Theoret. chim. Acta (Berl.) 30, 257—265 (1973)

Proton Magnetic Shielding in H_2O and $(H_2O)_2$

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Received January 24, 1973

The proton magnetic shielding constants in the water molecule and its linear perpendicular dimer are computed from SCF-MO-LCGO wave functions by using the uncoupled Hartree-Fock variation-perturbation procedure due to Karplus and Kolker. The convergence of the calculated shielding constants as well as their gauge dependence is studied. The final results for 17-term polynomial variation function indicate that the best choice for the gauge origin corresponds to the molecular electronic centroid.

The calculated proton magnetic shielding constant in the water molecule is in remarkable agreement with experimental data and favourably compares with the best coupled Hartree-Fock results. It follows from the calculations for the water dimer that the H-bond NMR-shift amounts in this case -1.0 ppm and qualitatively agrees with the experimental data for the liquid water.

Key words: Proton magnetic shielding – Hydrogen bond NMR shift of water molecule and dimer

Introduction

Recently we have reported [1] the results of the uncoupled Hartree-Fock (UCHF) variation-perturbation calculations of the proton magnetic shielding constant in the water molecule. It was shown that the simplified UCHF scheme due to Karplus and Kolker [2, 3] is able to reproduce the results of the time-consuming and laborious coupled Hartree-Fock (CHF) procedure [4]. Moreover, the gauge non-invariance of the Karplus-Kolker scheme was considerably less pronounced than in the case of the limited basis set CHF calculations [5]. In this way the results for the water molecule confirmed our previous conclusions concerning the validity and applicability of the Karplus-Kolker UCHF method for the calculation of the second-order energies related to pure imaginary operators [6–8].

More recently we have applied the same approach to the calculation of the hydrogen-bond NMR shift in the water dimer [9]. The preliminary results for the hydrogen-bonded proton indicated a down-field shift of the corresponding shielding constant in comparison with the isolated water molecule. It should be pointed out that the paramagnetic effect of the hydrogen-bond formation has been obtained without introducing any empirical parameter and all the calculations have been performed using the Gaussian SCF-MO-wave functions computed recently by Diercksen [10].

In the present paper we report the results of more extensive study of magnetic properties of the linear water dimer. A particular attention is paid to the influence of the hydrogen bonding on the proton magnetic shielding constant. We shall consider the hydrogen-bonded as well as the outer protons in the water dimer. The results for the water dimer will be compared with analogous calculations for the isolated water molecule. The influence of the choice of the origin for the magnetic field vector potential will also be discussed.

In comparison with previously reported calculations for the water molecule [1] and preliminary results for the water dimer [9] we have extended the polynomial representation of the variation functions. This extension leads to further improvement of the calculated proton shielding constant in the water molecule and lowers the shielding constant of the hydrogen-bonded proton in the water dimer.

Computational Details

The method employed in the present study — so-called Karplus-Kolker UCHF variation-perturbation procedure — has been extensively described in the previous paper [1] and we refer to this publication for the notation and general discussion. For the sake of clarity we only remind that within the Karplus-Kolker method the first-order perturbed orbitals are approximated in the form

$$u_{i\mu}^{(1,0)} = f_{i\mu}^{(1,0)} u_i^{(0)} - \sum_{k=1}^{n} \langle u_k^{(0)} | f_{i\mu}^{(1,0)} u_i^{(0)} \rangle u_k^{(0)} \tag{1}$$

(cf. Eq. (7) of Ref. [1]), where $f_{i\mu}^{(1,0)}$ is the variation function for the magnetic field perturbation in the μ-th direction. A usual procedure for the determination of $f_{1\mu}^{(1,0)}$ is to express it in a polynomial form

$$f_{i\mu}^{(1,0)} = \sum_{p}^{L} A_{p,i\mu} g_{p\mu} \tag{2}$$

where $g_{p\mu}$ are the products of the electronic coordinates with appropriate symmetry. The linear variation parameters $A_{p,i\mu}$ are then determined by extremizing the second-order energy functional of the Karplus-Kolker method [2, 3]. It should be mentioned that some additional problems arise when the calculated property is bilinear in external perturbations (e.g. the paramagnetic component of the magnetic shielding tensor) [1, 3, 11].

