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Ab initio Calculations on Small Hydrides Including Electron Correlation

IX. Equilibrium Geometries and Harmonic Force Constants of HF, OH^-, H_2F^+ and H_2O and Proton Affinities of F^-, OH^-, HF and H_2O

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Near Hartree-Fock *ab initio* SCF and correlation energy calculations based on the IEPA–PNO approximation are reported for F^-, HF, OH^-, H_2O, H_2F^+ and H_3O^+ using GTO-basis sets. The SCF values for the equilibrium geometries and harmonic force constants are corrected in the desired direction by inclusion of the correlation energy. The SCF errors are, however, always overcompensated. The agreement with experiment is improved for the symmetric stretching force constants of HF and H_2O, but bond lengths are nearly the same amount too long in the IEPA approximation as they are too short in the SCF calculations. In addition thereto protonation energies are computed and compared with experimental measurements.

Key words: Force constants – Proton affinities – Hydrides – Electron correlation.

1. Introduction

In previous papers of this series the effect of electron correlation on the molecular structure has been investigated for the hydrides of Li, Be, B and C. In the present paper computations on H_2O, HF and their protonated and deprotonated ions are reported.

Although these compounds are well known in chemistry, accurate spectroscopic gas phase data exist only for F^-, HF and H_2O [1]. In the last years mass-spectrometric experiments involving OH^- and H_3O^+ and their higher solvation complexes have been performed [2], which give important supplementary information on these molecules that are well-known from studies in solution and in solid state. H_2F^+ which is known to protonate even weak bases [3] has only been reported to exist as solute in the so-called "magic acid" [4].

Experimental information on the structure of atoms and molecules depends on the environment of the systems which are measured. In order to facilitate com-

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parison of different experimental results, data for the isolated species are desirable. Theory gives this information although the degree of accuracy depends on the various approaches used. Our intention was to perform as accurate calculations as possible with reasonable computation time. We checked the accuracy of our results a) by comparison with more sophisticated calculations which are only possible for smaller systems and b) by comparison with existing experimental data for the molecules in the gas phase. Proceeding this way it is possible to give a consistent theoretical treatment of a whole series of molecules and to estimate the reliability of our conclusions.

2. Method of Computation

As in the other papers of this series the method used is based on the independent-electron-pair approximation (IEPA) [5, 6] and direct calculation of approximate natural orbitals of electron-pair functions developped by Kutzelnigg, Ahlrichs, and co-workers [7, 8].

After performing a conventional Hartree-Fock calculation the canonical orbitals are transformed to localized ones using the criterion of Boys [9]. For each doubly occupied localized orbital φ_R one calculates a pair function in its natural expansion form in the effective field of the other electrons together with the intrapair correlation energy contribution ε_{RR}. Similarly, we find for pairs of different localized orbitals φ_R and φ_S singlet and triplet coupled pair functions in the effective field of the remaining electrons which give the interpair contributions ${}^s\varepsilon_{RS}$ and ${}^t\varepsilon_{RS}$.[1] The sum of the different intra- and interpair correlation energies is regarded as an approximation to the total correlation energy.

3. Choice of the Basis Set

For the O and F atom the (11*s*, 7*p*) GTO-basis set of Huzinaga [10] was used and contracted to a [7*s*, 4*p*] set, with the contraction coefficients taken from the atom. For the H atom we contracted Huzinaga's (6*s*) basis [11] to four groups[2]. Polarization functions of *d*-type on O and F and of *p*-type on H with optimized exponents were added. We simulate *p*- and *d*-functions by appropriate linear combinations of lobes which are shifted from the origin [12, 13]. Two basis sets were considered: for basis set *A* one set of *d*-functions (exponent 1.5) on F and O, respectively, and one set of *p*-functions (exp. 0.75) on H is used, for basis set *B* two *d*'s (exps. 0.75 and 3.0) and two *p*'s (exps. 0.65 and 2.6). Most of the calculations were done with basis set *A*, giving sufficient accuracy for a discussion of SCF- and IEPA effects on equilibrium geometries and force constants; only few selected points were computed with the larger basis *B*.

