floating function with an exponent close to the value of one exponent in the CGTO. These functions are necessary to provide the flexibility of the basis-set for the clusters. However, they do not improve the energy for the hydrogen atom. In addition the calculations for the systems up to H_5^+ were repeated with the larger basis set II. This was necessary to obtain an estimate of an error due to symmetry or near symmetry introduced in H_5^+ which will be discussed in the next paragraph. Applied to the hydrogen atom its deviation to the exact energy is 0.05 kJ/mol.

The six (or seven for basis set II) forces per hydrogen atom acting on the 5 (6) more diffuse basis functions and the nucleus with the steeper contraction, respectively, were calculated analytically, following Pulay's scheme [12]. For more details see Ref. [7]. A new method for geometry optimization by Smirnow [13] was adapted to our program. This method applied by Smirnow to CNDO calculations proved to be very efficient also for the *ab initio* calculations that we performed. Utilizing internal coordinates for the geometry optimization with a variable metric procedure it allows one to start with an experimental or estimated force matrix. Therefore, it combines the advantages of the force method by Pulay [14] with the advantages of the variable metric methods [15]. Nevertheless, the *ab initio* calculation can be performed in Cartesian coordinates yielding a gradient which is then linearly transformed into internal coordinates. The internal displacement vector predicted by the variable metric procedure is again transformed back linearly into external coordinates. This method is even more advantageous if calculations for a series of molecules are performed, where the larger contain the smaller ones as fragments. The approximate force constants (or rather pseudo force constants for the forces acting on the orbitals) obtained in the variable metric procedure for the smaller molecules can be used in the start matrix of the larger molecules which reduces the number of steps in the geometry optimization for these time-consuming calculations. Likewise the optimized positions of the orbitals in the fragments can be used as start positions in the larger systems.

The calculations were done on a Univac 1100/62 computer in single precision. The CPU-times needed for the full geometry optimizations were 530, 480 and 400 min for H_9^+, H_{11}^+ and H_{13}^+, respectively.

3. Results and Discussion

3.1. Energies

Table 2 shows the total energies for the different species. For comparison the energies obtained with the best basis set in the previous paper are tabulated in the first column. The new total energies are lower by 5 to 38 kJ/mol.

A drawback of the method applied is that floating orbitals cannot fully account for the polarization in highly symmetric molecules [7]. This is not valid for H, H_2 and H_3^+ where only a totally symmetric orbital is occupied. However, analyzing H_5^+ in D_{2d} symmetry, we find that the upper occupied orbital (b_2) is antisymmetric with respect to S_4. Whereas *p*-functions along the S_4-axis on the central hydrogen can participate in this MO, the floating *s*-functions cannot due to symmetry (they are actually fixed to the central hydrogen by symmetry). This is strongly true only in D_{2d} symmetry, but will apply in a less rigorous way also in C_{2v} symmetry. However, it is not true, even in D_{2d} symmetry, if the basis set is that large, that the basis functions on the other four hydrogen can account completely for the polarization at the central atom.

To explore the amount of this effect we carried out additional calculations. First, two additional *p*-functions with exponents 0.85 and 0.15, respectively, were

Table 2. Total energies (E/E_h)

Ion cluster	Previous paper [5]	Basis set I	Basis set II	(Estimated) Hartree–Fock-limit
H_2	−1.13126	−1.13337	−1.13356	−1.13364[a]
H_3^+	−1.29656	−1.29975	−1.30014	−1.30025[b]
H_5^+	−2.43698	−2.44182 −2.44208[c]	−2.44257 −2.44273[c]	−2.4429
H_7^+	−3.57412	−3.58149		−3.5826
H_9^+	−4.71021	−4.71966		−4.7210
H_{11}^+	−5.84278	−5.85490		−5.8566
H_{13}^+	−6.97514	−6.99010		−6.9921

[a] Ref. [16]
[b] Ref. [17]
[c] With additional *p*-functions on the central atom (see text).

added and the geometry reoptimized. This lowered the energy by 0.7 kJ/mol. Second, the calculations for the systems H_n^+, n(odd) ≤ 5, were repeated with the larger basis set. For H_5^+ we added six additional p-functions with the exponents equal to those of the floating s-functions. The energy was lowered by only 0.4 kJ/mol. These calculations were also of importance to make sure that the C_{2v} geometry was not favoured with respect to D_{2d} symmetry by this symmetry dependent basis set defect.