All the calculations presented in this paper were performed by using the method and formulae given in Ref. [1]. The ground state unperturbed wave functions for the isolated water molecule and water dimer are also the same as employed in our previous study [1, 9]. They were recently computed by Diercksen [10] and correspond to the experimental geometry and so-called "linear perpendicular" configuration of the water molecule and water dimer, respectively. The O ··· O distance in the water dimer equals 3 Å. A detailed description and discussion of the quality of these SCF-MO-LCGO-wave functions can be found in Diercksen's paper [10].

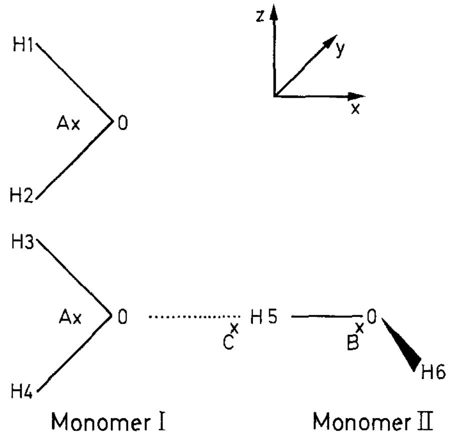

Fig. 1. The coordinate system for H_2O and $(H_2O)_2$. A, B, C denote the gauge origins; B and C lie in front of the monomer I plane

The variation functions $f_{i\lambda}^{(1,0)}$ were expressed in terms of the following $g_{p\lambda}$ functions:

$$\begin{aligned} g_{p\lambda}\colon\ & x_\mu,\ x_\nu,\ x_\mu x_\nu;\ x_\lambda x_\nu,\ x_\lambda x_\mu;\ x_\mu^2,\ x_\nu^2; \\ & x_\mu x_\lambda^2,\ x_\mu x_\mu^2,\ x_\mu x_\nu^2;\ x_\nu x_\lambda^2,\ x_\nu x_\mu^2,\ x_\nu x_\nu^2; \\ & x_\lambda x_\mu x_\nu;\ x_\mu x_\nu x_\lambda^2,\ x_\mu x_\nu x_\mu^2,\ x_\mu x_\nu x_\nu^2; \end{aligned} \tag{3}$$

where (λ, μ, ν) form a cycle and refer to the corresponding Cartesian coordinates. The origin of the coordinate system has been chosen at the oxygen atom [water I in the case of $(H_2O)_2$]. The coordinate systems employed for the water molecule and its linear dimer are shown in Fig. 1.

In comparison with previously adopted $g_{p\lambda}$ basis set [1, 9], the present one involves five additional functions and allows for a better representation of the first-order perturbed orbitals. However, it should be mentioned that also the present extension of the polynomial basis set does not remove the node-shift problems discussed in Ref. [1] and these can hardly be avoided within the Karplus-Kolker scheme [3, 12]. On the other hand, this should not significantly affect the results for non-linear molecules considered in this paper.

All the integrals which appear in the Karplus-Kolker functional for the second-order energy [2] as well as those arising in the calculation of the proton magnetic shielding constants were computed according to standard formulae [13, 14]. To evaluate the necessary $F_m(t)$ functions [14] the analytical approximations of Schaad and Morrell [15] have been employed. The calculations were programmed in Algol and run on the ODRA 1204 computer.

Results

For any approximate theory of the second-order magnetic properties the gauge dependence of final results is quite obvious and should be carefully examined. We have therefore repeated our calculations for several different ori-

Table 1. The convergence of the paramagnetic contribution to the proton magnetic shielding (in ppm)

L^b	Monomer[a]	Dimer[a]		
	H 1 = H 2	H 3 = H 4	H 5	H 6
3	2.919	69.102	−151.294	24.684
5	2.919	69.136	−151.485	25.157
7	2.919	69.161	−151.502	27.168
10	3.341	71.392	−154.108	27.187
13	3.257	71.397	−156.558	29.051
14	3.480	71.742	−156.565	29.154
17	3.776	72.242	−157.246	29.429

[a] The gauge origin is taken at the molecular electronic centroid. For the numbering of atoms see Fig. 1.

