Theoret. Chim. Acta (Berl.) 44, 109–127 (1977)

THEORETICA CHIMICA ACTA

Calculation of Molecular One-Electron Properties

A Comparative Study on FH and H_2O

Peter Swanstrøm*, Wolfgang P. Kraemer, and Geerd H. F. Diercksen

Max-Planck-Institut für Physik und Astrophysik, D-8 München 40, Föhringer Ring 6,
Federal Republic of Germany

A comprehensive analysis of the reliability of computed first- and second-order properties is attempted. The best and most recent experimental and theoretical data available in the literature have been compiled and compared to those obtained using moderately sized and extensive basis sets in calculations at the coupled Hartree-Fock level. It is concluded that prediction of the properties dealt with in this paper is, in general, safe though there are certain problems concerning the description of charge density polarization phenomena.

Key words: Electric moments – Polarizability – Susceptibility – Nuclear magnetic shielding

1. Introduction

The theoretical prediction of molecular properties is a field of growing interest to astrophysicists. This is because of the presence of molecular species in interstellar space, some of which are so unstable under terrestrial conditions that it has not yet been possible or it is at least extremely difficult to obtain the necessary data from laboratory measurements. In such cases, the identification and description of the properties of interstellar matter as well as the preparation of laboratory measurements would be greatly facilitated by means of accurate theoretical predictions. Due to the small size of most of these interstellar molecules, this seems also to be a field where *ab initio* methods are at the same time applicable and powerful.

In the present work we have focused on the reliability of some computed first- and second-order properties of two well-examined molecules, namely FH and H_2O. In particular, we have studied how a change of the molecular orbital basis affects the calculated properties, and we have compared our results extensively to other published theoretical results and to recent experimental data.

2. Calculations

The calculations of the molecular properties in this study are performed using the coupled Hartree-Fock approximation, i.e. they are all confined to the single determi-

---

* Permanent address: Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.

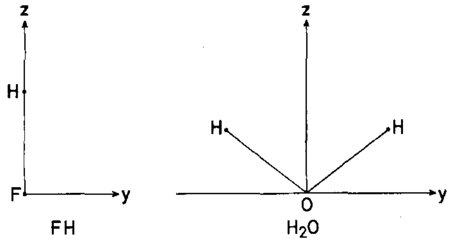

Fig. 1. Molecular geometries and definition of coordinate axes for FH and H_2O. d(FH) = 1.73290; d(OH) = 1.80889; (HOH) = 104.522 deg

nant self-consistent field level. The reader is referred to the paper by Thomsen and Swanstrøm [1] for a description of the coupled Hartree-Fock (CHF) scheme.

Two different Gaussian basis sets have been employed. The smaller one can be characterized as "improved double-zeta plus polarization". It consists of (11*s* 7*p* 1*d*) functions at the oxygen and fluorine centres, contracted to [5*s* 4*p* 1*d*], and of (6*s* 1*p*) functions at the hydrogen centres, contracted to [3*s* 1*p*], and is essentially the one proposed by Salez and Veillard [2]. The polarization functions have been optimized separately. The larger basis set is taken from van Duijnefeldt [3] and contains (13*s* 8*p* 2*d*) functions at oxygen and fluorine, contracted to [7*s* 5*p* 2*d*], and (8*s* 2*p*) functions at the hydrogens, contracted to [4*s* 2*p*], While the first set is already known to produce reliable molecular geometries (within the limits of about 0.005 Å) and total electronic energies which are off the Hartree-Fock limit by approximately 0.02 Hartree for the molecules considered [4, 5], the larger basis set was used to determine the influence of a change of the molecular orbital basis on the calculated properties and to check basis set saturation. We have used the experimental geometries for both molecules. The nuclear positions in the space-fixed coordinate systems are shown in Fig. 1. All results in this paper are given in atomic units. Conversion factors to SI units are listed under Tables 1-3.

The calculation of the Hartree-Fock molecular orbitals and the four-index transformation of the two-electron integrals to the molecular orbital basis were performed by the MUNICH molecular program system [6]. The one-electron properties were obtained using an IBM version (due to one of the authors (P.S.)) of the program system PERT/SCF [1] which has been interfaced to the MUNICH programs.

3. Results for FH

Hydrogen fluoride is a rather peculiar molecule from a theoretical point of view. The electronegativity of the fluorine atoms is so pronounced that the electronic charge distribution of this diatomic hydride is almost spherical, thus leaving the proton practically bare. This somewhat abnormal situation provides a crucial test for the calculation of molecular properties.

In Table 1 the following equilibrium electric properties are listed: SCF energy, centre of electronic charge (*EC*), sum of nuclear forces (f_z), force constant (k), dipole moment (μ), quadrupole moment (θ), and polarizabilities (α).

The sum of the Hellmann-Feynman forces acting on the nuclei along the z-axis is non-zero. This shows that the present SCF wave function is not yet a true Hartree-Fock

Table 1. Electric properties of FH. The experimental data are corrected for the effect of molecular vibration. Conversion factors: 1 a.u. of energy = 2.62556 x 10^6 J mol^{-1}; 1 a.u. of force = 8.23888 x 10^{-8} J m^{-1}; 1 a.u. of force constant = 1.55692 x 10^3 J m^{-2}; 1 a.u. of dipole moment = 8.47843 x 10^{-30} C m; 1 a.u. of quadrupole moment = 4.48659 x 10^{-40} C m^2; 1 a.u. of polarizability = 1.48185 x 10^{-31} m^3. The parenthesized numbers following some of the experimental data are the standard mean square deviations of the rightmost digits.

