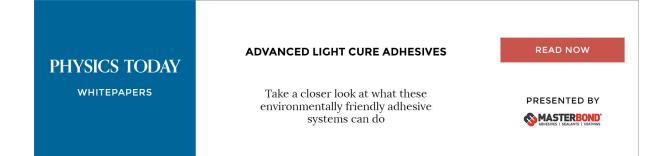# Conditions for invariance of molecular magnetic properties in Landau gauge transformations

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Conditions for invariance of molecular magnetic properties in Landau gauge transformations

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General constraints for invariance of magnetic properties in a gauge transformation are analyzed. Sum rules relative to the transformation from Coulomb to Landau gauges are examined in particular. Numerical tests for hydrogen fluoride, water, ammonia, and methane molecule have been carried out in large basis set calculations, using random-phase approximation. The conditions for invariance are severe conditions for accuracy of variational molecular wave functions. © *1995 American Institute of Physics.*

I. INTRODUCTION

The quality of an approximate variational wave function, describing a given electronic state of an atom or a molecule, can be assessed *a priori*, by checking the degree to which certain sum rules are satisfied, independently of any comparison between experimental data and corresponding quantities (i.e., electronic properties) estimated via the same wave function, which might be misleading in a number of cases. These sum rules are very general quantum mechanical relationships, fully obeyed by exact eigenfunctions to a model hamiltonian.[1] They furnish "internal" yardsticks of accuracy as by-products of the main calculation.

In particular, the ability of a variational electronic wave function to predict accurate magnetic properties in a molecule is necessarily related to the degree of gauge dependence of these properties. This is a major physical requirement, as gauge invariance is connected to charge and current conservation in the presence of magnetic field via the continuity equation.[2,3] Within the algebraic approximation, practicality of basis sets for determining theoretical magnetic properties can be estimated *a priori*, by checking their gauge invariance via proper sum rules.

In addition, a relevant theoretical question might be whether, if the approximate variational wave function is a good one, the gauge transformation also leads to a good approximate wave function. This question can be analyzed within the general framework of unitary invariance.[1] If one uses the same set of trial functions $\{\Psi\}$, invariant to the action of a unitary operator U (which transforms a given function of the set $\Psi' \rightarrow \Psi^{U\prime} = U^\dagger \Psi'$) to solve the variational problem for both Hamiltonians H and $H^U = U^\dagger H U$, then the optimum variational energy stays the same, i.e., $\hat{E}^U = \hat{E}$. In addition, the "best" variational wave function $\hat{\Psi}$ will have a series of physically desirable properties, in that it satisfies certain hypervirial theorems,[1] i.e., the aforementioned sum rules.

In three previous papers,[4–6] the Landau transformation of the vector potential in the Coulomb gauge has been investigated to obtain formulas for magnetic susceptibility and nuclear magnetic shieldings in a molecule in the presence of a static, time-independent, magnetic field. Quite remarkably, within the Landau gauge the diamagnetic contribution to susceptibility is a diagonal tensor, irrespective of coordinate system; besides, the diamagnetic contribution to nuclear shielding is fully described by a maximum of six independent components in the absence of molecular symmetry.

Numerical results[5–7] demonstrate that very accurate electronic wave functions are necessary to obtain paramagnetic contributions to magnetic susceptibility of the same quality as those obtainable within the Coulomb gauge for vector potential. On the other hand, nuclear magnetic shielding tensors in the Landau gauge are characterized by the same quality as those evaluated in the Coulomb gauge. In addition to direct comparison of total magnetic properties within Coulomb and Landau gauges, the accuracy of theoretical estimates can be also checked by analyzing sum rules for origin independence of magnetic properties in a change of coordinate system, which can be described as a gauge transformation of the Landau vector potential.[5,6] These topics have been recently reviewed.[8]

The present paper is aimed at deriving, and checking via extended numerical tests, more general constraints for invariance of magnetic properties under a gauge transformation for a molecule in a static homogeneous magnetic field. Besides their theoretical interest, these sum rules, as previously emphasized, can be applied to test the characteristics of excellent basis sets for evaluating magnetic properties. In particular, the sum rules for gauge invariance studied in this paper are helpful to sample a basis set in different regions of the molecular domain, as they involve a series of peculiar operators, able to weigh different portions of charge distribution. Accordingly, an analysis of sum rules for gauge invariance might help understand the conditions under which the gauge transformed wave function is also a good candidate for describing properties of a given electronic state in a molecule.