[b] See Eqs. (2), (3).

gins for the vector potential of the external magnetic field. In the case of the isolated water molecule the calculations were carried out in the coordinate system of the monomer *I* in the dimer (Fig. 1) and point *A* refers to the gauge origin at the monomer electronic centroid. Additionally, the proton shielding constant in the isolated monomer has also been computed for the gauge origin chosen at the shielded H atom.

As regards the gauge origin for the water dimer we tried the following choices:

(i) the electronic centroid of the monomer *I* in the dimer configuration (point *A* in Fig. 1),

(ii) the electronic centroid of the monomer *II* in the dimer configuration (point *B* in Fig. 1), and

(iii) the electronic centroid of the water dimer (point *C* in Fig. 1).

As will be explained in the next section, the gauge origins (i)–(iii) correspond to some supposedly best choices of the origin for the external magnetic field vector potential in monomers and in the dimer, respectively.

We studied the convergence of the calculated second-order energies using the $g_{p\lambda}$ basis sets with first 3, 5, 7, 10, 13 and 14, and with all the terms appearing in (3). It should be mentioned that some of these terms may not contribute to a given component of the magnetic susceptibility or magnetic shielding tensor. However, they were included in the basis set for symmetry reasons.

The second-order energies quadratic in the magnetic field or in the nuclear magnetic moment (see Ref. [1]) exhibit a monotonous, convergent behaviour with respect to the number of variation parameters. No violation of the variation principle for the Karplus-Kolker approximate UCHF functional has been noticed. For the present study the most interesting is the convergence of the calculated paramagnetic contribution (σ^p) to the proton shielding constants and this is illustrated by the data of Table 1. The corresponding figures refer to the gauge origin chosen at the electronic centroid of H_2O and $(H_2O)_2$, respectively. For the other gauge origins the convergence of σ^p is quite similar and in what follows we shall confine our considerations to the results obtained with the richest, 17-term representation of variationally determined first-order perturbed

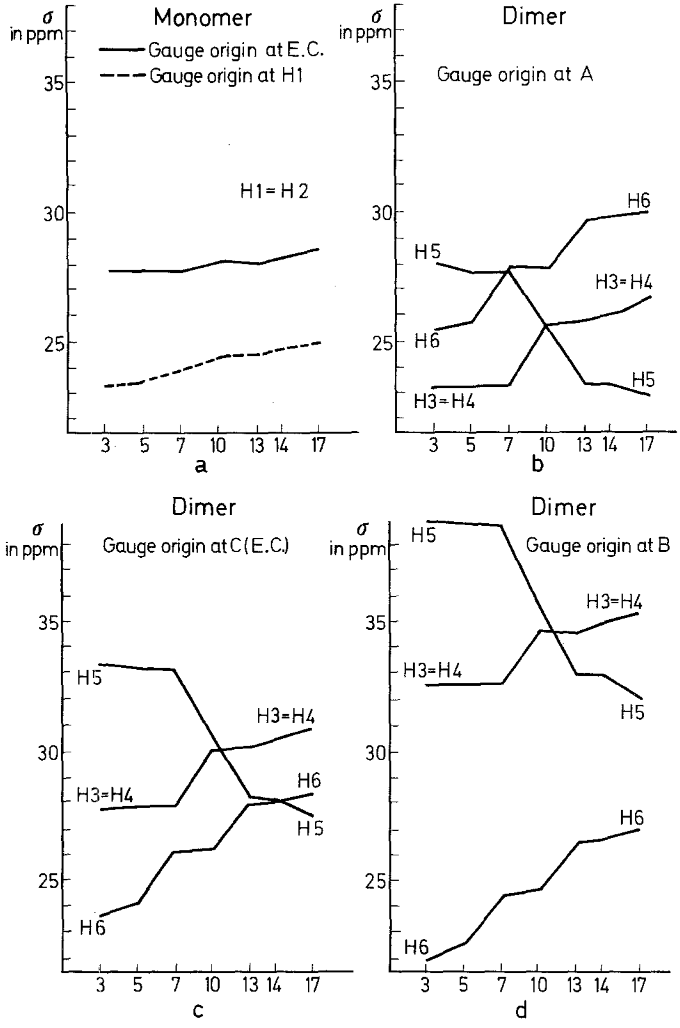

Fig. 2. A schematic plot of the convergence data for σ calculated with different gauge origins

orbitals. However, one can obtain some further information about the convergence of the total proton shielding constant for different gauge origins by looking at Fig. 2. Obviously Fig. 2 has only an illustrative meaning and the scale of the abscissa axis is quite arbitrary.

