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Electric quadrupole polarizabilities of nuclear magnetic shielding in some small molecules

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Computational procedures, based on (i) the Ramsey common origin approach and (ii) the continuous transformation of the origin of the quantum mechanical current density-diamagnetic zero (CTOCD-DZ), were applied at the Hartree-Fock level to determine electric quadrupole polarizabilities of nuclear magnetic shielding for molecules in the presence of a nonuniform electric field with a uniform gradient. The quadrupole polarizabilities depend on the origin of the coordinate system, but values of the magnetic field induced at a reference nucleus, determined via the CTOCD-DZ approach, are origin independent for any calculations relying on the algebraic approximation, irrespective of size and quality of the (gaugeless) basis set employed. On the other hand, theoretical estimates of the induced magnetic field obtained by single-origin methods are translationally invariant only in the limit of complete basis sets. Calculations of electric quadrupole polarizabilities of nuclear magnetic shielding are reported for H₂, HF, H₂O, NH₃, and CH₄ molecules. © 2008 American Institute of Physics. [DOI: 10.1063/1.2826342]

I. INTRODUCTION

The effects of a time-independent, spatially uniform electric field on molecular magnetic properties described by second-rank tensors, e.g., magnetic susceptibility¹ $\chi_{\alpha\beta}$ and magnetic shielding² $\sigma_{\alpha\beta}^I$ of the *I*th nucleus, can be studied in terms of third-rank tensors referred to as the corresponding (electric dipole) polarizabilities,³ e.g., $\chi_{\alpha\beta,\gamma}$.⁴ Shielding dipole polarizabilities, or hypershieldings, have been widely investigated^{3–23} and review articles are available.^{24–29}

When a polar molecule is dissolved, it polarizes the surrounding medium, giving rise to an electric field—a “reaction field”—at the solute.^{30,31} Buckingham proposed to calculate this field via the Onsager model.³ Electric fields produced by the induced charges on the solvent molecules in the vicinity of the highly polar groups of a nondipolar solute molecule lead to a nonuniform electric field at the nucleus of interest. Changes of shielding produced by the reaction field and reaction-field gradients were rationalized in terms of the dielectric constant of the solvent.³ Accurate theoretical evaluation of these changes via *ab initio* methods is expected to provide fundamental information about medium effects on NMR spectral parameters.

Contributions to nuclear magnetic shielding arising from molecular response to two perturbations, an external magnetic field and a nonuniform electric field, have been discussed in a few papers. The effects of the electric field gradient (EFG), first considered by Buckingham and Lawley,³² are expected to be sizeable for atoms heavier than

hydrogen.^{33–37} Theoretical procedures have been developed to estimate chemical shifts caused by a uniform EFG on nuclear magnetic shielding,^{38,39} allowing for the conventional common origin (CO) approach^{40–42} and for a computational scheme formally based on a continuous transformation of the origin of the current density setting the diamagnetic contribution to zero (CTOCD-DZ).^{43,44} Preliminary results were reported for the water molecule.³⁹ A more extended numerical test is presented in the following.

A short theoretical outline and few relationships employed in the calculations are given in Sec. II. *Ab initio* values of a fourth-rank tensor, called quadrupole polarizability of nuclear magnetic shielding, which provides quantitative estimates of the contribution of an external uniform electric field gradient to nuclear magnetic shielding in the molecules H₂, HF, H₂O, NH₃, and CH₄, are reported in Sec. III.

II. NUCLEAR MAGNETIC SHIELDING IN THE PRESENCE OF A STATIC NONUNIFORM ELECTRIC FIELD

The relationship for the electronic energy of a diamagnetic molecule with a nucleus *I* possessing a permanent magnetic dipole m_{Ia} , in the electronic reference state *a*, in the presence of two external perturbations, an external uniform magnetic field, and a nonuniform electric field with uniform gradient, contains mixed terms which account for linear and nonlinear responses to all orders in perturbation theory,

