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# Proton Magnetic Shielding in the Water Molecule

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The variation-perturbation uncoupled Hartree-Fock procedure of Karplus and Kolker is employed for the calculation of the second-order properties of the water molecule. The SCF MO LCGO ground state wave function was chosen and the first-order perturbed orbitals were approximated in the multiplicative form. The convergence of the method as well as the violation of the gauge independence are studied. For the preferred gauge origin at the electronic centroid the calculated proton shielding constant is 28.30 ppm and compares favourably with the experimental data (30.20, 30.03 ± 0.60 ppm). The results for the magnetic susceptibility of the water molecule are also in reasonable agreement with experimental values.

Die ungekoppelte Hartree-Fock Variationsstörungsrechnung von Karplus u. Kolker wird für die Berechnung von Eigenschaften 2. Ordnung des Wassermoleküls verwendet. Für die Berechnung wird die SCF MO SCGO-Wellenfunktion des Grundzustandes gewählt, und die gestörten Orbitale 1. Ordnung werden in der multiplikativen Form approximiert. Die Konvergenz der Methode und die Frage, ob die Eichinvarianz verletzt wird, werden untersucht. Für den gewählten Potential-Nullpunkt im Zentrum der negativen Ladungsverteilung beträgt die errechnete Protonenabschirmungskonstante 28,30 ppm in guter Übereinstimmung mit den experimentellen Werten (30.20, 30.03 ± 0.60 ppm). Die Ergebnisse für die magnetische Suszeptibilität des Wassermoleküls sind gleichfalls in vernünftiger Übereinstimmung mit dem Experiment.

## Introduction

The idea of the LCGO (Linear Combination of Gaussian Orbitals) approximation [1, 2] in the Hartree-Fock-Roothaan SCF procedure stimulated a rapid progress in large scale molecular calculations and a number of reliable, near-Hartree-Fock SCF MO LCGO wave functions for polyatomic molecules is now available [3–6]. In spite of very encouraging results for the molecular energies and several one-electron first-order properties [4, 7], the SCF MO LCGO wave functions were only seldom utilized for the calculation of the second-order properties related to external field perturbations [8–11]. To get more information about the usefulness of the LCGO molecular wave functions in the perturbation calculations we have undertaken a systematic study of the second-order magnetic properties of polyatomic molecules. Also the corresponding methods in the Hartree-Fock perturbation theory have recently been analysed [12–14].

The present paper is concerned with the calculation of the magnetic second-order properties of the water molecule from the SCF MO LCGO wave functions obtained recently by Diercksen [15]. A particular attention has been paid to the problem of the proton magnetic shielding in the water molecule. The results obtained are in remarkably good agreement with experimental data and indicate the usefulness of accurate SCF MO LCGO functions for the calculation of molecular magnetic properties. They also confirm our previous conclusions about the validity of the simplified variation-perturbation method [16] in the case of pure imaginary perturbing operators [12, 13].

## Method

In the Hartree-Fock approximation the accurate procedure for the calculation of the second-order energies is known as the coupled Hartree-Fock (CHF) method [17–19]. Applying this method one can circumvent almost all the sum-over-states and related problems but one has to calculate a number of two-electron integrals. Usually the corresponding solutions for the first-order perturbed orbitals $u_i^1$ are expressed in terms of the unperturbed virtual orbitals $u_k^0$ [18, 20]. However, the convergence of this expansion is rather slow [21, 22]. This can be improved by using a more general variation formulation of the CHF scheme [23] but even in this case the CHF procedure can hardly be applied to the calculation of the second-order properties of polyatomic molecules.

To avoid the computational difficulties of the CHF method several simpler, so-called uncoupled Hartree-Fock (UCHF) perturbation schemes were proposed [24–26, 12, 13]. The simplest one is due to Karplus and Kolker [16] and is based on the functional which contains only one-electron integrals. It was shown [13] that the validity of this approximate UCHF approach can be reasonably justified when the perturbation corresponds to a pure imaginary operator.

