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Theoretical study of magnetic properties of ammonia molecule in nonuniform magnetic field

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Abstract. The interaction Hamiltonian within the Bloch gauge for the potentials of the electromagnetic field has been used to define magnetic multipole moment operators and operators for the magnetic field of electrons acting on the nuclei of a molecule in the presence of nonhomogeneous external magnetic field. Perturbation theory has been applied to evaluate the induced electronic moments and magnetic field at the nuclei. Multipole magnetic susceptibility and nuclear magnetic shielding tensors have been introduced to describe the contributions arising in nonuniform fields, and their origin dependence has been analyzed. Extended numerical tests on the ammonia molecule in a static, nonuniform magnetic field have been carried out, using the random-phase approximation within the framework of accurate Hartree–Fock zero-order wavefunctions, and allowing for both angular momentum and torque formalisms in the calculation of paramagnetic contributions.

Key words: Nonuniform magnetic field – Magnetic multipoles – Magnetic susceptibility – Nuclear magnetic shielding

1 Introduction

The quantum mechanical theory of linear response properties of a molecule perturbed by an external, spatially uniform and time-independent magnetic field, and by internal nuclear magnetic moments is well established. The relevant quantities introduced to interpret the relative phenomenology are second-rank tensor properties, i.e., (static) magnetic susceptibility [1] and nuclear magnetic shielding [2].

Nonetheless only a few studies dealing with molecular properties which make themselves manifest in (linear) response to nonuniform static magnetic fields appeared so far [3–6]. The importance of well developed theories in this field can hardly be overemphasized: deeper knowledge of these topics would be rather important in view of both theoretical progress and practical purposes. Besides further insight on molecular structure and general comprehension of magnetic response, useful technological applications would possibly become available in several branches of activity, for instance, NMR imaging methods in diagnostical studies which are performed by using nonuniform magnetic fields.

The first theoretical problem one must tackle, in dealing with suitable definitions of response properties to nonuniform magnetic fields, is that of defining a proper set of magnetic multipole operators. Some of the proposals available in the literature are not suitable, as they suffer from a number of drawbacks (consult the critical paper of Raab [7]).

However, a nice, elegant and complete solution has been *ante litteram* made available by Bloch [8], by working out a proper series expansion for scalar and vector potentials, compatible with the Taylor series for the electric and magnetic fields. Unfortunately his paper, appeared in a collection of monographs (in German) [8] and does not appear known to many. At any rate, some similar results have been later rediscovered by Buckingham and Stiles [9], Barron and Gray [10], and Woolley [11].

The Bloch scalar and vector potentials are obtained via a gauge transformation. Then the interaction Hamiltonian is written in terms of electric and magnetic multipoles properly coupled with the electromagnetic field and its spatial derivatives [8].

Multipole magnetic susceptibilities and magnetic shieldings can be defined [4] according to the Bloch Hamiltonian [8]. Some numerical investigations on water and methane molecules have been already reported, showing the practicality of random-phase approximation (RPA) methods for near Hartree–Fock estimates of magnetic quadrupole contributions to magnetic properties [5, 6].

The fundamentals aspects of the theoretical methods developed in Ref. [4] are reviewed in Sect. 2 of the present paper, which is essentially aimed at reporting the numerical estimate of contributions to magnetic properties in the ammonia molecule arising from a time-independent magnetic field with spatially uniform gradient, see Sect. 3. To this end, some third-rank tensors, i.e., mixed magnetic dipole-magnetic quadrupole susceptibilities, and magnetic quadrupole contributions to nuclear shielding, have been calculated, using RPA procedures (fully equivalent to time-dependent Hartree–Fock methods [12]), within the framework of electronic wavefunctions of increasing accuracy.

Nonetheless, the theoretical approach outlined in Ref. [4] is basically suited for extensions describing higher-rank tensor interaction between electronic multipoles and derivatives of the magnetic field to any order. Time dependence of the field and its gradients are also easily accounted by means of those methods [4]. A general procedure can also be devised in terms of Cauchy moments expansion, according to previous studies [13]. Theoretical investigations of frequency-dependent response properties will be the object of future papers.

2 Molecule in nonuniform field

In the notation of previous papers [4–6], and adopting the Bloch normalization [8], the Hermitian operators for the electronic magnetic multipole moments, omitting contributions from electron spin, are

$$m_\alpha = -\frac{e}{2m_e c} \sum_{i=1}^{n} l_{i\alpha},$$

$$m_{\alpha\beta} = -\frac{e}{6m_e c} \sum_{i=1}^{n} (l_\alpha r_\beta + r_\beta l_\alpha)_i,$$

$$\begin{aligned} m_{\alpha\beta\gamma} &= -\frac{e}{16m_e c}\sum_{i=1}^{n}(l_\alpha r_\beta r_\gamma + r_\beta r_\gamma l_\alpha)_i, \\ &\vdots \\ m_{\alpha\alpha_1\ldots\alpha_k} &= -\frac{k+1}{(k+2)!}\frac{e}{2m_e c}\sum_{i=1}^{n}(l_\alpha r_{\alpha_1}\cdots r_{\alpha_k} + r_{\alpha_1}\cdots r_{\alpha_k} l_\alpha)_i \\ &= -\frac{\partial H^{(1)}}{\partial B_{\alpha_k\alpha_{k-1}\ldots\alpha_1\alpha}} \end{aligned} \tag{1}$$

It is easily shown that, whenever two tensor indices are repeated,

$$m_{\alpha\alpha} = 0 = m_{\alpha\alpha\beta\ldots}, \text{ etc.} \tag{2}$$

The electronic magnetic multipoles (1) are *unperturbed* or *permanent* moment operators. In the presence of a vector potential $A(r, t)$, the canonical momentum is replaced by the mechanical momentum,

$$P_\alpha = \sum_{i=1}^{n} p_{i\alpha} \rightarrow \Pi_\alpha = \sum_{i=1}^{n} \pi_{i\alpha}, \qquad \pi_{i\alpha} = p_{i\alpha} + \frac{e}{c}A_{i\alpha}, \tag{3}$$

and the angular momentum becomes

$$L'_\alpha = L_\alpha + \frac{e}{c}\varepsilon_{\alpha\beta\gamma}\sum_{i=1}^{n} r_{i\beta}A_{i\gamma} \qquad L_\alpha = \sum_{i=1}^{n} l_{i\alpha}. \tag{4}$$

According to Eqs. (1) and (4), within the Bloch gauge [8] for the vector potential, the operators for perturbed magnetic multipole moments become

$$\begin{aligned} m'_\alpha &= m_\alpha + \bar{\chi}^{\mathrm{d}}_{\alpha\beta}B(\mathbf{0}, t)_\beta + \bar{\chi}^{\mathrm{d}}_{\alpha\beta;\gamma}B(\mathbf{0}, t)_{\gamma\beta} \\ &\quad + \bar{\chi}^{\mathrm{d}}_{\alpha\beta;\gamma\delta}B(\mathbf{0}, t)_{\delta\gamma\beta} + \bar{\chi}^{\mathrm{d}}_{\alpha\beta;\gamma\delta\varepsilon}B(\mathbf{0}, t)_{\varepsilon\delta\gamma\beta} + \ldots, \end{aligned} \tag{5}$$

$$\begin{aligned} m'_{\alpha\beta} &= m_{\alpha\beta} + \bar{\chi}^{\mathrm{d}}_{\alpha\gamma;\beta}B(\mathbf{0}, t)_\gamma + \frac{16}{9}\bar{\chi}^{\mathrm{d}}_{\alpha\gamma;\beta\delta}B(\mathbf{0}, t)_{\delta\gamma} \\ &\quad + \frac{5}{2}\bar{\chi}^{\mathrm{d}}_{\alpha\gamma;\beta\delta\varepsilon}B(\mathbf{0}, t)_{\varepsilon\delta\gamma} + \ldots, \end{aligned} \tag{6}$$

