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Calculation of the fourth-rank molecular hypermagnetizability of some small molecules

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A computational scheme has been developed within the framework of Rayleigh–Schrödinger perturbation theory to evaluate nonlinear interaction energy contributions for a molecule in the presence of an external spatially uniform, time-independent magnetic field. Terms connected with the fourth power of the perturbing field, representing the fourth-rank hypermagnetizabilities of five small molecules, have been evaluated at the coupled Hartree–Fock level of accuracy within the conventional common-origin approach. Gaugeless basis sets of increasing size and flexibility have been employed in a numerical test, adopting two different coordinate systems to estimate the degree of convergence of theoretical tensor components. © 2004 American Institute of Physics. [DOI: 10.1063/1.1695551]

I. INTRODUCTION

Increasing attention is presently being paid to nonlinear response of molecules to intense electric and magnetic fields.^{1–16} The possibility of deviations from linear dependence of the resonance frequencies on the strength of the external magnetic field in nuclear magnetic resonance (NMR) experiments has been taken into account in early papers by Ramsey.^{17,18} A wider discussion was reported later in Ref. 19.

A quadratic dependence of magnetic susceptibility for a molecule in the presence of intense magnetic field has also been predicted.²⁰ The anisotropies of the dynamic fourth-rank hypermagnetizabilities at the wavelength $\lambda = 632.8$ nm, in H₂, N₂, C₂H₂, and HF have been reported by Rizzo and Rizzo.¹⁵

Raynes and Stevens have investigated the effects on the nuclear spin–spin coupling constants to second order in the magnetic field.²¹ Dependence of nuclear magnetic shielding in closed-shell atomic systems on even powers of a perturbing magnetic field has been analyzed by Vaara, Manninen, and Lounila.²²

Theoretical research in this field is expected to provide new fundamental information on molecular response and important indications to experimentalists, as current superconductor technology will soon allow routine use of strong homogeneous magnets. Techniques for high-field Bitter and hybrid magnets up to ≈ 30 T have been recently described.²³

This study is aimed at developing a computational scheme for a fourth-rank hypermagnetizability tensor denoted by $X_{\alpha\beta\gamma\delta}$. This is an intrinsic property of diamagnetic atoms and molecules, useful to rationalize their nonlinear response to intense magnetic field. An approach based on the Rayleigh–Schrödinger perturbation theory is outlined in Sec. III. Numerical estimates of the fourth-rank hypermagnetiz-

ability for the molecules H₂, HF, H₂O, NH₃, and CH₄ are reported in Sec. IV.

II. INTERACTION ENERGY

The energy of a diamagnetic molecule, i.e., a closed-shell system even under time reversal, in the electronic reference state a , in the presence of an external magnetic field \mathbf{B} which for the sake of simplicity is assumed spatially uniform and time independent, and of intramolecular perturbation, namely permanent magnetic dipoles μ_I at the I th nucleus, can be written as a Taylor series

$$\begin{aligned} W_a &= W_a^{(0)} + W_a^{(2)} + W_a^{(4)} + \dots \\ &= W_a^{(0)} - \frac{1}{2}\chi_{\alpha\beta}B_\alpha B_\beta - \frac{1}{24}X_{\alpha\beta\gamma\delta}B_\alpha B_\beta B_\gamma B_\delta + \dots \\ &\quad + \sigma_{\alpha\beta}^I \mu_{I\alpha} B_\beta + \frac{1}{6}\sum_{\alpha\beta\gamma\delta}^I \mu_{I\alpha} B_\beta B_\gamma B_\delta + \dots \\ &\quad + K_{\alpha\beta}^{IJ} \mu_{I\alpha} \mu_{J\beta} + \frac{1}{2}K_{\alpha\beta\gamma\delta}^{IJ} \mu_{I\alpha} \mu_{J\beta} B_\gamma + \dots, \quad (1) \end{aligned}$$

where $W_a^{(0)}$ is the energy of the isolated molecule, $\chi_{\alpha\beta}$ is the magnetic susceptibility, $\sigma_{\alpha\beta}^I$ is the magnetic shielding at nucleus I , and $K_{\alpha\beta}^{IJ}$ is the reduced nuclear spin–spin coupling tensor. The fourth-rank tensors $X_{\alpha\beta\gamma\delta}$, $\sum_{\alpha\beta\gamma\delta}^I$, and $K_{\alpha\beta\gamma\delta}^{IJ}$ account for nonlinear response in \mathbf{B} .