Both, the paramagnetic part of the magnetic susceptibility tensor $\chi^p_{\mu\nu}$ and the paramagnetic part of the nuclear magnetic shielding tensor $\sigma^p_{\mu\nu}(N)$ of the $N$-th nucleus are related to one-electron pure imaginary operators

$$H_\mu^{(1,0)}(\mathscr{H}_\mu) = \sum_{i=1}^{2n} h_\mu^{(1,0)}(i) = \sum_{i=1}^{2n} M_\mu^A(i)\,, \tag{1}$$

and

$$H_\mu^{(0,1)}(I_\mu^N) = \sum_{i=1}^{2n} h_\mu^{(0,1)}(i) = \sum_{i=1}^{2n} \frac{1}{r_{Ni}^3} M_\mu^N(i)\,, \tag{2}$$

respectively [27]. Thus, to calculate the magnetic susceptibility and the proton magnetic shielding constant for the water molecule we applied the Karplus-Kolker method. In Eqs. (1) and (2) the superscripts $(n, m)$ refer to the order with respect to the external magnetic field $\mathscr{H}_\mu$ and nuclear magnetic moment $I_\mu^N$ of the $N$-th nucleus, respectively. The symbol $M_\mu^B$ $(B = A, N)$ denotes the $\mu$-th component of the angular momentum operator with the origin at $\boldsymbol{R}_B$ and $2n$ corresponds to the number of electrons.

The tensors $\chi^p_{\mu\nu}$ and $\sigma^p_{\mu\nu}$ can be expressed in terms of the second-order energies $E_{\mu\nu}^{(2,0)}$ and $E_{\mu\nu}^{(1,1)}$

$$\chi^p_{\mu\nu} = -2E_{\mu\nu}^{(2,0)}\,, \tag{3}$$

$$\sigma^p_{\mu\nu} = E_{\mu\nu}^{(1,1)} \tag{4}$$

where (in atomic units)

$$\begin{aligned} E_{\mu\nu}^{(2,0)} &= \tfrac{1}{4}\alpha^2\, \mathscr{Re}\langle \Psi_\mu^{(1,0)} | H_\nu^{(1,0)} | \Psi^{(0)} \rangle \\ &= \tfrac{1}{2}\alpha^2\, \mathscr{Re} \sum_{i=1}^{n} \langle u_{i\mu}^{(1,0)} | h_\nu^{(1,0)} | u_i^{(0)} \rangle \end{aligned} \tag{5}$$

and

$$E_{\mu\nu}^{(1,1)} = \alpha^2\, \mathcal{R}e \langle \Psi_\mu^{(1,0)} | H_\nu^{(0,1)} | \Psi^{(0)} \rangle = 2\alpha^2\, \mathcal{R}e \sum_{i=1}^{n} \langle u_{i\mu}^{(1,0)} | h_\nu^{(0,1)} | u_i^{(0)} \rangle \tag{6}$$

$\Psi_\mu^{(1,0)}$ and $\Psi_\mu^{(0,1)}$ denote the first-order perturbed $2n$-electron wave functions while $u_{i\mu}^{(1,0)}$ and $u_{i\nu}^{(0,1)}$ correspond to the first-order perturbed orbitals resulting from the perturbations (1) and (2), respectively. Greek subscripts refer to a given cartesian component of the perturbing operator. An expression similar to (5) can also be written down for the second-order energy $E_{\mu\nu}^{(0,2)}$. Although $E_{\mu\nu}^{(0,2)}$ has no direct physical meaning, its numerical values can be useful in the study of the convergence of the variation procedure.

According to Karplus and Kolker [16, 28] we shall approximate the first-order perturbed orbitals in the multiplicative form (product-form approximation)

$$u_{i\mu}^{(1,0)} = f_{i\mu}^{(1,0)} u_i^{(0)} - \sum_{k=1}^{n} \langle u_k^{(0)} | f_{i\mu}^{(1,0)} u_i^{(0)} \rangle u_k^{(0)} , \tag{7}$$

$$u_{i\mu}^{(0,1)} = f_{i\mu}^{(0,1)} u_i^{(0)} - \sum_{k=1}^{n} \langle u_k^{(0)} | f_{i\mu}^{(0,1)} u_i^{(0)} \rangle u_k^{(0)} \tag{8}$$