$$m'_{\alpha\beta\gamma} = m_{\alpha\beta\gamma} + \bar{\chi}^{\mathrm{d}}_{\alpha\delta;\beta\gamma}B(\mathbf{0}, t)_\delta + \frac{5}{2}\bar{\chi}^{\mathrm{d}}_{\alpha\delta;\beta\gamma\varepsilon}B(\mathbf{0}, t)_{\delta\varepsilon} + \ldots, \tag{7}$$

$$\vdots$$

where

$$\bar{\chi}^{\mathrm{d}}_{\alpha\beta} = -\frac{e^2}{4m_e c^2}\sum_{i=1}^{n}(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta)_i, \tag{8}$$

$$\bar{\chi}^{\mathrm{d}}_{\alpha\beta;\gamma} = -\frac{e^2}{6m_e c^2}\sum_{i=1}^{n}[(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta)r_\gamma]_i, \tag{9}$$

$$\bar{\chi}^{\mathrm{d}}_{\alpha\beta;\gamma\delta} = -\frac{e^2}{16m_e c^2}\sum_{i=1}^{n}[(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta)r_\gamma r_\delta]_i, \tag{10}$$

$$\bar{\chi}^{\mathrm{d}}_{\alpha\beta;\gamma\delta\varepsilon} = -\frac{e^2}{60m_e c^2}\sum_{i=1}^{n}[(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta)r_\gamma r_\delta r_\varepsilon]_i, \tag{11}$$

$$\vdots$$

In these formulae a semicolon separates symmetric indices which can be freely permuted. The expectation values for the contributions to the magnetic moments induced within the electron cloud of a molecule in the presence of nonuniform magnetic field with harmonic dependence on time are written as follows:

$$\begin{aligned}\Delta\langle m'_{\lambda}\rangle &= \chi_{\lambda\alpha}B(\mathbf{0},t)_{\alpha} + \chi_{\lambda,\alpha\beta}B(\mathbf{0},t)_{\beta\alpha} \\ &\quad + \chi_{\lambda,\alpha\beta\gamma}B(\mathbf{0},t)_{\gamma\beta\alpha} + \cdots, \qquad (12)\\ \Delta\langle m'_{\lambda\mu}\rangle &= \chi_{\lambda\mu,\alpha}B(\mathbf{0},t)_{\alpha} + \chi_{\lambda\mu,\alpha\beta}B(\mathbf{0},t)_{\beta\alpha} \\ &\quad + \chi_{\lambda\mu,\alpha\beta\gamma}B(\mathbf{0},t)_{\gamma\beta\alpha} + \cdots, \qquad (13)\\ &\vdots\end{aligned}$$

Within the Bloch gauge for the electromagnetic potentials [8], the dynamic, i.e., frequency-dependent susceptibilities, are defined by the following:

$$\chi_{\alpha\beta}(\omega) = \chi^{\mathrm{p}}_{\alpha\beta}(\omega) + \chi^{\mathrm{d}}_{\alpha\beta}, \qquad (14)$$

$$\chi_{\alpha,\beta\gamma}(\omega) = \chi^{\mathrm{p}}_{\alpha,\beta\gamma}(\omega) + \chi^{\mathrm{d}}_{\alpha\beta;\gamma} \qquad (15)$$

$$\chi_{\beta\gamma,\alpha}(\omega) = \chi^{\mathrm{p}}_{\beta\gamma,\alpha}(\omega) + \chi^{\mathrm{d}}_{\beta\alpha;\gamma}, \qquad (16)$$

$$\vdots$$

where

$$\chi^{\mathrm{d}}_{\alpha,\beta} = -\frac{e^2}{4m_ec^2}\left\langle a\left|\sum_{i=1}^{n}(r_v^2\delta_{\alpha\beta} - r_{\alpha}r_{\beta})_i\right|a\right\rangle = \chi^{\mathrm{d}}_{\beta,\alpha} \equiv \chi^{\mathrm{d}}_{\alpha\beta}, \qquad (17)$$

$$\chi^{\mathrm{d}}_{\alpha\beta,\gamma} = -\frac{e^2}{6m_ec^2}\left\langle a\left|\sum_{i=1}^{n}[(r_v^2\delta_{\alpha\beta} - r_{\alpha}r_{\beta})r_{\gamma}]_i\right|a\right\rangle = \chi^{\mathrm{d}}_{\beta\alpha,\gamma}, \qquad (18)$$

$$\begin{aligned}\chi^{\mathrm{p}}_{\alpha,\beta}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2}\Re(\langle a|m_{\alpha}|j\rangle\langle j|m_{\beta}|a\rangle), \\ &= \chi^{\mathrm{p}}_{\beta,\alpha}(\omega) \equiv \chi^{\mathrm{p}}_{\alpha\beta}(\omega), \qquad (19)\end{aligned}$$

$$\begin{aligned}\chi^{\mathrm{p}}_{\alpha,\beta\gamma}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2}\Re(\langle a|m_{\alpha}|j\rangle\langle j|m_{\beta\gamma}|a\rangle), \\ &= \chi^{\mathrm{p}}_{\beta\gamma,\alpha}(\omega). \qquad (20)\end{aligned}$$

Within the definitions for paramagnetic contributions and total susceptibilities, tensor indices referring to different multipole moments are divided in groups (separated by a comma) which can be interchanged. For instance the same $\chi^{\mathrm{p}}_{\alpha,\beta\gamma}$ tensor can be used to describe the paramagnetic contributions to the magnetic dipole induced by a field gradient and to the magnetic quadrupole induced by a magnetic field.

The magnetic field induced on nucleus I by the electrons perturbed by the nonuniform magnetic field is [4],

$$\Delta\langle B^{n'}_{I\alpha}\rangle = -\sigma^{I}_{\alpha\beta}B(\mathbf{0},t)_{\beta} - \sigma^{I}_{\alpha,\beta\gamma}B(\mathbf{0},t)_{\gamma\beta} - \sigma^{I}_{\alpha,\beta\gamma\delta}B(\mathbf{0},t)_{\delta\gamma\beta} + \cdots \qquad (21)$$

The total dynamic magnetic shieldings are [4]

$$\sigma^{I}_{\alpha\beta}(\omega) = \sigma^{\mathrm{p}I}_{\alpha\beta}(\omega) + \sigma^{\mathrm{d}I}_{\alpha\beta}, \tag{22}$$

$$\sigma^{I}_{\alpha,\beta\gamma}(\omega) = \sigma^{\mathrm{p}I}_{\alpha,\beta\gamma}(\omega) + \sigma^{\mathrm{d}I}_{\alpha,\beta\gamma}, \tag{23}$$

where the diamagnetic contributions are defined by

$$\sigma^{\mathrm{d}I}_{\alpha\beta} = \frac{e}{2m_e c^2}\left\langle a \left| \sum_{i=1}^{n} (r_{i\lambda}E^{i}_{I\lambda}\delta_{\alpha\beta} - r_{i\alpha}E^{i}_{I\beta}) \right| a \right\rangle, \tag{24}$$

$$\sigma^{\mathrm{d}I}_{\alpha,\beta\gamma} = \frac{e}{3m_e c^2}\left\langle a \left| \sum_{i=1}^{n} (r_{i\lambda}E^{i}_{I\lambda}\delta_{\alpha\beta} - r_{i\alpha}E^{i}_{I\beta})r_{i\gamma} \right| a \right\rangle, \tag{25}$$

and the paramagnetic contributions are given by

$$\sigma^{\mathrm{p}I}_{\alpha,\beta}(\omega) = -\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^{2} - \omega^{2}}\Re(\langle a|B^{n}_{I\alpha}|j\rangle\langle j|m_{\beta}|a\rangle) \equiv \sigma^{\mathrm{p}I}_{\alpha\beta}(\omega), \tag{26}$$

$$\sigma^{\mathrm{p}I}_{\alpha,\beta\gamma}(\omega) = -\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^{2} - \omega^{2}}\Re(\langle a|B^{n}_{I\alpha}|j\rangle\langle j|m_{\beta\gamma}|a\rangle). \tag{27}$$