The final results for the proton magnetic shielding in the water molecule are shown in Table 2. For the gauge origin at the shielded H atom they are compared with the CHF results of Arrighini *et al.* [5] and with the experimental data [16]. Table 2 contains also our previous results obtained with a shorter variation function.

The corresponding results for the water dimer are given in Table 3. In this case we reported only the rotational average of the paramagnetic, diamagnetic

Table 2. Proton magnetic shielding in the water molecule (in ppm)

	Gauge origin	σ^p_{xx}	σ^p_{yy}	σ^p_{zz}	σ^p	σ
This work	e.c.	4.42	6.26	0.65	3.78	28.55
KK [1]	e.c.	3.66	6.26	0.65	3.52	28.30
This work	H 1	−75.54	−117.07	−39.01	−77.21	25.12
KK [1]	H 1	−76.65	−118.44	−39.01	−78.03	24.30
CHF [5]	H 1	−52.63	− 79.18	−25.76	−52.52	50.24
Exp.[a]	H 1	−71.79	−107.04	−36.57	−71.80	30.03 ± 0.60

[a] Taken from Ref. [5].

Table 3. Proton magnetic shielding in the water dimer (in ppm)

Proton[a]	Gauge[a] origin	σ^p	σ^d	σ
H 3 = H 4	*A*	− 18.92	45.69	26.77
	C	72.24	− 41.15	31.09
	B	162.93	−127.55	35.39
H 5	*A*	−259.29	282.31	23.02
	C	−157.24	184.80	27.56
	B	− 55.73	87.80	32.08
H 6	*A*	80.47	− 50.46	30.01
	C	29.43	− 0.90	28.53
	B	− 21.26	48.32	27.06

[a] See Fig. 1.

Table 4. Magnetic susceptibility (in erg/mole gauss^2)

	Monomer Gauge origin[a]		Dimer Gauge origin[a]		
	A (e.c.)	H 1	*A*	*C* (e.c.)	*B*
χ^p	1.119	25.854	269.906	134.414	268.957
χ	−14.290	−13.252	− 21.114	− 26.256	− 20.715

[a] See Fig. 1.

and the total shielding constant. There are no experimental data and other theoretical results to be directly compared with our calculations.

On calculating the first-order perturbed orbitals $u_{i\mu}^{(1,0)}$ we obtained as a by-product the paramagnetic contribution (χ^p) to the magnetic susceptibility tensor of H_2O and $(H_2O)_2$. The relevant results for χ^p as well as the final values of the total magnetic susceptibility (χ) calculated for different gauge origins were shown in Table 4. It is worth attention that the theoretical value of χ^p provides, according to Chan and Das [17], some criterion for the choice of the appropriate gauge origin in approximate calculations.

Discussion

It is evident from the data of Table 1 that even the 17-term representation of variation functions does not allow to reach a complete convergence of the calculated values of σ^p. Unfortunately, a further extension of the polynomial basis set (3) goes beyond the ability of our computing facilities but owing to a monotonous behaviour of the calculated shielding constants (Fig. 2) we can draw out rather general conclusions.

The gauge-dependence of the Karplus-Kolker method is also evident but appears to be less pronounced than in the case of the finite basis set CHF calculations. This is illustrated by the data of Table 2. Shifting the gauge origin from the central atom of H_2O to the shielded proton Arrighini *et al.* [5] found in their CHF calculations the gauge dependence of $+22.64$ ppm. In the present case, shifting the gauge origin from the electronic centroid (e.c.) of the monomer to the shielded proton we obtain the gauge dependence of -3.43 ppm. It should be pointed out that in the water molecule the central atom and e.c. almost coincide.

In comparison with the experimental data the calculated proton shielding constant in H_2O is much better when computed with the gauge origin at e.c. Our value (28.55 ppm) compares favourably with the best CHF result (28.94 ppm) obtained in rather cumbersome calculations by Arrighini *et al.* [5].