where $f_{i\mu}^{(1,0)}$ and $f_{i\mu}^{(0,1)}$ are the variation functions to be determined by extremizing an appropriate functional [16, 28]. It should be pointed out that both $E_{\mu\mu}^{(2,0)}$ and $E_{\mu\mu}^{(0,2)}$ are given by an extremum of the corresponding functionals and allow for an independent determination of the first-order perturbed orbitals $u_{i\mu}^{(1,0)}$ and $u_{i\mu}^{(0,1)}$. On the other hand, $E_{\mu\mu}^{(1,1)}$ is neither maximum nor minimum of an appropriate functional [28] which involves simultaneously both $u_{i\mu}^{(1,0)}$ and $u_{i\mu}^{(0,1)}$. Although Kolker and Karplus [28] in their calculations of the nuclear magnetic shielding determined these first-order perturbed orbitals by extremizing the functional for $E_{\mu\mu}^{(1,1)}$ we prefer to use the method which leads to $u_{i\mu}^{(1,0)}$ and $u_{i\mu}^{(0,1)}$ by an independent extremization of $E_{\mu\mu}^{(2,0)}$ and $E_{\mu\mu}^{(0,2)}$ respectively. Then, the energy $E_{\mu\nu}^{(1,1)}$ can be calculated from (6), or alternatively from

$$E_{\mu\nu}^{(1,1)} = \alpha^2\, \mathcal{R}e \langle \Psi_\mu^{(0,1)} | H_\nu^{(1,0)} | \Psi^{(0)} \rangle . \tag{9}$$

In general Eqs. (6) and (9) become completely equivalent in the limit of the exact solution for the first-order perturbed wave functions. This equivalence will also be obtained when the same analytical form of $f_{i\mu}^{(1,0)}$ and $f_{i\mu}^{(0,1)}$ is used.

A usual procedure for the determination of the variation functions $f_{i\mu}^{(1,0)}$ and $f_{i\mu}^{(0,1)}$ is to express them in a polynomial form [16, 28, 29], e.g.,

$$f_{i\mu}^{(1,0)} = \sum_{p=1}^{L} A_{p,i\mu} g_{p\mu} \tag{10}$$

where $g_{p\mu}$ are the products of the cartesian coordinates with appropriate symmetry properties. This approximation does not shift the nodes of the unperturbed orbitals and can lead to several difficulties [28, 30]. However, this should not be very important in the calculations of the paramagnetic susceptibility and proton magnetic shielding [16, 28]. The node shift problems can be avoided by using a generalized form of the multiplicative approximation (7) [31], but for the present purposes a simple product form of $u_{i\mu}^{(1,0)}$ seems to be sufficiently accurate [28].

Having determined the linear variation coefficients $A_{p,i\mu}$ by the extremization of the Karplus-Kolker functional [16] for $E^{(2,0)}_{\mu\mu}$ we can calculate the paramagnetic parts of the magnetic susceptibility and nuclear magnetic shielding tensor. The total magnetic susceptibility and nuclear magnetic shielding tensors are given by a sum of the corresponding diamagnetic ($\chi^d_{\mu\nu}$ and $\sigma^d_{\mu\nu}$) and paramagnetic components [32]

$$\chi_{\mu\nu} = \chi^d_{\mu\nu} + \chi^p_{\mu\nu}, \qquad \sigma_{\mu\nu} = \sigma^d_{\mu\nu} + \sigma^p_{\mu\nu} \tag{11}$$

where

$$\chi^d_{\mu\nu} = -\tfrac{1}{2}\alpha^2 \sum_{i=1}^{n} \langle u_i^{(0)} | \boldsymbol{r}_A \cdot \boldsymbol{r}_A \delta_{\mu\nu} - r_{A\mu} r_{A\nu} | u_i^{(0)} \rangle \tag{12}$$

and

$$\sigma^d_{\mu\nu} = \alpha^2 \sum_{i=1}^{n} \langle u_i^{(0)} | \frac{\boldsymbol{r}_N \cdot \boldsymbol{r}_A \delta_{\mu\nu} - r_{A\mu} r_{N\nu}}{r_N^3} | u_i^{(0)} \rangle \tag{13}$$

do not involve a knowledge of the perturbed orbitals. Their accuracy is only limited by the accuracy of the unperturbed SCF functions.