Molecular magnetic properties described via tensors of rank higher than two are not uniquely defined: they depend on the origin of the coordinate system [4–6]. Thus, in a change of origin,

$$\boldsymbol{r}'' = \boldsymbol{r}' + \boldsymbol{d}, \tag{28}$$

the transformation law of third-rank static tensors is [4]

$$\chi_{\gamma,\alpha\beta}(\boldsymbol{r}'') = \chi_{\gamma,\alpha\beta}(\boldsymbol{r}') - \chi_{\gamma\alpha}d_{\beta} + \tfrac{1}{3}\chi_{\gamma\delta}d_{\delta}\delta_{\alpha\beta}, \tag{29}$$

$$\sigma^{I}_{\gamma,\alpha\beta}(\boldsymbol{r}'') = \sigma^{I}_{\gamma,\alpha\beta}(\boldsymbol{r}') - \sigma^{I}_{\gamma\alpha}d_{\beta} + \tfrac{1}{3}\sigma^{I}_{\gamma\delta}d_{\delta}\delta_{\alpha\beta}\,. \tag{30}$$

Whereas the transformation formulae for the diamagnetic contributions are exactly obeyed in approximate calculations for any basis set, the corresponding equations for the paramagnetic contributions (and consequently relationships (29) and (30) for origin dependence of total dipole–quadrupole magnetizability and magnetic quadrupole effects on nuclear magnetic shielding) hold if $|a\rangle$ and $|j\rangle$ are the exact eigenstates to a model Hamiltonian [4], for instance the *true* Hartree–Fock states, as this automatically guarantees that a series of hypervirial theorems is fulfilled [14].

For the sake of generality, it should however be emphasized that this is a sufficient, but not necessary condition for the fulfillment of the hypervirial theorem. An example of a model satisfying this theorem is provided by the computational scheme adopted in this study, i.e., the random-phase approximation, where, in any event, the wavefunction is not an eigenstate of a (known) Hamiltonian.

At any rate, Eqs. (29) and (30) can be used to check the quality of a calculation, by comparing the estimates actually obtained corresponding to different choices of origin and those provided by these constraints: at the Hartree–Fock limit the results ought to be the same.

3 Results and discussion

A computational scheme based on the RPA, see Refs. [5, 6], has been applied in the present study. This theoretical method is particularly appealing, as *all* time-independent properties through second-order (in the acceptation of perturbation theory) are easily accessible by diagonalizing the non-Hermitian RPA matrix, i.e., from the spectrum of electron excitation energies and the corresponding transition amplitudes. Further extension to dynamic (frequency-dependent) susceptibilities and shieldings is straightforward according to the equations reported in Sect. 2, as documented by previous investigations on nuclear electromagnetic shieldings [15, 16].

Five Gaussian basis sets of increasing quality have been adopted to evaluate mixed dipole–quadrupole magnetic susceptibility and magnetic quadrupole contributions to nuclear magnetic shieldings of the ammonia molecule in the presence of a static magnetic field with spatially uniform gradient.

The essential features of these basis sets are available from Table 1.

Basis set I is a 6-31G* from Ref. [17], polarized according to methods previously described in Refs. [18, 19]. The (s/p) substratum for basis set II was taken from canonical (optimum-energy) van Duijneveldt tables [20], and the polarization functions are a set of two $3d$ functions on the nitrogen atom, with exponents 0.471168 and 0.139565, and one $2p$ function on hydrogen with exponent 1.0.

Basis set III adopts the $(13s8p/8s)$ substratum (energy optimized exponents) from the same tables [20]; the exponents of the $3d$ functions on nitrogen are 1.67, 0.45, 0.16, and 0.065; the exponents of the $2p$ functions on hydrogen are 4.84, 1.15, and 0.354. According to the suggestion of a referee, complete specification of this basis set is available in Table 11.

In basis set IV the same $(13s8p/8s)$ substratum has been augmented by two diffuse s functions on nitrogen, with exponents 0.0564372 and 0.02257488, to improve the description of the outer reaches in the molecular domain. These functions are expected to provide significant contributions to the transition matrix of the dipole length operator. The $3d$ exponents for nitrogen are 1.67, 0.45, 0.16, and 0.065, as in basis set III, and the $2p$ exponents for hydrogen are 1.50, 0.40 and 0.10.

Basis set V is the same as IV, with one set of $4f$ on nitrogen, with exponent 0.315, and one set of $3d$ functions on hydrogen, with exponent 0.15.

The overall quality of the Gaussian basis sets can be judged from the SCF energies and the average Thomas–Reiche–Kuhn (TRK) sum rules (within the dipole velocity formalism) reported in Table 1. This constraint is satisfied better

Table 1. Specification of basis sets and SCF energy

Basis set	Contraction scheme		Number of GTO	Number of CGTOS	SCF energy (au)	$1/3(P_\alpha, P_\alpha)^a$
	GTO	CGTO				
I	6–31G POL		124	52	– 56.1963699	9.115
II	$(11s7p2d/5s1p)$	$[6s5p1d/3s1p]$	68	45	– 56.2147163	9.230
III	$(13s8p4d/8s3p)$	$[8s6p4d/6s3p]$	112	95	– 56.2233781	9.907
IV	$(15s8p4d/10s3p)$	Uncontracted	120	120	– 56.2233509	9.927
V	$(15s8p4d1f/10s3p1d)$	Uncontracted	148	148	– 56.2235336	9.941

[a] Thomas–Reich–Khun sum rule for gauge invariance of magnetic properties (within dipole velocity formalism).

Table 2. Mixed dipole–quadrupole magnetic susceptibilities, $\chi_{\alpha,\beta\gamma}(r_{\mathrm{c.m.}})^{\mathrm{a}}$, of NH_3, in ppm au per molecule, evaluated with the origin on the center of mass

Component		Basis set				
		I	II	III	IV	V
111	χ^{d}	25.981	24.172	24.933	24.934	24.877
	χ^{p}	– 1.166	– 0.405	– 2.024	– 2.114	– 2.126
	χ	24.815	23.767	22.909	22.819	22.751
113	χ^{d}	27.323	25.170	20.930	20.982	21.007
	χ^{p}	– 4.018	– 3.696	– 4.074	– 4.201	– 4.353
	χ	23.305	21.474	16.906	16.781	16.654
131	χ^{d}	– 18.634	– 17.571	– 17.022	– 17.090	– 17.003
	χ^{p}	9.234	9.605	9.970	9.957	9.791
	χ	– 9.400	– 7.966	– 7.052	– 7.133	– 7.212
311	χ^{d}	– 18.634	– 17.571	– 17.022	– 17.090	– 17.003
	χ^{p}	5.370	5.425	6.567	6.597	6.610
	χ	– 13.264	– 12.146	– 10.455	– 10.493	– 10.393
333	χ^{d}	37.268	35.143	34.043	34.180	34.005
	χ^{p}	– 10.740	– 10.850	– 13.135	– 13.192	– 13.219
	χ	26.528	24.293	20.908	20.988	20.786

[a] Nonvanishing components,

$$\chi_{x,xz}(\mathrm{c.m.}) = \chi_{y,yz}(\mathrm{c.m.}),\ \chi_{x,zx}(\mathrm{c.m.}) = \chi_{y,zy}(\mathrm{c.m.}),$$

$$\chi_{x,yy}(\mathrm{c.m.}) = \chi_{y,xy}(\mathrm{c.m.}) = \chi_{y,yx}(\mathrm{c.m.}) = -\chi_{x,xx}(\mathrm{c.m.}),$$

$$\chi_{z,xx}(\mathrm{c.m.}) = \chi_{z,yy}(\mathrm{c.m.}),$$

by symmetry.

than 99% via basis sets III–V. Further information can be obtained from Refs. [21, 22], where wavefunction V has been used to calculate a number of properties in the same molecule.

