

Commentationes

SCF-CI Studies of Correlation Effects on Hydrogen Bonding and Ion Hydration

The Systems: H_2O , $\text{H}^+ \cdot \text{H}_2\text{O}$, $\text{Li}^+ \cdot \text{H}_2\text{O}$, $\text{F}^- \cdot \text{H}_2\text{O}$, and $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$

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Previous single-determinant Hartree-Fock studies on the equilibrium structures and stabilities of H_2O , H_3O^+ as well as of the monohydrated ionic systems $\text{Li}^+ \cdot \text{H}_2\text{O}$, $\text{F}^- \cdot \text{H}_2\text{O}$ and the hydrogen bonded water dimer, $\text{H}_2\text{O} \cdot \text{HOH}$, are extended by large scale configuration interaction calculations including all the possible single and double excitations arising from the canonical set of Hartree-Fock molecular orbitals. The correlation energy effects on the equilibrium geometrical parameters of the systems under consideration are found to be quite small. The contributions of the correlation energy to the total binding energies of the weakly interacting composed systems are obtained to be of the order of 1 kcal/mole, leading to a considerable increase of the hydrogen bond strength in $\text{F}^- \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdot \text{HOH}$ and to a small decrease of the binding energy in $\text{Li}^+ \cdot \text{H}_2\text{O}$. The observed strengthening of the hydrogen bonding interaction due to correlation is shown to be partly compensated by the change in the vibrational zero-point energy of the composed systems compared to the non-interacting subsystems. Approximate force constants corresponding to the intersystem vibrations in $\text{Li}^+ \cdot \text{H}_2\text{O}$, $\text{F}^- \cdot \text{H}_2\text{O}$, and $\text{H}_2\text{O} \cdot \text{HOH}$ are deduced from the calculated potential curve data on the SCF and the CI level of accuracy.

Key words: Configuration interaction – Hydrogen bonding – Ion hydration

1. Introduction

Over the past few years a large number of quantum mechanical studies on hydrogen bonding [1] and ion hydration [2] have been described in the literature. Experimentalists and theoreticians have been interested in hydrogen bonding since Latimer and Rodebush in 1920 first used this bond mechanism to describe the structure of water [3]. The interest greatly increased when Watson and Crick in 1953 postulated hydrogen bonding to be the key feature of the structure of DNA [4].

The process of ion hydration, on the other hand, is of tremendous importance in the whole field of the chemistry of aqueous solutions. In 1893 Nernst [5] and Thomson [6] pointed out independently that the degree of ionic dissociation in solutions depends on the dielectric constant of the solvent. Within the theory

of the electrolytic dissociation it is generally assumed that in solutions the dissociation products of an ionic compound are surrounded by a shell of solvent molecules. The structure and the size of this shell depends on the particular ion as well as on the solvent molecules. As has been established experimentally, the occurrence of these electrolytic dissociation reactions is not restricted to the liquid phase. Reactions, analogous to the well known acid-base reactions in aqueous solutions, and their reaction constants have been measured in the gas phase as well [7]. Recently a number of such reactions have been discovered in the D-region of the earth's ionosphere [8] and have later been studied in laboratory experiments [9]. They are of some interest for an understanding of the chemistry in the ionosphere [10] and in particular for the high abundance of the water clustered hydronium ion in that region.

The aim of the theoretical studies has been primarily to determine the minimum energy structure and stability (binding energy) of the hydrogen bonded and hydrated systems. In some cases parts of the energy hypersurface have been computed. This is necessary in order to discuss such properties as for example: vibrational spectra and their shifts relative to the non-hydrogen bonded systems, the structure of water by statistical methods [11] and thermodynamic properties [12].

All the quantum chemical investigations on hydrogen bonding and ion hydration (except for the hydronium ion H_3O^+) have hitherto been based on the single determinant Hartree-Fock method, or on semi-empirical approaches. Only very recently a study of the correlation effects in the dihydrated proton complex H_5O_2^+ has been published [13] which is based on a CI-calculation using nonorthogonal pseudo-natural orbitals.

The hydrogen bonded and hydrated systems discussed so far in the literature by theoretical methods are closed shell systems, that is, systems with an even number of electrons all of which are spin paired. It is generally agreed that for such a system the one-determinantal description of the wavefunction is an acceptable approximation for a wide range of studies. In the following the iterative single determinant Hartree-Fock approach will be abbreviated as "SCF-method". With such a wave function and a reasonable "good" and flexible expansion of the one-electron functions, selected properties can be computed in reasonable agreement with experiments: Typically, bond distances are within 0.05 Å, angles within 1–2° (if enough polarization functions are included in the basis set) and binding energies within a few kcal/mole of the experimental values. The most important dissociative reaction studied in this context, i.e. the dissociation of the hydrogen bonded and hydrated systems into the non-interacting subsystems, leads to closed shell fragments as well (an exception of this is H_3O^+ which separates into $\text{H}_2\text{O}^+ + \text{H}$ rather than $\text{H}_2\text{O} + \text{H}^+$). For such a particular path on the total energy hypersurface it is generally believed that the correlation energy changes are only small and that therefore the SCF surfaces are almost parallel to the experimental surfaces over a wide range.

All of these assumptions have to be carefully analyzed in view of the fact that the hydrogen bond energies are rather small, approximately 5–40 kcal/mole. In these cases contributions from the correlation energy, although small in magnitude, might be of rather strong influence on the shape of the energy hypersurface

and might effect therefore rather strongly the equilibrium parameters and properties of such systems (actually, when proton transfer within a hydrogen bonded system is considered even larger effects due to correlation have been observed, e.g. in H_5O_2^+ [13] and H_3O_2^- [14]). To justify (previous) SCF investigations on hydrogen bonded and hydrated systems it is thus necessary to study the correlation effects in some representative systems. The sample systems selected in this study are $\text{Li}^+-\text{H}_2\text{O}$, $\text{F}^--\text{H}_2\text{O}$, and $\text{H}_2\text{O}-\text{H}_2\text{O}$. As a byproduct and for the reason of comparison the systems H_2O and H_3O^+ are reconsidered as well.

2. Details of the Calculations

The SCF wavefunctions and energies have been calculated using Roothaan's SCF-MO-LCAO method [15]. The computations have been carried out on an IBM 360/91 computer, using the program system MUNICH [16]. The molecular orbitals are expanded into a set of Gaussian orbitals $\eta = x^l y^m x^n \exp(-\alpha r^2)$ (unnormalized) which are contracted to reduce the number of linear parameters. The basis sets used in these calculations consist of (11, 7, 1)-functions (which means in the well known terminology: 11 *s*-, 7*p*-, and 1*d*-type functions) centered on the fluorine and oxygen atoms; (11, 2) functions at the lithium atom and of (6, 1) functions at the hydrogen atoms. These functions are contracted to [5, 4, 1] (oxygen and fluorine), [5, 2] (lithium) and [3, 1] (hydrogen) functions. The basis sets used in these calculations have been described previously [17]. They are effectively taken from the literature [18, 19] and supplemented by polarization functions, the exponents of which have been optimized in suitable reference systems. The authors are aware that the contractions used here are not optimum, but they have been kept for the present investigation to avoid the recalculation of a large number of data used for comparison.

For the subsystems Li^+ , F^- , and H_2O the following total energies have been computed using the basis sets described (the best SCF energies found in the literature are given in brackets): $E_{\text{SCF}}(\text{Li}^+) = -7.23621$ a.u. (-7.23641 a.u. [20]), $E_{\text{SCF}}(\text{F}^-) = -99.45059$ a.u. (-99.45936 a.u. [20]), and $E_{\text{SCF}}(\text{H}_2\text{O}) = -76.05199$ a.u. (-76.06587 a.u. [21]).

After evaluating the accuracy of the SCF energies found in the literature it is believed that the SCF energies calculated in the present work are not more than 0.02 a.u. above the Hartree-Fock limit.

The transformation of the one and two-electron integrals from the basis of contracted Gaussian functions, available from the SCF calculations, to the basis of molecular SCF orbitals, needed for the CI calculations, have been performed by using the transformation package of the MUNICH program system. The algorithm for transforming the long list of two-electron integrals, the actual bottleneck of the transformation process, has been described elsewhere together with sample timings applicable to the present calculations [22]. The algorithm is based on a reordering procedure for a large list of indexed quantities which makes heavy use of direct access external storage [23].