For the exact theory the total magnetic susceptibility as well as the total nuclear magnetic shielding tensors should not depend on the choice of the origin $\boldsymbol{R}_A$ for the vector potential of the external magnetic field [33]. However, when an approximate theory is used this so-called gauge-invariance [32] of the final result can be violated and, in general, the results are origin-dependent. Thus, the study of the origin-dependence of $\chi_{\mu\nu}$ and $\sigma_{\mu\nu}$ provides an additional test of the accuracy of the calculated properties. Moreover, Chan and Das pointed out that there are some gauge origins which are better than others [33]. For the magnetic susceptibility the gauge origin at the electronic centroid [33], which maximizes the absolute value of the diamagnetic contribution, appears to be the best one. The same point is considered as a good one for the calculation of the nuclear magnetic shielding, though it does not lead to the extremum of the corresponding diamagnetic contribution. Sometimes the gauge origin which gives vanishing paramagnetic contribution to the nuclear magnetic shielding is considered as the best one [34, 35] but, in general, its determination requires a previous knowledge of $\sigma_{\mu\nu}$.

In the present calculations we have chosen two different origins for the vector potential of the external magnetic field and we studied the violation of the gauge invariance for both the magnetic susceptibility and nuclear magnetic shielding tensor. As it was mentioned, the paramagnetic contribution to $\sigma_{\mu\nu}$ was determined by using Eq. (6) or Eq. (9) with the first-order perturbed orbitals obtained by the extremization of the functionals corresponding to $E^{(2,0)}_{\mu\mu}$ [16] or $E^{(0,2)}_{\mu\mu}$. Some further details of the present approach are described in the next Section.

## Calculations

All the results presented in this paper were obtained with the SCF MO LCGO wave function computed recently by Diercksen [15] and we refer to his paper for its complete description and discussion. It should be pointed out that this wave function corresponds to the experimental geometry of the water molecule and the atomic coordinates (in a.u.) are given by: O(0, 0, 0), H1(−1.10717, 0, 1.43045), H2(−1.10717, 0, −1.43045) (see also Fig. 1 of Ref. [15]).

The variation functions $f_{i\mu}^{(1,0)}$ and $f_{i\mu}^{(0,1)}$ were expressed in the form (10) with the same set of $g_{p\mu}$ functions in both cases. For the $x$-component the following $g_{px}$ functions have been employed:

$$g_{px}: y, z, yz;\ yx^2, y^3, yz^2;\ zx^2, zy^2, z^3;\ yzx^2, y^3z, yz^3; \tag{14}$$

and the functions $g_{py}$ and $g_{pz}$ can be obtained from (14) by a cyclic permutation of the coordinates. The origin of the coordinate system in (14) has been chosen at the oxygen atom. Within the present form of $g_{p\mu}$ its particular choice does not have any influence on the final results. It also follows from the molecular symmetry that some of the terms included in the basis set (14) do not contribute to the second-order energies $E_{\mu\mu}^{(2,0)}$ and $E_{\mu\mu}^{(0,2)}$ depending on the component under consideration.

The form of the basis set (14) is different from that originally employed by Kolker and Karplus [16, 28]. For the sake of the computational convenience we have omitted all the terms involving the distance between an electron and a given center. The present approximation of the variation functions is similar to that recently employed by Chang [29] in the variation-perturbation study of the Faraday effect.

The integrals which appear in the Karplus-Kolker functionals [16] for $E_{\mu\mu}^{(2,0)}$ and $E_{\mu\mu}^{(0,2)}$ were calculated according to well known formulae [36, 37] with $F_m(t)$ functions [37] evaluated from the analytical approximations of Schaad and Morrell [38].

The calculations were performed for two different origins for the vector potential of the external magnetic field. The first origin has been chosen at the electronic centroid (e.c.) and the second one at the hydrogen atom which shielding constant is determined. The first choice corresponds to the prescription of Chan and Das [33] and is considered as a more justified and better than the second one. To study the convergence of the Karplus-Kolker scheme we performed the calculations of the second-order energies with first 3, 6 and 9 and with all the members of the basis set (14). The corresponding results are presented in Table 1.