Theoretical mixed dipole–quadrupole magnetic susceptibilities of ammonia, calculated assuming the origin of coordinates in the molecular center of mass, are collected in Table 2. Here and in following tables, tensor components are specified by $(x, y, z) \equiv (1, 2, 3)$. The reference system adopted in the calculation is specified by giving the coordinates of atoms in the footnotes to Tables 3–5.

A general indication clearly emerging from the present study on ammonia, confirming previous findings [5, 6], is that basis sets of low or intermediate quality are insufficient to furnish reliable theoretical predictions of the third-rank tensor properties examined here. In particular, it can be observed that, whereas quite accurate values of diamagnetic contributions to dipole susceptibility are obtained with basis sets of relatively modest quality, the diamagnetic contributions (18) to mixed magnetic dipole–quadrupole tensor (16) are sensibly affected by the quality of the basis set (although they are simply expectation values over the unperturbed wavefunction).

An even more marked dependence of the paramagnetic contributions (20) on the features of the electronic wavefunction was found in the present calculations.

Table 3. Mixed dipole–quadrupole magnetic susceptibilities of NH_3 in ppm au per molecule, corresponding to origin on $H_1^{\dagger}$, $\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$ and $\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$, calculated via Eqs. (15) and (29)[‡]

Component		Basis set				
		I	II	III	IV	V
111	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	260.845	267.180	257.201	256.997	256.752
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	258.351	261.457	257.163	257.029	256.647
	Diff.	2.494	5.723	0.037	− 0.032	0.105
113	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 96.466	− 99.165	− 100.175	− 100.520	− 100.677
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 93.787	− 97.700	− 100.547	− 100.649	− 100.617
	Diff.	− 2.679	− 1.465	0.371	0.129	− 0.060
122	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 144.993	− 148.466	− 141.352	− 140.516	− 139.853
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 141.583	− 142.612	− 140.036	− 139.924	− 139.699
	Diff.	− 3.410	− 5.854	− 1.316	− 0.592	− 0.154
131	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	4.527	10.132	− 6.272	− 6.678	− 6.512
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 9.399	− 7.967	− 7.051	− 7.132	− 7.212
	Diff.	13.926	18.099	0.780	0.454	0.700
133	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 115.853	− 118.714	− 115.849	− 116.480	− 116.900
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 116.768	− 118.845	− 117.128	− 117.105	− 116.948
	Diff.	0.915	0.131	1.279	0.625	0.048
212	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 36.907	− 33.768	− 24.429	− 23.752	− 23.228
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 24.815	− 23.768	− 22.908	− 22.823	− 22.749
	Diff.	− 12.092	− 10.000	− 1.521	− 0.929	− 0.479
221	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	397.218	411.781	340.315	337.186	332.969
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	325.489	332.766	328.475	328.498	328.089
	Diff.	71.731	79.015	11.840	8.688	4.880
223	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 103.369	− 105.626	− 97.919	− 98.717	− 101.239
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 93.787	− 97.700	− 100.547	− 100.650	− 100.614
	Diff.	− 9.582	− 7.926	2.829	1.731	− 0.625
232	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	0.714	2.498	− 3.535	− 4.702	− 6.414
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 9.399	− 7.967	− 7.051	− 7.133	− 7.212
	Diff.	10.113	10.465	3.516	2.431	0.798
311	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	34.410	40.068	26.512	26.403	26.964
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	24.299	25.321	26.343	26.339	26.483
	Diff.	10.111	14.747	0.169	0.064	0.481
313	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 11.918	− 8.436	− 0.074	− 0.103	− 0.423
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	0.0	0.0	0.0	0.0	0.0
	Diff.	− 11.918	− 8.436	− 0.074	− 0.103	− 0.423
322	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	23.129	22.310	25.895	25.866	26.593
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	24.299	25.321	26.343	26.339	26.483
	Diff.	− 1.170	− 3.011	− 0.448	− 0.473	0.110
331	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	386.725	383.313	332.766	332.408	333.559
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	337.135	336.271	330.263	330.569	330.967
	Diff.	49.590	47.042	2.504	1.839	2.592
333	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	− 57.539	− 62.378	− 52.407	− 52.269	− 53.557
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	− 48.599	− 50.642	− 52.687	− 52.675	− 52.966
	Diff.	− 8.940	− 11.736	0.280	0.406	− 0.591

[†] Nonvanishing components.

[‡] Coordinates in bohr: $H_1 = (1.770988, 0.0, -0.591964)$.

Table 4. Mixed dipole–quadrupole magnetic susceptibilities of NH_3 corresponding to origin on $H_2^\ddagger$, $\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$ and $\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$, in ppm au per molecule, calculated via Eqs. (15) and (29)‡

Component		Basis set				
		I	II	III	IV	V
111	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−113.352	−119.479	−97.602	−96.968	−95.799
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−91.078	−95.078	−94.221	−94.286	−94.197
	Diff.	−21.398	−24.401	−3.381	−2.682	−1.602
112	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−353.862	−364.765	−312.622	−310.217	−307.163
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−303.375	−308.770	−304.309	−304.250	−303.842
	Diff.	−50.487	−55.995	−8.313	−5.967	−3.321
113	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−101.643	−104.011	−98.332	−99.319	−101.102
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−93.787	−97.700	−100.547	−100.649	−100.617
	Diff.	−7.856	−6.311	2.215	1.330	−0.485
121	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	22.106	21.097	3.258	2.365	1.311
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	22.106	21.097	3.258	2.365	1.311
122	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	55.425	60.122	39.677	38.730	37.349
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	33.569	35.655	35.656	35.734	35.723
	Diff.	21.856	24.467	4.021	2.996	1.626
123	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−2.989	−2.798	1.064	0.693	−0.244
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	−2.989	−2.798	1.064	0.693	−0.244
131	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	1.668	4.406	−4.219	−5.197	−6.438
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−9.399	−7.967	−7.051	−7.133	−7.212
	Diff.	11.067	12.373	2.832	1.936	0.774
132	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−1.651	−3.306	1.185	0.873	0.036
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	−1.651	−3.306	1.185	0.873	0.036
133	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	57.927	59.357	57.925	58.237	58.450
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	58.385	59.423	58.564	58.552	58.474
	Diff.	−0.458	−0.065	−0.639	−0.315	−0.024
211	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	115.712	120.429	104.517	103.489	102.311
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	101.125	102.923	101.436	101.417	101.280
	Diff.	14.587	17.506	3.081	2.072	1.031
212	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	1.382	2.773	−18.785	−19.655	−20.963
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−24.815	−23.768	−22.908	−22.823	−22.749
	Diff.	26.197	26.541	4.123	3.167	−1.786
221	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−215.683	−220.005	−201.159	−200.126	−199.062
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−199.969	−202.036	−198.601	−198.478	−198.172
	Diff.	−15.714	−17.969	−2.558	−1.648	−0.890
222	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−216.044	−223.239	−204.847	−204.365	−203.546
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−202.250	−205.847	−202.873	−202.834	−202.559
	Diff.	−13.794	−17.392	−1.974	−1.531	−0.987
223	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−98.192	−100.780	−99.561	−100.120	−100.812
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−93.787	−97.700	−100.547	−100.650	−100.614
	Diff.	−4.405	−3.080	0.986	0.530	−0.198

Table 4. (Continued)