The CI calculations have been performed by means of the program system MOLECULE, developed in Stockholm. The details of the method have been described elsewhere [24]. Basically, the method avoids the space and time con-

Table 1. Timing data for the CI calculations (CPU time on an IBM 360/91 computer)

Molecule	$n_{\text{occ}}^{\text{a}}$	$n_{\text{virt}}^{\text{b}}$	$N_{\text{conf}}^{\text{c}}$	CPU-time (min/iteration)
H ₂ O	4	29	1917	0.5
H ₂ O	5	30	3304	0.8
H ₃ O ⁺ (planar)	4	35	5420	1.5
H ₂ O ⁺ (non planar)	4	35	10010	3.0
Li ⁺ · (H ₂ O) (planar)	5	39	5613	1.7
Li ⁺ · (H ₂ O) (non planar)	5	39	10101	3.6
F ⁻ · (H ₂ O)	8	46	36204	10.5
(H ₂ O) ₂	8	58	56268	22.1

^a Number of occupied molecular orbitals.

^b Number of unoccupied (virtual) molecular orbitals.

^c Number of configuration of correct spin and space symmetry.

suming step of explicitly constructing the Configuration-Interaction matrix via symbolic matrix elements [25]. Instead, the CI expansion coefficients are constructed directly from the list of molecular integrals in an iterative procedure. In the program version used in the present work, the reference state is a single (closed shell) Hartree-Fock determinant, and all singly and doubly excited configurations are taken into account. All configurations are constructed to have the correct spin and space symmetry, and thus consist in general of a number of Slater determinants. A maximum of around 60000 of such configurations can be taken into account in the present version of the program (a total of approximately 1500 K bytes of IBM processor storage is used in this limiting case). Timing data for the CI calculations of the systems studied in the present work are listed in Table 1. The values are given in central processor time of the IBM 360/91 computer for one iteration in the matrix diagonalization procedure. The efficiency of the program (CPU time/elapsed time) in a single job environment is approximately 90%.

Convergence in the energy to 10^{-7} a.u. is usually reached within 7–9 iterations. An analysis of the timing data given in Table 1 shows that the time is approximately a linear function of the number of configurations (N_{conf}) for $N_{\text{conf}} < 10000$. For larger numbers the timing is approximately proportional to $N_{\text{conf}}^{3/2}$.

The programs have been linked via standard data interfaces, a common feature of the MUNICH program system, practically without any further adaptations, although they have been developed at different places.

3. Results

3.1. The System H₂O

A number of quantum chemical calculations for the water molecule, both on the SCF and the CI level, have been reported in the literature [26].

The most accurate SCF calculation on this molecule has been performed by Clementi and Popkie [21], who calculated the total SCF energy to be $E_{\text{SCF}}(\text{H}_2\text{O}) = -76.0659$ a.u. using a basis set including *d*- and *f*-type (Gaussian)

Table 2. Total SCF and CI energies for the H₂O molecule in different geometrical configurations

$d(\text{OH})$ Å	$\angle(\text{HOH})$	E_{SCF} a.u.	E_{corr} a.u.	E_{CI} a.u.
0.9572	100°	-76.051251	-0.214861	-76.266112
	104°52	-76.051977	-0.214477	-76.266454
	108°	-76.051808	-0.214239	-76.266047
0.92	104°52	-76.051020	-0.212027	-76.263047
0.94		-76.052309	-0.213338	-76.265647
0.98		-76.049746	-0.215999	-76.265745
0.9572	104°52	-76.051977	-0.230578	-76.282555 ^a

^a Including 1s excitations and all virtual orbitals.

polarization functions at the oxygen atom as well as p - and d -type functions at the hydrogens. Based on this result, the Hartree-Fock limit for water has been estimated to be $E_{\text{HF}}(\text{H}_2\text{O}) = -76.068$ a.u.

The lowest total variational energy reported so far has been obtained by Meyer [27] in a CI calculation using configurations built from non-orthogonal pseudo-natural orbitals, and has been computed to be $E(\text{H}_2\text{O}) = -76.3683$ a.u. Estimating the exact non-relativistic energy at the equilibrium geometry to $E_{\text{NR}}(\text{H}_2\text{O}) = -76.431$ a.u. [27], the total correlation energy would be $E_{\text{corr}}(\text{H}_2\text{O}) = -0.363$ a.u. Thus the above calculation accounts for approximately 83% of the total correlation energy.

A multiconfigurational wavefunction for the water molecule has been reported by Schaefer and Bender [28]. Within the iterative natural orbital method, using 1027 configurations the authors calculated a total energy of $E_{\text{INO}}(\text{H}_2\text{O}) = -76.2418$ a.u. and a corresponding SCF energy of $E_{\text{SCF}}(\text{H}_2\text{O}) = -76.0488$ a.u. In a later note Schaefer *et al.* [29] gave geometry parameters and force constants for the water molecule obtained with a 277 term INO-CI wave function.

A determination of energies, geometry parameters, and force constants for the water molecule, using the independent electron pair approach (IEPA) has been performed by Lischka [30]. With this method a total energy of $E_{\text{IEPA}}(\text{H}_2\text{O}) = -76.3232$ a.u. has been obtained starting from a SCF energy of $E_{\text{SCF}}(\text{H}_2\text{O}) = -76.0593$ a.u. It has to be noticed, however, that the total energy, computed within the framework of this method, is not an upper bound to the exact non-relativistic energy, and therefore cannot be directly compared to the other energies referenced. Actually, the sum of the pair energies (-0.2640 a.u.) is seen to overestimate by approximately 10% the variational correlation energy obtainable with the basis set used.

Calculations on the water molecule have been included in the present investigation for two reasons: (1) to test the accuracy of the wavefunction computed within the CI-scheme outlined, using the basis set described above, and (2) to have theoretical data of the same relative accuracy available to compare to the results obtained for the ion hydrates and the water dimer.

The computed total (SCF and CI) energies of the water molecule for a number of different nuclear configurations are listed in Table 2. In all the calculations,

Table 3. Pair energies for H₂O (in atomic units)

	I^a	II^b	Meyer [27]
$1a_1 - 1a_1$	—	-0.0124	-0.0388
$2a_1 - 1a_1$	—	-0.0017	-0.0038
$3a_1 - 1a_1$	—	-0.0011	-0.0043
$1b_1 - 1a_1$	—	-0.0011	-0.0048
$1b_2 - 1a_1$	—	-0.0008	-0.0033
$2a_1 - 2a_1$	-0.0098	-0.0098	-0.0114
$3a_1 - 2a_1$	-0.0170	-0.0169	-0.0219
$1b_1 - 2a_1$	-0.0173	-0.0172	-0.0235
$1b_2 - 2a_1$	-0.0201	-0.0200	-0.0249
$3a_1 - 3a_1$	-0.0195	-0.0194	-0.0223
$1b_1 - 3a_1$	-0.0302	-0.0301	-0.0353
$1b_2 - 3a_1$	-0.0317	-0.0315	-0.0340
$1b_1 - 1b_1$	-0.0191	-0.0189	-0.0223
$1b_2 - 1b_1$	-0.0284	-0.0283	-0.0317
$1b_2 - 1b_2$	-0.0212	-0.0211	-0.0224
Total	-0.2141	-0.2303	-0.3056

^a No $1s$ - excitations included.

^b All single and double excitations included.

except the one listed in the last line of the table, excitations from the energetically lowest orbital (the $1s$ -orbital on oxygen) have been excluded, as well as excitations to the highest virtual orbital. For H₂O in its experimental equilibrium geometry the valence shell correlation energy is computed to be $E_{\text{vcorr}}(\text{H}_2\text{O}) = -0.2145$ a.u., which amounts to approximately 70% of the total estimated valence shell correlation energy. If excitations from the $1s$ oxygen orbital are taken into account in constructing the total wavefunction (last row of Table 2) a total correlation energy of $E_{\text{corr}}(\text{H}_2\text{O}) = -0.2306$ a.u. is obtained, which corresponds to only 64% of the estimated total correlation energy [27]. This indicates that only a small fraction of the $1s$ -correlation energy (-0.0161 a.u.) is included in this calculation. The reason is that the Gaussian basis set has primarily been constructed to give a good description of the valence shell electron distribution and that it is not flexible enough to account adequately for the inner shell correlation effects.