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[1] In the following text we shall tabulate the sum $\varepsilon_{RS} = {}^s\varepsilon_{RS} + {}^t\varepsilon_{RS}$ only.

[2] In constructing the contracted functions always those with the largest exponents were grouped together, i.e. (5 1 1 1 1 1 1) for the (11*s*) set, on O and F, respectively, (4 1 1 1) for the (7*p*) set and (3 1 1 1) for (6*s*) set on H.

4. Results and Discussion

a) *Equilibrium Geometries and Force Constants for* HF, OH^-, H_2O *and* H_2F^+

The SCF energy and the pair correlation increments for the valence shell were calculated with basis *A* for HF and OH^- at seven internuclear distances. The results for HF are collected in Table 1. If not stated otherwise, all energies are given in atomic units and are negative; the labels *b* and *n*[3] refer to bond pair and lone pair, respectively. The dependence of the correlation energy on the distance *r* is dominated by ε_{bb} and ε_{bn} which both increase in absolute value, $|\varepsilon_{nn}|$ is slightly increasing, $|\varepsilon_{nn'}|$ decreasing; an analogous situation is found for OH^-. The correlation of the inner shell electrons have been shown to remain approximately constant in other calculations [14, 15] and should therefore not change the shape of the potential energy curve significantly. Therefore it is not taken into account here.

For H_2O and H_2F^+ the dependence of ε_{nn}, ε_{bn} and $\varepsilon_{nn'}$ on *r* (keeping $\alpha = \text{const}$) is the same as for HF and OH^-. Variation of the bond angle α (at $r = \text{const}$) shows the expected dominating increase of $|\varepsilon_{bb'}|$ with decreasing α (Table 2).

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[3] The Boys localization procedure yielded in all cases equivalent lone pair orbitals.

Table 1. Variation of SCF-, pair-correlation- and total energies (a.u.) with the bond distance *r* (a.u.) for HF

r	1.50	1.65	1.69	1.733	1.79	1.85	2.10
E_{SCF}	100.0457	100.0640	100.0650	100.0647	100.0624	100.0583	100.0287
ε_{bb}	0.0257	0.0279	0.0285	0.0292	0.0301	0.0310	0.0350
ε_{nn}	0.0210	0.0211	0.0211	0.0211	0.0212	0.0212	0.0213
ε_{bn}	0.0266	0.0277	0.0280	0.0283	0.0287	0.0291	0.0305
$\varepsilon_{nn'}$	0.0280	0.0279	0.0279	0.0279	0.0279	0.0279	0.0277
$\sum_{R\leq S} \varepsilon_{RS}$	0.2523	0.2581	0.2595	0.2612	0.2632	0.2653	0.2735
E_{tot}	100.2980	100.3221	100.3245	100.3258	100.3256	100.3236	100.3022

Table 2. Variation of SCF-, pair-correlation- and total energies (a.u.) with the bond distance r_{OH} (a.u.) and bond angle α for H_2O

	$\alpha = 104.5°$			$r = 1.809$	
	$r = 1.70$	1.809	1.95	$\alpha = 90°$	120°
E_{SCF}	76.0552	76.0593	76.0452	76.0522	76.0546
ε_{bb}	0.0280	0.0295	0.0316	0.0296	0.0291
ε_{nn}	0.0227	0.0228	0.0230	0.0229	0.0227
$\varepsilon_{bb'}$	0.0230	0.0244	0.0263	0.0259	0.0235
ε_{bn}	0.0260	0.0265	0.0272	0.0268	0.0265
$\varepsilon_{nn'}$	0.0290	0.0288	0.0285	0.0281	0.0295
$\sum_{R\leq S} \varepsilon_{RS}$	0.2572	0.2640	0.2729	0.2661	0.2629
E_{tot}	76.3124	76.3232	76.3180	76.3183	76.3176

The net effect of correlation is to increase the bond length (the same behaviour was observed in other cases [15]) and to decrease the bond angle.