	This work	This work	Exp.	UCHF [10]	CHF [13]	TDCHF [14]	SPPA [15]	FPTM SCF [44]	FPTM CEPA [44]
Basis	[5.4.1/3.1]	[7.5.2/4.2]		(3.1/1)	(See Text)	(See Text)	(12.6/3.3)	(11*s*6*p*3*d*/5*s*2*p*)	
Energy	−100.0565	−100.0685	−100.530[a]	−99.5361	−100.0462		−100.0438	−100.0582	−100.2853
EC	0.0941	0.0971							
Σf_z	−0.052	−0.024	(0)						
k	0.623	-	0.620[a]						
$\mu_\parallel$	0.792	0.762	0.707[b]		0.755			0.757	0.703
$\Theta_\parallel$	1.696	1.745	1.755 (22)[c]						
$\alpha_\perp$	2.45	3.40	<5.1[d]	2.46	4.20	4.04	2.50	4.47	5.17
$\alpha_\parallel$	4.62	5.31	>5.1[d]	5.34	5.80	5.33	5.38	5.75	6.44
α	3.18	4.04	5.59[e]	3.42	4.73	4.47	3.46	4.90	5.59
$\alpha_\parallel - \alpha_\perp$	2.17	1.91		2.88	1.60	1.29	2.88	1.28	1.27

[a] Experimental estimate by Cade and Huo [17].

[b] Molecular beam electric resonance spectrum by Muenter and Klemperer [18].

[c] Molecular beam electric resonance spectrum by de Leeuw and Dymanus [8].

[d] Ionic polarizability from refractive index estimated by Tessman *et al.* [9].

[e] Refractive index measurements by Perkins [43], without vibrational correction.

Table 2. Magnetic susceptibility (in ppm) and rotational magnetic moment of FH. The experimental data are corrected for the effect of molecular vibration. Conversion factors: 1 a.u. of susceptibility = 8.92394×10^{-8} m3 mol^{-1}; 1 nuclear magneton (μ_N) = 5.05094×10^{-27} J T^{-1}

	This Work	This Work	Exp.	UCHF [20]	CHF [13]	UCHF [21]	CHF [22]
Basis	[5.4.1/3.1]	[7.5.2/4.2]		(3.1/1)	See Text	[5.3/5.1]	[5.4.1/3.1]
$\chi_{\perp}^{d}$	−127.0	−126.1				−124.1	−127.0
$\chi_{\parallel}^{d}$	−112.6	−112.4				−111.2	−112.6
$\chi_{\perp}^{p}$	7.6	7.8	9.38 (1)[a]	15.8	10.8	5.7	8.4
$\chi_{\parallel}^{d} - \chi_{\perp}^{d}$	14.4	13.7	15.04 (28)[a]			12.9	14.4
$\chi_{\parallel} - \chi_{\perp}$	6.8	5.9	5.90 (27)[a]			7.2	6.0
χ^{d}	−122.8	−121.5		−107.4	−122.3	−119.8	−122.2
χ^{p}	5.0	5.2	6.25 (1)[a]	10.5	7.2	3.8	5.6
χ	−117.1	−116.3		−96.9	−115.1	−116.0	−116.6
$G_{\perp}/\mu_N$	0.767	0.760	0.74104 (15)[a]		0.738		

[a] Molecular beam electric resonance spectrum by de Leeuw and Dymanus [8].

function although quite extended Gaussian basis sets have been employed [5]. The agreement between the computed and the experimental force constant supports earlier conclusions that *ab initio* calculated harmonic force constants at the SCF level lead to reliable results if the wave function used is close enough to the Hartree-Fock limit ([7], and reference therein). In contrast to the dipole moment, the quadrupole moment is in good agreement with the molecular beam result of de Leeuw and Dymanus [8]. Tessmann *et al.* [9] have measured ionic polarizabilities in crystals by means of refractive indices. They have estimated the polarizability of the F^- ion to be about 5.1 a.u. Anticipating the perpendicular and the parallel components in FH to be smaller and larger, respectively, than this value we notice that this is only fulfilled in the case of the larger basis set employed here. Perkins [43] measured the refractive index of liquid anhydrous FH at several wavelengths. Assuming a density of 0.9552 g cm^{-3} we calculate an average polarizability of 5.59 a.u. at infinite wavelength. This result is included in Table 1, although it ought to deviate significantly from the ideal gas phase result.

There are a number of previous theoretical calculations of the electric properties of FH using partly different approaches or different basis sets. The corresponding data available from the literature are added to Table 1 for comparison. These calculations are briefly described as follows:

Kolker and Karplus [10] used an uncoupled Hartree-Fock (UCHF) procedure employing the best limited basis molecular orbitals (BLMO) of Ransil [11]. We have to recall, however, the critical analysis by Sadlej and Jaszuński [12] who show that the Karplus-Kolker scheme is not in general acceptable for the calculation of the electric properties.

Stevens and Lipscomb [13] used a CHF procedure combined with explicit optimization of the first-order perturbed molecular orbitals. They used a $(7\sigma 3\pi)$ and a $(3\sigma 1\pi)$ Slater type orbital (STO) basis set at the fluorine and hydrogen centres, respectively, as zeroth-order wave function, augmented to a $(8\sigma 5\pi 1\delta)$ and a $(5\sigma 2\pi)$ basis for the perpendicular component and to a $(9\sigma 5\pi)$ and $(4\sigma 2\pi)$ basis for the parallel component of the electric field perturbation.