Component		Basis set				
		I	II	III	IV	V
232	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	3.574	8.224	− 5.587	− 6.180	− 6.495
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	− 9.399	− 7.967	− 7.051	− 7.133	− 7.212
	Diff.	12.973	16.191	1.464	0.953	0.717
233	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	100.332	102.810	100.329	100.876	101.234
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	101.125	102.923	101.436	101.417	101.280
	Diff.	− 0.793	− 0.113	− 1.107	− 0.541	− 0.046
311	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	25.949	26.749	26.049	25.999	26.680
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	24.299	25.321	26.343	26.338	26.483
	Diff.	1.650	1.428	− 0.294	− 0.339	0.197
312	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	4.885	7.690	0.267	0.215	0.170
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	4.885	7.690	0.267	0.215	0.170
313	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	5.959	4.218	0.037	0.050	0.211
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	5.959	4.218	0.037	0.050	0.211
321	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	4.885	7.700	0.267	0.236	0.164
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	4.885	7.700	0.267	0.236	0.164
322	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	31.590	35.629	26.358	26.272	26.868
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	24.299	25.321	26.343	26.337	26.482
	Diff.	7.291	10.308	0.014	− 0.065	0.386
323	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	10.321	7.306	0.064	0.090	0.363
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0	0.0	0.0
	Diff.	10.321	7.306	0.064	0.090	0.363
331	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	− 193.365	− 191.659	− 166.385	− 166.195	− 166.776
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	− 168.569	− 168.137	− 165.133	− 165.281	− 165.486
	Diff.	− 24.796	− 23.522	− 1.252	− 0.914	− 1.290
332	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	− 334.918	− 331.963	− 288.187	− 287.863	− 288.853
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	− 291.970	− 291.222	− 286.019	− 286.281	− 286.629
	Diff.	− 42.948	− 40.741	− 2.168	− 1.582	− 2.224
333	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	− 57.539	− 62.378	− 52.407	− 52.271	− 53.548
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	− 48.699	− 50.642	− 52.687	− 52.675	− 52.966
	Diff.	− 8.940	− 11.736	0.280	0.404	− 0.582

[†] Nonvanishing components

$$\chi_{y,xz}(\mathrm{H}_2) = \chi_{x,yz}(\mathrm{H}_2),$$

$$\chi_{x,zy}(\mathrm{H}_2) = \chi_{y,zx}(\mathrm{H}_2).$$

[‡] Coordinates in bohr: $\mathrm{H}_2 = (-0.885499,\ 1.533729,\ -0.591964)$.

In any event, from the general trend observed in Table 2 (collecting data evaluated corresponding to the center of mass), it can be resonably argued that the results provided by (high quality) larger basis sets III–V have apparently converged to the Hartree–Fock limit. The same judgment can be achieved by inspection of the

Table 5. Magnetic quadrupole contribution to nuclear magnetic shielding of nitrogen N[†], $\sigma^{\mathrm{N}}_{\alpha,\beta\gamma}$[‡], in ppm au, from basis sets IV and V

	Component	$\sigma^{\mathrm{d}}_{\alpha,\beta\gamma}(\mathrm{N})$	$\sigma^{\mathrm{p}}_{\alpha,\beta\gamma}(\mathrm{N})$	$\sigma^{\mathrm{d}}_{\alpha,\beta\gamma}(\mathrm{c.m.})$	$\sigma^{\mathrm{p}}_{\alpha,\beta\gamma}(\mathrm{c.m.})$	$\sigma_{\alpha,\beta\gamma}(\mathrm{N})$	$\sigma_{\alpha,\beta\gamma}(\mathrm{c.m.})$	$\sigma^{¶}_{\alpha,\beta\gamma}(\mathrm{c.m.})$
IV	111	4.244	− 122.784	4.244	− 122.780	− 118.540	− 118.536	− 118.540
	113	7.946	− 161.909	52.924	− 171.866	− 153.964	− 118.942	− 118.779
	131	− 4.189	50.293	− 4.189	50.293	46.104	46.104	46.104
	311	− 4.189	45.337	− 19.337	50.430	41.148	31.093	31.092
	333	8.379	− 90.703	38.674	− 100.885	− 82.325	− 62.212	− 62.212
V	111	4.241	− 122.991	4.241	− 122.981	− 118.749	− 118.740	− 118.749
	113	7.942	− 160.899	52.914	− 170.808	− 152.957	− 117.894	− 117.787
	131	− 4.181	51.211	− 4.181	51.211	47.029	47.029	47.029
	311	− 4.181	45.492	− 19.331	50.582	41.310	31.251	31.251
	333	8.363	− 90.985	38.663	− 101.166	− 82.622	− 62.503	− 62.503

[†] Coordinates in bohr: N = (0, 0, 0.127799).

The entries in brackets specify the origin of the coordinate system.

[‡] Nonvanishing components,

$$\sigma_{x,xx}(\mathrm{N}) = -\sigma_{x,yy}(\mathrm{N}) = -\sigma_{y,xy}(\mathrm{N}) = \sigma_{y,yx}(\mathrm{N}),$$

$$\sigma_{x,xz}(\mathrm{N}) = \sigma_{y,yz}(\mathrm{N})$$

[¶] Calculated via Eq. (30).

results of Tables 3 and 4, where mixed dipole–quadrupole magnetic susceptibilities (corresponding to origin on hydrogen nuclei H_1 and H_2 respectively) calculated directly from formula (16) are compared with those obtained via the results of Table 2 by applying Eq. (29) for origin dependence. As discussed in the text, Eq. (29) is exactly fulfilled only in the limit of a complete set of expansion.

Although rather large differences between corresponding estimates are found in Table 3 in the case of smaller basis sets, the discrepancies smoothly decrease, and almost vanish, in the case of largest basis set V in most of the cases. One can notice, however, some slightly disappointing results (compare for 111, 131, 311, and 331 components in Table 3, where smaller differences are apparently obtained via basis set IV rather than V). Even if these differences are quite small in absolute value, compare for -0.032 and 0.454, 0.105 and 0.700 respectively for basis sets IV and V, and smaller than 0.1% for the 111 component, they are relatively larger for 131 component (they amount to $\approx$10% in this case).

In any event, according to these findings, it can be assumed that the results yielded by the last two basis sets have fairly converged to the HF limit.

It is quite remarkable that both diamagnetic and paramagnetic contributions to dipole–quadrupole susceptibility from basis set III, evaluated with the origin of the gauge on the center of mass, are quite close to those obtained via much larger basis sets IV–V, see Table 2. This result can be useful for studies of larger molecules, and may be helpful to build up *ad hoc* basis sets for mixed dipole–quadrupole magnetic susceptibilities (18) and (20).

However, as can be observed from the results of Table 3, basis set III does not guarantee a good degree of origin independence of theoretical dipole–quadrupole susceptibilities. To this end, it seems necessary to use large basis sets any way.

Also the paramagnetic components of calculated magnetic-quadrupole contributions to nuclear magnetic shielding of hydrogen and nitrogen are largely affected by the characteristics of the basis sets I–V. The same behavior has been found for diamagnetic terms of nitrogen shielding using smaller basis sets. On the other hand, the diamagnetic components of hydrogen shielding are much less dependent on the quality of electronic wavefunction. Only the results furnished by basis sets IV and V have been reported in Tables 5–7 to show convergence of theoretical estimates.

Magnetic quadrupole contributions to nuclear magnetic shieldings have been evaluated corresponding to origin on the center of mass and on the nucleus in question. These values are not the same, as static magnetic properties beyond dipole sus- ceptibility (14) and shielding (22) basically depend on origin, compare for Eq. (30). However, as regards the theoretical estimates corresponding to origin on the center of mass, the values obtained in a direct calculation and those arrived at by Eq. (30) are extremely close, see the last two columns in Tables 5–7. This is a further proof of near Hartree–Fock level of quality.

Similar trends and conclusions have been found in previous studies on water and methane molecules [5, 6].