The effects of correlation on bond distances and harmonic force constants are clearly demonstrated in Tables 3 and 4. For HF and OH^- we fitted a function of the form $\sum_i a_i x^i e^{-\alpha_i x}$ (α_i also optimized) to 7 points at different internuclear distances and computed the equilibrium geometries and the force constants analytically. In the case of the triatomic molecules H_2O and H_2F^+ 17–20 points on the two-dimensional energy surface were calculated to determine the force constants of the totally symmetric vibrations; in analogy to the linear case these points were interpolated by the following sum: $\sum_{ij} a_{ij} x^i y^j e^{-\alpha_i x} e^{-\beta_j y}$. In addition to that we considered for H_2O also the antisymmetric vibration.

For the triatomic molecules two equivalent forms of the harmonic potential are used [1c, part II]:

$$2V = 2V_0 + F_{11}(r_1^2 + r_2^2) + F_{33}\alpha^2 + 2F_{12}r_1r_2 + 2F_{13}(r_1 + r_2)\alpha$$

and

$$2V = 2V_0 + c_{11}S_1^2 + 2c_{12}S_1S_2 + c_{22}S_2^2 + c_{33}S_3^2 .$$

The symmetry coordinates S_1, S_2 and S_3 are given in terms of the internal displacement coordinates r_1, r_2 and α:

$$S_1 = \alpha$$

$$S_2 = \frac{1}{\sqrt{2}}(r_1 + r_2)$$

$$S_3 = \frac{1}{\sqrt{2}}(r_1 - r_2) .$$

The c's and F's are related in the following way:

$$F_{11} = \frac{c_{22} + c_{33}}{2}$$

$$F_{12} = \frac{c_{22} - c_{33}}{2}$$

$$F_{13} = \frac{c_{12}}{\sqrt{2}}$$

and

$$F_{33} = c_{11} .$$

A comparison of the SCF results (see Table 3 and 4) with experimental values shows the following characteristics: bond lengths are too short by 2% and stretching force constants too large by about 15%. Inclusion of the electron correlation by means of the IEPA–PNO approximation shifts the calculated equilibrium geometries and force constants in the desired direction but always overcorrects

Table 3. Calculated and experimental bond distances R_0 (Å) and harmonic force constants k_0 (mdyn/Å) for HF and OH^-

		Hartree-Fock limit [16, 17]	This work		exp[a]
			SCF	IEPA	
HF	R_0	0.897	0.900	0.929	0.917
	k_0	11.261	11.36	9.407	9.657
OH^-	R_0	0.942	0.945	0.974	0.970
	k_0	9.334	9.001	7.438	–

[a] experimental values were taken from [16] and [17].

Table 4. Equilibrium geometries, harmonic force constants (mdyn/Å) and harmonic vibration frequencies (cm^{-1}) for H_2O and H_2F^+ [a]

		Dunning *et al.* [19]	This work		exp	Ref.
		SCF	SCF	IEPA		
H_2O	R_0(Å)	0.941	0.942	0.973	0.958	[21]
	α_0	106.6	106.5	103.3	104.5	
	F_{11}	9.38	9.31	8.37	8.45	
	F_{12}	−0.078	0.395	−0.550	−0.101	[22]
	F_{13}/R_0	0.249	0.232	0.222	0.227	
	F_{33}/R_0^2	0.867	0.821	0.722	0.761	
	$\bar{\nu}_1$ A_1	–	1695.1	1590.3	1653.9	[23]
	$\bar{\nu}_2$ A_1	–	4143.4	3725.5	3825.3	
	$\bar{\nu}_3$ B_1	–	4045.3	4034.5	3935.6	
H_2F^+	R_0(Å)	–	0.942	0.970	–	
	α_0	–	116.0	111.8	–	
	c_{11}/R_0^2	–	0.549	0.543	–	
	c_{22}	–	8.227	6.896	–	
	c_{12}/R_0	–	0.0857	0.127	–	
	$\bar{\nu}_1$ A_1	–	1384.2	1378.2	–	
	$\bar{\nu}_2$ A_1	–	3790.8	3475.4	–	

[a] For H_2F^+ we did not consider the antisymmetric vibration – therefore only the force constants corresponding to the symmetry coordinates are given.

the SCF errors. The agreement with experiment is improved for the symmetric stretching force constants (deviation from experimental value approx. −5%); the bond distances (with IEPA), however, are nearly the same amount too long as they are too short in the SCF calculations (see Tables 3 and 4). Recently Meyer [18] showed also for the CH_4 molecule by a comparison of his PNO–CI and CEPA methods with the IEPA approach that IEPA tends to overestimate the correlation energy changes with increasing bond length.