The computed pair energies are listed in Table 3 together with the values reported by Meyer [27], which will be used as reference values in the following. As expected only about 30% of the pair correlation energy are obtained for the inner shell orbital. A comparison of the pair correlation energies of the valence shell shows, that pairs including the $2a_1$ valence orbital (which is mainly $2s$ oxygen in character) are less well described than the pairs including higher orbitals, for which approximately 90% of the values reported by Meyer have been obtained. The basis set selected for the present investigation thus appears to be well suited for a good description of the correlation effects in the more diffuse orbitals which are the most important ones for the bond formation.

The geometry parameters and force constants computed both with the SCF wavefunction and the 1917 term CI wavefunction have been listed in Table 4.

Table 4. Calculated geometries and force constants for H₂O. The parameters have been obtained with the expansion: $V = V_e + f_r(\Delta r)^2 + (2/r_e) f_{rrr}(\Delta r)^3 + 1/2 f_x r_e^2 \Delta \alpha^2$

	SCF	CI	exp ^a
Bond distance, r_e (Å)	0.944	0.960	0.957
Bond angle, α (degrees)	105°3	103°8	104°5
Stretching force			
Constant, f_r (md/Å)	9.50	8.44	8.35
Anharmonicity, f_{rrr} (md/Å)	– 10.00	– 9.84	– 9.55
Bending force constant, f_x (md/Å)	0.816	0.752	0.76
Interpolated total energy (a.u.)	– 76.051998	– 76.266471	– 76.431 ^b

^a Kuchits, K., Morino, Y.: Bull. Chem. Soc. Japan **38**, 814 (1965)

^b Meyer, W.: Intern. J. Quantum Chem. **5**, 341 (1971).

At the SCF level the geometrical parameters agree with the values reported in the literature which have been obtained with similar basis sets [29–31].

At the CI level a bond distance of $d(\text{OH}) = 0.960$ Å has been computed which is by 0.003 Å larger than the experimental value (while the SCF bond distance is by 0.013 Å shorter than the experimental one). A comparison with calculations using larger basis sets [30, 31] seems to indicate that part of the remaining discrepancy is due to an insufficient basis set. In general, calculations using the present scheme and basis sets yield bond distances reliable to ± 0.003 Å. If a higher accuracy is required configurations corresponding to excitations out of an antibonding reference state have to be included in the CI expansion and also a larger basis set must be employed.

The bond angle has been determined to be 0.8 degrees too large on the SCF level, but 0.7 degrees too small on the CI level compared to experimental values. For a more accurate determination of the bond angle again a larger basis set would be needed including in particular more d - and f -type polarization functions.

The calculation of vibrational parameters had to be limited to the symmetric stretch and bend force constants (including the anharmonicity parameter) because of the small number of points computed on the energy hypersurface. The stretching force constant has been calculated by a third order polynomial fit to the appropriate parts of the surface. The value calculated on the SCF level is in good agreement with the values reported by Dunning *et al.* [31] and Lischka [30]. – It should be noticed that a parabolic fit to three calculated points on the hypersurface leads to values ranging between 8–10 mdyn/Å, depending on the choice of the points. – The two force constants computed on the CI level are in good agreement with the experimental values with a deviation in both values of approximately 1%. The error in the computed value for the anharmonicity parameter is about 3%. In the present work it is thus found, that taking into account correlation effects, lowers the stretching force constant by 1.06 mdyn/Å, while McLaughlin *et al.* [29] predicted almost no change.

3.2. The Hydronium Ion H₃O⁺

The first non-empirical quantum chemical study of the hydronium ion, based on the molecular orbital and valence bond methods has been performed

Table 5. Total SCF and CI energies for the system H_3O^+ in different geometrical configurations

$d(\text{OH})$ Å	$\sphericalangle(\text{HOH})$	E_{SCF} a.u.	E_{corr} a.u.	E_{CI} a.u.
0.94	120°	-76.326 610	-0.208 942	-76.535 552
0.96		-76.327 701	-0.210 434	-76.538 135
0.98		-76.326 439	-0.211 916	-76.538 355
0.971 86		-76.327 216	-0.211 315	-76.538 531
	119°25	-76.327 694	-0.211 373	-76.539 067
	117°05	-76.328 786	-0.211 590	-76.540 376
	113°55	-76.329 536	-0.212 009	-76.541 545
	108°94	-76.328 541	-0.212 697	-76.541 238
0.95	117°05	-76.328 815	-0.209 906	-76.538 721
	113°55	-76.329 292	-0.210 263	-76.539 555
	108°94	-76.327 918	-0.210 885	-76.538 803
0.99	117°05	-76.326 768	-0.212 982	-76.539 750
	113°55	-76.327 733	-0.213 455	-76.541 188
	108°94	-76.327 035	-0.214 205	-76.541 240

by Grahn [32]. In this investigation the hydronium ion was found to be planar (or almost planar), and the proton affinity of water was calculated to be approximately 250 kcal/mole.

Later the structure of this ion has been re-investigated by Bishop [33], using a nine-term single centre expansion of the molecular wavefunction. The HOH-angle was found to be $\alpha(\text{HOH}) = 114.5^\circ$ and the inversion barrier was computed to be 0.5 kcal/mole.

In the past few years a number of SCF MO studies on different levels of accuracy have been reported for the hydronium ion [30, 34–37]. In most of these calculations the hydronium ion has been either explicitly assumed or found to be planar, with a very shallow potential for the symmetric HOH angle variation.

Recently Lischka [30] has performed extended SCF and IEPA calculations for H_3O^+ . In the SCF approximation the ion has been found to be slightly non-planar with an inversion barrier of 0.94 kcal/mole. For the proton affinity of the water molecule a value of 176.6 and 174.0 kcal/mole has been calculated in the SCF and IEPA approximation, respectively.

In the present work, the hydronium ion was studied both in the SCF approximation and on the CI level of accuracy, using a 10010 configuration wavefunction (5420 terms for the planar structure). A number of points on the energy hypersurface have been calculated for different distances $d(\text{OH})$ and angles $\sphericalangle(\text{HOH})$, with the symmetry of the ion kept to be C_{3v} . The geometry parameters and computed total energies are listed in Table 5.

From this energy hypersurface the most stable structure can be determined, and the symmetric stretching and bending force constants be computed. For this purpose, the following polynomial in r ($r = d(\text{OH})$) and θ (angle between the OH bonds and the inversion plane) has been fitted to the energy hypersurfaces in the SCF and CI approximations by least square techniques:

$$E = E_0 + a_{10}r + a_{20}r^2 + a_{30}r^3 + a_{02}\theta^2 + a_{04}\theta^4 + a_{06}\theta^6 + a_{12}r\theta^2 + a_{14}r\theta^4 + a_{22}r^2\theta^2 + a_{24}r^2\theta^4. \quad (3.1)$$

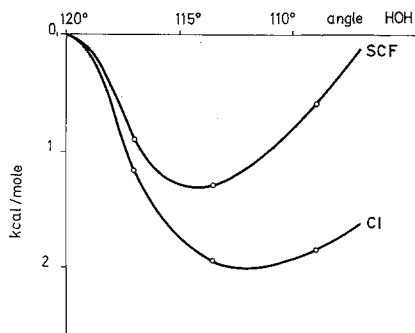


Fig. 1. Potential curves for the angular variation (angle HOH) in H_3O^+ on the SCF and the CI level of accuracy

The geometry parameters and force constants computed from this polynomial are listed in Table 6.

The present investigation thus predicts the hydronium ion to have a pyramidal structure and estimates the inversion barrier to be 2.0 kcal/mole. The SCF values for the geometry parameters agree well with the parameters obtained by Kollman and Allen [37] in a recent SCF study, using a slightly smaller basis set. It is well known that polarization functions on the central atom are essential for a correct description of the inversion motion of XY_3 molecules. In the present work only one set of d -orbitals on oxygen has been included in the basis set. On the other hand Rauk *et al.* have shown [38] in the case of ammonia that the inclusion of a second set of d -orbitals on nitrogen increases the inversion barrier from 4 to 5 kcal/mole, i.e. by about 20% of the SCF barrier. A similar, but smaller effect of the same kind can be expected for the hydronium ion. If we assume that the correction is roughly proportional to the barrier on the SCF level we would expect an error of 0.2–0.3 kcal/mole. We can therefore predict the inversion barrier of the hydronium ion to be in the range of 2.0–2.5 kcal/mole. A comparison of the SCF and the CI results shows that 0.65 kcal/mole, or 32% of the energy barrier are due to correlation, and it can be seen that correlation favours the pyramidal structure with a smaller bond angle (cf. Fig. 1). The lengthening of the bond distance in the CI calculation (compared to SCF) is the same in H_3O^+ as in H_2O (0.016 Å).