As a final check of accuracy for the theoretical values, the paramagnetic contribution to mixed magnetic dipole–quadrupole susceptibilities have also been calculated allowing for the torque formalism [23], formally replacing the angular momentum operator with the torque operator in all the relevant formulae via an off-diagonal hypervirial relationship [23]. The results provided by angular momentum and torque gauges would be the same only within a *true* Hartree–Fock

Table 6. Magnetic quadrupole contribution to nuclear magnetic shielding of proton H$_1^{\dagger}$, $\sigma^{\mathrm{H}_1}_{\alpha,\beta\gamma}$‡, in ppm au, from basis sets V and VI

	Component	$\sigma^{\mathrm{d}}_{\alpha,\beta\gamma}(\mathrm{H}_1)$	$\sigma^{\mathrm{p}}_{\alpha,\beta\gamma}(\mathrm{H}_1)$	$\sigma^{\mathrm{d}}_{\alpha,\beta\gamma}(\mathrm{c.m.})$	$\sigma^{\mathrm{p}}_{\alpha,\beta\gamma}(\mathrm{c.m.})$	$\sigma_{\alpha,\beta\gamma}(\mathrm{H}_1)$	$\sigma_{\alpha,\beta\gamma}(\mathrm{c.m.})$	$\sigma^{\P}_{\alpha,\beta\gamma}(\mathrm{c.m.})$
IV	111	33.576	2.783	96.126	− 12.390	36.360	83.736	84.217
	113	− 18.547	− 12.547	− 49.209	− 6.034	− 31.095	− 55.243	− 55.502
	122	− 13.888	6.349	− 42.821	9.658	− 7.540	− 33.163	− 32.702
	131	25.710	36.663	38.983	14.071	62.373	53.055	54.996
	133	− 19.688	− 9.132	− 53.305	2.732	− 28.820	− 50.573	− 51.516
	212	− 13.888	− 18.814	− 13.888	− 18.525	− 32.702	− 32.413	− 32.702
	221	116.735	101.677	245.379	19.202	218.411	264.581	269.094
	223	− 40.836	− 37.213	− 86.211	− 5.560	− 78.049	− 91.772	− 94.990
	232	3.421	3.443	3.421	4.308	6.864	7.730	6.864
	311	25.710	31.713	50.095	6.872	57.423	56.967	57.561
	313	− 19.688	− 26.384	− 25.372	− 17.679	− 46.072	− 43.052	− 43.355
	322	3.421	− 3.112	13.092	− 5.329	0.309	7.763	8.576
	331	110.935	104.907	234.896	27.551	215.842	262.446	265.721
	333	− 29.131	− 28.601	− 63.187	− 1.543	− 57.732	− 64.730	− 66.137
V	111	33.567	2.750	96.122	− 12.462	36.317	83.660	84.037
	113	− 18.557	− 12.634	− 49.215	− 6.189	− 31.192	− 55.404	− 55.539
	122	− 13.897	6.040	− 42.852	9.675	− 7.857	− 33.177	− 32.976
	131	25.722	36.581	38.994	14.130	62.304	53.124	54.770
	133	− 19.670	− 8.789	− 53.269	2.787	− 28.460	− 50.483	− 51.061
	212	− 13.897	− 18.987	− 13.897	− 18.907	− 32.884	− 32.804	− 32.884
	221	116.717	101.603	245.329	19.572	218.320	264.901	267.869
	223	− 40.850	− 35.522	− 86.228	− 5.338	− 76.372	− 91.565	− 92.934
	232	3.429	4.161	3.429	4.402	7.591	7.831	7.591
	311	25.722	31.627	50.121	6.941	57.349	57.062	57.349
	313	− 19.670	− 26.544	− 25.365	− 18.025	− 46.215	− 43.390	− 43.437
	322	3.429	− 3.653	13.108	− 5.393	− 0.223	7.715	8.085
	331	110.944	104.027	234.912	27.366	214.971	262.278	264.683
	333	− 29.152	− 27.974	− 63.229	− 1.548	− 57.126	− 64.777	− 65.434

[†] Coordinates in bohr: $\mathrm{H}_1 = (1.770998, 0, -0.591964)$. Entries in brackets specify the origin.

[‡] Nonvanishing components.

[¶] Calculated via Eq. (30).

Table 7. Magnetic quadrupole contribution to nuclear magnetic shielding of proton $H_2^\ddagger$, $\sigma^{H_2\,\ddagger}_{\alpha,\beta\gamma}$, in ppm au, from basis sets IV and V

	Component	$\sigma^{d}_{\alpha,\beta\gamma}(H_2)$	$\sigma^{p}_{\alpha,\beta\gamma}(H_2)$	$\sigma^{d}_{\alpha,\beta\gamma}$(c.m.)	$\sigma^{p}_{\alpha,\beta\gamma}$(c.m.)	$\sigma_{\alpha,\beta\gamma}(H_2)$	$\sigma_{\alpha,\beta\gamma}$(c.m.)	$\sigma^{\P}_{\alpha,\beta\gamma}$(c.m.)
IV	111	− 37.556	− 33.802	− 82.767	− 2.327	− 71.358	− 85.094	− 86.911
	112	89.105	69.342	192.469	11.709	158.446	204.177	207.176
	113	− 35.264	− 31.046	− 76.961	− 5.678	− 66.310	− 82.639	− 85.118
	121	− 24.018	− 35.004	− 32.064	− 20.962	− 59.022	− 53.026	− 54.186
	122	27.712	29.236	56.114	3.693	56.948	59.807	61.153
	123	− 9.651	− 10.680	− 16.023	0.206	− 20.331	− 15.817	− 17.099
	131	8.993	11.748	12.312	6.749	20.741	19.060	18.897
	132	− 9.651	− 14.386	− 15.399	− 4.228	− 24.038	− 19.627	− 20.842
	133	9.844	4.566	26.652	− 1.366	14.410	25.287	25.758
	211	− 24.018	− 13.214	− 57.121	3.444	− 37.232	− 53.676	− 32.702
	212	− 27.712	41.817	41.648	17.784	69.529	59.432	61.154
	213	− 9.651	− 10.680	− 16.023	0.206	− 20.331	− 15.817	− 17.099
	221	− 37.599	− 18.427	− 87.986	− 1.078	− 56.026	− 89.064	− 89.744
	222	41.068	21.122	103.284	− 5.810	62.191	97.474	98.802
	223	− 24.119	− 18.714	− 58.459	− 5.916	− 42.833	− 64.375	− 65.374
	232	20.138	28.360	30.093	11.630	48.497	41.723	42.966
	233	− 17.050	− 7.909	− 46.163	2.366	− 24.959	− 43.798	− 44.615
	311	8.993	5.595	22.343	− 2.279	14.588	20.064	20.822
	312	− 9.651	− 15.080	− 16.023	− 5.283	− 24.732	− 21.306	− 21.211
	313	9.844	13.192	12.686	8.840	23.036	21.526	21.677
	321	− 9.651	− 15.079	− 16.023	− 5.283	− 24.730	− 21.306	− 21.210
	322	20.138	23.006	40.844	3.822	43.144	44.666	45.314
	323	− 17.050	− 22.849	− 21.973	− 15.311	− 39.899	− 37.284	− 37.546
	331	− 55.467	− 52.454	− 117.448	− 13.775	− 107.922	− 131.223	− 132.861
	332	96.072	90.855	203.426	23.859	186.927	227.285	230.122
	333	− 29.131	− 28.601	− 63.187	− 1.543	− 57.732	− 64.730	− 66.137
V	111	− 37.542	− 33.591	− 82.733	− 2.320	− 71.133	− 85.053	− 86.259
	112	89.095	69.395	192.444	12.014	158.490	204.458	206.442
	113	− 35.277	− 29.801	− 76.974	− 5.551	− 65.078	− 82.526	− 83.586
	121	− 24.020	− 35.044	− 32.053	− 21.310	− 59.064	− 53.363	− 54.021