In the case of H_2O (Table 4) our SCF force constants agree with other treatments [19, 20], with the exception of F_{12} for which we obtain the opposite sign. F_{12} is here calculated as the difference of two large numbers, an error of a few percent in c_{22} and c_{33} is sufficient to change the sign of F_{12}. Here it is interesting to look at the effect of correlation in more detail: the constant c_{33} for the antisymmetric vibration is hardly influenced by correlation, because the stretching of one bond implies the shortening of the other, which causes the changes of the different pair energies to cancel each other approximately. In our calculations the constant c_{22} for the symmetric stretching vibration (and therefore also F_{11}) decreases with inclusion of correlation, as one would expect from the results for diatomic hydrides (Table 3). Quite the same behaviour has also been observed by Staemmler and Jungen [24][4] for the BH_2 radial. We disagree with Mc Laughlin, Bender and Schaefer [25] who find no change in the stretching force constant F_{11} when correlation is included. In our SCF calculation the vibration with the largest frequency corresponds to symmetry A_1, which is in contradiction to the experimental result – correlation produces then the correct order of the frequencies although the overshooting of the IEPA correction is manifested here also.

Using the same size of the basis set for H_2F^+ no new aspects appear which would make the computed results less reliable than those for H_2O. To our knowledge no experimental values exist for the equilibrium geometry and harmonic force constants; a direct comparison of the calculated harmonic frequencies with the IR-spectrum measured by Hyman *et al.* [4] is not possible because of solvation effects and inharmonic contributions to the vibrations which were not considered in our calculations.

b) Energies of Protonation

At the equilibrium geometries SCF and IEPA calculations were performed with the larger basis set *B*. Results are given in Table 5. Our SCF values for F^-, HF and OH^- are all less than 0.005 a.u. above the Hartree-Fock limit, 0.006 a.u. for H_2O (estimated Hartree-Fock limit by Clementi and Popkie [28] – 76.068 a.u.), the same should hold for H_2F^+. It is difficult to compare our correlation energies with values of the other authors (Table 5) because they used canonical orbitals for their CI calculation in contrast to our localized ones. It is known that the pair energies are not invariant under unitary transformations of the SCF–MO's [32]. Moreover our basis set does not contain *f*-functions.

For H_3O^+ a pyramidal configuration is found to be slightly more stable than the planar one. The height of the barrier of inversion is too small (0.0015 a.u. in SCF) to allow a definite decision whether it exists at all, inclusion of correlation enlarges this barrier [33]. This uncertainty, however, does not affect our calculated proton affinities (a detailed study of the structure of H_3O^+ is in preparation [33]).

The proton affinity is defined here as the difference between the energies of the protonated species and the parent molecule at the minimum of the potential energy surface, i.e. we have not included the zero point energy. Protonation energies from SCF calculations with various smaller GTO-basis sets than ours

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[4] There is a misprint in Table 3 of [24]. F_{12} should read as -0.14 instead of 0.14 (private communication).

