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Magnetizability and nuclear shielding constants of solvated water

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Abstract

We apply a recently developed model for calculating gauge origin independent molecular magnetic properties of solvated molecules to determine the magnetizability and nuclear shielding constants of solvated water. The solute is surrounded by a solvation shell and this supermolecule is enclosed in a spherical cavity immersed in a dielectric medium.

1. Introduction

In this Letter we apply a recently developed rigorous method for calculating gauge-origin independent magnetic properties of solvated molecules to determine the magnetic properties of solvated water. Our method is based on previous work establishing an electronic Hamiltonian for origin independent studies of magnetic properties [1–3], and on dielectric-medium response methods for calculating the molecular properties of solvated molecules [4–8]. In particular, we shall consider the magnetizability and nuclear shielding constants of a water molecule solvated in water. We do this by taking the water molecule of interest together with a first solvation shell, surrounding this supermolecule by the bulk of the solvent. The latter is represented as a homogeneous, isotropic and linear dielectric medium. The charge distribution of the supermolecule within the spherical cavity induces polarization charge densities in the dielectric medium, which in turn give rise to an extra polarization potential felt by the supermolecule.

The magnetizability ξ and the nuclear magnetic shielding constants $\sigma(K)$ are defined as [2,3]

$$\xi = - \left. \frac{\partial^2 E(\mathbf{B})}{\partial^2 \mathbf{B}} \right|_{\mathbf{B}=0} \quad (1)$$

and

$$\sigma(K) = 1 + \left. \frac{\partial^2 E(\mathbf{B}, \mathbf{m})}{\partial \mathbf{B} \partial \mathbf{m}_K} \right|_{\mathbf{B}=\mathbf{m}=0} \quad (2)$$

where \mathbf{m}_K is the nuclear magnetic moment of nucleus K , \mathbf{m} is the collection of nuclear magnetic moments and \mathbf{B} is the magnetic field induction. The energy functional is

$$E(\mathbf{B}, \mathbf{m}) = E_{\text{vac}}(\mathbf{B}, \mathbf{m}) + E_{\text{sol}}(\mathbf{B}), \quad (3)$$

where the first term is the energy corresponding to the Hamiltonian for the molecular compound in vacuum and the second term is the solvation energy given as [4–8]

$$E_{\text{sol}}(\mathbf{B}) = \sum_{lm} g_l (\langle T_{lm} \rangle)^2, \quad (4)$$

where we have utilized the expression for the solvation energy where the solvent response is in equilib-

rium with the charge distribution of the molecules within the cavity [4,8–10]. The charge distribution of the solute is expanded in a multipole series where the charge moments are

$$\langle T_{lm} \rangle = T_{lm}^n - \langle T_{lm}^e \rangle, \quad (5)$$

$$T_{lm}^n = \sum_K Z_K R_K^{lm}(\mathbf{R}_K), \quad (6)$$

$$T_{lm}^e = R^{lm}(r) = \sum_{pq} R_{pq}^{lm} E_{pq}, \quad (7)$$

where Z_K and \mathbf{R}_K are the nuclear charge and position of nucleus K , and the functions R^{lm} are transformed spherical harmonics. The moment $T_{lm}^n(\langle T_{lm}^e \rangle)$ is the nuclear (electronic) contribution to the charge moment $\langle T_{lm} \rangle$. For a spherical cavity of radius R_{cav} embedded in a medium with dielectric constant ϵ and having the moment expansion of l , we have the following expression for g_l :

$$g_l = -\frac{1}{2} R_{\text{cav}}^{-(2l+1)} \frac{(l+1)(\epsilon-1)}{l+\epsilon(l+1)}. \quad (8)$$

We refer to Refs. [4–8] for further details.

The theoretical background for obtaining gauge-origin independent magnetic properties for solvated compounds has been presented in Ref. [11]. Presently no other method exists for performing such calculations. There have been investigations concerning solvent effects on nuclear shielding constants but these have mainly involved studies of dimers, trimers or placing solvent molecules around the solute for simulating the solvent effects [12–19]. A recent study by Chesnut and Rusiloski [20] used a rather crude model for estimating the effect of an outer dielectric medium on the nuclear shielding constants. The electronic wavefunction was optimized in the presence of a dielectric medium employing the Onsager model (only the dipolar solvent reaction field is included) and the response of the wavefunction to the magnetic induction and the magnetic moments entering the solvation energy was neglected. They also performed molecular dynamics simulations of liquid water and used the obtained structures as input to electronic structure calculations of NMR chemical shieldings of liquid water. Their latter approach gave much better agreement with experimental data than their dielectric medium approach.

