Electric-field Dependence of Nuclear Magnetic Shielding and Susceptibility of Hydrogen and Hydrogen Fluoride Molecules

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Z. Naturforsch. **34 a**, 1279—1282 (1979); received September 5, 1979

The components of the tensors $\sigma^{(1)}$, $\sigma^{(2)}$ and $\chi^{(1)}$, $\chi^{(2)}$, which describe the linear and quadratic electric-field dependences of the nuclear magnetic shielding and susceptibility are computed for H_2 and HF molecules using a gauge invariant double finite perturbation SCF approach. This approach is suitable for the discussion of intramolecular and intermolecular environmental effects and the effect of electric-field gradient is pointed out.

1. Introduction

An electric field distorts the electron distribution in a molecule which causes changes in the molecular susceptibility and in the magnetic shielding of nuclei. The dependence of the magnetic shielding on the electric field was calculated by Buckingham [1]. He showed that the shielding change $\Delta\sigma_{\mathrm{E}}$ due to a uniform electric field $\boldsymbol{E}$ for a proton in an X-H bond is given by

$$\Delta\sigma_{\mathrm{E}} = -A\,E_2 - B\,E^2\,, \tag{1}$$

where A and B are bond parameters which are independent of the electric field, but dependent of the nature of X. The z-axis is taken along the X-H bond from X to H, so that for an electric field along the bond the shielding will be reduced if A and B are positive.

Direct experimental evidence for the existence of an electric field effect on shielding has been found by many authors not only for protons but also for fluorine and ^{13}C nuclei. There have been also some ab-initio theoretical calculations of the electric-field dependence of molecular magnetic properties [2—4].

In the present paper a simple but general method for the calculation of the electric field effect upon the molecular susceptibility and magnetic shielding is presented.

2. Details of Calculations

In the presence of a uniform electric field $\boldsymbol{E}$ the nuclear magnetic shiedling tensor $\sigma_{\alpha\beta}$ can be expanded as a power series in E

$$\sigma_{\alpha\beta} = \sigma^{(0)}_{\alpha\beta} + \sigma^{(1)}_{\alpha\beta\gamma}\,E_\gamma + \tfrac{1}{2}\,\sigma^{(2)}_{\alpha\beta\gamma\delta}\,E_\gamma\,E_\delta + \cdots\,, \tag{2}$$

where $\sigma^{(0)}_{\alpha\beta}$ is the shielding in the absence of $\boldsymbol{E}$. Averaging over all directions of the magnetic field we obtain for a nucleus of $C_{\infty\mathrm{v}}$ site symmetry [5]

$$\sigma = \sigma^{(0)} - A\,E_{\parallel} - B_{\parallel}\,E_{\parallel}{}^2 - B_{\perp}\,E_{\perp}{}^2\,, \tag{3}$$

where $E_{\parallel}$ and $E_{\perp}$ are the electric-field components parallel and perpendicular to the internuclear axis and the parameters A, $B_{\parallel}$ and $B_{\perp}$ are defined (using the tensor summation convention) by

$$A = -\tfrac{1}{3}\,\sigma^{(1)}_{\alpha\alpha z}\,; \quad B_{\parallel} = -\tfrac{1}{6}\,\sigma^{(2)}_{\alpha\alpha zz}\,;$$
$$B_{\perp} = -\tfrac{1}{6}\,\sigma^{(2)}_{\alpha\alpha xx}\,. \tag{4}$$

In these expressions the negative signs have been introduced to make more easy the comparison with Equation (1).

Similar equations can be written also for the magnetic susceptibility.

The procedure used to obtain the electric-field dependence of the nuclear shielding tensor is a double finite perturbation theory. For a given magnitude and direction of the external electric field the SCF-Hartree-Fock equation has been solved and the magnetic field perturbation has been determined by use of a standard finite perturbation procedure [6—9]. Such calculations were carried out for an external magnetic field density of 5000 T (~ 0.021 a.u.) for several values of the external electric field between $2.5 \cdot 10^9$ V/m (~ 0.005 a.u.) and $10 \cdot 10^9$ V/m (~ 0.02 a.u.). Derivatives with respect to both external fields were obtained by numerical differentiation. The numerical technique is computationally convenient although it requires very high accuracy because of the relatively small

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external field dependence. The threshold for molecular integrals was set to 10^{-10} a.u.

External electric fields were generated by point charges at very large distances. The charges used were up to $3 \cdot 10^{-13}$ As ($\sim 2 \cdot 10^6$ a.u.) at a distance of $5 \cdot 10^{-7}$ m ($\sim 10^4$ a.u.). The homogenity of thus generated electric fields is good enough for the evaluation of the field dependence. The field difference at the sites of the nuclei in H_2 is less than $3 \cdot 10^6$ V/m (0.03%). This procedure is simple enough and can be used to show also the effect of inhomogenity of external electric fields — a true reallity in all experimental measurements.