III. FOURTH-RANK HYPERMAGNETIZABILITIES

The relevant formulas of the Rayleigh–Schrödinger (RS) theory for a quantum-mechanical system in the presence of first- and second-order perturbations, denoted, respectively, by $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, have been reported in Ref. 24. We suppose that the zero-order eigenvalue problem $\hat{H}^{(0)}|\Psi_j^{(0)}\rangle = E_j^{(0)}|\Psi_j^{(0)}\rangle$ has been solved to determine the complete set of unperturbed electronic wave functions $|\Psi_j^{(0)}\rangle$. We will indicate by $|a\rangle \equiv |\Psi_a^{(0)}\rangle$ the reference electronic state and by

TABLE I. Basis sets employed in the calculations.

| Basis set | | SCF energy (hartree) |
|------------------|--------------|----------------------|
| H ₂ | | |
| I | aug-cc-pCVDZ | -1.128 806 |
| II | aug-cc-pCVTZ | -1.133 041 |
| III | aug-cc-pCVQZ | -1.133 478 |
| IV | aug-cc-pCV5Z | -1.133 590 |
| HF | | |
| I | aug-cc-pCVDZ | -100.035 366 |
| II | aug-cc-pCVTZ | -100.068 891 |
| III | aug-cc-pCVQZ | -100.069 244 |
| IV | aug-cc-pCV5Z | -100.070 595 |
| H ₂ O | | |
| I | aug-cc-pCVDZ | -76.042 670 |
| II | aug-cc-pCVTZ | -76.061 347 |
| III | aug-cc-pCVQZ | -76.066 184 |
| IV | aug-cc-pCV5Z | -76.067 201 |
| NH ₃ | | |
| I | aug-cc-pCVDZ | -56.206 300 |
| II | aug-cc-pCVTZ | -56.220 869 |
| III | aug-cc-pCVQZ | -56.224 149 |
| IV | aug-cc-pCV5Z | -56.224 831 |
| CH ₄ | | |
| I | aug-cc-pCVDZ | -40.200 263 |
| II | aug-cc-pCVTZ | -40.213 756 |
| III | aug-cc-pCVQZ | -40.216 291 |
| IV | aug-cc-pCV5Z | -40.216 790 |

$|j\rangle \equiv |\Psi_j^{(0)}\rangle$ the j th excited state. Introducing the natural transition frequencies $\omega_{ja} = \hbar^{-1}(E_j^{(0)} - E_a^{(0)})$, the RS second-order energy correction is

$$W_a^{(2)} = \langle a | \hat{H}^{(2)} | a \rangle - \frac{1}{\hbar} \sum_{i \neq a} \omega_{ia}^{-1} \langle a | \hat{H}^{(1)} | i \rangle \langle i | \hat{H}^{(1)} | a \rangle. \quad (2)$$

The third-order energy

TABLE II. Magnetic hypersusceptibility $X_{\alpha\beta\gamma\delta}$ of the H₂ molecule in SI a.u.^a

| Basis set | Component ^b | $X_{\alpha\beta\gamma\delta}$ (c.m.) | $X_{\alpha\beta\gamma\delta}(H_1)^c$ |
|-----------|------------------------|--------------------------------------|--------------------------------------|
| I | xxxx | 5.02 | 3.67 |
| II | | 5.85 | 5.49 |
| III | | 6.07 | 5.91 |
| IV | | 6.18 | 6.12 |
| I | xxyy | 1.67 | 1.22 |
| II | | 1.95 | 1.83 |
| III | | 2.02 | 1.97 |
| IV | | 2.06 | 2.04 |
| I | xxzz | 1.94 | 1.88 |
| II | | 1.98 | 1.96 |
| III | | 1.99 | 1.98 |
| IV | | 1.99 | 1.99 |
| I | zzzz | 5.11 | 5.11 |
| II | | 5.67 | 5.67 |
| III | | 5.69 | 5.69 |
| IV | | 5.71 | 5.71 |

^aHere and in the following tables, the conversion factor to SI units is $1.428\,259\,51 \times 10^{-39} \text{ JT}^{-4}$ per molecule. $X_{yyyy} = X_{xxxx}$, $X_{yyzz} = X_{xxzz}$ by symmetry.