2. Calculations

The calculations were carried out using the Hermit-Sirius-Abacus suite of programs [21–23]. In all calculations we used the 6-311++G(2d,2p) basis set [24], which is known to give good results for magnetizabilities as well as nuclear shieldings [25]. The size of the cavity is chosen to be the distance from the center of mass to the most distant atom plus the Van der Waals distance of this atom. For a single solvated water molecule this gives a cavity radius of 3.94 au, whereas for a central water molecule surrounded by its first solvation shell the radius is 8.73 au. The dielectric constant of the medium is given by the static dielectric constant of water, 78.54. The multipole expansion is truncated at $l_{\text{max}} = 10$. The dependence of the magnetic properties on the size of cavity and truncation of the multipole expansion was investigated in Refs. [11,26] and is not considered further here. For all molecules investigated in Ref. [11], the magnetic properties were converged with respect to the truncation of the multipole expansion for $l_{\text{max}} \geq 6$. The structure of the solvation shell around the central water molecule is taken from Ref. [27], and has previously been used for investigating the sign change of the hyperpolarizability of water undergoing gas-to-liquid transition [6].

The properties considered here are the chemical shielding constants and the magnetizability of water. We investigate the changes in both the paramagnetic and the diamagnetic contributions to these properties, made possible by the use of the natural connection [28,29].

Buckingham has proposed the following classification of the contributions to the solvent shifts of nuclear shieldings, σ_{solvent} [30]

$$\sigma_{\text{solvent}} = \sigma_b + \sigma_a + \sigma_w + \sigma_E. \quad (9)$$

These contributions arise from the bulk magnetic susceptibility (σ_b), the anisotropy in the molecular susceptibility of close-lying solvent molecules (σ_a), the Van der Waals interactions (σ_w) and the solvent polarization field (σ_E). The approach presented in Ref. [11] calculates σ_E , and by including a first solvation shell in the calculation we can give a better account of the σ_E and σ_a contributions, as well as include the Van der Waals interaction contribution, σ_w . However, there is currently no ab initio procedures for obtaining σ_b .

2.1. Magnetizability

We have summarized our results for the magnetizability of water in Table 1. Our gas phase value for the magnetizability is in excellent agreement with previous Hartree–Fock calculations of the magnetizability of water [2], and also within the error bars of the experiment. We note that the effect of the dielectric medium is to increase the diamagnetic character of the molecule, but the change is small.

The magnetizability of the central water molecule solvated by a first solvation shell poses a problem. The magnetizability is not a local property but rather the response of the supermolecule to a magnetic field induction. To solve this problem we use the differential shell approach of Ref. [6]. We perform four calculations:

- (i) Central water molecule + first solvation shell; ξ_i .
- (ii) First solvation shell; ξ_{ii} .
- (iii) Central water molecule + first solvation shell + dielectric medium; ξ_{iii} .
- (iv) First solvation shell + dielectric medium; ξ_{iv} .

The magnetizability of the central molecule including the first solvation shell is obtained as

$$\xi_{\text{shell}} = \xi_i - \xi_{ii}, \quad (10)$$

and the magnetizability of the central molecule including the first solvation shell and the outer dielectric medium is obtained as

$$\xi_{\text{solv}} = \xi_{iii} - \xi_{iv}. \quad (11)$$

From Table 1 we see that there are dramatic changes in the magnetizability when the molecule is enclosed in the first solvation shell. In contrast to the diamagnetic shift of the outer dielectric medium, the

effect of the solvation shell is to reduce the diamagnetic character of the molecule. Adding a dielectric medium to the supermolecule only leads to small changes in the magnetizability of the central molecule, once more increasing the diamagnetic character.

It is noteworthy that our value for the central molecule is in excellent agreement with the experimental values for ice at 223 K ($-204 \times 10^{-30} \text{ J T}^{-2}$), in particular if we assume that the correlation effect amounts to a scaling by 1.02, as indicated in several papers [31,32]. The excellent agreement with experiments on ice, but large deviation for the gas-phase results supports the need for a re-evaluation of the gas-phase magnetizabilities [31].

Both the dia- and paramagnetic parts of the magnetizability are significantly enhanced by the addition of a solvation shell, but the change in the paramagnetic term is almost three times larger than the shift in the diamagnetic term, explaining the strong paramagnetic shift observed, both experimentally and in this investigation, upon solvation of the water molecule.

It is particularly noteworthy that upon solvation the paramagnetic contribution to the magnetizability changes by a factor of 3–4. This dramatic change may be understood as a consequence of the lowering of the excited states upon solvation (as seen, for instance, in the narrowing of the HOMO–LUMO gap). Indeed, this effect appears to be the single most important factor that determines the paramagnetic solvation shift of the magnetizability of water.

Finally, we note the large change in the anisotropy. Although water is considered a fairly isotropic medium, this does not seem to be the case for a rigid ice structure.