Epstein [14] employed a time-dependent CHF method to calculate the dynamic polarizability. He used the minimal STO basis set of Stevens and Lipscomb [13] for the zeroth-order wave function augmented to $(4\sigma 4\pi 1\delta)$ and $(3\sigma 1\pi)$ for the perpendicular component and to $(5\sigma 4\pi)$ and $(2\sigma 1\pi)$ for the parallel component of the electric field perturbation. The results quoted in Table 1 are obtained with the dipole-length operator formulation.

Oddershede *et al.* [15] used a self-consistent polarization propagator approximation to compute the dynamic polarizability. They used the STO basis set of Bender and Davidson [16] consisting of $(12\sigma 6\pi)$ functions on fluorine and of $(3\sigma 3\pi)$ functions on hydrogen. The corresponding results in Table 1 are those obtained using the dipole-length formulation, with two-particle/two-hole excitation corrections included.

Recently Werner and Meyer [44] reported a number of polarizability calculations. They used the finite perturbation method (FTPM), computing the dipole moment at

Table 3. Proton magnetic shielding (in ppm) and proton spin rotation constant in FH. The experimental data are corrected for the effect of molecular vibration. Conversion factor: 1 kHz = 6.62620 x 10^{-31} J

	This Work			This Work			Exp.	CHF [13]	UCHF [27]	UCHF [21]	CHF [22]	CHF [28]	CHF [29]
Basis	[5.4.1/3.1]			[7.5.2/4.2]				See Text	(3.1/1)	[5.3/3.1]	[5.4.1/3.1]	(3.1/1)	(5.2/2)
Gauge	*EC*	H	H*	*EC*	H	H*	H	H	H	H	H	-	-
$\sigma_{\perp}^{d}$	10.7	140.8	140.8	9.8	140.8	140.8			143.7	140.3	140.5		
$\sigma_{\parallel}^{d}$	43.8	43.8	43.8	44.1	44.1	44.1			44.8	43.5	43.8		
$\sigma_{\perp}^{p}$	10.2	−83.7	−119.9	9.9	−110.2	−121.1	−119.6 (3)[a]	−116.3	−124.8	−111.9	−119.5	(−114.8)	
σ^{d}	21.8	108.5	108.5	21.2	108.6	108.6	108.9 (8)[a]	108.4	110.7	108.0	108.3	(110.7)	
σ^{p}	6.8	−55.8	−80.0	6.6	−73.4	−80.7	−79.7 (3)[a]	−77.5	−83.2	74.6	−79.7	(−76.5)	
σ	28.6	52.7	28.6	27.8	35.1	27.8	29.2 (5)[a]	30.9	27.5	33.4	28.6	34.2	30.6
$\sigma_{\parallel}^{d} - \sigma_{\perp}^{d}$	33.1	−97.0	−97.0	34.3	−96.7	−96.7	−96 (9)[b]	−98.9	−98.9	−96.8	−96.7		
$\sigma_{\parallel} - \sigma_{\perp}$	22.9	−13.3	22.9	24.4	13.4	24.4	24 (9)[b]		26.0	15.1	22.8		
C_H/kHz			−70.3			−65.7	−71.5 (13)[a]	−70.7				−90.2	

[a] Vibrational corrections to nuclear magnetic shielding by Hindermann and Cornwell [26].

[b] Molecular beam electric resonance spectrum by de Leeuw and Dymanus [8].

several finite electric field strengths. The basis sets employed in this work are especially adapted and optimized for the determination of polarizability. On top of the SCF level they performed several calculations at the pseudo-natural orbital configuration interaction (PNO-CI) and the pseudo-natural orbital correlated electron-pair approximation (PNO-CEPA) levels. At the SCF level this procedure is virtually identical to the CHF method. The results quoted in Table 1 are those obtained using the more extensive uncontracted Gaussian basis set: ($11s6p3d$) functions at the fluorine and ($5s2p$) functions at the hydrogen centres.

Besides the basic difficulty to calculate reliable polarizabilities using a single determinant wave function, the theoretical results given in Table 1 indicate that within the present approach this quantity seems to depend crucially on the choice of the basis set.

First we discuss the results for the perpendicular components $\alpha_\perp$ of the polarizability. In the calculation reported by Oddershede *et al.* [15] the basis set contained many σ- and π- but no δ-type functions. They obtain a poor value for $\alpha_\perp$. In the calculations by Stevens and Lipscomb [13], by Epstein [14], and by Werner and Meyer [44], the basis set did contain δ-type functions and these authors obtain good values for $\alpha_\perp$. This indicates that the presence of diffuse δ-type functions is essential to a proper description of the perpendicular charge density polarization. This conclusion is supported by our own results: addition of a d-function to the smaller basis set improves the value for $\alpha_\perp$ from 2.45 a.u. to 3.40 a.u.

Stevens and Lipscomb [13], Epstein [14], and Oddershede *et al.* [15] all obtain approximately the same values for $\alpha_\parallel$ ranging from 5.3 to 5.8 a.u. The relative improvement achieved by Stevens and Lipscomb is probably attributable to the specific optimization of the perturbed molecular orbitals performed by these authors. The basis sets did not include δ- but only σ- and π- type functions. Although both of our basis sets do include d-functions only the larger basis set leads to a value for $\alpha_\parallel$ which is comparable to the above results. We conclude that δ-type functions are not essential to the description of the parallel charge density polarization. This conclusion is supported by the following observation: The SCF results of Werner and Meyer [44] with d-functions in the basis set are fairly close to those of Stevens and Lipscomb without d-functions.

The PNO-CEPA results of Werner and Meyer seem to be superior to any other results obtained hitherto. They indicate that correlation effects are by no means negligible when calculating the polarizability.

In Table 2 we list the magnetic susceptibility (χ) and the rotational magnetic moment (G) of FH. The results are obtained with the gauge origin at the centre of mass. The table has no entry for the parallel component of the paramagnetic (high frequency) susceptibility since it vanishes identically.