According to the data of Table 1 both $E_{\mu\mu}^{(2,0)}$ and $E_{\mu\mu}^{(0,2)}$ exhibit a monotonous behaviour with respect to the number of variation parameters. Apparently, we did not reach a complete convergence for all the components of these second-order energies and the poorest result is expected for $E_{xx}^{(2,0)}$. In this latter case the molecular

Table 1. The study of the convergence of the calculated second-order energies[a]

| $L$[b] | $-E^{(2,0)}$ | | | $-E^{(0,2)}$ | | | $E^{(1,1)}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $xx$ | $yy$ | $zz$ | $xx$ | $yy$ | $zz$ | $xx$ | $yy$ | $zz$ |
| 3 | 0.170 | 0.745 | 0.165 | 0.263 | 0.403 | 0.138 | 3.360 | 4.573 | 0.824 |
| 6 | 0.170 | 0.913 | 0.165 | 0.277 | 0.416 | 0.138 | 3.360 | 5.838 | 0.824 |
| 9 | 0.170 | 0.913 | 0.194 | 0.277 | 0.434 | 0.148 | 3.360 | 5.838 | 0.576 |
| 12 | 0.189 | 0.938 | 0.198 | 0.287 | 0.440 | 0.151 | 3.656 | 6.261 | 0.647 |

[a] The gauge origin is taken at e.c. Both $E^{(2,0)}$ and $E^{(0,2)}$ are expressed in a.u.

$$\chi_{\mu\mu}^{p}(\text{erg/mole}\cdot\text{gauss}^2) = -2.375964\,E_{\mu\mu}^{(2,0)}$$

$E^{(1,1)}$ is given in ppm.

[b] The number of the first terms of the basis set (14) employed in the calculation.

symmetry eliminates eight terms of the largest 12-term set (14) employed in the present study. However, we believe that, in general, the calculated second-order energies should not appreciably change upon addition of higher terms in (10). It should be also pointed out that for all the components of $E^{(0,2)}$ the convergence is remarkably good.

The oscillatory behaviour of $E^{(1,1)}_{\mu\mu}$ can easily be understood if we recall that in contrary to $E^{(2,0)}_{\mu\mu}$ and $E^{(0,2)}_{\mu\mu}$ this second-order energy is neither maximum nor minimum of an appropriate functional [28]. In this paper the energy $E^{(1,1)}_{\mu\mu}$ has been calculated from Eq. (6) (or, equivalently from Eq. (9)) and, thus, depends on the accuracy of previously determined first-order perturbed orbitals. For the variation method the best first-order perturbed orbitals are those which extremize $E^{(2,0)}_{\mu\mu}$ (or $E^{(0,2)}_{\mu\mu}$), and therefore, we treat the energies $E^{(1,1)}_{\mu\mu}$ calculated with 12-term representation of $f^{(1,0)}_{i\mu}$ ($f^{(0,1)}_{i\mu}$) as the best ones.

The data of Table 1 refer to the gauge origin at the electronic centroid. Quite similar behaviour of the gauge-dependent second-order energies is also observed for the origin taken at the hydrogen atom which shielding constant is considered. However, the convergence of $E^{(2,0)}_{\mu\mu}$ and $E^{(1,1)}_{\mu\mu}$ appears to be somewhat better when the origin of the vector potential is taken at the electronic centroid.

All the calculations reported in this paper were programed in Algol and performed on the ODRA 1204 computer. Almost all the final results obtained for the magnetic susceptibility and proton magnetic shielding in the water molecule refer to 12-term basis set (14). The corresponding paramagnetic contributions for shorter variation functions can easily be calculated from the data of Table 1.

## Results and Discussion

### *a) Magnetic Susceptibility*

The components of the paramagnetic contribution to the magnetic susceptibility tensor were calculated according to Eq. (3). The corresponding numerical values for the gauge origin at the electronic centroid (e.c.) are shown in Table 2. They are compared with recent results of Arrighini *et al.* [39] obtained by using the CHF approach and also with the experimental data of Taft and Dailey [40].