The valence shell correlation energy of the hydronium ion has been calculated to be -0.2120 a.u. at the equilibrium geometry, while the corresponding value for the water molecule is -0.2145 a.u. Thus, the correlation energy of the hydronium ion is estimated to be approximately 1.5 kcal/mole *smaller* in magnitude than that of the water molecule. A similar correlation energy difference has been obtained by Lischka [30], using the IEPA approach. It has been argued, that the correlation energy of the hydronium ion should have a value between those of H_2O and NH_3 [36, 39]. The correlation energy difference between these two molecules has been estimated to be 28 kcal/mole [40]. Taking this estimate the correlation energy difference between H_2O and H_3O^+ has been expected to be as large as approximately 20 kcal/mole [36]. However, estimates of the correlation

Table 6. Calculated properties for H_3O^+

	SCF	CI
Total energy (a.u.) ^a	- 76.329 776	- 76.541 803
Correlation energy (a.u.) ^a		- 0.212 027
$d(\text{OH})$ (Å)	0.959	0.972
Angle (HOH) (degrees)	113.5	111.6
Inversion barrier (kcal/mole)	1.30	2.05
Energy difference (kcal/mole) ^b	174.3	172.8
Zero-point energy difference (kcal/mole)	5.28	5.28
Proton affinity of H_2O (kcal/mole)	169.0	167.5
Symmetric stretching force constant (md/Å) ^c	8.49	7.58
Symmetric bending force constant (md/Å) ^c	0.34	0.40

^a At the equilibrium geometrical structure.

^b $\Delta E = E(\text{H}_2\text{O}) - E(\text{H}_3\text{O}^+)$.

^c Defined according to: $V = V_0 + (3/2)f_r(\Delta r)^2 + (3/2)r_e^2 f_\theta(\Delta\theta)^2$.

energy difference between H_2O and NH_3 based on recent accurate SCF calculations [21, 38], indicated much smaller values of approximately 5–10 kcal/mole. Moreover, the electronic structure of the hydronium ion is much more similar to that of the water molecule, than to that of the ammonia molecule. Thus the small correlation energy difference between the water molecule and the hydronium ion found in the present investigation seems to be reasonable.

The proton affinity of the water molecule is defined as the difference of the total energies of the hydronium ion and the water molecule. The proton affinity can be estimated from the difference of the electronic energies *and* the changes in the zero-point energies of the two systems. From the observed fundamental vibrational frequencies [41] the zero-point energy of the water molecule may be determined to be 13.47 kcal/mole. The zero-point energy of the hydronium ion on the other hand cannot be calculated along this line, because the infrared spectrum of the free ion has not been observed. However, it is possible to determine all vibrational frequencies by the so called "valence force method" [42] from the symmetric force constants only. To check this approach, the vibrational frequencies of the water molecule have been calculated, using the computed symmetric (CI) force constants listed in Table 4. This gives the following frequencies (the experimental values are given in brackets): $\nu_1 = 3860.8$ (3825.3) cm^{-1} , $\nu_2 = 1649.0$ (1654.9) cm^{-1} , $\nu_3 = 3914.4$ (3935.6) cm^{-1} . The zero-point energy of the water molecule computed from these frequencies is found to be 13.46 kcal/mole, which is almost identical to the value calculated from the experimental frequencies.

The same approach has been applied to the calculation of the zero-point energy of the hydronium ion. The following frequencies have been obtained using the symmetric (CI) force constants listed in Table 6 (the experimental values for the hydronium ion in crystalline oxonium salts are given in brackets [43, 44]):

$$\begin{aligned} \nu_1(a_1) &= 3603.5 \text{ (2800–3200) } \text{cm}^{-1}, \nu_2(a_1) = 887.0 \text{ (1100–1200) } \text{cm}^{-1}, \\ \nu_3(e) &= 3390.5 \text{ (2600–2800) } \text{cm}^{-1}, \nu_4(e) = 1636.0 \text{ (1600–1700) } \text{cm}^{-1}. \end{aligned}$$

Table 7. Symmetric bending and stretching vibration frequencies in H_3O^+

Quantum numbers		Frequency in cm^{-1}
stretching	bending	
0	1	83
0	2	596
0	3	1037
0	4	1606
0	5	2238
0	6	2927
1	0	3598
0	7	3666
1	1	3739
1	2	4228

From these frequencies the zero point energy of the hydronium ion follows to be 20.79 kcal/mole, while experimental crystal data give a value of approximately 18.4 kcal/mole.

The present approach seems to be unsatisfactory in case of the hydronium ion for the following reason: The valence force method to compute vibrational frequencies is based on the assumption of a harmonic potential. But the lowest frequency of the hydronium ion, that is the symmetric bending frequency, has been calculated to be $\nu_2(a_1) = 887.0 \text{ cm}^{-1}$ ($= 2.54 \text{ kcal/mole}$) which is well above the calculated inversion barrier of 2.05 kcal/mole. As a result large deviations from harmonicity have to be expected.

Therefore, for a more realistic determination of the vibrational frequencies the symmetric vibrational modes are calculated directly by solving the two-dimensional vibrational problem: For this purpose the vibrational wavefunction is expanded in products of Hermitefunctions, and the linear combination coefficients are determined by an energy minimisation (energy variation principle). This calculation has been done by a computer program written by Almlöf [45]. In the present investigation, the 11-term analytical potential (3.1) has been used to be fitted to the calculated energy hypersurface. The vibrational wavefunction has been approximated by a 144 term expansion in which both the linear coefficients and the Gaussian exponents have been optimized.

The lowest vibrational frequencies are listed in Table 7: The zero-point energy contribution from the symmetrical vibrational frequencies is calculated to be 1530.8 cm^{-1} , while the valence force method leads to 2245.3 cm^{-1} . The fundamental stretching frequency is determined to be $\nu = 3598 \text{ cm}^{-1}$, which is almost identical to the value of $\nu = 3604 \text{ cm}^{-1}$ computed by the valence force method. Therefore the asymmetric stretching frequency $\nu_3 = 3390.5 \text{ cm}^{-1}$ and the bending frequency $\nu_4 = 1636.0 \text{ cm}^{-1}$ obtained by the valence force method are believed to be in reasonable agreement with the actual frequencies.

The zero-point energy of the hydronium ion is determined from these frequencies to be 18.75 kcal/mole; the zero-point energy of the water molecule is similarly determined to be 13.47 kcal/mole. Thus the proton affinity of water is computed to be 169.0 kcal/mole at the SCF level and to be 167.5 kcal/mole at

the CI level; the contribution of the vibrational motion is calculated to be -5.28 kcal/mole. The proton affinity is seen to decrease by 1.5 kcal/mole if electron correlation is taken into account. The calculated proton affinity is in very good agreement with the values of 166 ± 2 kcal/mole [46] and 168 ± 3 kcal/mole [47] recently determined experimentally by cross section measurements for some ion molecule reactions.

3.3 The System $\text{Li}(\text{H}_2\text{O})^+$

A number of semiempirical and *ab initio* self-consistent field calculations on the monohydrate of the lithium cation have been reported in the literature [21, 48–51]. The most extensive calculations have been performed by Diercksen and Kraemer (DK) [50] and by Clementi and Popkie, (CP) [21], using large, contracted Gaussian basis sets. In both studies the system $\text{Li}(\text{H}_2\text{O})^+$ has been found to be planar. Clementi and Popkie, using their largest basis set, have calculated the equilibrium Li–O distance to be $d(\text{LiO}) = 1.842 \text{ \AA}$, and a binding energy (hydration energy) value of $B^{\text{Hydr}}(\text{Li}^+) = 35.20$ kcal/mole. Both, DK and CP, have studied the influence of the lithium cation on the geometry of the attached water molecule (on the SCF-level) and found the effect to be very small.

In the present investigation emphasis has been put primarily on the study of the correlation energy effects in the equilibrium structure of the lithium monohydrate. Therefore only a limited geometry variation has been considered. In the case of the planar structure the (LiO)-bond distance has been varied keeping the geometry of the water molecule fixed at the experimental values. Further, because the $\text{Li}(\text{OH}_2)^+$ might be expected to favour a non-planar structure in analogy to the OH_3^+ , some calculations with out of plane positions of the lithium cation have been performed as well. – In the present calculations, a 5613 (non-zero) term expansion of the wavefunction has been used for the planar structure, and a 10101 term expansion for the non-planar structure. All single and double excitations have been taken into account in forming the wavefunctions, except those from the energetically lowest molecular orbital (of $1s$ -oxygen character).