Similar considerations apply to the larger systems. In H_7^+, e.g. the second occupied orbital (b_1) is antisymmetric with respect to the C_2-axis. Therefore, we added two p-functions at the hydrogen on the axis to the basis set and reoptimized the structure. In this case, however, the energy was not lowered at all (and the coefficients of the p-functions in the MO were pretty small). Evidently, here the basis functions on the relatively close neighbouring atoms were able to account for the polarization.

Table 3 presents calculated dissociation energies D_e and experimental reaction enthalpies $\Delta H^\ominus(T)$ for reaction (1). For a rigorous comparison we would have to evaluate all terms in the following equation

$$D_e = \Delta H^\ominus(T) - \Delta E_v(T) - \Delta(E_{\text{rot}}(T) + E_{\text{kin}}(T) + pV) \tag{2}$$

A calculation of $\Delta E_v(T)$ in an adequate way is not feasible at the moment. However, the last term in Eq. (2) can be treated classically. In the third column of table 3 we show the experimental results minus this last term. These values are best suited for a comparison with the calculated values in the second column. Their difference (column 4) is due to the change in electron correlation and vibrational energy.

The most accurate $\Delta H^\ominus$ value for H_3^+ is a calculated one, which is in good agreement with the experimental values (see [9] and references therein). The term in column 4 (−18.0 kJ/mol) consists of 7.9 kJ/mol due to electron correlation and −25.9 kJ/mol due to zero point vibration.

For H_5^+ four experimental $\Delta H^\ominus$ values are available [2], one of them being assumed not to be very accurate. The remaining three values 40.6 ± 0.8 kJ/mol

Table 3. Experimental and calculated energies for the dissociation reaction (kJ/mol)

Ion cluster	D_e^{SCF} [5]	D_e^{SCF} (this work)	$\Delta H - \Delta(E_{\text{rot}} + E_{\text{kin}} + PV)$	$\Delta E_{\text{corr}} + \Delta E_v$	$\Delta H^\ominus(T)$, exp.
H_3^+	434.0	437.4	419.4[a]	−18.0	419.4[a] (0 K)
H_5^+	24.4	23.7	31.8	8.1	40.2[b] (290 K)
H_7^+	15.8	15.9	12.6	−3.3	17.2[b] (158 K)
H_9^+	13.1	12.6	11.8	−0.8	15.9[b] (140 K)
H_{11}^+	3.8	4.9	6.9	2.0	10.0[b] (108 K)
H_{13}^+	3.3	4.8	—		

[a] Most accurate theoretical value, see text.

[b] From Hiroaka et al.; Ref. [2]

(370 K), 40.2 kJ/mol (290 K) and 33.9±3 kJ/mol (250 K) yield $\Delta E_{\mathrm{corr}}+\Delta E_v$ values of 6.1, 8.1 and 2.9 kJ/mol, respectively. Assuming the value for ΔE_{corr} (9.6 kJ/mol) calculated by Ahlrichs [10] being correct, ΔE_v is between −6.7 and −1.5 kJ/mol. Evidently, the experimental values are not accurate enough for a rigorous analysis, but we might conclude that the two terms cancel each other to a good extent. The same is suggested by the larger systems H_7^+ to H_{11}^+.

3.2. Structures

Table 4 shows the structural data for the clusters up to H_9^+. The main features of the structures did not change, i.e. H_3^+ is a regular triangle which acts as a nucleating centre for the H_2 molecules. Investigating the distances as a function of the basis set (including the four basis sets of the previous study [5]) we find that no distance converges monotonously. The direction of approaching and overshooting the Hartree–Fock value is different, however, for the different distances. All structures in this study were optimized till the norm of the gradient of all internal coordinates (including the coordinates of all floating orbitals) was smaller than $0.0008E_h/a_0^2$.