Table 5. Comparison of different SCF and CI results with experimental values

		r(a.u.)	α	IEPA					Variational CI		exp energy[b]
				E_{SCF}	E^{K}_{corr} [a] (*K*-shell)	E^{V}_{corr} (valence shell)	E^{T}_{corr} (total	E_{tot}	E_{corr}	E_{tot}	
F^-	This work			99.4571[c]	0.0495	0.3007	0.3502	99.8073	—	—	
	Weiss [26]			99.4594	0.0598	0.3219	0.3817	99.8411	—	—	99.858
HF	This work	1.733	—	100.0660	0.0485	0.2860	0.3345	100.4005	—	—	
	Cade and Huo [16]	1.733	—	100.0703	—	—	—	—	—	—	100.477
	Bender and Davidson [27]	1.733	—	100.0703	0.0563	0.3083	0.3646	100.4349	0.2861	100.3564	
OH^-	This work	1.781	—	75.4128	0.0492	0.3009	0.3501	75.7629	—	—	75.781
	Cade [17]	1.781	—	75.4175	—	—	—	—	—	—	
H_2O	This work	1.809	104.5	76.0620	0.0479	0.2832	0.3311	76.3931	—	—	
	Clementi [28]	1.809	104.5	76.0659	—	—	—	—	—	—	76.436
	Meyer [29]	1.809	104.5	76.0628	0.0560	0.3020	0.3580	76.4208	0.3056	76.3683	
H_2F^+	This work	1.81	113	100.2612	—	0.2833	0.2833	100.5444	—	—	
	Hopkinson *et al.* [30]	1.733	105	100.2082	—	—	—	—	—	—	
H_3O^+	Basis set *B*	1.81	10	76.3418		—	—	—	—	—	
	Basis set *A*	1.85	15	76.3386	—	0.2629	0.2629	76.6015	—	—	
	Diercksen [31]	1.82	0	76.3280	—	—	—	—	—	—	

[a] Sum of the *intra* and inter pair contributions of the inner (*K*-) shell to the correlation energy. In this case all of the 11*s* and 7*p* functions were decontracted.

[b] The values are taken from table 3 of [30] and are defined as the sum of the atomic-, dissociation- and zero-point vibrational energy, but corrected for relativistic effects.

[c] One set of *p*-functions with exponents 0.08 was added.

Table 6. Calculated and experimental proton affinities (in kcal/mole) (all energies are negative)

	This work				Hartree-Fock limit[a]	Hopkinson *et al.* [30]	exp[b]
	SCF Basis set		With correlation[d] Basis set				
	A	*B*	*A*	*B*			
F^-	380.9	382.1	374.3	372.9	383.5	386.6	388.6[c] 361 — 368
HF	121.8	122.5	121.8	120.8	—	108.4	—
OH^-	406.4	407.5	398.2	396.4	408.0	403.2	411.1[c] 370 — 392
H_2O	176.6	175.6	174.0	—	—	181.2	151 — 181

[a] The energy for F^- is taken from [35], for HF and OH^- from [16] and [17] and for H_2O from [28].

[b] Values taken from Table 5 of [30].

[c] From spectroscopic data (see also Table 5, last column).

[d] Only the correlation energy for the valence shell is taken into account.

are compared by Hopkinson *et al.* [30], Schuster [34] gives semiempirical (CNDO/2) values. The SCF-approximation gives already the main contributions, inclusion of correlation modifies these results only to a very small extent (Table 6). Even over the whole series of molecules given in Table 5 correlation does not change enough to have a significant influence on energy differences in the order of magnitude of some 100 kcal/mole.

Our basis sets are supposed to have enough flexibility to insure an approximately equal accuracy of the total energy for the isoelectronic series of systems considered here, as far as protonation energies are concerned. This means that our values for the proton affinities should be of comparable quality for the whole series. Experimental results, especially for H_2O vary over a relative wide range depending on the method of determination; from our point of view the larger values are favoured for H_2O (this is also found in recent measurements of De Paz *et al.* [2b]).

5. Conclusions

The present investigations show what improvements can be obtained for the calculation of equilibrium geometries and force constants by taking into account electron correlation in the framework of the IEPA–PNO approximation, but also what limits are connected with this method. The best results are obtained for the symmetric stretching force constants – the too large SCF values (+15%) are decreased substantially and then agree reasonably with experiment (−5%). The bond distances, however, are approximately the same amount too long with inclusion of the IEPA correlation energy as they are too short in the SCF calculation. This overcorrection of the SCF error is not so large for the bond angle of H_2O. The comparison of our calculated results with experimental values indicates also the reliability of our predictions for the molecular properties of the experimentally less known systems H_2F^+ and H_3O^+.

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