Theoretical study of the magnetic properties of a methane molecule in a nonuniform magnetic field

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Contributions to magnetic susceptibility and magnetic shielding of the nuclei, arising from electronic magnetic-quadrupole moments interacting with a magnetic field with a spatially uniform gradient, have been determined for a methane molecule, by a large-basis-set calculations within the random-phase approximation. The Hartree-Fock limit of accuracy has been achieved and the quality of the calculations has been confirmed via tests based on sum rules for the origin dependence of the response properties.

I. INTRODUCTION

A molecule linearly responding to an external, spatially uniform and time-independent magnetic field and internal nuclear magnetic moments can be studied by means of well-known quantum-mechanical theories, introducing second-rank tensor properties, i.e., magnetic susceptibility [1] and nuclear magnetic shielding [2].

Quite recently, theoretical methods have been reported to investigate effects arising in nonhomogeneous magnetic fields. As a matter of fact, one has to go beyond the "quadrupole approximation," [3] according to which the magnetic field and the electric-field gradient are both assumed spatially uniform all over the molecular domain: to any higher approximation, electric and magnetic multipoles are to be introduced in the interaction Hamiltonian in a consistent way, keeping terms of the same order of magnitude. This is achieved introducing a suitable expansion for electric and magnetic multipoles [4].

Bloch [5] has first shown that the solution is obtained by working out a proper series expansion for the scalar and vector potentials, compatible with the Taylor series for the electric and magnetic fields: multipole magnetic susceptibilities and magnetic shieldings [6,7] can be defined according to the Bloch Hamiltonian [5] in a very general and compact formulation.

The contributions to magnetic properties arising from nonuniformity of the magnetic field are expected to be very small and hardly measurable on a macroscopic scale. At the molecular level, however, it has been proven that higher magnetic multipoles can make detectable contributions to the nuclear magnetic shielding and to NMR chemical shift [8,9] As a matter of fact, at very large distances from a probe, i.e., a nuclear magnetic dipole, the magnetic field induced by an electronic current density is basically due to the magnetic dipole associated with the charge flow. In any event, in closer regions, contributions arising from higher magnetic multipoles become significant: the local field acting upon 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 [8,9]. In other words, an analysis of nuclear magnetic shieldings in terms of magnetic multipoles of neighboring groups may help us to understand the role played by different domains of the electron distribution: the pseudo-contact term, according to Buckingham and Stiles [9], can be rationalized via multipole magnetic susceptibilities.

Accordingly, the present paper is aimed at reporting numerical estimates of near Hartree-Fock accuracy for contributions to magnetic properties in the methane molecule, arising from magnetic quadrupoles interacting with the spatially uniform gradient of a time-independent magnetic field: mixed dipole-quadrupole magnetic susceptibilities and magnetic-quadrupole contributions to nuclear shielding have been calculated, using time-dependent Hartree-Fock methods, equivalent to the random-phase approximation (RPA) [10] within the framework of electronic wave functions of increasing quality.

II. MOLECULE IN A NONUNIFORM FIELD

In the notation of previous papers [6,7], the contributions to the magnetic moments induced within the electron cloud of a molecule in the presence of a nonuniform magnetic field with harmonic dependence on time are written

$$\Delta \langle m'_\lambda \rangle = \chi_{\lambda\alpha} B(0,t)_\alpha + \chi_{\lambda,\alpha\beta} B(0,t)_{\beta\alpha}$$
$$+ \chi_{\lambda,\alpha\beta\gamma} B(0,t)_{\gamma\beta\alpha} + \cdots , \qquad (1)$$

$$\Delta \langle m'_{\lambda\mu} \rangle = \chi_{\lambda\mu,\alpha} B(0,t)_\alpha + \chi_{\lambda\mu,\alpha\beta} B(0,t)_{\beta\alpha}$$
$$+ \chi_{\lambda\mu,\alpha\beta\gamma} B(0,t)_{\gamma\beta\alpha} + \cdots , \qquad (2)$$

etc. Within the Bloch gauge for the electromagnetic potentials [5], the frequency-dependent susceptibilities are

defined,

$$\chi_{\alpha\beta}(\omega)=\chi^p_{\alpha\beta}(\omega)+\chi^d_{\alpha\beta} , \tag{3}$$

$$\chi_{\alpha,\beta\gamma}(\omega)=\chi^p_{\alpha,\beta\gamma}(\omega)+\chi^d_{\alpha\beta;\gamma} \tag{4}$$