The results of these calculations are listed in Table 8. In agreement with previous SCF investigations we find the most stable geometry to be planar. The variation of the correlation energy for the out of plane motion of the lithium ion is very small. Looking at the $d(\text{LiO})$ bond length variation a six term polynomial in $1/d(\text{LiO})$ has been fitted to the calculated points of the potential energy curves by the least square method, both on the SCF and on the CI level. From these analytical approximations to the computed potential energy curves, the equilibrium Li–O distance is calculated to be $d(\text{LiO}) = 1.831 \text{ \AA}$ within the SCF accuracy and to be $d(\text{LiO}) = 1.842 \text{ \AA}$, if correlation effects are taken into account. This indicates that the correlation correction has apparently only very little effect on the SCF result in this case. In the SCF study of CP a value of $d(\text{LiO}) = 1.842 \text{ \AA}$ has been reported. Kebarle *et al.* [52] on the other hand deduced from their measurements a bond length of $d(\text{LiO}) = 1.92 \text{ \AA}$. This discrepancy between the theoretically determined $d(\text{LiO})$ -value and the experimental one is hard to understand because of the high accuracy of the theoretical calculations, which gives normally agreement with experimental bond distances within a few thousands of an Ångstrom.

Table 8. SCF and CI energies for the system $\text{Li}^+ \cdot (\text{H}_2\text{O})$ in different geometrical configurations

$d(\text{LiO})$ a.u.	θ^a	E_{SCF} a.u.	E_{corr} a.u.	E_{CI} a.u.
3.0	0°	-83.335626	-0.239211	-83.574837
3.3		-83.344799	-0.239555	-83.584354
3.4		-83.345591	-0.239670	-83.585261
3.5		-83.345663	-0.239780	-83.585443
3.6		-83.345190	-0.239885	-83.585075
3.7		-83.344310	-0.239982	-83.584292
4.0		-83.340206	-0.240229	-83.580435
4.5		-83.331827	-0.240509	-83.572336
5.0		-83.324138	-0.240676	-83.564814
10.0		-83.296905	-0.241132	-83.538037
100.0		-83.288274	-0.241380	-83.529654
3.5	5°	-83.345604	-0.239785	-83.585389
3.6		-83.345135	-0.239889	-83.585024
3.7		-83.344258	-0.239987	-83.584245
3.5	10°	-83.345427	-0.239798	-83.585225
3.6		-83.344969	-0.239904	-83.584873
3.7		-83.344103	-0.240002	-83.584105

^a θ is the angle between the bisector of the HOH-angle and the O-Li vector. The Li^+ ion is located in the symmetry plane perpendicular to the plane of the water molecule.

The correlation energy of the composed system $\text{Li}(\text{H}_2\text{O})^+$ is smaller in magnitude than the sum of the correlation energies calculated for the isolated subsystems; the difference is 1.16 kcal/mole. This is consistent with a similar result obtained for the hydronium ion. A reasonable explanation for this result may be found looking at the corresponding density difference graphs obtained with the MUNICH graphics program package [16]. From these plots it can be seen that in both cases an electron delocalization onto the positive ion takes place. As a result the effective nuclear charge observed by an individual electron is decreased leading to the observed correlation difference. We note, however, that this finding disagrees with the result obtained by Kistenmacher *et al.* [51], who used the Wigner statistical model to estimate the correlation energy effects. Using their SCF electron densities they calculate the correlation energy difference to be -0.26 kcal/mole, that is a larger correlation energy (in magnitude) for the complex than for the isolated subsystems.

In order to compute the hydration energy of the lithium cation to some accuracy, the change of the zero-point energy in forming the hydrate from the isolated subsystems has to be estimated. This has been done by using the valence force approximation [42]. The force constant for the stretching of the O-H bonds and the variations of the H-O-H angle were taken from the CI calculations on the free water molecule. These force constants do not change very much going to the monohydrate as has been shown by Kistenmacher *et al.* [51]. The force constants for the Li-O stretching (k_1) and the out of plane motion of the lithium ion (k_A) has been deduced from the present CI calculations. The resulting values are $k_1 = 0.903$ mdyne/Å and $k_A/d(\text{Li-O})^2 = 0.020$ mdyne/Å, respectively.

Table 9. Calculated properties for $\text{Li}^+ \cdot \text{H}_2\text{O}$

	SCF	CI
Total energy (a.u.) ^a	-83.345706	-83.585814
Correlation energy (a.u.) ^a		-0.240108
$d(\text{LiO})$ (Å)	1.831	1.842
Energy difference (kcal/mole) ^b	36.08	34.92
Zero-point energy difference (kcal/mole)	2.05	2.05
Binding energy (kcal/mole) ^c	34.03	32.87
Vibrational frequencies (cm^{-1})		
ν_1 (O-H stretch)	3861.52	(3860.84) ^a
ν_2 (H-O-H angle)	1690.76	(1649.04) ^d
ν_3 (Li-O stretch)	552.36	
ν_4 (O-H stretch)	3914.43	(3914.36) ^d
ν_5 (Li, in plane bend)	390.59	
ν_6 (Li, out of plane bend)	449.98	

^a At the interpolated equilibrium geometry.

^b $\Delta E = E(\text{Li}^+) + E(\text{H}_2\text{O}) - E(\text{Li}^+ \cdot \text{H}_2\text{O})$.

^c Including vibrational energy correction (O°K).

^d Calculated values for a free water molecule are given in brackets.

The force constant for the in-plane motion of Li^+ may be assumed to be equal to k_A . Using these force constants the fundamental frequencies listed in Table 9 can be calculated. Kistenmacher *et al.* have reported similar values obtained from their more extensive SCF energy hypersurface. In view of the accuracy of the valence force approximation as discussed by Herzberg and the accuracy of our computed energy surface we believe the zero-point energy computed from the frequencies listed in Table 9 to be accurate to ± 0.4 kcal/mole. The hydration energy of the lithium cation is thus calculated, with the estimated zero-point energy changes included, to be $B^{\text{Hydr}} = 34.03$ kcal/mole and 32.87 kcal/mole at the SCF and CI level, respectively. The experimental value reported by Kebarle *et al.* [52] is 34.0 kcal/mole. Kistenmacher *et al.* [51] have obtained the value 34.1 kcal/mole in their SCF study. It should, however, be noted that their corrections for vibrational and correlation energy changes are slightly different from ours.

Finally an interesting decomposition of the total interaction energy between the lithium cation and the water molecule into physically meaningful subparts may be performed. In the case of hydrogen bonds it is well known that the dominant contribution to the bond energy originates in general in a purely electrostatic interaction between the associated subsystems. The same can be expected to hold for the interactions between a positive ion and a polar molecule like H_2O . To get this part of the bond energy in a particular point of the energy hypersurface the energy expectation value has to be calculated in that point from a wavefunction, which has been constructed from the molecular orbitals of the non-interacting subsystems after a proper Schmidt orthogonalization of the corresponding orbital sets among each other. The electrostatic contribution is then

Table 9a. Different contributions to the binding energy for the system $\text{Li}^+ \cdot \text{H}_2\text{O}$ (kcal/mole)

$d(\text{LiO})$ a.u.	ΔE (electrostatic)	ΔE (delocalization)	ΔE (correlation)	ΔE (total)
3.0	-28.36	-1.36	1.36	-28.36
3.3	-34.54	-0.94	1.15	-34.33
3.4	-35.12	-0.86	1.07	-34.91
3.5	-35.24	-0.78	1.00	-35.02
3.6	-35.00	-0.72	0.94	-34.78
3.7	-34.50	-0.67	0.88	-34.29
4.0	-32.04	-0.56	0.72	-31.88
4.5	-26.93	-0.43	0.55	-26.81
5.0	-22.21	-0.30	0.44	-22.07
10.0	- 5.40	-0.02	0.16	- 5.26

determined as the difference between this energy expectation value and the sum of the SCF energies of the separated subsystems. On the other hand, the difference between this energy expectation value and the actual iterative SCF energy of the total interacting system has been defined by Kollman and Allen [57] as the delocalization energy. This second contribution to the bond energy accounts for the effect of polarization and charge transfer which takes place in the process of bond formation. A third part, the correlation contribution, is obtained from the difference between the calculated correlation energies of the total interacting system and the non-interacting subsystems. The different contributions are listed in Table 9a for the monohydrated lithium cation. The data show that the binding in $\text{Li}^+ \cdot \text{H}_2\text{O}$ originates more or less purely in the electrostatic interaction. Delocalization and correlation give only very small effects, which cancel out each other to some extent as the correlation energy decreases during bond formation in $\text{Li}^+ \cdot \text{H}_2\text{O}$.