Table 2. The paramagnetic contribution to the magnetic susceptibility of the water molecule (in erg/mole · gauss$^2$)

| | This work[a] | CHF [39] | Exp.[b] [40] |
|---|---|---|---|
| $\chi^p_{xx}$ | 0.45 | 1.03 | 1.40 |
| $\chi^p_{yy}$ | 2.23 | 2.06 | 2.33 |
| $\chi^p_{zz}$ | 0.47 | 0.54 | 0.79 |
| $\chi^p_{Av}$ | 1.05 | 1.21 | 1.51 |

[a] These results correspond to the gauge origin at e.c. while the CHF and the experimental data refer to the gauge origin at the nuclear center of mass. The difference can be estimated as $-\Delta\chi^d$ and does not exceed 0.02 erg/mole · gauss$^2$.

[b] There are also several other experimental data [45, 46] but the differences are unimportant from the point of view of the present comparison.

Table 3. Total magnetic susceptibility of the water molecule (in erg/mole gauss$^2$)

| | This work | | Reference theoretical results | | | | Exp.[g] |
|---|---|---|---|---|---|---|---|
| | I[a] | II[b] | CHF[c] | VP[d] | GIAO[e] | DG[f] | |
| $\chi_{xx}$ | −14.88 | −14.48 | −14.55 | −14.56 | −13.70 | −12.10 | −13.5 ± 2.0 |
| $\chi_{yy}$ | −14.21 | −11.85 | −14.35 | −14.41 | −12.67 | −13.27 | −13.7 ± 1.8 |
| $\chi_{zz}$ | −13.99 | −13.81 | −14.22 | −13.68 | −12.15 | −11.68 | −12.1 ± 1.6 |
| $\chi_{\mathrm{Av}}$ | −14.36 | −13.38 | −14.37 | −14.22 | −12.84 | −12.38 | −13.1 ± 1.8 |

[a] Gauge origin at e.c.

[b] Gauge origin at the hydrogen.

[c] CHF results of Arrighini *et al.* [39] calculated using an extended STO basis set function. The gauge origin is at the nuclear center of mass.

[d] Variation-perturbation results for the LCGO wavefunction of Neumann and Moskowitz [4] with first three terms of (14) [49]. The gauge origin is at the oxygen.

[e] Calculated using the gauge invariant approach [47] with the SCF function of Ellison and Shull [48].

[f] Variation-perturbation results of Das and Ghose [43] obtained with approximate localized orbitals. The gauge origin is at the electronic centroid.

[g] The experimental data from Ref. [40] for the gauge origin at the nuclear center of mass. See also Footnote b to Table 2.

From the point of view of the theory involved in the present approach a comparison with the CHF results seems to be especially important. According to [12] and [13] the Karplus-Kolker scheme has a reliable justification for pure imaginary perturbations and the calculated paramagnetic contributions to the magnetic susceptibility should not differ remarkably from the corresponding CHF values. This is observed for the $y$- and $z$-component. A worse result for $\chi^p_{xx}$ can be explained by the fact, that $f^{(1,0)}_{ix}$ has, by symmetry, only four non-zero variation parameters while for e.g. $f^{(1,0)}_{iz}$ almost all the terms (14) do contribute to the second-order energy. It should be also pointed out that the CHF value of $\chi^p_{xx}$ agrees much better with the experimental value. In spite of some differences between the present and CHF components of the paramagnetic contribution, the rotational average $\chi^p_{\mathrm{Av}}$ is almost the same as calculated by Arrighini *et al.* and compares favourably with the experimental value.

In Table 3 we presented a comparison of the calculated and experimental results for the total magnetic susceptibility tensor of the water molecule. Due to significant inaccuracies in the corresponding experimental data for the diamagnetic contribution one can hardly ascribe a definite priority to any theoretical result. However, it is worth attention that the results obtained with very poor wave functions are in general closer to the mean experimental value. It should be also pointed out that our variation-perturbation result for the total magnetic susceptibility tensor (with gauge origin at e.c.) is practically the same as that obtained by Arrighini *et al.* within the CHF approach with extended basis set of the Slater-type orbitals [39]. This indicates the usefulness of the SCF MO LCGO wavefunctions as well as the applicability of the simplified variation-perturbation UCHF approach to the calculation of molecular magnetic properties.