^bNonvanishing components.

^c $H_1 = (0,0,0.70)$ bohr.

TABLE III. Magnetic hypersusceptibility $X_{\alpha\beta\gamma\delta}$ of the HF molecule in SI a.u.^a

| Basis set | Component ^b | $X_{\alpha\beta\gamma\delta}$ (c.m.) | $X_{\alpha\beta\gamma\delta}(H_1)^c$ |
|-----------|------------------------|--------------------------------------|--------------------------------------|
| I | xxxx | 7.19 | 3.53 |
| II | | 7.85 | 7.08 |
| III | | 7.97 | 7.11 |
| IV | | 7.99 | 7.46 |
| I | xxyy | 2.40 | 1.18 |
| II | | 2.66 | 2.36 |
| III | | 2.66 | 2.37 |
| IV | | 2.66 | 2.49 |
| I | xxzz | 1.81 | 2.39 |
| II | | 2.07 | 2.19 |
| III | | 2.07 | 2.19 |
| IV | | 2.04 | 2.09 |
| I | zzzz | 5.27 | 5.27 |
| II | | 5.80 | 5.80 |
| III | | 5.80 | 5.80 |
| IV | | 5.71 | 5.71 |

^a $X_{yyyy} = X_{xxxx}$, $X_{yyzz} = X_{xxzz}$ by symmetry.

^bNonvanishing components.

^c $H_1 = (0,0,1.645\,027)$ bohr.

$$W_a^{(3)} = \frac{1}{\hbar^2} \sum_{i \neq a} \sum_{j \neq a} \omega_{ia}^{-1} \omega_{ja}^{-1} \langle a | \hat{H}^{(1)} | i \rangle \langle i | \hat{H}^{(1)} | j \rangle \langle j | \hat{H}^{(1)} | a \rangle - \frac{2}{\hbar} \sum_{i \neq a} \omega_{ia}^{-1} \Re \{ \langle a | \hat{H}^{(1)} | i \rangle \langle i | \hat{H}^{(2)} | a \rangle \}, \quad (3)$$

vanishes identically for a closed-shell molecule if $\hat{H}^{(1)}$ involves only magnetic perturbations. The fourth-order contribution becomes

$$W_a^{(4)} = -\frac{1}{\hbar^3} \sum_{i \neq a} \sum_{j \neq a} \sum_{k \neq a} \omega_{ia}^{-1} \omega_{ja}^{-1} \omega_{ka}^{-1} \times \langle a | \hat{H}^{(1)} | i \rangle \langle i | \hat{H}^{(1)} | j \rangle \langle j | \hat{H}^{(1)} | k \rangle \langle k | \hat{H}^{(1)} | a \rangle + \frac{1}{\hbar^3} \sum_{i \neq a} \sum_{j \neq a} \omega_{ia}^{-2} \omega_{ja}^{-1} \times \langle a | \hat{H}^{(1)} | i \rangle \langle i | \hat{H}^{(1)} | a \rangle \langle a | \hat{H}^{(1)} | j \rangle \langle j | \hat{H}^{(1)} | a \rangle + \frac{1}{\hbar^2} \sum_{i \neq a} \sum_{j \neq a} \omega_{ia}^{-1} \omega_{ja}^{-1} \langle a | \hat{H}^{(1)} | i \rangle \langle i | \hat{H}^{(2)} | j \rangle \langle j | \hat{H}^{(1)} | a \rangle + \frac{2}{\hbar^2} \sum_{i \neq a} \sum_{j \neq a} \omega_{ia}^{-1} \omega_{ja}^{-1} \Re \times \{ \langle a | \hat{H}^{(2)} | i \rangle \langle i | \hat{H}^{(1)} | j \rangle \langle j | \hat{H}^{(1)} | a \rangle \} - \frac{1}{\hbar} \sum_{i \neq a} \omega_{ia}^{-1} \langle a | \hat{H}^{(2)} | i \rangle \langle i | \hat{H}^{(2)} | a \rangle, \quad (4)$$

where barred fluctuation operators are defined by, e.g.,

$$\overline{\hat{H}^{(1)}} \equiv \hat{H}^{(1)} - \langle a | \hat{H}^{(1)} | a \rangle, \quad \overline{\hat{H}^{(2)}} \equiv \hat{H}^{(2)} - \langle a | \hat{H}^{(2)} | a \rangle. \quad (5)$$