122	27.707	29.197	56.098	3.713	56.904	59.811	60.728
123	− 9.653	− 9.911	− 16.027	0.368	− 19.565	− 15.659	− 16.193
131	9.003	12.264	12.320	6.834	21.267	19.155	19.384
132	− 9.653	− 14.037	− 15.400	− 4.212	− 23.690	− 19.612	− 20.428
133	9.835	4.394	26.635	− 1.393	14.229	25.242	25.530
211	− 24.020	− 13.369	− 57.129	3.442	− 37.389	− 53.687	− 54.099
212	27.707	41.710	41.620	18.005	69.417	59.625	60.680
132	− 9.653	− 9.911	− 16.027	0.368	− 19.564	− 15.659	− 16.192
221	− 37.600	− 18.588	− 87.993	− 1.236	− 56.188	− 89.229	− 89.696
222	41.055	20.982	103.262	− 5.856	62.037	97.407	98.320
223	− 24.131	− 18.358	− 58.468	− 5.978	− 42.489	− 64.446	− 64.889
232	20.149	28.479	30.103	11.699	48.628	41.802	42.977
233	− 17.035	− 7.612	− 46.133	2.413	− 24.647	− 43.720	− 44.221
311	9.003	5.168	22.361	− 2.309	14.171	20.052	20.403
312	− 9.653	− 15.275	− 16.027	− 5.340	− 24.928	− 21.367	− 21.333
313	9.835	13.272	12.683	9.013	23.108	21.695	21.720
321	− 9.653	− 15.276	− 16.027	− 5.340	− 24.929	− 21.367	− 21.330
322	20.149	22.808	40.867	3.858	42.957	44.725	45.031
323	− 17.035	− 22.987	− 21.967	− 15.609	− 40.022	− 37.576	− 37.616
331	− 55.472	− 52.015	− 117.456	− 13.683	− 107.487	− 131.139	− 132.342
332	96.080	90.094	203.440	23.701	186.174	227.141	229.224
333	− 29.152	− 27.976	− 63.229	− 1.548	− 57.127	− 64.777	− 65.434

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† Entries in brackets specify the origin, coordinates in bohr: $H_2 = (-0.885499, 1.533729, -0.591964)$.

‡ Nonvanishing components,

$$\sigma_{x,yz}(H_2) = \sigma_{y,xz}(H_2).$$

¶ Calculated via Eq. (30).

Table 8. Mixed dipole–quadrupole magnetic-susceptibilities, $\chi_{\alpha,\beta\gamma}(r_{\mathrm{c.m.}})^{\dagger}$, of NH_3 within the torque formalism, in ppm au per molecule, evaluated with the origin on the center of mass via basis sets III–V

Component		Basis set		
		III	IV	V
111	χ^{d}	24.933	24.934	24.877
	χ^{p}	− 2.177	− 2.121	− 2.098
	χ	22.756	22.813	22.779
113	χ^{d}	20.980	20.982	21.007
	χ^{p}	− 4.263	− 4.114	− 4.326
	χ	16.717	16.868	16.681
131	χ^{d}	− 17.022	− 17.090	− 17.003
	χ^{p}	10.042	9.697	9.645
	χ	− 6.979	− 7.393	− 7.357
311	χ^{d}	− 17.022	− 17.090	− 17.003
	χ^{p}	6.558	6.496	6.553
	χ	− 10.463	− 10.594	− 10.449
331	χ^{d}	34.043	34.180	34.005
	χ^{p}	− 13.116	− 12.991	− 13.106
	χ	20.927	21.190	20.900

† Nonvanishing components,

$$\chi_{x,xz}(\mathrm{c.m.}) = \chi_{y,yz}(\mathrm{c.m.}),\ \chi_{x,zx}(\mathrm{c.m.}) = \chi_{y,zy}(\mathrm{c.m.}),$$

$$\chi_{x,yy}(\mathrm{c.m.}) = \chi_{y,xy}(\mathrm{c.m.}) = \chi_{y,yx}(\mathrm{c.m.}_1) = -\chi_{x,xx}(\mathrm{c.m.})$$

$$\chi_{z,xx}(\mathrm{c.m.}) = \chi_{z,yy}(\mathrm{c.m.})$$

by symmetry.

calculation (off-diagonal hypervirial relations are fulfilled exactly [23] in this limit case). Somewhat rewardingly, comparison of Tables 2 and 8 for the origin in the center of mass, Tables 3 and 9, and Tables 4 and 10, for origin on different hydrogen nuclei, shows an excellent overall agreement.

At this point some comments are helpful to weigh the magnitude of the effects observable at macroscopic level, in relation to the calculated quantities.

For $\sigma_{\alpha,\beta\gamma}$ the conversion factor from ppm atomic units used in the tables to (irrational) ppm cgs emu (i.e. ppm cm) is the Bohr radius, i.e., $a_0 \approx 0.529177249 \times 10^{-8}$ cm (from the 1986 adjustment of the fundamental physical constants by Cohen and Taylor [24]). To convert to corresponding ppm SI units (i.e., ppm m) one should further multiply by 10^{-2}.

For $\chi_{\alpha,\beta\gamma}$ the conversion factor from ppm au per molecule to ppm cgs emu (i.e., cm^4) per mole is $a_0^4 N \approx 4.7223184 \times 10^{-10}$ (from Ref. [24]). The conversion factor from ppm egs emu per mole to ppm SI units (i.e., ppm $\mathrm{J\,T^{-2}\,m\,mol^{-1}}$) is 0.1.

This means that the effects discussed in this study are hard to detect with any experimental apparatus developed so far. The minute quantitities estimated in the present theoretical study are probably extremely difficult to measure.

The problem is actually related to technical difficulties of building up magnets with a very high, spatially uniform gradient. The authors hope, however, that the

Table 9. Mixed dipole–quadrupole magnetic susceptibilities of NH_3 within the torque formalism, corresponding to origin on H_1†, $\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$ and $\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$, in ppm au per molecule, calculated via Eqs. (15) and (29) from basis sets III–V‡

Component		Basis set		
		III	IV	V
111	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	256.695	258.124	257.783
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	257.108	257.423	257.009
	Diff.	−0.413	0.700	0.775
113	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−101.582	−100.717	−100.814
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−100.784	−100.761	−100.757
	Diff.	−0.798	0.044	0.056
122	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	140.730	−140.777	−140.238
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−139.932	−140.117	−139.894
	Diff.	−0.798	−0.659	−0.344
131	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−7.021	−4.732	−4.427
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−6.979	−7.392	−7.358
	Diff.	−0.042	2.661	2.930
133	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−115.965	−117.347	−117.546
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−117.176	−117.306	−117.115
	Diff.	1.211	−0.041	−0.431
212	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−28.094	−21.638	−21.186
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−22.756	−22.816	−22.776
	Diff.	−5.338	1.177	1.590
221	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	338.325	340.438	337.098
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	338.773	329.106	328.563
	Diff.	9.552	11.332	8.535
223	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−95.456	−101.821	−104.571
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−100.784	−100.762	−100.753
	Diff.	5.327	−1.059	−3.818
232	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−2.162	−5.161	−6.833
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−6.979	−7.394	−7.357
	Diff.	4.817	2.233	0.525
311	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	25.394	28.412	28.709
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	26.378	26.409	26.553
	Diff.	−0.984	2.003	2.156
313	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−3.410	−0.208	−0.402
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	0.0	0.0	0.0
	Diff.	−3.410	−0.208	−0.402
322	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	26.801	25.552	26.394
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	26.378	26.406	26.553
	Diff.	0.423	−0.854	−0.159
331	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	331.266	339.765	340.365
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	330.661	332.108	332.110
	Diff.	0.605	7.657	8.255
333	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_1})$	−52.196	−53.964	−55.103
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_1})$	−52.756	−52.816	−53.106
	Diff.	0.561	−1.148	−1.997

† Nonvanishing components.

‡ Coordinates in bohr: $H_1 = (1.770998, 0.0, -0.591964)$.