The results obtained with the two different basis sets do not differ very much from each other, and they show good agreement with the molecular beam results of de Leeuw and Dymanus [8]. To the authors' knowledge there is no recent experimental determination of the total susceptibility available in the literature. Ehrlich [19] reported in 1942 a value of –96.4 ± 1.1 ppm based on liquid phase measurements, but we hesitate to compare this value directly to the other (gas phase) results of Table 2. We observe that, in general, an increased basis set size corresponds to a slightly improved agreement with the experimental results. It is striking, however, that the diamagnetic anisotropy shows the opposite trend, and this supports the conclusion that our two basis sets do not span the r^2 operator equally well in all directions.

We have added the results from a number of other theoretical works in Table 2:

Karplus and Kolker [20] used the same wave function [11] as above [10] to calculate the susceptibility in an UCHF variation-perturbation approach.

In the work [13] referred to above, Stevens and Lipscomb also calculated the susceptibility and the rotational magnetic moment. They used the same zeroth-order STO wave function, but the basis set was augmented to a $(8\sigma 5\pi 1\delta)$ basis for fluorine and a $(5\sigma 3\pi 1\delta)$ basis for hydrogen when the perpendicular magnetic field perturbation was calculated, and the first-order perturbed orbitals were optimized with special reference to this perturbation.

Sadlej and co-workers have performed both uncoupled and coupled Hartree-Fock calculations of the magnetic properties. In the UCHF work, Okniński and Sadlej [21] use the Gaussian basis set of Noble and Kortzeborn [23] ($(5s3p)$ functions at the F centre and $(5s1p)$ functions at H) in an approximate variation-perturbation method. In fact they have extended the virtual orbital spectrum of the Fock operator without extending the original basis set and a considerable improvement of the first-order perturbed orbitals is achieved. In the CHF work, Sadlej and Raynes [22] introduce a similar pseudo extension of the virtual orbital spectrum, but in this case they define the contribution from the additional orbitals by requiring the magnetic properties to be gauge invariant as they must be in an infinite basis [25]. Since the basis set used in this calculation is identical to our smaller basis a direct comparison between the two methods is possible. It appears that Sadlej and Raynes do obtain better agreement with experiment than we do even with the extended basis set.

As further magnetic properties the proton and fluorine shieldings (σ) are given in Tables 3 and 4, respectively, together with the spin rotation constants (C). Our results are given for three different gauge origins: EC, X, and X^* where X denotes a particular nuclear centre. The asterisk at the gauge origin indicates that the paramagnetic shielding has been obtained by a gauge invariant translation of the total shielding from EC to X, i.e. $\sigma^p(X^*) = \sigma(EC) - \sigma^d(X)$. This procedure has formerly been applied by Thomsen and Swanstrøm [7]. It is based on the assumption that EC is an appropriate gauge origin for the determination of magnetic properties, as originally proposed by Chan and Das [24]. Although there are objections against the arguments leading to this proposal, it seems to be acceptable from an empirical point of view.

The results for the proton shielding obtained with the two different basis sets do not differ much and they compare favourably both to the molecular beam results of de Leeuw and Dymanus [8], and to the experimental estimates by Hindermann and Cornwell [26]. The fact that in this case the smaller basis leads to results which are slightly, though not significantly better than those obtained with the larger basis sup-

Table 4. Fluorine magnetic shielding (in ppm) and fluorine spin rotation constant in FH. The experimental data are corrected for the effect of molecular vibration

	This Work			This Work			Exp.	CHF [13]	UCHF [27]	CHF [28]	CHF [29]
Basis	[5.4.1/3.1]			[7.5.2/4.2]				See Text	(3.1/1)	(3.1/1)	(5.2/2)
Gauge	*EC*	F	F*	*EC*	F	F*	F	F	F	-	-
$\sigma_{\perp}^{d}$	481.7	482.3	482.3	481.6	482.4	482.4			480.9		
$\sigma_{\parallel}^{d}$	482.0	482.0	482.0	481.9	481.9	481.9			482.9		
$\sigma_{\perp}^{p}$	−120.4	−121.7	−121.0	−103.9	−105.0	−104.7		−101.6	−155.4	(−97.4)	
σ^{d}	481.8	482.2	482.2	481.7	482.2	482.2	482.5 (20)[a]	481.6	481.6	(481.7)	
σ^{p}	−80.3	−81.1	−80.7	−69.3	−70.0	−69.8	−62.8 (3)[a]	−67.7	−103.6	(−64.9)	
σ	401.5	401.1	401.5	412.4	412.3	412.4	419.7 (3)[a]	413.9	378.0	416.8	411.7
$\sigma_{\parallel}^{d} - \sigma_{\perp}^{d}$	0.3	−0.3	−0.3	0.4	−0.5	−0.5	−1 (9)[b]		2.0		
$\sigma_{\parallel} - \sigma_{\perp}$	120.8	121.4	120.8	104.3	104.5	104.3	108 (9)[b]		159.2		
C_F/kHz			379.8			321.2	283.6 (15)[a]	312.4		294.9	

[a] Vibrational corrections to nuclear magnetic shielding by Hindermann and Cornwell [26].

[b] Molecular beam electric resonance spectrum by de Leeuw and Dymanus [8].

ports the assumption that these results cannot be improved any further within the CHF scheme employed. For the fluorine shielding the larger basis set is clearly superior to the smaller one. It is probable that an improved description of the electron density distribution around the fluorine nucleus would lead to still better agreement with experiment.