TABLE IV. Magnetic hypersusceptibility $X_{\alpha\beta\gamma\delta}$ of the H_2O molecule in SI a.u.^a

| Basis set | Component ^d | $X_{\alpha\beta\gamma\delta}(\text{c.m.})$ | $X_{\alpha\beta\gamma\delta}(H_1)^b$ |
|-----------|------------------------|--|--------------------------------------|
| I | xxxx | 21.48 | 12.46 |
| II | | 23.43 | 22.49 |
| III | | 23.69 | 23.26 |
| IV | | 23.79 | 23.51 |
| I | xxyy | 4.67 | 4.09 |
| II | | 5.16 | 5.34 |
| III | | 5.19 | 5.27 |
| IV | | 5.16 | 5.18 |
| I | xxzz | 6.45 | 3.59 |
| II | | 7.12 | 7.02 |
| III | | 7.19 | 7.16 |
| IV | | 7.20 | 7.17 |
| I | xxyz | 0.0 | -1.72 |
| II | | 0.0 | -0.08 |
| III | | 0.0 | -0.02 |
| IV | | 0.0 | -0.01 |
| I | yyyy | 14.12 | 13.87 |
| II | | 14.74 | 14.73 |
| III | | 14.77 | 14.69 |
| IV | | 14.71 | 14.65 |
| I | yyyz | 0.0 | -0.74 |
| II | | 0.0 | -0.07 |
| III | | 0.0 | -0.10 |
| IV | | 0.0 | -0.06 |
| I | yyzz | 6.14 | 4.47 |
| II | | 6.44 | 6.22 |
| III | | 6.47 | 6.32 |
| IV | | 6.45 | 6.38 |
| I | yzzz | 0.0 | -3.15 |
| II | | 0.0 | -0.39 |
| III | | 0.0 | -0.22 |
| IV | | 0.0 | -0.12 |
| I | zzzz | 14.38 | 9.26 |
| II | | 15.91 | 15.68 |
| III | | 16.12 | 15.77 |
| IV | | 16.12 | 15.88 |

^aNonvanishing components.^b $H_1 = (0, 1.431\ 530, -0.985\ 265)$ bohr.

It is expedient to introduce symbols for response properties explicitly showing the operators \hat{A}, \hat{B}, \dots involved and the total order in the transition frequencies as a subindex. To first order in ω_{ia}

$$\{\hat{A}, \hat{B}\}_{-1} \equiv \frac{2}{\hbar} \sum_{i \neq a} \omega_{ia}^{-1} \Re\{\langle a|\hat{A}|i\rangle\langle i|\hat{B}|a\rangle\}, \quad (6)$$

to second order in ω_{ia}

$$\{\hat{A}, \hat{B}, \hat{C}\}_{-2} \equiv \mathbf{S}(\hat{A}, \hat{B}, \hat{C}) \left(\frac{1}{\hbar^2} \sum_{j \neq a} \sum_{k \neq a} \omega_{ja}^{-1} \omega_{ka}^{-1} \langle a|\hat{A}|j\rangle \times \langle j|\hat{B}|k\rangle\langle k|\hat{C}|a\rangle \right), \quad (7)$$

and to third order in ω_{ia} TABLE V. Magnetic hypersusceptibility $X_{\alpha\beta\gamma\delta}$ of the NH_3 molecule in SI a.u.^a