Table 1

The magnetizability of water for the different models. All numbers in units of $10^{-30} \text{ J T}^{-2}$

	Gas phase	Dielectric	1. Solv. shell	1. Solv. shell and dielectric
ξ	-234.1	-234.7	-199.7	-199.8
ξ^{dia}	-258.7	-257.2	-280.9	-282.8
ξ^{para}	24.6	22.5	81.2	83.1
$\Delta \xi_i$	-3.6	-3.3	-23.5	-18.0
$\Delta \xi_1$	4.8	3.3	7.1	7.3
CRC ^a ξ	-218 ± 30			-204 (s, 223 K)

^a Handbook of Physics and Chemistry.

Table 2

The nuclear shielding constant of hydrogen for the various models. The isotropic shielding constant, σ^H , the diamagnetic contribution, σ_{dia}^H , the paramagnetic contribution, σ_{para}^H , the anisotropy and the asymmetry

Hydrogen	Gas phase	Dielectric	1. Solv. shell	1. Solv. shell and dielectric
σ^H	30.91	29.96	27.36	26.94
σ_{dia}^H	25.09	24.56	136.35	136.35
σ_{para}^H	5.82	5.41	-108.99	-109.41
anisotropy	20.29	21.56	31.15	31.73
experiment ^a , $\Delta\sigma$				28.7 ± 1
experiment ^b , $\Delta\sigma$				34.2 ± 1

^a Ref. [34]. Temperature was 195 K.

^b Ref. [35]. Temperature was 173 K.

2.2. Nuclear shielding constants

In Tables 2 and 3 we present the nuclear shielding constants of oxygen and hydrogen for the various solvent models. The solvent affects the nuclear shielding constants quite significantly, and the dominating effect arises from the interactions between the solute and the first solvation shell.

For hydrogen, we notice that σ^H decreases steadily with the complexity of the solvent models. In contrast, σ^O increases with the introduction of the dielectric medium but decreases as the first solvation shell is included. As the dielectric medium is added outside the first solvation shell, the shielding once more increases. This is due to the fact that the dielectric medium only affects the paramagnetic part by reducing its absolute value. In contrast, the solvation shell increases the absolute value of both the dia- and paramagnetic terms, the paramagnetic term being slightly larger. It is interesting to note that the solvation shell leads to an enormous change in both the dia- and paramagnetic contributions to the hydrogen shielding, but the effects almost cancel out. The anisotropy for σ^H (σ^O) increases (decreases) substantially with the inclusion of the first solvation

shell, although the effect is not quite as dramatic as for the anisotropy of the magnetizability.

The agreement with experiment is quite satisfactory for the hydrogen shielding (the experimental solvation shift being -4.26 ppm), whereas for the most sophisticated model we only manage to recover about half of the experimental solvation shift for oxygen, which is -36.2 ppm. It is interesting to note that the addition of a dielectric medium changes the hydrogen anisotropy by 0.6 ppm, which may be compared to the change of 0.9 ppm that was observed by Pulay et al. [33] when going from the (H₂O)₅ water cluster to the (H₂O)₁₇ cluster, implying that the dielectric model gives a fair description of the long-range interactions on the central water molecule.

As for the magnetizability, we notice that the most dramatic solvation effect in water appears to be the large paramagnetic shift in the paramagnetic part of the shieldings (as induced by the first solvation shell). Again, this effect appears to be related to the lowering of the excited states upon solvation.

As regards comparison with experiment it is important to bear in mind that our solvent structure is just one of many possible ones. It would be interest-

Table 3

The nuclear shielding constant of oxygen for the various models. The isotropic shielding constant, σ^O , the diamagnetic contribution, σ_{dia}^O , the paramagnetic contribution, σ_{para}^O , the anisotropy and the asymmetry

Oxygen	Gas phase	Dielectric	1. Solv. shell	1. Solv. shell and dielectric
σ^O	336.6	346.0	318.8	320.2
σ_{dia}^O	424.4	424.6	529.2	529.2
σ_{para}^O	-87.7	-78.6	-210.4	-209.0
anisotropy	52.1	54.7	33.5	33.1

ing to perform a complete geometry optimization of the five water molecules surrounded by the dielectric medium, as the geometry is known to be important in order to get a proper description of the solvent shift [26]. Another aspect of interest is to perform a rotational-vibrational averaging or to perform calculations on a large number of solvent structures obtained from molecular dynamics simulations. A combination of molecular dynamics simulations and electronic structure calculations for obtaining NMR chemical shieldings has been introduced in Ref. [20].