$$\chi_{\beta\gamma,\alpha}(\omega)=\chi^p_{\beta\gamma,\alpha}(\omega)+\chi^d_{\beta\alpha;\gamma} , \tag{5}$$

etc., where

$$\chi^d_{\alpha,\beta}=-\frac{e^2}{4m_ec^2}\left\langle a\left| \sum_{i=1}^n (r^2_\nu\delta_{\alpha\beta}-r_\alpha r_\beta)_i \right| a\right\rangle$$

$$=\chi^d_{\beta,\alpha}\equiv\chi^d_{\alpha\beta} , \tag{6}$$

$$\chi^d_{\alpha\beta;\gamma}=-\frac{e^2}{6m_ec^2}\left\langle a\left| \sum_{i=1}^n [(r^2_\nu\delta_{\alpha\beta}-r_\alpha r_\beta)r_\gamma]_i \right| a\right\rangle$$

$$=\chi^d_{\beta\alpha;\gamma} , \tag{7}$$

$$\chi^p_{\alpha,\beta}(\omega)=\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega^2_{ja}-\omega^2}\mathrm{Re}(\langle a|m_\alpha|j\rangle\langle j|m_\beta|a\rangle)$$

$$=\chi^p_{\beta,\alpha}(\omega)\equiv\chi^p_{\alpha\beta}(\omega) , \tag{8}$$

$$\chi^p_{\alpha,\beta\gamma}(\omega)=\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega^2_{ja}-\omega^2}\mathrm{Re}(\langle a|m_\alpha|j\rangle\langle j|m_{\beta\gamma}|a\rangle)$$

$$=\chi^p_{\beta\gamma,\alpha}(\omega) . \tag{9}$$

In the formulas for the diamagnetic contributions, a semicolon separates symmetric indices which can be freely permuted; 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 $\chi^p_{\alpha,\beta\gamma}$ 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 [6,7]

$$\Delta\langle B^{n'}_{I\alpha}\rangle=-\sigma^I_{\alpha\beta}B(0,t)_\beta$$
$$-\sigma^I_{\alpha,\beta\gamma}B(0,t)_{\gamma\beta}-\sigma^I_{\alpha,\beta\gamma\delta}B(0,t)_{\delta\gamma\beta}+\cdots . \tag{10}$$

The total dynamic magnetic shieldings are [6,7]

$$\sigma^I_{\alpha\beta}(\omega)=\sigma^{pI}_{\alpha\beta}(\omega)+\sigma^{dI}_{\alpha\beta} , \tag{11}$$

$$\sigma^I_{\alpha,\beta\gamma}(\omega)=\sigma^{pI}_{\alpha,\beta\gamma}(\omega)+\sigma^{dI}_{\alpha,\beta\gamma} , \tag{12}$$

the diamagnetic contributions are defined,

$$\sigma^{dI}_{\alpha\beta}=\frac{e}{2m_ec^2}\left\langle a\left| \sum_{i=1}^n (r_{i\lambda}E^i_{I\lambda}\delta_{\alpha\beta}-r_{i\alpha}E^i_{I\beta}) \right| a\right\rangle , \tag{13}$$

$$\sigma^{dI}_{\alpha,\beta\gamma}=\frac{e}{3m_ec^2}\left\langle a\left| \sum_{i=1}^n (r_{i\lambda}E^i_{I\lambda}\delta_{\alpha\beta}-r_{i\alpha}E^i_{I\beta})r_{i\gamma} \right| a\right\rangle , \tag{14}$$

and the paramagnetic contributions are

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

$$\equiv\sigma^{pI}_{\alpha\beta}(\omega) , \tag{15}$$

$$\sigma^{pI}_{\alpha,\beta\gamma}(\omega)=-\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega^2_{ja}-\omega^2}\mathrm{Re}(\langle a|B^n_{I\alpha}|j\rangle\langle j|m_{\beta\gamma}|a\rangle) . \tag{16}$$