In Table 3 we have also reported our previous variation-perturbation results obtained with the SCF MO LCGO wave function of Neumann and Moskowitz [4]. Concerning the total molecular energy they obtained slightly better result than that reported by Diercksen [15] and their wave function should be closer to that corresponding to the Hartree-Fock limit. However, the components of the magnetic susceptibility tensor calculated with these two SCF MO LCGO wave functions do not differ significantly.

The gauge dependence of our results can be seen by a comparison of the calculated components of the total magnetic susceptibility for the origin at e.c. with those obtained for the origin at H atom. According to Moccia [41], when the results are gauge dependent, the maximum of the total magnetic susceptibility gives the best approximation to the Hartree-Fock limit. Thus, following the results of Arrighini *et al.* [39], the magnetic susceptibility obtained using the electronic centroid for the gauge origin is probably more reliable.

### *b). Proton Magnetic Shielding*

The proton magnetic shielding is undoubtedly one of the most important molecular magnetic properties of the water molecule but there were only few attempts to calculate it non-empirically. The only reliable result is that obtained recently by Arrighini *et al.* [39, 42] by using the CHF method. The variation-perturbation scheme, similar to that applied in the present study, has also been employed by Das and Ghose [43]. However, they used rather poor ground state wave function and their results were rather disappointing. The best result of Das and Ghose does not exceed even 60 percent of the experimental value.

The present variation-perturbation results obtained with 12-term expansion for $f_i^{(1,0)}$ are shown in Table 4. The convergence of the calculated components of the proton shielding constant for the gauge origin at e.c. has been analysed in Table 1. The gauge dependence as well as the convergence for the rotational average of the shielding tensor has been presented in Table 5.

Table 4. Results for the proton magnetic shielding in the water molecule (in ppm)

| | Gauge origin | Component | | | Rotation average |
|---|---|---|---|---|---|
| | | $xx$ | $yy$ | $zz$ | |
| $\sigma^p$ | e.c. | 3.66 | 6.26 | 0.65 | 3.52 |
| $\sigma^d$ | e.c. | 23.21 | 14.04 | 37.08 | 24.78 |
| $\sigma$ | e.c. | 26.87 | 20.30 | 37.73 | 28.30 |
| $\sigma^p$ | H | − 76.65 | −118.44 | −39.01 | − 78.03 |
| $\sigma^d$ | H | 100.96 | 130.37 | 75.67 | 102.33 |
| $\sigma$ | H | 24.31 | 11.93 | 36.66 | 24.30 |

Table 5. The convergence of the proton shielding constant (in ppm)

| | Gauge origin | $L^a = 3$ | 6 | 9 | 12 |
|---|---|---|---|---|---|
| $\sigma^p_{Av}$ | e.c. | 2.92 | 3.34 | 3.26 | 3.52 |
| $\sigma_{Av}$ | e.c. | 27.70 | 28.12 | 28.04 | 28.30 |
| $\sigma^p_{Av}$ | H | −79.00 | −78.37 | −78.31 | −78.03 |
| $\sigma_{Av}$ | H | 23.33 | 23.96 | 24.02 | 24.30 |

[a] See footnote b to Table 1.

The experimental rotation average of the proton shielding constant in the water molecule is estimated as 30.20 ppm [4] or 30.03 ± 0.60 ppm [44]. Hence, according to the data of Table 5, the results obtained for each gauge origin improve upon the addition of new variation parameters. The best result, 28.30 ppm, is apparently for the gauge origin chosen at the electronic centroid. This conclusion agrees with our previous remarks concerning the best gauge origin for the calculation of the magnetic susceptibility. It should be also pointed out that the best value obtained by Arrighini *et al.* [44] for a particular choice of the gauge origin as suggested by Moccia [41], is 28.94 ppm.

It follows from the data of Table 4 that shifting the gauge origin from e.c. to the shielded H atom we induce the gauge dependence of 4 ppm and according to Table 5 this gauge dependence is reduced with increasing number of terms in the variation function. It is worth attention that $\sigma_{xx}$ and $\sigma_{zz}$ are almost gauge-invariant, and therefore, these values appear to be more reliable than the results for $\sigma_{yy}$. This is also illustrated by the numerical data presented in Table 6. It follows from a comparison with the experimental data for the gauge origin at H atom, that the worst result is obtained for $\sigma^p_{yy}$.