3. Results and Discussion

3.1. *Proton Shielding in H_2*

Computed values of the components $\sigma^{(0)}$, $\sigma^{(1)}$ and $\sigma^{(2)}$ for proton shielding in H_2 are given in Table 1. Computations are done with two slightly different basis sets. The first basis is a double-zeta basis set [10] implemented with polarization functions with exponent one. Basis set II consists of the same functions, but with orbital exponents of polarization functions equal to 0.5.

There are some differences between the computed values with different bases, especially in components including also paramagnetic parts. Components of $\sigma^{(1)}$ computed with both bases are not much different and are similar to those of earlier works given in Table 1 in separate columns. The sign of the components of $\sigma^{(1)}$ depends on the nucleus in question.

The difference between the components $\sigma^{(2)}_{\alpha\alpha xx}$ computed with the two bases sets is substantial showing that the basis sets used are too small to give a satisfactory description of the electric-field dependence of the shielding. This is perhaps also the reason why the inequality $B_\perp > B_\parallel$ predicted in earlier work [3] is not confirmed.

3.2. *Nuclear Shieldings in HF*

Computed values of the shielding components for the nuclei of HF are given in Table 2. The basis set used (III) is that of Dunning [11]. The computed values A, $B_\perp$ and $B_\parallel$ agree well with those of Day and Buckingham [2], though there are some differences in the values of the components $\sigma^{(2)}$. The basis set we used is smaller than the one of Day and Buckingham, but due to the use of field dependent factors [6], [7] our results are gauge invariant.

Table 1. Components of the tensors $\sigma^{(0)}$, $\sigma^{(1)}$ and $\sigma^{(2)}$ for nuclear shielding in the hydrogen molecule. The molecular axis is taken as the z-axis and the results are computed for an internuclear distance of 1.4 a.u. The first two suffixes denote the directions of the magnetic dipole and the magnetic induction, the third and fourth ones denote the direction of the external electric field. Values of $\sigma^{(0)}$ are given in units 1×10^{-6}, values of $\sigma^{(1)}$ in units 1×10^{-16} mV^{-1} and values of $\sigma^{(2)}$ in units 1×10^{-28} m^2 V^{-2}. The signs of $\sigma^{(1)}$ and A are taken for the proton H′ and the electric field with the direction H → H′.

Component	Basis set I	Basis set II	Ref. [4]	Ref. [3]
$\sigma_{xx}^{(0)}$	26.09	26.37	25.58	
$\sigma_{zz}^{(0)}$	27.84	27.98	27.83	
$\sigma_{av}^{(0)}$	26.68	26.91	26.33	
$\sigma_{xzz}^{(1)}$	−1.26	−1.08	−1.15	−1.33
$\sigma_{zzz}^{(1)}$	−0.63	−0.63	−0.63	−0.61
$\sigma_{xxxx}^{(2)}$	−0.1	−0.8	−5.86	−0.65
$\sigma_{yyxx}^{(2)}$	−2.1	−3.5	−7.12	−2.85
$\sigma_{zzxx}^{(2)}$	−0.5	−2.0	−6.37	−2.80
$\sigma_{xxzz}^{(2)}$	−7.4	−5.3	−7.12	−2.09
$\sigma_{zzzz}^{(2)}$	−3.6	−4.2	−2.43	−1.54
A	1.05	0.93	0.97	1.09
$B_\parallel$	3.07	2.47	2.53	0.95
$B_\perp$	0.45	1.05	3.35	1.05

Table 2. Components of the tensors $\sigma^{(0)}$, $\sigma^{(1)}$ and $\sigma^{(2)}$ for nuclear shielding in HF. Results are computed for an internuclear distance of 1.733 a.u. Suffixes and units as in Table 1. The signs of $\sigma^{(1)}$ and A correspond to the electric field direction H → F.

	H		*F*	
Component	Basis set III	Ref. [2]	Basis set III	Ref. [2]
$\sigma_{xx}^{(0)}$	23.32	18.85	367.2	378.3
$\sigma_{zz}^{(0)}$	43.25	44.10	482.8	481.9
$\sigma_{av}^{(0)}$	29.97	27.27	405.7	412.8
$\sigma_{xxz}^{(1)}$	1.80	1.94	− 20.5	− 18.3
$\sigma_{zzz}^{(1)}$	0.58	0.64	0.03	− 0.027
$\sigma_{xxxx}^{(2)}$	−1.0	0.71	4.0	− 46.7
$\sigma_{yyxx}^{(2)}$	−1.0	−2.55	− 89.0	− 26.0
$\sigma_{zzxx}^{(2)}$	−1.1	−2.90	− 69.0	−158.3
$\sigma_{xxzz}^{(2)}$	16.0	19.3	−505.0	−462.0
$\sigma_{zzzz}^{(2)}$	1.67	0.24	1.0	− 87.4
A	−1.39	−1.50	13.7	12.2
$B_\parallel$	−5.6	−6.46	168.0	168.9
$B_\perp$	0.5	0.79	25.7	38.5

Comparison of the proton components in HF and H_2 shows a great increase in the value of $\sigma^{(2)}_{xxzz}$. The sign of $B_\parallel$ is negative, though the signs of $B_\parallel$ for all protons were believed to be positive [12].