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$$W_a = W_a^{(0)} + \cdots + \sigma_{\alpha\beta}^I m_{I\alpha} B_\beta + s_{\alpha\beta,\gamma}^I m_{I\alpha} B_\beta E_\gamma + s_{\alpha\beta,\gamma\delta}^I m_{I\alpha} B_\beta E_{\delta\gamma} + \cdots, \quad (1)$$

where $W_a^{(0)}$ is the energy of the isolated molecule and E_α , B_α , and $E_{\beta\alpha} \equiv \nabla_\beta E_\alpha$ denote electric field, flux density of the magnetic field, and electric field gradient at the origin of the coordinate system. Tensor notation is employed, and the Einstein convention for summing over repeated Greek indices is in force. $\sigma_{\alpha\beta}^I$ is the nuclear magnetic shielding in the absence of additional external electric perturbations,^{41,42} $s_{\alpha\beta,\gamma}^I$ and $s_{\alpha\beta,\gamma\delta}^I$ account for nonlinear response of the electrons to first order in the external electric field and electric field gradient, respectively.

An expression analogous to Eq. (1) holds for the magnetic shielding at nucleus I ,^{3,37,38}

$$\sigma_{\alpha\beta}^I(\mathbf{E}) = \sigma_{\alpha\beta}^I + s_{\alpha\beta,\gamma}^I E_\gamma + s_{\alpha\beta,\gamma\delta}^I E_{\delta\gamma} + \cdots. \quad (2)$$

According to Eq. (2), the tensors $s_{\alpha\beta,\gamma}^I$ and $s_{\alpha\beta,\gamma\delta}^I$ are interpreted as dipole and quadrupole shielding polarizabilities, or nuclear magnetic hypershieldings. Explicit definitions in terms of polarization propagators have been given in previous papers,^{38,39} e.g., within the CO approach, the second-rank tensor $\sigma_{\alpha\beta}^I$ in Eqs. (1) and (2) is the Ramsey nuclear magnetic shielding.^{41,42} Definitions of $s_{\alpha\beta,\gamma}^I$ and $s_{\alpha\beta,\gamma\delta}^I$ are arrived at by the Rayleigh-Schrödinger perturbation theory.³⁸ The magnetic tensors in relationships (1) and (2) can be expressed as the sum of diamagnetic and paramagnetic contributions within the canonical CO formulation. The corresponding CTOCD-DZ definitions for dipole and quadrupole shielding polarizabilities can be obtained by formal annihilation of the diamagnetic contribution to the current density induced in the electrons by the uniform external magnetic field in the presence of an external electric field with a uniform electric field gradient.⁴⁵ However, approaches allowing for commutators *à la* Geertsens⁴⁶ are easier to handle.

In the CO scheme,^{40,41} values of magnetic properties calculated via approximated quantum chemical methods allowing for gaugeless basis sets depend on the origin of the coordinate system. London orbitals⁴⁷ are commonly used to construct gauge including atomic orbitals (GIAO).⁴⁸ Then, theoretical predictions for, say, nuclear magnetic shielding polarizabilities,²² are origin independent. The CTOCD schemes provide a viable alternative tool to compute nuclear magnetic shieldings and dipole polarizabilities of magnetic shielding invariant in a gauge translation.³⁸

The question is more complicated in the case of quadrupole polarizability of nuclear magnetic shielding because this property is intrinsically dependent on the coordinate system.^{38,39} In a translation of origin

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}, \quad (3)$$

the operator for the electric quadrupole of n electrons changes as

$$\hat{\mu}_{\alpha\beta}(\mathbf{r}'') = \hat{\mu}_{\alpha\beta}(\mathbf{r}') - \frac{1}{2}\hat{\mu}_\alpha(\mathbf{r}')d_\beta - \frac{1}{2}\hat{\mu}_\beta(\mathbf{r}')d_\alpha - \frac{1}{2}ned_\alpha d_\beta, \quad (4)$$

where $\hat{\mu}_\alpha$ is the operator for the electric dipole, and the CTOCD-DZ quadrupole polarizability varies accordingly as^{38,39}

$$s_{\alpha\beta,\gamma\delta}^I(\mathbf{r}'') = s_{\alpha\beta,\gamma\delta}^I(\mathbf{r}') - \frac{1}{2}d_\delta s_{\alpha\beta,\gamma}^I(\mathbf{r}') - \frac{1}{2}d_\gamma s_{\alpha\beta,\delta}^I(\mathbf{r}'). \quad (5)$$