| Basis set | Component ^d | $X_{\alpha\beta\gamma\delta}(\text{c.m.})$ | $X_{\alpha\beta\gamma\delta}(H_1)^b$ |
|-----------|------------------------|--|--------------------------------------|
| I | xxxx | 46.68 | 33.66 |
| II | | 50.56 | 49.62 |
| III | | 50.96 | 50.51 |
| IV | | 51.19 | 50.98 |
| I | xxxy | 0.0 | -2.06 |
| II | | 0.0 | -0.18 |
| III | | 0.0 | -0.06 |
| IV | | 0.0 | -0.03 |
| I | xxyy | 13.52 | 12.78 |
| II | | 14.26 | 14.27 |
| III | | 14.29 | 14.28 |
| IV | | 14.30 | 14.29 |
| I | xyyy | -5.06 | -5.52 |
| II | | -5.23 | -5.22 |
| III | | -5.19 | -5.20 |
| IV | | -5.18 | -5.18 |
| I | xxzz | 13.52 | 10.50 |
| II | | 14.26 | 14.56 |
| III | | 14.29 | 14.47 |
| IV | | 14.30 | 14.36 |
| I | xyzz | 5.06 | 5.06 |
| II | | 5.23 | 5.32 |
| III | | 5.19 | 5.27 |
| IV | | 5.18 | 5.21 |
| I | yyyy | 37.58 | 37.32 |
| II | | 39.15 | 39.13 |
| III | | 39.36 | 39.36 |
| IV | | 39.48 | 39.48 |
| I | yyzz | 12.53 | 12.50 |
| II | | 13.05 | 13.16 |
| III | | 13.12 | 13.16 |
| IV | | 13.16 | 13.16 |
| I | zzzz | 37.58 | 27.36 |
| II | | 39.15 | 38.67 |
| III | | 39.36 | 38.88 |
| IV | | 39.48 | 39.22 |

^aNonvanishing components.^b $H_1 = (-0.591\ 964, 1.770\ 998, 0)$ bohr.

$$\{\hat{A}, \hat{B}, \hat{C}, \hat{D}\}_{-3} \equiv \mathbf{S}(\hat{A}, \hat{B}, \hat{C}, \hat{D})$$

$$\begin{aligned} & \times \left(\frac{1}{\hbar^3} \sum_{i \neq a} \sum_{j \neq a} \sum_{k \neq a} \omega_{ia}^{-1} \omega_{ja}^{-1} \omega_{ka}^{-1} \right. \\ & \times \langle a|\hat{A}|i\rangle\langle i|\hat{B}|j\rangle\langle j|\hat{C}|k\rangle\langle k|\hat{D}|a\rangle \\ & - \frac{1}{\hbar^3} \sum_{i \neq a} \sum_{j \neq a} \omega_{ia}^{-2} \omega_{ja}^{-1} \\ & \left. \times \langle a|\hat{A}|i\rangle\langle i|\hat{B}|a\rangle\langle a|\hat{C}|j\rangle\langle j|\hat{D}|a\rangle \right). \quad (8) \end{aligned}$$

In these expressions $\mathbf{S}(\hat{A}, \hat{B}, \hat{C}, \hat{D}, \dots)$ implies a sum of all terms arising from permuting the operators $\hat{A}, \hat{B}, \hat{C}, \hat{D}, \dots$ on the r.h.s. of a given relationship.

Within the Coulomb gauge for the vector potential $\mathbf{A}^{\mathbf{B}}$ of the magnetic field \mathbf{B}

$$\mathbf{A}^{\mathbf{B}} = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{r}_0), \quad (9)$$

and using a well-established notation,²⁴ the first- and second-order perturbing Hamiltonians are written

TABLE VI. Magnetic hypersusceptibility $X_{\alpha\beta\gamma\delta}$ of the CH_4 molecule in SI a.u.^a

| Basis set | Component ^d | $X_{\alpha\beta\gamma\delta}(\text{c.m.})$ | $X_{\alpha\beta\gamma\delta}(H_1)^b$ |
|-----------|------------------------|--|--------------------------------------|
| I | xxxx | 86.66 | 67.15 |
| II | | 91.51 | 90.50 |
| III | | 91.75 | 91.27 |
| IV | | 91.88 | 91.75 |
| I | xxyy | 10.72 | 5.53 |
| II | | 11.43 | 10.98 |
| III | | 11.49 | 11.30 |
| IV | | 11.54 | 11.47 |
| I | xxyz | 0.0 | 1.12 |
| II | | 0.0 | 0.24 |
| III | | 0.0 | 0.10 |
| IV | | 0.0 | 0.03 |
| I | xxzz | 37.97 | 32.40 |
| II | | 40.04 | 40.10 |
| III | | 40.13 | 40.12 |
| IV | | 40.17 | 40.18 |
| I | yyyy | 86.66 | 78.93 |
| II | | 91.51 | 91.52 |
| III | | 91.75 | 91.72 |
| IV | | 91.88 | 91.88 |
| I | yyyz | 0.0 | 4.97 |
| II | | 0.0 | 0.01 |
| III | | 0.0 | 0.03 |
| IV | | 0.0 | 0.0 |
| I | yyzz | 37.97 | 35.11 |
| II | | 40.04 | 39.94 |
| III | | 40.13 | 40.07 |
| IV | | 40.17 | 40.16 |
| I | yzzz | 0.0 | 4.17 |
| II | | 0.0 | 0.36 |
| III | | 0.0 | 0.16 |
| IV | | 0.0 | 0.05 |
| I | zzzz | 59.41 | 44.81 |
| II | | 62.90 | 61.98 |
| III | | 63.12 | 62.69 |
| IV | | 63.24 | 63.12 |