The magnitude of A, $B_{\|}$ and $B_{\perp}$ for the fluorine nucleus is greater than for the proton as was predicted before considering the ease of polarization along and perpendicular to the bond direction.

3.3. Magnetic Susceptibility of H_2 and HF

The magnetic susceptibility components of H_2 in an electric field are given in Table 3. The values are calculated with the same basis sets as the nuclear shieldings. To our knowledge there have not been published any data for the components $\chi^{(2)}$ for the hydrogen molecule. The components $\chi^{(1)}$ are zero for H_2 due to the molecular symmetry.

Table 3. Magnetic susceptibility components of $\chi^{(0)}$ and $\chi^{(2)}$ calculated for the hydrogen molecule in an electric field. For the molecule the z-axis is defined as the intermolecular axis and the internuclear separation is 1.4 a.u. The first two suffixes denote the directions of the magnetic induction, the third and fourth ones denote the direction of the electric field. Values of $\chi^{(0)}$ are in units of 1×10^{-29} JT^{-2}, those of $\chi^{(2)}$ are in units of 1×10^{-52} JT^{-2} m^2 V^{-2}.

Component	Basis set I	Basis set II	Ref. [4]
$\chi_{xx}^{(0)}$	− 6.77	− 6.68	−6.921
$\chi_{zz}^{(0)}$	− 5.82	− 5.85	−6.143
$\chi_{av}^{(0)}$	− 6.45	− 6.40	−6.662
$\chi_{xxxx}^{(2)}$	0.19	− 1.35	
$\chi_{yyxx}^{(2)}$	47.5	37.2	
$\chi_{zzxx}^{(2)}$	0.25	− 0.48	
$\chi_{xxzz}^{(2)}$	− 7.36	−11.0	
$\chi_{zzzz}^{(2)}$	−15.2	−15.1	

Table 4. Magnetic susceptibility components of $\chi^{(0)}$, $\chi^{(1)}$ and $\chi^{(2)}$ for HF. The z-axis is in the H → F direction and the internuclear separation is 1.733. Suffixes as in Table 3. Values of $\chi^{(0)}$ are in units of 1×10^{-29} JT^{-2}, those of $\chi^{(1)}$ are in units of 1×10^{-41} JT^{-2} mV^{-1} and those of $\chi^{(2)}$ are in units of 1×10^{-52} JT^{-2} m^2 V^{-2}.

Component	Basis set III	Ref. [2]
$\chi_{xx}^{(0)}$	−17.01	−17.54
$\chi_{zz}^{(0)}$	−16.28	−16.65
$\chi_{av}^{(0)}$	−16.77	−17.24
$\chi_{xxz}^{(1)}$	6.21	0.486
$\chi_{zzz}^{(1)}$	2.38	4.116
$\chi_{xxxx}^{(2)}$	− 2.8	− 6.17
$\chi_{yyxx}^{(2)}$	− 7.1	−10.18
$\chi_{zzxx}^{(2)}$	− 0.5	− 6.85
$\chi_{xxzz}^{(2)}$	17.2	− 4.15
$\chi_{zzzz}^{(2)}$	− 4.08	− 5.13

The susceptibility components of HF are given in Table 4. The greatest differences between our values and those of reference [2] occur with the components $\chi^{(1)}_{xxz}$ and $\chi^{(2)}_{xxzz}$. These components are most sensitive to the quality of the basis set; so the great discrepancy between these results can be due to the different basis sets used.

3.4. Electric Field Gradient Effects

From the results calculated for different distances of the point charge it is possible to evaluate the dependence of the magnetic properties on the gradient of the electric field. For instance, we can develop the susceptibility in a series

$$\chi = \chi^{(0)} + \chi^{(1)} E + \frac{1}{2} \chi^{(2)} E^2 + \Theta^{(1)} \frac{dE}{dr} + \frac{1}{2} \Theta^{(2)} \frac{d^2E}{dr^2} . \qquad (5)$$

We hope to present the dependence of magnetic properties on electric field gradients in a later paper. Let us note here only that this dependence is considerable and should be taken into account.

For a hydrogen molecule in perpendicular magnetic field and parallel electric field (point charge on molecular axis) the field gradient components are:

$$\Theta^{(1)} = - 2.3 \cdot 10^{-51} \, JT^{-2} \, m^2 \, v^{-1} ,$$
$$\Theta^{(2)} = - 2.7 \cdot 10^{-60} \, JT^{-2} \, m^3 \, v^{-1} .$$

This means that for the electric field of a point charge of 100 a.u. at a distance of 100 a.u. from H_2 the perturbation of the quadratic electric field term ($\chi^{(2)}$) is only twice as big as the perturbation of the first electric field gradient term ($\Theta^{(1)}$). That is one of the reasons why the approach of Day and Buckingham with point charges at smaller distances [2] did not succeed. For such small distances there is even a need for higher terms in the series (5).

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