Terms arising from a change of gauge of the vector potential,

$$A_\alpha^{\mathbf{B}'} \rightarrow A_\alpha^{\mathbf{B}''} = A_\alpha^{\mathbf{B}'} + \nabla_\alpha f, \quad (6)$$

in which

$$A_\alpha^{\mathbf{B}''} = \frac{1}{2}\epsilon_{\alpha\beta\gamma} B_\beta (r_\gamma - r''_\gamma), \quad f = (\mathbf{r}'' - \mathbf{r}') \cdot \mathbf{A}^{\mathbf{B}'}, \quad (7)$$

associated with translation (3), appear in the transformation laws of diamagnetic and paramagnetic contributions to the total quadrupole polarizability evaluated via CO and CTOCD-DZ procedures. However, the latter is invariant to the gauge translation (6) and (7) for any basis set due to the exact cancellation of terms of the same type but different sign.^{38,39} Therefore, the induced magnetic field at the nucleus,

$$\Delta\langle \hat{B}_{I\alpha}^{\mathbf{B}''} \rangle = -\sigma_{\alpha\beta}^I(\mathbf{E}) B_\beta, \quad (8)$$

evaluated via the CTOCD-DZ method, is *origin independent*.³⁸

For a freely tumbling molecule, it is expedient to define a mean quadrupole shielding polarizability tensor.³⁷ Averaging over all molecular orientations in the external magnetic field and keeping the electric field gradient fixed with respect to the molecule, the contribution to the shielding of nucleus I is

$$\Delta\sigma_{\delta\gamma}^I(\mathbf{E}) = -C_{\delta\gamma}^I E_{\delta\gamma}. \quad (9)$$

The $C_{\delta\gamma}^I$ values are evaluated via quadrupole shielding polarizabilities,

$$C_{\delta\gamma}^I = -\left(\frac{1}{3}\right)s_{\alpha\alpha,\gamma\delta}^I. \quad (10)$$

III. RESULTS AND DISCUSSION

Some numerical tests have been made to investigate how the predictions for $s_{\alpha\beta,\gamma\delta}^I$ depend on the quality of the gaugeless basis sets employed, i.e., the aug-cc-pCVDZ, aug-cc-pCVTZ, and aug-cc-pCVQZ from Refs. 49 and 50 referred to as I–III, respectively, for NH₃ and CH₄. For H₂, HF, and H₂O, the aug-cc-pCV5Z basis set,^{49,50} referred to as IV, has also been used. The molecular geometries employed in the calculations are taken from a previous paper.⁵¹ The calculations have been carried out by means of the DALTON code,⁵² employing the CTOCD-DZ routines implemented by Ligabue *et al.*,⁵³ within the scheme of quadratic response function at the level of random-phase approximation (RPA).

The results obtained via the largest basis set adopted for each molecule are reported in Ref. 54, giving calculated tensor components in Tables 1–6. The atomic coordinates are specified in bohr in these tables. Additional tables and tests on convergence of theoretical results from basis sets I–IV for

TABLE I. Average quadrupole shielding polarizabilities (in a.u.). The conversion factor to SI units is $(ea_0^2/E_h) \times 10^{-6} = 1.029\,085\,93 \times 10^{-28} \text{ V}^{-1} \text{ m}^2$ via the CODATA tabulation (Refs. 55 and 56).

Molecule	Atom	C_{xx}	C_{xy}	C_{yy}	C_{yz}	C_{zz}
H ₂ O	H ₁	-16.1	0.0	29.2	-48.6	10.5
	O ₁	-416.8	0.0	-488.2	0.0	-155.7
H ₂	H ₁	-20.0	0.0	-15.4	0.0	-22.7
HF	H ₁	-7.7	0.0	-16.8	0.0	64.9
	F ₁	29.4	0.0	312.0	0.0	-679.3
NH ₃	H ₁	-10.1	-33.3	58.6	0.0	-30.4
	N ₁	269.3	0.0	-136.3	0.0	-136.3
CH ₄	H ₁	-28.0	0.0	33.7	47.9	5.9
	C ₁	-26.5	0.0	-26.5	0.0	-54.8

water molecule are also available in Ref. 54. They document the degree of closeness to the Hartree-Fock limit for the paramagnetic contribution $S_{\alpha\beta,\gamma\delta}^{pl}$ and for the diamagnetic contribution $S_{\alpha\beta,\gamma\delta}^{dl}$ in the conventional CO representation and $S_{\alpha\beta,\gamma\delta}^{\Delta I}$ in the CTOCD-DZ scheme. The corresponding total property is obtained as a sum of these contributions, e.g., $S_{\alpha\beta,\gamma\delta}^{(\Delta+p)I} = S_{\alpha\beta,\gamma\delta}^{\Delta I} + S_{\alpha\beta,\gamma\delta}^{pl}$. However, the predictions from basis sets III and IV are fairly close. A significant improvement of accuracy on earlier computations³⁹ was achieved.