Molecular magnetic properties described via tensors of rank higher than 2 are not uniquely defined: they depend on the origin of the coordinate system [6,7]. Thus, in a change of origin,

$$\mathbf{r''}=\mathbf{r'}+\mathbf{d} , \tag{17}$$

the third-rank tensors transforming,

$$\chi_{\gamma,\alpha\beta}(\mathbf{r''})=\chi_{\gamma,\alpha\beta}(\mathbf{r'})-\chi_{\gamma\alpha}d_\beta+\tfrac{1}{3}\chi_{\gamma\delta}d_\delta\delta_{\alpha\beta} , \tag{18}$$

$$\sigma^I_{\gamma,\alpha\beta}(\mathbf{r''})=\sigma^I_{\gamma,\alpha\beta}(\mathbf{r'})-\sigma^I_{\gamma\alpha}d_\beta+\tfrac{1}{3}\sigma^I_{\gamma\delta}d_\delta\delta_{\alpha\beta} . \tag{19}$$

Whereas the transformation formulas for the diamagnetic contributions are exactly obeyed in approximate calculations for any basis set, the corresponding equations for the paramagnetic contributions [and consequently relationships (18) and (19) for origin dependence of total dipole-quadrupole magnetizability and magnetic-quadrupole effects on nuclear magnetic shielding] hold only if $|a\rangle$ and $|j\rangle$ are the exact eigenstates to a model Hamiltonian [6], for instance the *true* Hartree-Fock states, as this implies that a series of hypervirial theorems is fulfilled [11].

Accordingly, Eqs. (18) and (19) can be used to check the quality of a calculation, by comparing the estimates actually obtained corresponding to different choices of

TABLE I. Mixed dipole-quadrupole magnetic susceptibility $\chi_{\alpha,\beta\gamma}(C)$ [in a.u., $\chi_{x,xz}(C)=\chi_{x,zx}(C)$; $\chi_{y,yz}(C)=\chi_{y,zy}(C)$ and $-\chi_{z,yy}(C)=\chi_{x,xz}(C)=\chi_{z,xx}(C)=-\chi_{y,yz}(C)$ by symmetry] of CH_4, evaluated with the origin on carbon via basis sets I–VI.

Component[a]		Basis set					
		I	II	III	IV	V	VI
113	χ^d	−51.438	−51.137	−51.472	−51.036	−51.011	−50.986
	χ^p	4.499	25.368	22.754	26.345	26.323	26.381
	χ	−46.939	−25.769	−28.718	−24.691	−24.688	−24.605

[a]Nonvanishing components.

TABLE II. Mixed dipole-quadrupole magnetic susceptibilities of CH_4 corresponding to origin on H_1, calculated from basis sets I–VI [in a.u., coordinates in bohr of H_1 are (0, 1.683 40, 1.190 34)] via Eq. (4), $\chi^a_{\alpha,\beta\gamma}(R_{H_1})$, and via Eq. (18), $\chi^b_{\alpha,\beta\gamma}(R_{H_1})$.

Component[a]		I	II	III	IV	V	VI
				Basis set			
112	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	553.023	418.318	427.381	361.757	360.059	359.495
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	400.203	361.655	373.133	358.530	358.522	357.871
	Diff.	152.820	56.663	54.249	3.227	1.537	1.624
113	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	375.294	273.305	278.721	233.903	232.759	230.206
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	236.048	229.959	235.127	228.828	228.825	228.448
	Diff.	139.247	43.345	43.594	5.075	3.934	1.758
121	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−77.529	−6.014	−15.701	−2.630	−2.683	−0.793
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	0.0	0.0	0.0	0.0	0.0	0.0
	Diff.	−77.529	−6.014	−15.701	−2.630	−2.683	−0.793
131	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−70.573	−26.743	−34.586	−23.757	−23.744	−24.562
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	−46.939	−25.769	−28.718	−24.691	−24.689	−24.604
	Diff.	−23.634	−0.974	−5.868	0.934	0.945	0.042
211	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−148.103	−122.097	−126.845	−120.827	−120.842	−119.573
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	−133.401	−120.522	−124.378	−119.510	−119.508	−119.291
	Diff.	−14.702	−1.546	−2.467	−1.317	−1.335	−0.283
222	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	306.601	259.532	264.072	240.536	239.978	239.143
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	266.802	241.103	248.755	239.020	239.015	238.581
	Diff.	39.799	18.429	15.317	1.516	0.963	0.562
223	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	392.097	296.595	311.006	279.279	278.883	278.211
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	329.925	281.498	292.563	278.210	278.203	277.654
	Diff.	62.172	15.098	18.443	1.069	0.680	0.556
232	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−53.770	−3.453	−2.301	21.618	22.382	23.446
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	46.939	25.769	28.718	24.691	24.689	24.608
	Diff.	−100.709	−29.222	−31.019	−3.073	−2.308	−1.163
233	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−158.498	−137.435	−137.227	−119.709	−119.136	−119.570
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	−133.401	−120.552	−124.378	−119.510	−119.508	−119.291
	Diff.	−25.097	−16.883	−12.849	−0.199	0.371	−0.280
311	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−120.477	−108.826	−113.177	−107.335	−107.306	−108.559
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	−141.268	−111.012	−116.666	−109.197	−109.194	−108.956
	Diff.	20.791	2.186	3.489	1.862	1.888	0.397
322	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−103.674	−85.536	−80.892	−61.959	−61.179	−60.547
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	−47.390	−59.474	−59.230	−59.815	−59.815	−59.746
	Diff.	−56.284	−26.062	−21.661	−2.144	−1.363	−0.800
323	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	−87.924	−21.352	−26.083	−1.512	−0.962	−0.792
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	0.0	0.0	0.0	0.0	0.0	0.0
	Diff.	−87.924	−21.352	−26.083	−1.512	−0.962	−0.792
332	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	542.628	402.980	417.000	362.875	361.788	359.523
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	400.203	361.655	373.133	358.530	358.523	357.872
	Diff.	142.424	41.326	43.867	4.345	3.265	1.651
333	$\chi^a_{\alpha,\beta\gamma}(R_{H_1})$	224.150	194.362	194.068	169.294	168.485	169.105
	$\chi^b_{\alpha,\beta\gamma}(R_{H_1})$	188.658	170.486	175.896	169.013	169.009	168.702
	Diff.	34.493	23.876	18.172	0.281	−0.524	0.403