3.4. The System $\text{F} \cdot (\text{H}_2\text{O})^-$

Abinitio SCF studies of the monohydrated fluoride anion have been reported recently by Diercksen and Kraemer (DK) [54], as well as by Kistenmacher, Popkie, and Clementi (KPC) [51, 53]. Semiempirical CNDO/2 calculations on this system have been performed by Lischka *et al.* [55] and by Breitschwerdt and Kistenmacher [48].

In both *ab-initio* studies the structure of the $\text{F}(\text{HOH})^-$ with a linear hydrogen bond between the F^- ion and the attached water molecule has been determined to have a (FO)-bond length of $d(\text{FO}) = 2.51 \text{ \AA}$, keeping the H_2O geometry fixed. Apart from this optimization an additional variation of the (FHO)-bond angle has been performed by KPC leading to a very small deviation from the linear H-bond by 4.5° . The hydration energy values reported in the two investigations are both very similar:

$$B^{\text{Hydr}} = 24.07 \text{ kcal/mole (DK) and } B^{\text{Hydr}} = 23.7 \text{ kcal/mole (KPC).}$$

Both CNDO/2 calculations have failed to predict realistic bond energies.

Table 10. SCF and CI energies for the system $F^- \cdot (H_2O)$ in different geometrical configurations

$d(FO)$ a.u.	$\sphericalangle(OHF)$	E_{SCF} a.u.	E_{corr} a.u.	E_{CI} a.u.
4.5	180°	-175.539525	-0.415452	-175.955628
4.6		-175.540475	-0.415137	-175.955612
4.7		-175.540874	-0.414828	-175.955702
4.8		-175.540847	-0.414594	-175.955441
5.0		-175.539902	-0.414063	-175.953965
10.0		-175.509965	-0.411663	-175.921628
100.0		-175.502617	-0.411717	-175.914334
4.7	178°	-175.541116	-0.414852	-175.955968
	176°	-175.541211	-0.414808	-175.956019
	174°	-175.541165	-0.414756	-175.955921

Table 11. Calculated properties for the system $F^- \cdot (H_2O)$

	SCF	CI
Total energy (a.u.) ^a	-175.541213	-175.956023
Correlation energy (a.u.) ^a		-0.414810
$d(FO)$ (Å)	2.509	2.471
Angle (FHO) (degrees)	175.67	176.44
F-O stretching force constant (md/Å)	0.590	0.596
Energy difference (kcal/mole) ^b	24.22	26.16
Binding energy (kcal/mole) ^c	21.04	22.98

^a At the interpolated equilibrium geometry.

^b $\Delta E = E(F^-) + E(H_2O) - E(F^- \cdot H_2O)$.

^c Including a zero-point energy correction of 3.18 kcal/mole [51]. The experimental value is 23.3 kcal/mole [55].

The present study has been restricted to an investigation of the monohydrated fluoride anion near to its equilibrium geometry, varying the (FO)-bond length and the (FHO)-bond angle in a quite limited range. The geometry of the water molecule has been kept fixed at its experimental equilibrium value. – The calculations have been performed using a 36204 (non-zero) term expansion of the wavefunction. All single and double excitations have been taken into account in forming this wavefunction, except excitations from the energetically lowest molecular orbital (of 1s fluorine and oxygen character).

For the different points on the energy hypersurface the computed SCF and CI energies, and the correlation energies are listed in Table 10. For the linear hydrogen bonded structure ($\sphericalangle(FHO) = 180^\circ$) a fourth degree polynomial in $d(FO)$ has been fitted to the calculated SCF and CI results. From these polynomials the equilibrium bond distance is determined to be $d^{SCF}(FO) = 2.51 \text{ \AA}$, and $d^{CI}(FO) = 2.47 \text{ \AA}$, respectively. The value calculated on the SCF level is in complete agreement with the values reported by DK [54] and KPC [53]. The

hydrogen bond angle has been calculated to be $\angle^{\text{SCF}}(\text{FHO}) = 175.5^\circ$, and $\angle^{\text{CI}}(\text{FHO}) = 176.4^\circ$. The value determined within the SCF approximation agrees with the value reported by KPC [53].

It has already been pointed out that in the monohydrates of the proton and the lithium cation the charge delocalization is the dominating effect leading to the observed decrease of the total correlation energy in the composed system compared to the sum of the correlation energies of the non-interacting subsystems.

An analogous study of the monohydrated fluoride anion shows that in connection with the strong polarizability of the F^- ion (which can already be realized on the SCF level looking at the corresponding density difference plots [16]) a considerable dispersion energy contribution can be expected which gives rise to an increase of the correlation energy in the composed system $\text{F}^- \cdot \text{H}_2\text{O}$.

In agreement with the qualitative considerations, a correlation energy difference of $\Delta E_{\text{corr}} = -2.01$ kcal/mole (i.e. the difference between the correlation energy of the composed system and the sum of the correlation energies of the subsystems) has been obtained at the equilibrium bond length of $d^{\text{CI}}(\text{FO}) = 2.47$ Å. This value is somewhat larger than the one reported by Kistenmacher *et al.*, who calculated the correlation energy difference to be -0.75 kcal/mole, using Wigner's statistical model [51].

Only a very limited part of the energy hypersurface near the equilibrium geometry of the hydrated fluoride anion has been studied in the present investigation. Therefore the difference between the zero-point vibrational energies of the monohydrate and the isolated subsystems (the water molecule) cannot be calculated rigorously from the data obtained here. Using the analytic approximations to the potential energy curves of the linear hydrogen bonded $\text{F}(\text{HOH})^-$ system, the force constants for the FO stretching have been computed to be $k^{\text{SCF}} = 0.590$ mdyn/Å and $k^{\text{CI}} = 0.596$ mdyn/Å. This shows that the inclusion of correlation effects is of little influence on the stretching force constants, and it should be of even less influence on the bending force constants. Therefore the zero-point energy difference can safely be calculated within the SCF approximation, using for example the vibrational frequencies of the hydrated fluoride anion determined by Kistenmacher *et al.* in their extensive SCF study. From these frequencies the zero-point energy difference has been determined to be 3.18 kcal/mole (Kistenmacher *et al.* are reporting a value of 2.27 kcal/mole, which seems not to be consistent with the listed frequencies).

Taking this estimated zero-point energy change into account, the hydration energy of the fluoride anion is thus calculated to be $B^{\text{Hydr}} = 21.04$ kcal/mole at the SCF level, and $B^{\text{Hydr}} = 22.98$ kcal/mole at the CI level. This latter energy value deduced from the CI results is in excellent agreement with the experimental value of $B^{\text{Hydr}} = 23.3$ kcal/mole reported by Kebarle *et al.* [56]. – In an extensive SCF study Kistenmacher *et al.* obtained for the hydration energy a value of $B^{\text{Hydr}} = 22.18$ kcal/mole, using an approximation to estimate the correlation energy contribution. The difference in the SCF energies for the hydrated fluoride anion and the isolated subsystems has been computed by these authors to be 23.70 kcal/mole, which is close to the corresponding value of 24.22 kcal/mole obtained in the present work.