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References

- [1] T. Helgaker and P. Jørgensen, *J. Chem. Phys.* 95 (1991) 2595.
- [2] K. Ruud, T. Helgaker, K.L. Bak, P. Jørgensen and H.J.Aa. Jensen, *J. Chem. Phys.* 99 (1993) 3847.
- [3] K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K.L. Bak and H.J.Aa. Jensen, *J. Chem. Phys.* 100 (1994) 8178.
- [4] K.V. Mikkelsen, E. Dalgaard and P. Swanstrøm, *J. Phys. Chem.* 79 (1987) 587.
- [5] K.V. Mikkelsen, *Z. Physik. Chem.* 170 (1991) 129.
- [6] K.V. Mikkelsen, P. Jørgensen and H.J.Aa. Jensen, *J. Chem. Phys.* 100 (1994) 6597.
- [7] K.V. Mikkelsen, Y. Luo, H. Ågren and P. Jørgensen, *J. Chem. Phys.* 100 (1994) 8240.
- [8] K.V. Mikkelsen, H. Ågren, H.J.Aa. Jensen and T. Helgaker, *J. Chem. Phys.* 89 (1988) 3086.
- [9] H.J. Kim and J.T. Hynes, *J. Chem. Phys.* 93 (1990) 5194.
- [10] R.A. Marcus, *J. Chem. Phys.* 24 (1956) 979.
- [11] K.V. Mikkelsen, K. Ruud, T. Helgaker and P. Jørgensen, to be published (:995).
- [12] R. Ditchfield, *J. Chem. Phys.* 65 (1976) 3123.
- [13] R. Höller and H. Lischka, *Chem. Phys. Letters* 84 (1981) 94.
- [14] F.R. Prado and C. Giessner-Prettre, *J. Magn. Reson.* 47 (1982) 103.
- [15] C.M. Rohlfing, L.C. Allen, and R. Ditchfield, *Chem. Phys. Letters* 86 (1982) 380.
- [16] J.F. Hinton, P. Guthrie, P. Pulay and K. Wolinski, *J. Am. Chem. Soc.* 114 (1992) 1604.
- [17] D.B. Chesnut and B.E. Rusiloski, *J. Phys. Chem.* 97 (1993) 2839.
- [18] K. Jackowski, *Chem. Phys. Letters* 194 (1992) 167.
- [19] A.C. de Dios, J.G. Pearson and E. Oldfield, *Science* 260 (1993) 1491.
- [20] D.B. Chesnut and B.E. Rusiloski, *J. Mol. Struct.* 314 (1994) 19.
- [21] T. Helgaker, P.R. Taylor, K. Ruud, O. Vahtras and H. Koch, HERMIT, a molecular integral program.
- [22] H.J.Aa. Jensen, H. Ågren and J. Olsen, in: *Modern techniques in computational chemistry: MOTEC-90*, ed. E. Clementi (ESCOM, Leiden, 1990).
- [23] T. Helgaker, K.L. Bak, H.J.Aa. Jensen, P. Jørgensen, R. Kobayashi, H. Koch, K.V. Mikkelsen, J. Olsen, K. Ruud, P.R. Taylor and O. Vahtras, ABACUS, a second order MCSCF molecular property program.
- [24] M.J. Frisch, J.A. Pople and J.S. Binkley, *J. Chem. Phys.* 80 (1984) 3265.
- [25] P. Dahle, K. Ruud, T. Helgaker, K.L. Bak and P. Jørgensen, to be published (1995).
- [26] P.-O. Åstrand, K.V. Mikkelsen, K. Ruud and T. Helgaker, *J. Am. Chem. Soc.* (1995), submitted for publication.
- [27] A.H. Narten, *J. Chem. Phys.* 55 (1971) 2268.
- [28] J. Olsen, K.L. Bak, K. Ruud, T. Helgaker and P. Jørgensen, *Theoret. Chim. Acta* 90 (1995) 421.
- [29] K. Ruud, T. Helgaker, J. Olsen and P. Jørgensen, *Chem. Phys. Letters* 235 (1995) 47.
- [30] A.D. Buckingham, T. Schaefer and W.G. Schneider, *J. Chem. Phys.* 32 (1960) 1227.
- [31] K. Ruud, H. Skaane, T. Helgaker, K.L. Bak and P. Jørgensen, *J. Am. Chem. Soc.* 116 (1994) 10135.
- [32] S.M. Cybulski and D.M. Bishop, *J. Chem. Phys.* 100 (1994) 2019.
- [33] P. Pulay, J.F. Hinton and K. Wolinski, in: *Nuclear magnetic shieldings and molecular structure*, ed. J.A. Tossell, NATO ASI Series C, vol. 386 (Kluwer, Dordrecht, 1993).
- [34] D.P. Burum and W.K. Rihm, *J. Chem. Phys.* 70 (1979) 3553.
- [35] A. Pines, D.J. Ruben, S. Vegga and M. Mehring, *Phys. Rev. Letters* 36 (1976) 110.