[a]Nonvanishing components.

TABLE III. Magnetic quadrupole contribution to nuclear-magnetic shielding of carbon, $\sigma^C_{\alpha,\beta\gamma}$ [in a.u., $\sigma_{x,xz}(C) = \sigma_{x,zx}(C) = \sigma_{z,xx}(C) = -\sigma_{z,yy}(C) = -\sigma_{y,yz}(C) = -\sigma_{y,zy}(C)$], from basis sets I to VI.

	Component[a]	$\sigma^d_{\alpha,\beta\gamma}(C)$	$\sigma^p_{\alpha,\beta\gamma}(C)$	$\sigma_{\alpha,\beta\gamma}(C)$
I	113	−6.619	32.463	25.843
II	113	−6.604	33.833	27.229
III	113	−6.528	39.960	33.432
IV	113	−6.626	36.779	30.153
V	113	−6.626	36.842	30.216
VI	113	−6.632	36.903	30.272

[a]Nonvanishing components.

origin and those provided by these constraints; at the Hartree-Fock limit, the results ought to be the same.

III. RESULTS AND DISCUSSION

Six 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 a methane molecule in the presence of a static magnetic field with a spatially uniform gradient.

Basis sets I and II (of triple-ζ quality plus polarization) were taken from Ref. [12]; they share similar (s,p) substrate, but are characterized by different exponents for the polarization functions. The relative results have been reported, choosing from a large set of similar data, to document the strong dependence on these exponents when the extension of the basis set is limited. Basis sets III to VI are the same as I–IV from Ref. [13]: their increasing quality has been exhaustively tested to estimate convergence to the Hartree-Fock limit for a number of response properties, in particular basis VI, which includes $3d$ and $4f$ functions on carbon, and $2p$ and $3d$ functions on hydrogen. The extremely good features of these basis sets can be judged from the results obtained in Refs. [12,13].

Theoretical dipole-quadrupole magnetic susceptibilities of methane, calculated assuming the origin of coordinates on carbon, are collected in Table I. It can be observed

that the diamagnetic contributions, calculated as expectation values over the unperturbed wave function, are very slightly affected by the quality of the basis set, at variance with the case of the water molecule [7]. On the other hand, the paramagnetic contributions heavily depend on the features of the electronic wave function. Even little variation of exponents in the polarization functions (compare for the results from basis sets I and II) essentially of the same size turn out in large differences of the calculated property. However, from the general trend observed in Table I, it can be concluded that the results yielded by larger basis sets IV–VI have converged to the Hartree-Fock limit. The same judgment can be achieved by inspection of the results of Table II, where the magnetic susceptibility corresponding to the origin on the hydrogen nucleus calculated directly from definition (9), is compared with those results obtained from Table I via Eq. (18). As discussed in the text, Eq. (18) is exactly fulfilled only in the limit of a complete set of expansions.