In all the computations, the electric quadrupole operator [Eq. (4)] is referred to the origin \mathbf{r}' of the coordinate system at the center of mass. Values of shielding polarizabilities, in ppm au, were calculated taking the gauge origin on the nucleus of interest. However, the total CTOCD-DZ predictions are invariant in a gauge translation.³⁹ The number of linearly independent components of $S_{\alpha\beta,\gamma\delta}^I$ depends on the nuclear site symmetry (i.e., the symmetry of the site occupied by the nucleus of interest in relation to the molecule as a whole), and it is obtained by methods discussed by Raynes and Ratcliffe.⁹ Table 3 of this reference can be used also for $S_{\alpha\beta,\gamma\delta}^I$ which is symmetric in the exchange $\gamma \leftrightarrow \delta$, owing to the Maxwell equation $\nabla \times \mathbf{E} = 0$ for time independent fields.

In the limit of a complete basis set, the CO results, $S_{\alpha\beta,\gamma\delta}^{(d+p)I}$ would be the same as the corresponding CTOCD-DZ $S_{\alpha\beta,\gamma\delta}^{(\Delta+p)I}$. Only in this ideal case would the CO results be independent of a gauge translation, whereas the CTOCD-DZ are invariant for any basis set. However, both CO and CTOCD-DZ values depend on the origin according to Eq. (5).

Theoretical $C_{\delta\gamma}^I$ average values, expressed in au, are reported in Table I.

IV. CONCLUDING REMARKS

Quadrupole polarizabilities of nuclear magnetic shielding were calculated at the random-phase approximation level of accuracy for the H₂, HF, H₂O, NH₃, and CH₄, molecules using the conventional common origin approach and the procedure referred to as continuous transformation of the origin of the quantum mechanical current density-diamagnetic zero. Convergence to the limit of RPA accuracy for the CTOCD-DZ predictions was estimated for the water mol-

ecule, employing four basis sets of increasing quality. The indications clearly emerging from this numerical test are that, whereas the diamagnetic contributions $S_{\alpha\beta,\gamma\delta}^{dl}$ in the conventional CO representation are comparatively less affected, the accuracy of the paramagnetic contributions $S_{\alpha\beta,\gamma\delta}^{pl}$ and of the diamagnetic CTOCD-DZ contributions $S_{\alpha\beta,\gamma\delta}^{\Delta I}$ depends critically on the quality of the basis set.

It was observed that the aug-cc-pCVQZ (Refs. 49 and 50) basis is sufficient to obtain quite good convergence for ¹H in the water molecule. For some components of the paramagnetic contributions to ¹⁷O quadrupole shielding polarizability, convergence is still incomplete. Similar trends were found for the other molecules studied. Therefore, the aug-cc-pCVQZ basis set is suitable for theoretical evaluation of CTOCD-DZ quadrupole polarizabilities of proton shielding also in larger molecular systems, but it may be insufficient for heavier atoms.

It can be asked whether the theoretical predictions arrived at in the present study could be confirmed by an experiment. The biggest value calculated for the $xxzz$ component of ¹⁹F is ≈ 1010 ppm au, corresponding to $\approx 1.040 \times 10^{-25} \text{ V}^{-1} \text{ m}^2$. To observe a shift as big as ≈ 1 ppm of σ_{xx}^F , in an experiment in ordered phase, an electric field gradient E_{zz} of $\approx 1 \times 10^{19} \text{ V m}^{-2}$ should be applied, which would seem out of reach on macroscopic scale. On the other hand, strong intramolecular gradients can arise within polar molecules. Quadrupole shielding polarizabilities are expected to play a significant role in some species and they can help rationalise chemical shifts via contributions provided by chemical moieties in the proximity of the probe.

Eventually, it should be noted that the RPA calculations reported in this paper do not include either electron correlation effects or vibrational corrections. Further studies are needed to examine these points.

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