In Table 3 and 4 these data are compared to a number of previous theoretical results that have been obtained essentially within the approaches described above. Thus the shielding results of Kolker and Karplus [27] have been determined using the UCHF approximation on the basis of Ransil's BLMO wave function. The results of Stevens and Lipscomb [13], quoted in Table 3, were calculated with hydrogen as gauge origin. Choosing fluorine as origin they obtained the slightly better value of 28.45 ppm for the proton shielding due to the fact that in FH the centre of electronic charge (*EC*) is very close to the F centre.

The other results listed in Tables 3 and 4 have been obtained in the following way:

Ditchfield [28, 29] has performed CHF calculations of the shielding factors using gauge invariant atomic orbitals. With a minimal basis he obtained a better fluorine shielding and a poorer proton shielding than Kolker and Karplus [27] did with the same basis set size. This difference must therefore be attributed to the neglect of two-electron coupling terms in the UCHF procedure. With a split-shell basis he gets results in good agreement with experiment.

Sadlej and co-workers have also performed uncoupled and coupled Hartree-Fock calculations of the proton shielding using the same procedures as above for the magnetic susceptibility. The UCHF result of Okniński and Sadlej [21] deviates about 10% from the experimental value, whereas the CHF calculation of Sadlej and Raynes [22] essentially reproduces our result with the same basis set. This agreement is very satisfactory in view of the fact that the computational procedures are quite different.

There is no obvious correlation between basis set size and the quality of the calculated magnetic properties. As pointed out above the fluorine and proton shielding factors exhibit opposite behaviour upon an extension of the basis set and similar strange behaviour is found for the diamagnetic susceptibility anisotropy. In general we find the same lack of correlation when we examine the other results quoted in Tables 2, 3, and 4. In some cases, even very small basis sets do lead to results which compare favourably to those obtained with very elaborate basis sets. The only conclusion possible is that the properties mentioned are not crucially dependent on the basis set.

4. Results for H_2O

The importance of water and its properties and hence the particular interest of theoreticians for this molecule is not to be explicitly stressed here. In Table 5 we give the electric properties of H_2O calculated at its experimental geometry. The results corresponding to the smaller basis have in fact been produced by Thomsen and Swanstrøm

Table 5. Electric properties of H_2O. The experimental data are corrected for the effect of molecular vibration. Conversion factors, see text of Table 1

	This Work	This Work	Exp.	FPTM [35]	CHF [36]	UCHF [37]	FPTM SCF [44]	FPTM CEPA [44]
Basis	[5.4.1/3.1]	[7.5.2/4.2]		[5.3.2/2.1]	(5.3.1/2.1)	[5.3.2/2.1]	(11*s*6*p*3*d*/5*s*2*p*)	
Energy	−76.0520	−76.0643	−76.481[a]	−76.0440	−76.0384	−76.0440	−76.0553	−76.2799
EC	0.135	0.143		0.137		0.137		
Σf_z	−0.060	−0.023	(0)					
μ_z	0.868	0.782	0.7268 (4)[b]	0.823	0.758	0.823	0.782	0.723
θ_{xx}	−1.78	−1.83	−1.86 (1)[c]	−1.78	−2.04	−1.78		
θ_{yy}	1.87	1.91	1.96 (1)[c]	1.85	2.07	1.85		
θ_{zz}	−0.097	−0.076	−0.097 (2)[c]	−0.079	−0.029	−0.079		
α_{xx}	4.95	7.00		3.98	7.21	6.63	7.99	9.59
α_{yy}	7.54	8.69		7.23	8.63	9.54	9.04	9.81
α_{zz}	6.11	7.78		5.06	7.84	7.97	8.47	9.64
α	6.20	7.82	9.74[d]	5.42	7.90	8.04	8.50	9.68

[a] Estimate including correlation and relativistic effects by Neumann and Moskowitz [31].

[b] Stark effect measurements by Clough *et al.* [32].

[c] Beam maser Zeeman spectroscopy by Verhoeven and Dymanus [33].

[d] Extrapolation of dynamic polarizability to infinite wavelength, as quoted by Eisenberg and Kauzmann ([34, p. 16).

[7] for a slightly different geometry[1]. As is expected, the sum of the Hellmann-Feynman forces along the z-axis is non-vanishing though decreasing when the basis set is extended. Again the dipole moment is too large, as is frequently observed for Hartree-Fock wave functions. The quadrupole moment tensor is in good agreement with the beam maser results of Verhoeven and Dymanus [33], and it appears that the agreement is improved with the larger basis set. As was the case for FH, the small basis set fails to satisfactorily describe the polarization of the electronic distribution. Even the result obtained with the extended basis only accounts for 80% of the experimental value.

The results are compared to those of five other approaches which are described briefly as follows:

Liebmann and Moskowitz [35] determined the electric properties using the wave function of Neumann and Moskowitz [31]. They used the finite perturbation method but in spite of its equivalence to the CHF approach their results are, however, in slightly worse agreement with experiment than the data of the present study. The same authors also calculated the polarizability using the Karplus-Kolker uncoupled approach. They are able to reproduce exactly the experimental value, but for the reasons mentioned above in the FH analysis we hesitate to include this result in Table 5.

Arrighini *et al.* [36] calculated the electric properties within the CHF approach using a STO basis set which consists of ($5s3p1d$) functions at the oxygen centre and of ($2s1p$) functions at the hydrogens. The polarizability obtained in this way is almost identical to ours for the large basis set, but the dipole and quadrupole moments differ slightly from our results. The first-order properties are apparently rather sensitive to the choice of basis functions.