^aNonvanishing components.^b $H_1 = (0, 1.683\ 396, 1.190\ 341)$ bohr.

$$\hat{H}^{\mathbf{B}} = \frac{e}{m_e c} \sum_{i=1}^n \hat{\mathbf{A}}_i^{\mathbf{B}} \cdot \hat{\mathbf{p}}_i = -\hat{m}_\alpha B_\alpha, \quad (10)$$

$$\hat{H}^{\mathbf{B}\mathbf{B}} = \frac{e^2}{2m_e c^2} \sum_{i=1}^n \hat{\mathbf{A}}_i^{\mathbf{B}} \cdot \hat{\mathbf{A}}_i^{\mathbf{B}} = -\frac{1}{2} \hat{\chi}_{\alpha\beta}^{\text{d}} B_\alpha B_\beta. \quad (11)$$

The Einstein convention for repeated Greek indices is in force. In these relationships

$$\hat{m}_\alpha = -\frac{e}{2m_e c} \hat{L}_\alpha, \quad (12)$$

is the operator for the orbital magnetic dipole moment of electrons, and

$$\hat{\chi}_{\alpha\beta}^{\text{d}} = -\frac{e^2}{4m_e c^2} \sum_{i=1}^n (r_\gamma r_\gamma \delta_{\alpha\beta} - r_\alpha r_\beta)_i, \quad (13)$$

is the second-rank diamagnetic susceptibility operator. The magnetic susceptibility, $\chi_{\alpha\beta}$, of a molecule in the presence of the magnetic field \mathbf{B} is defined by the relationship^{4,11,25}

$$\chi_{\alpha\beta}(\mathbf{B}) = \chi_{\alpha\beta} + \frac{1}{2} X_{\alpha\beta\gamma\delta} B_\gamma B_\delta + \dots, \quad (14)$$

where

$$\chi_{\alpha\beta} = -\frac{\partial^2 W_a^{(2)}}{\partial B_\alpha \partial B_\beta} = \chi_{\alpha\beta}^{\text{d}} + \chi_{\alpha\beta}^{\text{p}}. \quad (15)$$

The diamagnetic and paramagnetic contributions to the second-rank susceptibility are, respectively,

$$\chi_{\alpha\beta}^{\text{d}} = \langle a | \hat{\chi}_{\alpha\beta}^{\text{d}} | a \rangle, \quad \chi_{\alpha\beta}^{\text{p}} = \{ \hat{m}_\alpha, \hat{m}_\beta \}_{-1}. \quad (16)$$

The fourth-rank hypermagnetizability tensor $X_{\alpha\beta\gamma\delta}$ accounts for nonlinear response of the electron cloud to fourth order in \mathbf{B} . It is defined as minus the fourth derivative of the molecular energy in the limit of vanishingly small magnetic field, that is

$$X_{\alpha\beta\gamma\delta} = -\frac{\partial^4 W_a^{(4)}}{\partial B_\alpha \partial B_\beta \partial B_\gamma \partial B_\delta}. \quad (17)$$