The parameters in Table 4 are used in the following way. R_1 is the bond-length of the H_2-like subunits. R_2 and R_3 are the sides of the H_3^+ triangle. R_4 is the distance from a corner of the triangle to the middle of a H_2 sub-unit. H_5^+ and H_7^+ have C_{2v}-symmetry, H_9^+ shows D_{3h} symmetry. The change in R_1 from H_2 to H_9^+ suggests that we are dealing with a real H_2 sub-unit which is perturbed mostly in H_5^+ and least in H_9^+. This is exactly what we also would expect from the increasing distance R_4. Likewise we find a corresponding behaviour for the nucleating H_3^+ triangle. In H_9^+ it is hardly perturbed, showing a sidelength only $0.008a_0$ larger than in H_3^+. H_5^+ and H_7^+ show a stronger perturbation. In H_5^+ the bond-length R_2 opposite to the corner where the H_2 is attached is shortened by about the same amount as the others are increased. In H_7^+ the bond-length R_2 between the corners where the H_2 are attached is decreased only little whereas the others are increased similarly as in H_5^+.

Table 4. Structures

Ion cluster	Basis set	R_1/a_0	R_2/a_0	R_3/a_0	R_4/a_0
H_2	I	1.387			
	II	1.386			
H_3^+	I		1.642		
	II		1.639		
H_5^+ [a]	I	1.413	1.577	1.704	3.017
	II	1.412	1.571	1.710	2.970
H_7^+	I	1.406	1.629	1.709	3.295
H_9^+	I	1.402	1.650		3.476

[a] With p-functions added on the central hydrogen.

The H_5^+ structure shows no tendency towards D_{2d} symmetry even if p-functions were added, which proves that this change [10] is a pure correlation effect. H_{11}^+ and H_{13}^+ have the structure of H_9^+ with H_2 about $5.8a_0$ above and below the H_3^+-plane, respectively. The H_9^+ sub-unit is structurally not perturbed within the accuracy of the calculations. The relative potential between the H_2 and H_9^+ sub-units is extremely flat. Therefore their relative position depends much on the starting geometry for the convergence threshold used.

3.3. Positions of the Floating Basis Functions

In molecules the electrons of one atom are polarized by the other atoms. Standard calculations take care of polarization by adding atomic functions with higher angular momentum than the highest occupied AO has, i.e. at least p-functions for hydrogen, to the basis set. Depending on the amount of polarization these will contribute with larger or smaller coefficients to the molecular orbitals. In our scheme polarization will make the orbitals float more or less away from their nucleus. With a simple model, assuming a polarization due to a static external field, we would expect for a function the farther away, the smaller the exponent [18]. However, we find a more complicated situation. Table 5 shows the floating distances (from the nucleus) as a percentage of the H_2 bond-length and of the height of the triangle for H_2 and H_3^+, respectively. At first sight the behaviour is fully erratic. An analysis of the floating in the course of the geometry optimization shows, nevertheless, that the basis functions with the two (three for basis set II) smallest exponents hardly change their starting position. These functions are too diffuse to change the energy much by changing their position. The function with the largest exponent has floated away extremely from the nucleus. This can be explained by the fact, that the contraction on the nucleus contains a very similar primitive function. Therefore, the electron density near the nucleus is modelled pretty well by the contraction on the nucleus and the next function cannot contribute much in that area. This is confirmed by a relatively small coefficient of this basis function in the occupied molecular orbital.

Table 5. Percentage of floating of the basis functions in H_2 and H_3^+

	Exponent	H_2	H_3^+
Basis set I	1.9	41.4	29.2
	0.6435	6.9	12.4
	0.2179	8.3	17.9
	0.0738	14.7	10.7
	0.025	18.0	14.1
Basis set II	1.9	35.0	24.8
	0.79908	5.2	10.5
	0.33607	7.4	16.0
	0.14134	15.1	10.8
	0.5944	21.1	14.6
	0.025	24.8	14.6

4. Conclusions

The approach to obtain near-Hartree–Fock energies with relatively small basis sets where all functions float independently proved to be quite successful. A disadvantage of the method is a basis set defect in highly symmetric species which is only unimportant, if the basis set is sufficiently flexible. Another disadvantage is the limitation to geometry optimization, i.e. the method is for example not very efficient for potential energy surface searches. The advantages are the small basis set and the transferability of information (position of the floating basis functions, force constants) from smaller fragments to larger systems.

The calculated dissociation energies are in accordance with the measured $\Delta H^{\ominus}$ values and allow one to predict that the value for H_{13}^+ should be equal to the one for H_{11}^+ within the experimental accuracy.

The change from C_{2v} to D_{2d} symmetry for H_5^+ is a pure correlation effect.

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