The results for the monomer indicate some significance of e.c. as the gauge origin in the Karplus-Kolker method. According to Chan and Das [17] this choice leads to the lowest (positive) value of χ^p (see also Table 4) and one can also expect that it minimizes the absolute error of the computed χ^p and $u_{i\mu}^{(1,0)}$. For this reason one can expect rather good results for σ^p calculated with the gauge origin at e.c. This qualitative reasoning is nicely supported by the corresponding numerical data [17, 1, 9]. Moreover, it is important that e.c. can be defined for any molecule while some other concepts, e.g. the origin at the central atom, are in general rather arbitrary.

According to the discussion presented in [1] we attribute more significance to the results obtained for the gauge origin at the molecular electronic centroid, especially when we compare the data for different molecules. Thus, comparing the proton shielding constants in H_2O and $(H_2O)_2$ (Tables 2 and 3) we find for the gauge origins at e.c. the H-bond NMR shift of -1.0 ppm. Additionally, examining Fig. 2c we observe that the calculated value provides a sort of the "upper bound" to the H-bond NMR shift in the water dimer and unambigously indicates a decrease of σ for the H-bonded proton. Qualitatively the same effect is obtained for the gauge origin at A (Fig. 2) but at B the corresponding shielding constant unexpectedly increases in comparison with that in the monomer. To explain this rather peculiar result it is worth attention that for all the gauge origins considered in this paper an extension of the polynomial basis set, in general results in increase of σ for H 3($=$H 4) and H 6 while σ of H 5 simultaneously decreases. This also leads to rather systematic increase of σ in the monomer. Thus, on augmenting the basis set we should reach the desired sequence also for the gauge origin B.

For the monomer I in the dimer its protons should resemble to some extent those in the isolated molecule and it appears that $\sigma(\text{H}\,3)=\sigma(\text{H}\,4)$ must not be higher than σ(H 5). On the other hand, in the liquid an average proton surrounding resembles rather that of H 5 and in this respect our calculation predicts a down-field shift of the corresponding NMR signal. It is worth attention that qualitative considerations [18] predict rather an up-field shift and disagree with experiment [19].

Recently Guidotti *et al.* [20] reported the CHF calculations of several properties of the water molecule in an ice-like cluster. The surrounding molecules were taken into account by an appropriate perturbation-like modification of the SCF function of the isolated molecule. The calculated change in the proton shielding constant (-3.81 ppm and -5.83 for the gauge origins at O and H, respectively) is rather close to the observed association shift (-4.58 ppm at 0° C [19]). However, the observed shift is strongly temperature-dependent [19]. The Boltzmann average of σ which is reported in [20] takes into account only the existence of several configurations of the cluster but does not include the influence of the $\mathrm{O} \cdots \mathrm{O}$ stretching motion. To our feeling the computed values must not be directly compared with the experimental data and only the direction of the chemical shift appears to be meaningful. In this respect the result of the Karplus-Kolker method agrees with that of Guidotti *et al.*

Guidotti *et al.* [20] calculated also the change of the magnetic susceptibilty of H_2O upon the cluster formation but their result (-0.355 erg/mole gauss^2) differs in sign from the quoted experimental value ($+0.45$ erg/mole gauss^2) for the liquid. From the data of Table 4 we find $+1.16$ erg/mole gauss^2 (per mole of H_2O) for the change of χ upon the hydrogen bond formation. We believe that the direction of the computed change of χ can be compared with that in the liquid.

Summing up we want to stress that the method applied in this paper to the study of the H-bond induced changes in the magnetic properties of H_2O is much simpler than the CHF approach and does not offer any computational difficulties. Obviously, this method is approximate but it works quite well. In this respect we refer the reader to Tables 2 and 3 to recognize the order of magnitude of the computed dia- and paramagnetic contributions which result in rather small final value of σ. These final results compare rather favourably with the corresponding CHF data. It should be also pointed out that in the case of real perturbing operators (e.g. electric polarizability calculations) some modification of the Karplus-Kolker scheme is necessary [6, 8].

Acknowledgments. The authors wish to thank Dr. G. H. F. Diercksen for the original computer outputs of the SCF-MO-LCGO-functions and one-electron properties.

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