Very large differences between corresponding estimates are found in Table II in the case of smaller basis sets. The discrepancies, however, monotonically decrease, and eventually become negligibly small, in the case of basis sets IV–VI. One can therefore assume that the results for these basis sets are close to the Hartree-Fock limit.

The paramagnetic components of calculated magnetic-quadrupole contributions to nuclear magnetic shielding are also significantly affected by the characteristics of the basis set [7]. This is confirmed here for carbon and hydrogen shielding, but the results obtained via the largest basis set (see Tables III and IV) have converged to the Hartree-Fock limit.

A final comment is necessary on the order of magnitude of the calculated quantities. Within the (irrational) cgs emu system of units, the conversion factor from atomic units for $\sigma_{\alpha,\beta\gamma}$ is the Bohr radius, i.e., $a_0 \approx 0.52917 \times 10^{-8}$ cm. To convert to Système International (SI) units, i.e., m, one should further multiply by 10^{-2}.

For $\chi_{\alpha,\beta\gamma}$ the conversion factor from a.u. per molecule to cgs emu per mole is $a_0^4 N \approx 4.7223 \times 10^{-10}$. The conversion factor from cgs emu per mole to SI units, i.e.,

TABLE IV. Magnetic quadrupole contribution to nuclear magnetic shielding of proton H_1 [in a.u., coordinates in bohr of H_1 are (0, 1.683 40, 1.190 34) $\sigma^d_{\alpha,\beta\gamma}$ via Eq. (19)], $\sigma_{\alpha,\beta\gamma}$ (nonvanishing components) from basis set VI.

Component	$\sigma^d_{\alpha,\beta\gamma}(H_1)$	$\sigma^d_{\alpha,\beta\gamma}(H_1)$	$\sigma^d_{\alpha,\beta\gamma}(c.m.)$	$\sigma^p_{\alpha,\beta\gamma}(c.m.)$	$\sigma_{\alpha,\beta\gamma}(H_1)$	$\sigma_{\alpha,\beta\gamma}(c.m.)$	$\sigma_{\alpha,\beta\gamma}{}^a(c.m.)$
112	99.084	95.377	212.554	28.809	194.461	241.363	242.313
113	67.850	64.532	148.085	17.450	132.382	165.535	166.219
121	−10.622	−16.101	−10.622	−16.095	−26.722	−26.717	−26.722
131	−9.724	−14.293	−9.724	−14.301	−24.017	−24.025	−24.017
211	−10.622	−1.070	−37.480	4.441	−11.692	−33.038	−33.044
222	40.109	27.495	104.790	−0.203	67.604	104.587	104.908
223	45.596	34.491	110.324	11.017	80.087	121.341	121.564
232	−31.978	−44.333	−47.485	−20.734	−76.311	−68.219	−68.673
233	−29.487	−26.425	−67.311	−4.238	−55.912	−71.549	−72.864
311	−9.724	−3.665	−28.715	0.219	−13.389	−28.496	−28.488
322	−31.978	−33.705	−66.477	−6.213	−65.683	−72.690	−73.143
323	−29.487	−41.454	−40.453	−24.773	−70.941	−65.226	−65.541
332	80.218	70.018	182.723	20.128	150.236	202.851	203.493
333	41.702	37.370	95.192	5.994	79.072	101.186	101.631

$J T^{-2} m mol^{-1}$, for $\chi_{\alpha,\beta\gamma}$ is 0.1. This means that measuring the tiny quantities introduced in the present study with any experimental setup so far available is probably out of reach. 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 theoretical estimates reported in this work may spur experimental studies in this field.

However, as emphasized in the Introduction, the situation is different at the microscopical level, when short-range intramolecular effects play an important role, and detectable contributions arising from magnetic quadrupoles are experienced by a resonating nucleus. Plots of streamlines of the current density induced by a magnetic field within the electron cloud of a molecule evidence the typical pattern of toroidal vortices [14]. Whereas ordinary axial vortices have angular momentum and interact with a magnetic field, these doughnut-shaped vortices, due to stagnation lines forming close loops, do not possess a dipole moment, but have a quadrupole moment and can therefore interact with the gradient of inhomogeneous fields [15]. Accordingly, the analysis of streamline plots and the theoretical determination of the magnetic-quadrupole effects in large molecules can provide insight into the pseudocontact mechanism in a chemical shift.

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