Table 12. Different contributions to the binding energy for the system $F^- \cdot H_2O$ (kcal/mole)

$d(FO)$ a.u.	ΔE (electrostatic)	ΔE (delocalization)	ΔE (correlation)	ΔE (total)
4.5	-21.25	-1.91	-2.34	-25.50
4.6	-22.10	-1.66	-2.15	-25.91
4.7	-22.56	-1.45	-1.95	-25.96
4.8	-22.74	-1.26	-1.81	-25.81
5.0	-22.41	-0.98	-1.47	-24.86

Concluding the discussion of the monohydrated fluoride anion the same decomposition of the total binding energy has been performed as has already been described in the lithium case. The corresponding data are summarized in Table 12. As can be expected, the largest part of the interaction energy arises from the electrostatic interaction again. In the equilibrium structure its contribution accounts for 87% of the binding energy, while delocalization and correlation give only minor effects. However, as there is in contrast to $Li^+ \cdot H_2O$ an increase of the correlation energy forming the hydrated complex, the correlation contribution leads to a stabilization of the hydrogen bond in this case. On the three different levels of accuracy (pure electrostatic approximation, SCF accuracy, CI accuracy) the following optimum FO-bond distances can be derived from the data in Table 12: $d(FO) = 2.55 \text{ \AA}$, 2.51 \AA , and 2.47 \AA , respectively. This demonstrates that inclusion of the higher interaction effects (delocalization and correlation) leads to shorter FO-distance.

3.5. The Water Dimer

Quite a number of SCF studies have been performed dealing with the water dimer [1, 58] since the first quantum theoretical treatment by Sokolov [59] in 1947. There are obvious reasons for the particular interest of theoreticians into the hydrogen bonding interaction between water molecules – namely because liquid water plays a fundamental role in many chemical and in most biochemical processes. An understanding of the water-water interactions appears therefore to be a necessary basis for a more detailed discussion of a number of chemical phenomena. In this context the water dimer is used as a suitable model system accessible to purely theoretical calculations accurate enough to study the basic physical principles of hydrogen bonding between water molecules. An extensive survey on the properties of the water dimer has been given by Rao [63] including references to earlier *ab initio* and semiempirical investigations.

The interaction between two H_2O molecules via a hydrogen bond is found to be a rather weak one. The most accurate SCF calculations published in the past few years favour a binding energy close to 5 kcal/mole [58] for the isolated dimer. From experimental measurements in ice crystals a value of about 5.7 kcal/mole may be deduced.

For such a weak hydrogen bond the question about the correlation influence arises even more to be of particular importance. Already in 1937 London [61] estimated the dispersion energy between two water molecules to follow a $(-K/R^6)$

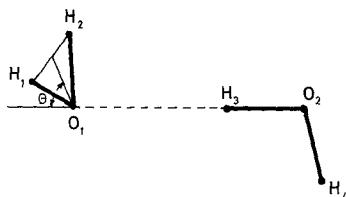


Fig. 2. Geometric structure of the water dimer system

dependence, where K was given the value 47×10^{-12} erg \AA^6 . This corresponds to a dispersion energy of 1.14 kcal/mole at an oxygen-oxygen separation of 2.9 \AA . An estimate based on the known values for the Neon dispersion attraction (appropriately scaled with the square of the polarizability ratio) yields a dispersion energy value of 0.9 kcal/mole at a distance of 2.76 \AA [62]. From a comparison of these data with the total dimerisation energy value of water the correlation contribution can be expected to be rather important in water-water interactions.

In the present investigation an attempt has been made to calculate this correlation contribution to the water dimerisation energy directly by means of the configuration interaction approach. For the generation of the CI wavefunction canonical Hartree-Fock orbitals have been used, and within this orbital basis all possible single and double excitations have been included except those from the 1s orbitals of the oxygen atoms. This leads to a total of 56 268 spin and space symmetrized configurations.

Previous SCF calculations have shown that in the equilibrium geometry of the dimer the two water molecules are attached to each other via a linear hydrogen bond with the outer hydrogen centres in a *trans* position (cf. Fig. 2). Thus we have limited the present study to this linear structure, varying the oxygen-oxygen distance and the angle θ only. As in the foregoing calculations the water molecules themselves have been kept fixed at the experimentally determined geometry.

The calculated energy values are listed in Table 13. From the SCF results an equilibrium geometry has been obtained which is in good agreement with previous SCF studies [58, 62]: $d(\text{OO}) = 3.00$ \AA , $\theta = 41.5^\circ$. The corresponding SCF binding energy follows to be $B = 5.14$ kcal/mole, without including any zero-point vibration energy correction.

Correlation has been found, however, to have a significant effect on these SCF results. The CI data summarized in Table 13 show that the absolute value of the correlation energy increases with decreasing oxygen-oxygen bond distance. The difference in the calculated correlation energies at the two positions on the potential curve with $d(\text{OO}) = 2.9$ \AA and $d(\text{OO}) = 100.0$ \AA is -1.03 kcal/mole. Thus inclusion of the correlation contribution results in a somewhat smaller $d(\text{OO})$ equilibrium distance and in a considerably larger binding energy value. The equilibrium CI results are: $d(\text{OO}) = 2.919$ \AA , $\theta = 42.4^\circ$, and $B = 6.05$ kcal/mole (zero-point energy not included).

Because of the difficulties in studying the structure of the isolated water dimer experimentally there are no reliable experimental data available for a direct comparison. Recently Torsi and Nixon [64] have performed a study of the

Table 13. SCF and CI energies for the water dimer, (H₂O)₂, in different geometrical configurations

$d(\text{OO})$ Å	θ^a	E_{SCF} a.u.	E_{corr} a.u.	E_{CI} a.u.
2.7	0°	-152.109425	-0.410433	-152.519858
2.8	0°	-152.110832	-0.410032	-152.520864
2.9	0°	-152.111489	-0.409717	-152.521206
3.0	0°	-152.111654	-0.409471	-152.521125
3.1	0°	-152.111507	-0.409275	-152.520782
100.0	0°	-152.103954	-0.408083	-152.512037
3.0	10°	-152.111802	-0.409467	-152.521269
3.0	20°	-152.111954	-0.409486	-152.521440
3.0	30°	-152.112082	-0.409512	-152.521594
3.0	40°	-152.112147	-0.409532	-152.521679
3.0	50°	-152.112099	-0.409538	-152.521637

^a θ is the angle between the plane of the proton acceptor H₂O molecule and the hydrogen bond axis (cf. Fig. 2).

Table 14. Calculated properties for the water dimer

	SCF	CI
Total energy (a.u.) ^a	-152.112148	-152.521683
Correlation energy (a.u.) ^a		-0.409533
$d(\text{OO})$ (Å)	2.994	2.924
Angle θ (degrees) ^b	41.5	42.4
O-O stretching force constant (md/Å)	0.137	0.163
Binding energy (kcal/mole) ^c	5.14	6.05

^a At the interpolated equilibrium geometry.

^b Angle between the plane of the proton acceptor H₂O molecule and the hydrogen bond axis (cf. Fig. 2).

^c Not including the vibrational energy correction (see text for discussion).

infrared spectrum of matrix isolated (solid nitrogen) water dimer molecules. They predict a linear structure with a single hydrogen bond. The frequency shifts they obtained seem to indicate a larger oxygen-oxygen distance compared to that one which has been deduced from measurements in ice. A more quantitative estimate of this difference in the bond lengths may be obtained by a comparison with corresponding data reported for formic acid and acetic acid [65]. In the vapor phase the oxygen-oxygen bond distances of these two acid dimers have been measured to be 2.73 Å and 2.76 Å, respectively, while in crystals a decrease of these distances to 2.58 Å, and 2.61 Å, respectively, has been obtained. Assuming a similar change of the bond distance to occur in the water case as well, one would expect an oxygen-oxygen distance in the water dimer of $d(\text{OO}) = 2.91$ Å in the gas phase. This value would be in excellent agreement with the one inferred from the present CI calculations.

Table 15. Different contributions to the binding energy for the water dimer (kcal/mole)

$d(\text{OO})^a$ Å	ΔE^b (electrostatic)	ΔE^b (delocalization)	ΔE (correlation)	ΔE (total)
2.7	-3.11	-0.32	-1.48	-4.91
2.8	-4.08 (-4.50)	-0.23 (-3.05)	-1.22	-5.53
2.9	-4.55	-0.18	-1.03	-5.76
3.0	-4.70 (-5.48)	-0.13 (-1.73)	-0.87	-5.70
3.1	-4.64	-0.10	-0.75	-5.49

^a Angle $\theta = 0^\circ$ (cf. Fig. 2).

^b Corresponding values obtained by Kollman and Allen [57] are given in parenthesis.