Jaszuński *et al.* [37] performed UCHF calculations using a modified Karplus-Kolker approach. Like Liebmann and Moskowitz, they employed the wave function of Neumann and Moskowitz [31]. Their results for the polarizability reproduce the experimental value slightly better than those of the present study.

As they did for FH, Werner and Meyer [44] performed extensive polarizability calculations at both the SCF and the correlated CEPA levels. Their SCF results are better than any other results published so far though it still deviates some 12% from the experimental value. Their correlated result, however, almost reproduces the experimental value. The employed basis set is of the same type as for FH: ($11s6p3d/5s2p$).

From the results quoted in Table 5 we see that one crucial property in these calculations is the electric polarizability. Although all the employed basis sets did contain d functions, none of the CHF results is in very good agreement with experiment. And it is seen that the same statement holds for the calculated dipole moment. We may

---

[1] Attention is drawn to the fact that there was a program coding error in the former CDC version of PERT/SCF [1]. This has affected the paramagenetic contributions to the magnetic properties. The discrepancy between the H_2O properties presented here, and those obtained formerly [7], is essentially due to this error, though the slightly different geometry does also influence the results.

thus conclude that the self-consistent Hartree-Fock molecular orbitals fail to span the r operator sufficiently well, even when extended basis sets are used. The fact that the UCHF approximation of Jaszuński *et al.* [37] leads to a large improvement over the FPTM (= CHF) results of Liebmann and Moskowitz [35] with the same basis set supports this conclusion. The quadrupole moments quoted in Table 5 are all in reasonable agreement with the experimental values and we conclude that the molecular orbitals do span the r^2 operator well. Also the fact that the correlated (CEPA) result of Werner and Meyer [44] is so much better than any of the other results gives further emphasis to this statement.

Table 6 gives the magnetic susceptibility (χ) and the rotational magnetic moment (G) tensors for the H_2O. In order to make a direct comparison with experiment possible, the calculations have been performed with the gauge origin at the centre of mass. The results corresponding to the two basis sets do not differ much, though the larger basis leads to a slight improvement of the paramagnetic contribution in particular. The agreement with the high resolution microwave measurements of Taft and Dailey [38] and with the beam maser Zeeman spectroscopic results of Verhoeven and Dymanus [33] is satisfactory.

The CHF results of Arrighini *et al.* [36] are not very different from ours. The same statement holds for the UCHF calculations of Jaszuński and Sadlej [39], with the exception of the paramagnetic component along the molecular figure axis.

The proton and oxygen magnetic shieldings (σ) are given in Tables 7 and 8, respectively. As for FH, our results are given for three different gauge origins: *EC*, X, and X^* where the value at X^* has been obtained by a gauge invariant translation through the space from *EC* to X.

In the case of the proton shielding, the effect of augmenting the basis is nearly negligible and the values obtained reproduce almost exactly the beam maser results of Verhoeven and Dymanus [33]. For the total shielding Pople, Schneider and Bernstein ([30], p. 90) give $\sigma(H_2O) = \sigma(H_2) + 3.60$ ppm based on gas phase measurements. Raynes *et al.* [40] have estimated $\sigma(H_2) = 26.58 \pm 0.36$ ppm on the basis of combined theoretical and experimental results. In this way a value of $\sigma(H_2O) = 30.2 \pm 0.4$ ppm is obtained.

Arrighini *et al.* [41] calculated the proton shielding using the hydrogen and oxygen centres as gauge origins. Since the centre of electronic charge, *EC*, is only 0.1 a.u. distant from the oxygen the results obtained with the latter centre as gauge origin can serve for comparison with the results that we obtain at *EC*. They obtain a total shielding of 28.2 ppm which compares reasonably well to experiment and their results are, in general, not very different from ours. The UCHF calculation of Jaszuński and Sadlej [39] is based on the same wave function that we have used in the smaller calculation. Using *EC* as gauge origin they achieve reasonable agreement with experiment for the total shielding and their results are, generally, not very different from ours or from those of Arrighini *et al.*

Ditchfield [29] used a split-shell basis set (without polarization functions at the nuclear centres) of gauge invariant atomic orbitals in a CHF procedure. He obtains good agreement with experiment. The separation of the shielding into a diamagnetic and a para-

Table 6. Magnetic susceptibility and rotational magnetic moment of H_2O. Conversion factors, see text of Table 2

	This work	This Work	Exp.	CHF [36]	UCHF [39]
Basis	[5.4.1/3.1]	[7.5.2/4.2]		(5.3.1/2.1)	[5.4.1/3.1]
χ^d_{xx}	−184.2	−182.7	−179 (20)[a]	−183.9	−184.2
χ^d_{yy}	−162.1	−161.5	−145 (18)[a]	−165.4	−162.0
χ^d_{zz}	−171.7	−170.9	−167 (22)[a]	−174.6	−171.8
χ^p_{xx}	25.0	26.1	26.1[a]	23.1	25.0
χ^p_{yy}	6.6	7.3	8.9[a]	6.1	5.3
χ^p_{zz}	13.3	14.0	15.7[a]	11.6	5.0
χ^d	−172.7	−171.7	−164 (20)[a]	−174.6	−172.7
χ^p	15.0	15.8	16.9[a]	13.6	11.8
χ	−157.7	−155.9	−147 (20)[a]	−161.1	−160.9
G_{xx}/μ_N	0.681	0.669	0.645 (6)[b]		
G_{yy}/μ_N	0.716	0.692	0.657 (1)[b]		
G_{zz}/μ_N	0.755	0.743	0.718 (7)[b]		

[a] High resolution microwave spectroscopy by Taft and Dailey [38].

[b] Beam maser Zeeman spectroscopy by Verhoeven and Dymanus [33].