Table 10. Mixed dipole–quadrupole magnetic susceptibilities of NH_3 within the torque formalism, corresponding to origin on $H_2^\dagger$, $\chi^a_{\alpha,\beta\gamma}(R_{H_2})$ and $\chi^b_{\alpha,\beta\gamma}(R_{H_2})$, in ppm au per molecule, calculated via Eqs. (15) and (29), from basis sets III–V[‡]

Component		Basis set		
		III	IV	V
111	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 95.653	− 99.024	− 98.100
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 94.420	− 94.492	− 94.336
	Diff.	− 1.233	− 4.532	− 3.764
112	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 311.884	− 312.176	− 309.715
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 304.433	− 304.768	− 304.273
	Diff.	− 7.451	− 7.408	− 5.442
113	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 96.989	− 101.546	− 103.636
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 100.784	− 100.761	− 100.757
	Diff.	3.795	− 0.785	− 2.879
121	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	5.454	1.398	0.575
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0
	Diff.	5.454	1.398	0.575
122	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	37.670	40.354	39.327
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	35.832	35.841	35.778
	Diff.	1.838	4.513	3.548
123	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 2.652	0.479	1.629
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0
	Diff.	− 2.652	0.479	1.629
131	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 3.377	− 5.055	− 6.232
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 6.979	− 7.394	− 7.357
	Diff.	3.603	2.339	1.125
132	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 2.104	0.169	1.048
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.001	0.0
	Diff.	− 2.104	0.170	1.048
133	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	57.983	58.671	58.773
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	58.588	58.652	58.557
	Diff.	− 0.605	0.019	0.216
211	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	103.000	104.576	103.675
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	101.478	101.590	101.423
	Diff.	1.523	2.988	2.252
212	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 18.648	− 19.218	− 20.198
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 22.756	− 22.816	− 22.776
	Diff.	4.108	3.598	2.578
221	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 201.863	− 200.261	− 199.346
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 198.520	− 198.770	− 198.448
	Diff.	− 3.343	− 1.491	− 0.898
222	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 203.429	− 206.203	− 205.469
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 202.955	− 203.180	− 202.847
	Diff.	− 0.474	− 3.024	− 2.623
223	$\chi^a_{\alpha,\beta\gamma}(R_{H_2})$	− 100.051	− 100.944	− 101.748
	$\chi^b_{\alpha,\beta\gamma}(R_{H_2})$	− 100.784	− 100.762	− 100.753

Table 10. (Continued)

Component		Basis set		
		III	IV	V
	Diff.	0.733	−0.232	−0.994
232	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−5.806	−4.836	−5.037
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−6.979	−7.394	−7.357
	Diff.	1.173	2.558	2.320
233	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	100.429	101.627	101.794
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	101.478	101.417	101.423
	Diff.	−1.048	0.037	0.370
311	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	26.450	26.266	26.968
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	26.378	26.408	26.554
	Diff.	0.072	−0.142	0.414
312	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−0.609	1.222	1.012
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	−0.001	0.0
	Diff.	−0.609	1.223	1.012
313	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	1.706	0.104	0.201
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0
	Diff.	1.706	0.104	0.201
321	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−0.609	1.242	1.007
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0
	Diff.	−0.609	1.242	1.007
322	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	25.747	27.702	28.128
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	26.378	26.407	26.553
	Diff.	−0.631	1.295	1.575
323	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	2.955	0.183	0.346
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	0.0	0.0	0.0
	Diff.	2.955	0.183	0.346
331	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−165.638	−169.877	−170.182
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−165.330	−166.049	−166.055
	Diff.	−0.307	−3.828	−4.127
332	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−286.893	−294.239	−294.753
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−286.361	−287.611	−287.616
	Diff.	−0.532	−6.628	−7.137
333	$\chi^{a}_{\alpha,\beta\gamma}(R_{H_2})$	−52.197	−53.968	−55.096
	$\chi^{b}_{\alpha,\beta\gamma}(R_{H_2})$	−52.756	−52.815	−53.106
	Diff.	0.559	−1.153	−1.989

† Nonvanishing components

$$\chi_{y,xz}(H_2) = \chi_{x,yz}(H_2),$$

$$\chi_{x,zy}(H_2) = \chi_{y,zx}(H_2),$$

‡ Coordinates in bohr: $H_2 = (-0.885499, 1.533729, -0.591964)$.

very accurate theoretical estimates reported in this work may provide an incentive for experimental studies in this field: reliable predictions via quantum mechanical studies might be very helpful to bridge the gap between theory and experiment, and would certainly offer practical guidance to develop a proper experimental setup.

Table 11. Basis set $(13s8p4d/8s3p)$-$[8s6p4d/6s3p]$ for H and N employed in the calculations[†]

Atom	*s* subset				*p* subset				*d* subset			
	CGTO	GTO	Orbital exponent	Contraction coefficient	CGTO	GTO	Orbital exponent	Contraction coefficient	CGTO	GTO	Orbital exponent	Contraction coefficient
N	1	1	74761.715106	0.000050	1	1	126.666567	0.001152	1	1	1.67	1.0
		2	11123.653813	0.000394		2	29.837389	0.009016	1	1	0.45	1.0
		3	2512.685697	0.002088		3	9.394038	0.040814	1	1	0.16	1.0
		4	703.777285	0.008906	2	1	3.405104	0.130101	1	1	0.065	1.0
		5	225.478793	0.032081	3	1	1.350000	0.277697				
		6	79.615810	0.097424	4	1	0.557696	0.380736				
	2	1	30.237283	0.231728	5	1	0.232449	0.314966				
	3	1	12.263622	0.377540	6	1	0.094264	0.094498				
	4	1	5.265086	0.318623								
	5	1	2.333471	0.082578								
	6	1	0.901856	0.003101								
	7	1	0.358336	0.000537								
	8	1	0.141093	0.000084								
H	1	1	402.009948	0.000279	1	1	4.84	1.0				
		2	60.241959	0.002165	1	1	1.15	1.0				
		3	13.732173	0.011200	1	1	0.354	1.0				
	1	1	3.904505	0.044899								
	1	1	1.282709	0.142300								
	1	1	0.465544	0.330883								
	1	1	0.181120	0.436328								
	1	1	0.072791	0.176456								

[†] The *s*/*p* contraction scheme is taken from Van Duijneveldt's basis sets Ref. [17].

Progress in magnet design and construction technology has made magnets with continuous fields of nearly 50 T routinely available. In addition to these magnets already operational, it has been very recently reported that at Los Alamos campus pulsed magnets of over 1000 T have been detonated [25]. These dramatic advances seem to imply that measurements of multipole susceptibilities and shieldings would become feasible in the very near future.

In addition, although contributions to magnetic properties originating from nonuniformity of the magnetic field are expected to be very small on a macroscopic scale, higher magnetic multipoles can provide detectable contributions to the nuclear magnetic shielding and to NMR chemical shift *at molecular level*, as it has been proved [26, 9].

As a matter of fact, at very large distances from a nuclear magnetic dipole used as a probe, the induced magnetic field is essentially due to the magnetic dipole associated to the electron current density. In closer regions, effects arising from higher magnetic multipoles become appreciable: the local field exerted on a nucleus carrying an intrinsic magnetic moment will be affected by terms beyond the electronic magnetic dipole, compare for the experimentally well-known "pseudo-contact" shift [26, 9]. In other words, an analysis of nuclear magnetic shieldings in terms of magnetic multipoles of neighboring groups may be helpful to gauge the role played by different domains of the electron distribution: the pseudo-contact term, according to Buckingham and Stiles [9], can in fact be rationalized via multipole magnetic susceptibilities. Numerical information available from this study could be used to this purpose.

4 Conclusions

The theoretical magnetic properties of ammonia molecule in a static magnetic field with uniform spatial gradient, that is, dipole–quadrupole magnetic susceptibility and magnetic quadrupole contributions to nuclear magnetic shielding of hydrogen and nitrogen nuclei evaluated in the present study are very close to the Hartree–Fock limit of accuracy. Convergence of theoretical estimates has been proved over a series of wavefunctions of increasing size and quality. Theoretical predictions obtained within the angular momentum and torque formalism for the paramagnetic contributions (which should be exactly the same for a complete set of expansion) are practically identical in the case of larger basis sets, suggesting that basis set saturation has been virtually achieved. Sum rules for origin dependence have also been evaluated to furnish a benchmark of accuracy, in order to confirm the reliability of theoretical response properties.

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