Similar difficulties arise for a comparison of the theoretically calculated dimerisation energy of water with experimental results. From a relation for the second order virial coefficient of water vapor Rowlinson [66] has determined an energy value of 4.86 kcal/mole for the water dimerisation. More recently maser studies [67] have revealed the existence of water dimers in the upper atmosphere and have established a stability of the dimer of 5.2 ± 1.5 kcal/mole against the dissociation reaction. Using a semiempirical statistical method Bolander *et al.* [65] have obtained for the water dimerisation a binding energy value between 2.9 and 3.1 kcal/mole including a zero-point vibration correction which has been estimated from the water force constants in ice and which is therefore expected to be somewhat too large. – Del Bene and Pople [68] have tried to determine the force constants of the water dimer molecule from an *ab initio* SCF energy hypersurface based on minimal STO-4G basis set calculations. From their data the zero-point energy change in the dimerisation process is obtained to be 1.5 kcal/mole. In the present calculations, however, the O–O stretching force constant and the force constant associated with the θ variation (cf. Fig. 2) have been computed to be considerably smaller than Del Bene and Pople's values. A reasonable estimate of the zero-point vibration correction based on the present results would thus lead to a smaller value of about 1 kcal/mole. With this correction the dimerisation energy of water is finally obtained to be 5.1 ± 0.3 kcal/mole, where the error limits account for the uncertainty in the zero-point vibration correction.

This binding energy value for the water dimer molecule is seen to be close to the originally calculated SCF value. Obviously the correlation and the zero-point vibration energy corrections, both of similar absolute magnitude, have opposite signs and thus cancel out each other to some extent. An analogous effect we have already observed in the case of the hydrogen bonded $\text{F}^- \cdot \text{HOH}$ system. This explains the success of previous SCF studies in predicting equilibrium geometries as well as the binding energies of these weakly interacting closed shell systems to an accuracy comparable in many cases to that obtained in experimental measurements.

Different contributions to the total interaction energy as have already been defined above are summarized in Table 15 for a number of oxygen-oxygen separations with $\theta = 0^\circ$ in the water dimer system. As in the previously discussed ion

Table 16. Energy lowering due to the basis set superposition effects for the single water molecules using the total set of basis functions as in the water dimer system

$d(\text{OX})$ Å	ΔE_{SCF} kcal/mole	ΔE_{corr} kcal/mole	ΔE_{Cl} kcal/mole
(a) proton acceptor molecule:			
2.70	0.53	0.59	1.12
2.80	0.48	0.50	0.98
2.90	0.44	0.43	0.87
3.00	0.39	0.38	0.77
3.10	0.36	0.34	0.70
(b) proton donor molecule:			
2.70	0.58	0.47	1.05
2.80	0.53	0.42	0.95
2.90	0.47	0.39	0.86
3.00	0.42	0.35	0.77
3.10	0.37	0.32	0.69

hydrates the pure electrostatic interaction is obtained as the most important part in this decomposition. In the case of the planar dimer structure ($\theta = 0^\circ$) it is found to account for as much as 79% of the total binding energy, while delocalization and charge transfer effects take part only with 3%. The correlation contribution has already been determined to be about 18%. The small effect of the delocalization obtained in the present study is quite different from the results of Kollman and Allen [59]. They have performed an equivalent analysis based on their SCF calculations and determined the electrostatic contribution to account for 76% and the delocalization effect for 24% of the total interaction energy. The discrepancy particularly in the delocalization value might be due to the fact, that Kollman and Allen did not include polarization functions in their basis sets. This deficiency of the basis set might possibly lead to a so-called "superposition error", which arises if the basis functions on one of the water molecules are used to some extent to improve the wavefunction on the second water molecule.

To have a rough estimate of the effect of the basis set superposition error on the results obtained in the present study some additional calculations have been performed for a single water molecule employing the total set of basis functions used for the water dimer. Two different cases have been considered in this context and the corresponding numerical results have been summarized in Table 16: in the first case the basis set effect has been determined for the proton acceptor molecule with the additional basis functions of the second water in the positions of the proton donor part [the $d(\text{OX})$ -values in Table 16 represent the distances between the acceptor oxygen and the centre X of the functions belonging originally to the proton donor oxygen], while in the second case the analogous calculations have been performed for the proton donor water molecule. The data in Table 16 show that the basis set effects are of almost equal magnitude for both cases (acceptor and donor molecule), particularly for $d(\text{OX})$ -values close to the actual equilibrium oxygen-oxygen distance. Compared to the small dimerization energy of water the computed energy effects are surprisingly large. It has to be pointed out, however,

that the improvement of the wavefunctions of the two single water molecules obtained from these model calculations is, of course, much bigger than the one which has to be expected for each of the two water molecules in the dimer because the nuclear charges of the second water are missing and the additional function set can exclusively be used by the single water molecule. Thus the calculated values have to be considered as very high upper limits to the actual basis set effects in the water dimer.

4. Conclusion

The main topic of the present study on hydrogen bonding and on ion hydration has been to discuss in some detail the influence of the correlation energy effects on the structure and stability of weakly interacting closed shell molecular systems. The accuracy needed for this purpose has been achieved by using extended and flexible gaussian basis sets on the nuclear centres, including on each centre one set of polarization functions, and by expanding the CI wavefunctions over all the single and double excitations of the valence electrons, that can arise within the associated molecular orbital basis. Using this approach it has been possible to account approximately for as much as 70% of the valence electron correlation energy.

Good agreement has been obtained with measurements in those cases where experimental results are available from the literature. Particularly, the calculated binding energies are within the experimental error limits and in most cases the difference between the theoretical and the experimental value is even less than 1 kcal/mole. For the single water molecule the calculated bond distance has been found to differ by only 0.003 Å from the measured value. This accuracy can of course not be expected for the bond distances between the weakly interacting systems as well, because the interaction potential curve is found to be quite flat. In these cases the error in the calculated bond distances is estimated to be certainly not larger than 0.02 Å.

For a further discussion of the accuracy of the approach used in this study essentially two sources of errors in the calculations should be considered arising namely from the incompleteness of the atomic basis sets employed and from the exclusion of the higher excitations in the present CI wavefunctions.

As has already been pointed out the basis set limitation may give rise to the so-called superposition error in the calculated potential curve leading to an artificial lowering of the potential curve in the minimum region and therefore to binding energies which are too large. The additional calculations which have been performed to study this effect in the water dimer case show that this error can be expected to be much smaller than about 0.4 kcal/mole and 0.8 kcal/mole on the SCF and the CI level of accuracy, respectively, where these values have to be considered as very upper limits to the actual effects. There is no easy way to determine this basis set effect directly. For the weakly interacting two water molecules its influence on the theoretically calculated binding energy value might be non-negligible. For the hydrated ionic systems of this study, however, treated within the same absolute accuracy the superposition error can be expected to be of very small influence since the absolute magnitude of the binding energy values is much larger.

Among the higher excitations the most important ones are the so-called "unlinked clusters", the CI expansion coefficients of which are obtained as products of the coefficients weighting the single and double excitations. For covalent bonds these terms have been found to depend strongly on the bond distance and to have therefore a non-negligible effect on the equilibrium geometries [69]. In the case of the weakly interacting closed shell systems of the present study, however, these terms can reasonably be expected to be almost independent of the intersystem separation. The actual contribution arising from the unlinked clusters may be estimated from the re-normalization equation:

$$E_{u.c.} = (1 - C_0^2) E^{(2)},$$

where $E^{(2)}$ represents the correlation energy contribution obtained from the double excitations only and where C_0 is the CI coefficient of the leading configuration, usually the Hartree-Fock determinant. From this formula the unlinked cluster contributions to the total binding energy have been estimated to be less than 0.1 kcal/mole for the water dimer and less than 0.2 kcal/mole for the $F^- \cdot H_2O$ system.

Summarizing it can be concluded that the correlation energy contributions to the total binding energy of the weakly interacting closed shell systems studied here are of the order of 1 kcal/mole. In the case of the monohydrated positive ions it has been found that in the process of bond formation the correlation contribution decreases due to electron delocalization and thus leads to smaller binding energies compared to the SCF results. A further lowering of the bond energy is obtained by inclusion of a zero-point vibration energy correction. In hydrogen bonded systems, on the other hand, the dispersion attraction is apparently the dominating correlation effect leading to an increase in magnitude of the correlation energy in the composed system. The resulting increase of the total binding energy is however partly compensated by the change in the vibrational zero-point energy which is of the same order of magnitude and which has therefore to be included at this level of accuracy. This finding provides finally a plausible explanation for the fact that a number of pure SCF studies on the structure and stability of hydrogen bonded systems, neglecting any zero-point corrections, have been able to give results which are in a surprisingly good agreement with experimental values.

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