Table 7. Proton magnetic shielding (in ppm) in H_2O

	This Work			This Work			Exp.	CHF [41]		UCHF [39]		CHF [29]
Basis	[5.4.1/3.1]			[7.5.2/4.2]				(5.2.1/2.1)		[5.4.1/3.1]		(5.2/2)
Gauge	*EC*	H	H*	*EC*	H	H*	H	H	O	*EC*	H	-
σ_{xx}^{d}	14.3	130.6	130.6	13.6	130.6	130.6		130.2	9.3	14.0	130.4	
σ_{yy}^{d}	37.2	75.8	75.8	37.3	75.9	75.9		75.3	32.1	37.1	75.7	
σ_{zz}^{d}	23.3	101.1	101.1	22.8	101.2	101.2		102.8	25.2	23.2	101.0	
σ_{xx}^{p}	9.0	−77.0	−107.3	8.9	−100.2	−108.1	−108.3[a]	−79.2	11.3	6.3	−118.4	
σ_{yy}^{p}	1.9	−26.5	−36.7	1.3	−34.2	−37.3	−37.7[a]	−25.8	4.4	0.7	−39.0	
σ_{zz}^{p}	6.2	−51.2	−71.6	6.7	−65.5	−71.7	−71.3[a]	−52.6	2.4	3.7	−76.7	
σ^{d}	24.9	102.5	102.5	24.6	102.6	102.6	102.4[a]	102.8	22.2	24.8	102.3	
σ^{p}	5.7	−51.6	−71.9	5.6	−66.7	−72.4	−72.2[a]	−52.5	6.0	3.5	−78.0	
σ	30.6	50.9	30.6	30.2	35.9	30.2	30.2 (4)[b]	50.2	28.2	28.3	24.3	32.8

[a] Beam maser Zeeman spectroscopy by Verhoeven and Dymanus [33].

[b] Based on NMR measurements by Pople, Schneider and Bernstein ([30], p. 90) and on the estimate by Raynes *et al.* [40].

Table 8. Oxygen magnetic shielding (in ppm) in H_2O

	This Work			This Work			CHF [42]	CHF [29]
Basis	[5.4.1/3.1]			[7.5.2/4.2]			(5.2.1/2.1)	(5.2/2)
Gauge	*EC*	O	O*	*EC*	O	O*	O	-
σ^d_{xx}	415.9	417.0	417.0	415.7	417.1	417.1	415.6	
σ^d_{yy}	414.3	415.3	415.3	413.9	415.2	414.2	414.3	
σ^d_{zz}	415.7	415.7	415.7	415.8	415.8	415.8	415.2	
σ^p_{xx}	−133.2	−134.2	−134.3	−112.1	−112.9	−113.5	−90.3	
σ^p_{yy}	−60.1	−65.3	−61.1	−49.9	−51.6	−51.2	−53.4	
σ^p_{zz}	−122.0	−122.0	−122.0	−105.8	−105.8	−105.8	−108.2	
σ^d	415.3	416.0	416.0	415.1	416.0	416.0	415.0	
σ^p	−105.1	−107.1	−105.8	−89.3	−90.1	−90.2	−84.0	
σ	310.2	308.9	310.2	325.9	326.0	325.9	331.1	328.1

magnetic part does not have the conventional meaning when gauge invariant perturbation theory is employed. For this reason only the total shielding is quoted.

For the oxygen shielding we observe that the change of basis substantially alters the paramagnetic components and we expect that an improved description of the electron density distribution at the oxygen may change the shielding still more. Our result of 325.9 ppm agrees reasonably well with the 331.1 ppm obtained by Arrighini *et al.* [42] and with the 328.1 ppm obtained by Ditchfield [29].

The magnetic properties quoted in Tables 6, 7, and 8 are all in reasonable agreement with each other, and with available experimental data. This is particularly true for the CHF calculations though it should be stressed that rather elaborate basis sets have been employed in all the calculations that we have referred to. We conclude that the molecular orbitals employed do span the operators of type r^2 and $1/r$ reasonably well.

Recently, Rosenberg and Shavitt [45] published a detailed comparative investigation on various one-electron properties of water, and their dependence on the choice of basis set and on the level of approximation - SCF or CI. They conclude that the inclusion of electronic correlation has an appreciable effect on, among other properties, the dipole moment. This statement parallels our own conclusion: that the SCF molecular orbitals fail to span r-type operators satisfactorily.

5. Conclusion

The results of the theoretical investigations reported in this paper indicate that a prediction of molecular first- and second-order properties is quite safe when the coupled Hartree–Fock procedure is adopted for the second-order properties, i.e. when the molecular orbitals are kept self-consistent during the perturbative measuring operation. The results obtained this way will generally deviate less than 10% from the experimental results.

There is, however, one notorious exception to this statement: the molecular orbitals fail to span r-type operators sufficiently well. Those properties which depend on matrix elements of this operator, e.g. the dipole moment and the dipole polarizability, will thus generally be in error. Typical deviations from the experimental values are ranging from 10% to 40%, depending on the basis set. Diffuse d-type orbitals seem to have a positive effect on the final result. Basically an improvement of the theoretically determined properties of an r-type operator can only be expected if configuration interaction (CI) type wave functions are used instead of Hartree–Fock functions. As has been shown by Green in the case of the dipole moment, even limited CI expansions with properly selected configurations are able to produce reliable results. The inclusion of electronic correlation seems to be imperative for the satisfactory determination of polarizabilities.

Of the two basis sets which we have employed only the larger one gives a reasonable description at the SCF level of the charge density distribution near the heavy nucleus.