Allowing for relationships (7) and (8) of the Rayleigh–Schrödinger perturbation theory

$$\begin{aligned} X_{\alpha\beta\gamma\delta} = & \{ \hat{m}_\alpha, \hat{m}_\beta, \hat{m}_\gamma, \hat{m}_\delta \}_{-3} + \{ \hat{\chi}_{\alpha\beta}^{\text{d}}, \hat{m}_\gamma, \hat{m}_\delta \}_{-2} \\ & + \{ \hat{\chi}_{\alpha\gamma}^{\text{d}}, \hat{m}_\beta, \hat{m}_\delta \}_{-2} + \{ \hat{\chi}_{\alpha\delta}^{\text{d}}, \hat{m}_\gamma, \hat{m}_\beta \}_{-2} \\ & + \{ \hat{\chi}_{\gamma\beta}^{\text{d}}, \hat{m}_\alpha, \hat{m}_\delta \}_{-2} + \{ \hat{\chi}_{\delta\beta}^{\text{d}}, \hat{m}_\gamma, \hat{m}_\alpha \}_{-2} \\ & + \{ \hat{\chi}_{\gamma\delta}^{\text{d}}, \hat{m}_\alpha, \hat{m}_\beta \}_{-2} + \{ \hat{\chi}_{\alpha\beta}^{\text{d}}, \hat{\chi}_{\gamma\delta}^{\text{d}} \}_{-1} \\ & + \{ \hat{\chi}_{\gamma\beta}^{\text{d}}, \hat{\chi}_{\alpha\delta}^{\text{d}} \}_{-1} + \{ \hat{\chi}_{\alpha\gamma}^{\text{d}}, \hat{\chi}_{\delta\beta}^{\text{d}} \}_{-1}. \end{aligned} \quad (18)$$

IV. RESULTS AND DISCUSSION

Five molecules, H_2 , HF , H_2O , NH_3 , and CH_4 , have been considered in a series of preliminary calculations aimed at estimating the magnitude of their fourth-rank hypermagnetizability. An algorithm based on the coupled Hartree–Fock (CHF) approach, exploiting full molecular symmetry to speed-up computations and to reduce disk occupancy by a factor depending on the order of the molecular point group has been applied. Full details on the iterative density-matrix approach employed are available in Ref. 26.

Some tests have been made to investigate how the theoretical results depend on the quality of basis sets I–IV from Refs. 27 and 28 adopted for H_2 , HF , NH_3 , and CH_4 . They are specified in Table I. The basis sets I–IV are, respectively, the aug-cc-pCVDZ, aug-cc-pCVTZ, aug-cc-pCQZ, and aug-cc-pCV5Z in which basis functions higher than f have been eliminated for the heavier nucleus, and f functions have been eliminated for hydrogen in all molecules except H_2 .

The internuclear distance for H_2 used in the calculation is 1.40 bohr. Molecular geometries are from Ref. 29 for HF , from Ref. 30 for H_2O , NH_3 , and CH_4 .

Calculated tensor components are reported in Tables II–VI for two different origins of the vector potential (9), the center-of-mass (c.m.) and a hydrogen nucleus. The results would be origin independent only for a complete basis set. Their closeness is, therefore, a measure of basis set quality. A sufficient degree of convergence to the Hartree–Fock limit for the property seems to have been attained from the values reported in the Tables.

The CHF predictions suggest that the hypermagnetizabilities of small molecules like those considered in the

present study are quite small. Allowing for the CODATA recommended values from Ref. 31, the conversion factor from (SI) atomic units for $X_{\alpha\beta\gamma\delta}$ to SI units is $(e^2 a_0^2 m_e^{-1})^2 E_h^{-1} = 1.428\,259\,51 \times 10^{-39} \text{ JT}^{-4}$ per molecule. Since the conversion factor for second-rank magnetizabilities is $e^2 a_0^2 m_e^{-1} = 7.891\,036\,417 \times 10^{-29}$, and their order of magnitude is ~ 1 a.u. for the molecules considered,³² the contribution quadratic in \mathbf{B} to the magnetizability from the second term on the r.h.s. of Eq. (14) is $\approx 10^{-11} |\mathbf{B}|^2$ smaller than the first one. Thus, in a magnetic field with magnetic field density of 10 tesla, the second term would be $\approx 10^{-9}$ smaller than the first one, which implies that the $X_{\alpha\beta\gamma\delta}$ tensors are difficult to measure, unless diamagnetic molecules like aromatics, showing peculiar magnetic exaltation of second-rank magnetizabilities, are also characterized by anomalously high hypermagnetizabilities.

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