In Table 6 we included also the CHF results of Arrighini *et al.* [44]. Evidently, they do not agree with the corresponding experimental values, though for the gauge origin at the central atom the agreement was relatively good [44]. This indicates a much stronger gauge-dependence of the incomplete basis set CHF calculations, than that found in the present approach.

A comparison of the total components of the shielding tensor calculated in the present paper with those obtained by Arrighini *et al.* [44] for several gauge origins is shown in Table 7. It can be seen that our values are in general better

Table 6. Paramagnetic contribution to the proton magnetic shielding for the gauge origin at the hydrogen atom (in ppm)

| | This work | CHF[a] | Exp.[b] |
|---|---|---|---|
| $\sigma^p_{xx}$ | − 76.65 | −52.63 | − 71.79 |
| $\sigma^p_{yy}$ | −118.44 | −79.18 | −107.04 |
| $\sigma^p_{zz}$ | − 39.01 | −25.76 | − 36.57 |
| $\sigma^p_{\mathrm{Av}}$ | − 78.03 | −52.52 | − 71.80 |

[a] The CHF results of Arrighini *et al.* [44].

[b] The experimental data of Bluyssen *et al.* [50] taken from Ref. [44].

Table 7. A comparison of the results for the proton magnetic shielding in the water molecule (in ppm)

| | Gauge origin | $\sigma_{xx}$ | $\sigma_{yy}$ | $\sigma_{zz}$ | $\sigma_{\mathrm{Av}}$ |
|---|---|---|---|---|---|
| This work | e.c. | 26.87 | 20.30 | 37.73 | 28.30 |
| This work | H | 24.31 | 11.93 | 36.66 | 24.30 |
| CHF[a] | O | 27.57 | 20.60 | 36.52 | 28.23 |
| CHF[a] | H | 50.21 | 50.98 | 49.52 | 50.24 |
| Exp.[b] | — | — | — | — | 30.20 |

[a] Results of Arrighini *et al.* [44].

[b] Taken from Ref. [4].

than those calculated within the CHF scheme. It follows that when the gauge origin is chosen at e.c., both the CHF method and the Karplus-Kolker variation-perturbation scheme lead to remarkably good results. However, comparing the calculations for the gauge origin at H atom we find that the Karplus-Kolker scheme gives much better estimate of the proton shielding constant. Undoubtedly, extending the basis set of virtual orbitals one would obtain better results within the CHF approach. This, however, increases enormously the computational effort involved in this scheme. On the other hand, using the variation-perturbation method of Karplus and Kolker we can greatly simplify the computations without a considerable loss of accuracy of final results. The present calculations indicate also the usefulness of the SCF MO LCGO wave functions which allow for a very simple evaluation of all the one-electron integrals appearing in the treatment.

The results of the calculations described in this paper confirm our previous conclusions [12, 13] that for pure imaginary perturbing operators the corrections to the Karplus-Kolker scheme derived from the CHF functional should not be very important. However, one has also to point out some intrinsic limitations of the Karplus-Kolker method which do not arise in the CHF approach. The derivation of the Karplus-Kolker functional is based on the multiplicative approximation (7) for the first-order perturbed orbitals [16, 13]. A rigid form of the perturbed wave functions cannot account for the necessary node shifts, and thus, some properties, e.g., the magnetic shielding constants of heavy nuclei, cannot be accurately calculated within the Karplus-Kolker scheme [28]. Apparently, these difficulties do not arise when the first-order perturbed orbitals are expanded into a set of virtual Hartree-Fock orbitals [51] and from this point of view the method applied by Arrighini *et al.* [22, 39, 44, 51] seems to be more successful. However, in the case of the magnetic susceptibility and proton shielding, the rigidity of the multiplicative approximation appears to be less important [16, 28].

To summarize our discussion we conclude that the Karplus-Kolker scheme can be considered as a simple, practical and probably sufficiently accurate method for the calculation of molecular magnetic susceptibilities and proton shielding constants. To support this conclusion the corresponding calculations for other molecules are in progress. Also the problem of the proton magnetic shielding in the hydrogen-bonded systems will be considered in a subsequent paper.

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