This fact is reflected by the nuclear magnetic shielding results for the fluorine and oxygen nuclei. It can be stated further that the smaller basis set completely fails to describe the charge density polarization, as can be seen from the calculated dipole polarizabilities.

Acknowledgement. One of the authors (P.S.) wishes to express his gratitude to the Max-Planck-Institut für Physik und Astrophysik for the hospitality and the financial support during the author's two recent stays at the Institute.

References

1. Thomsen, K., Swanstrøm, P.: Mol. Phys. **26**, 735 (1973)
2. Salez, C., Veillard, A.: Theoret. Chim. Acta (Berl.) **11**, 441 (1968)
3. Van Duijnefeldt, F. B.: IBM J. Res. RJ 945 (1971)
4. Diercksen, G. H. F., Kraemer, W. P., Roos, B. O.: Theoret. Chim. Acta (Berl.) **36**, 249 (1975)
5. Von Niessen, W., Diercksen, G. H. F., Kraemer, W. P.: Quantum Chemistry: State of the Art. Proceedings of the SCR Atlas Symposium No. 4 (Oxford 1974)
6. Diercksen, G. H. F., Kraemer, W. P.: MUNICH Molecular Program System, Technical Report (Max-Planck-Institut für Physik und Astrophysik, München), to be published
7. Thomsen, K., Swanstrøm, P.: Mol. Phys. **26**, 751 (1973)
8. De Leeuw, F. H., Dymanus, A.: J. Mol. Spectry. **48**, 427 (1973)
9. Tessman, J. R., Kahn, A. H., Shockley, W.: Phys. Rev. **92**, 890 (1953)
10. Kolker, H. J., Karplus, M.: J. Chem. Phys. **39**, 2011 (1963)
11. Ransil, B. J.: Rev. Mod. Phys. **32**, 245 (1960)
12. Sadlej, A. J., Jaszuński, M.: Mol. Phys, **22**, 761 (1971)
13. Stevens, R. H., Lipscomb, W. N.: J. Chem. Phys. **41**, 184 (1964)
14. Epstein, I. R.: J. Chem. Phys. **53**, 1881 (1970)
15. Oddershede, J., Jørgensen, P., Beebe, N. H. F.: J. Chem. Phys. **63**, 2996 (1975)
16. Bender, C. F., Davidson, E. R.: J. Chem. Phys. **49**, 4989 (1968)
17. Cade, P. E., Huo, W. H.: J. Chem. Phys. **47**, 614 (1967)
18. Muenter, J. S., Klemperer, W.: J. Chem. Phys. **52**, 6033 (1970)
19. Ehrlich, P.: Z. Anorg. Allgem. Chem. **249**, 219 (1942)
20. Karplus, M., Kolker, H. J.: J. Chem. Phys. **38**, 1263 (1963)
21. Okniński, A., Sadlej, A. J.: Acta Phys. Polon. **A48** (3) (1975)
22. Sadlej, A. J., Raynes, W. T.: Chem. Phys. **7**, 383 (1975)
23. Noble, P. N., Kortzeborn, R. N.: J. Chem. Phys. **52**, 5375 (1970)
24. Chan, S., Das, T. P.: J. Chem. Phys. **37**, 1527 (1962)
25. Epstein, S. T.: J. Chem. Phys. **42**, 2897 (1965)
26. Hindermann, D. K., Cornwell, C. D.: J. Chem. Phys. **48**, 4148 (1968)
27. Kolker, H. J., Karplus, M.: J. Chem. Phys. **41**, 1259 (1964)
28. Ditchfield, R.: J. Chem. Phys. **56**, 5688 (1972)
29. Ditchfield, R.: Mol. Phys. **27**, 789 (1974)
30. Pople, J. A., Schneider, W. G., Bernstein, H. J.: High resolution nuclear magnetic resonance. New York: McGraw-Hill 1959
31. Neumann, D., Moskowitz, J. W.: J. Chem. Phys. **49**, 2056 (1968)
32. Clough, S. A., Beers, Y., Klein, G. P., Rothman, L. S.: J. Chem. Phys. **59**, 2254 (1973)
33. Verhoeven, J., Dymanus, A.: J. Chem. Phys. **52**, 3222 (1970)
34. Eisenberg, D., Kauzmann, W.: The structure and properties of water. Oxford: University Press 1969
35. Liebmann, S. P., Moskowitz, J. W.: J. Chem. Phys. **54**, 3622 (1971)
36. Arrighini, G. P., Guidotti, G., Salvetti, O.: J. Chem. Phys. **52**, 1037 (1970)
37. Jaszuński, M., Okniński, A., Sadlej, A. J.: Acta Phys. Polon. **A41**, 595 (1972)
38. Taft, H., Dailey, B. P.: J. Chem. Phys. **51**, 1002 (1969)

39. Jaszuński, M., Sadlej, A. J.: Theoret. Chim. Acta (Berl.) **27**, 135 (1972)
40. Raynes, W. T., Davies, A. M., Cook, D. B.: Mol. Phys. **21**, 123 (1971)
41. Arrighini, G. P., Maestro, M., Moccia, R.: J. Chem. Phys. **52**, 6411 (1970)
42. Arrighini, G. P., Maestro, M., Moccia, R.: Chem. Phys. Letters 7, 351 (1970)
43. Perkins, A. J.: J. Chem. Phys. **68**, 654 (1969)
44. Werner, H.-J., Meyer, W.: Mol. Phys. **31**, 855 (1976)
45. Rosenberg, B. J., Shavitt, I.: J. Chem. Phys. **63**, 2162 (1975)
46. Green, S.: J. Chem. Phys. **54**, 827 (1971)

Received June 9, 1976/September 29, 1976