In Sec. II the general case of an arbitrary gauge transformation is analyzed. Section III deals in particular with sum rules for invariance under a Landau transformation, and corresponding numerical results are discussed in Sec. IV. They lead to insights as to when the Landau gauge transformation will affect the accuracy of the approximations retained in a calculation of magnetic properties.

II. SUM RULES FOR INVARIANCE IN A GENERAL CHANGE OF GAUGE

Let us consider a molecule with n electrons, with mass m_e, charge $-e$, coordinates $\mathbf{r}_i$, canonical momenta $\mathbf{p}_i$, angular momenta $\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$, $(i = 1, 2, \ldots, n)$, and N nuclei, with corresponding quantities M_I, $Z_I e$, $\mathbf{R}_I$, etc.

The "particle" Hamiltonian of the electrons is

$$H^{(0)} = \sum_{i=1}^{n} \left(\frac{p_i^2}{2m_e} - \sum_{I=1}^{N} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{j \neq i}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right)$$
$$+ \frac{1}{2} \sum_{I}^{N} \sum_{J \neq I}^{N} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}, \tag{1}$$

with eigenstates $|j\rangle$ and energy eigenvalues $E_j^{(0)}$; the reference state is denoted by $|a\rangle$ {the notation of previous papers[4-6] is retained here, e.g., $L_\alpha = \sum_{i=1}^{n} l_{i\alpha}$, $\omega_{ja} = (1/\hbar)[E_j^{(0)} - E_a^{(0)}]$, etc.}.

In the presence of a magnetic field $\mathbf{B}$ with vector potential

$$\mathbf{A}^{\mathscr{E}}(\mathbf{r}) = \tfrac{1}{2} \mathbf{B} \times \mathbf{r}, \quad \nabla \cdot \mathbf{A}^{\mathscr{E}} = 0, \tag{2}$$

in the Coulomb gauge, the "interaction" Hamiltonian is

$$V = \frac{e}{2m_e c} \sum_{i=1}^{n} (\mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{p}_i + \mathbf{p}_i \cdot \mathbf{A}_i^{\mathscr{E}}) + \frac{e^2}{2m_e c^2} \sum_{i=1}^{n} \mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{A}_i^{\mathscr{E}}, \tag{3}$$

where $\mathbf{A}_i^{\mathscr{E}} = \mathbf{A}^{\mathscr{E}}(\mathbf{r}_i)$.

If a permanent magnetic dipole μ_I on nucleus I is also present, with vector potential

$$\mathbf{A}^{\mu_I}(\mathbf{r}) = -\mu_I \times \nabla \frac{1}{|\mathbf{r} - \mathbf{R}_I|}, \tag{4}$$

the interaction Hamiltonian (3) contains the additional terms

$$\frac{e}{m_e c} \sum_{i=1}^{n} \mathbf{A}_i^{\mu_I} \cdot \mathbf{p}_i + \frac{e^2}{m_e c} \sum_{i=1}^{n} \mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{A}_i^{\mu_I}. \tag{5}$$

In a gauge transformation of the Coulomb vector potential,

$$\mathbf{A}^{\mathscr{E}} \to \mathbf{A}^{\mathscr{E}\prime} = \mathbf{A}^{\mathscr{E}} + \nabla \lambda, \tag{6}$$

induced by the generating function λ, the unitary operator acting on the electronic wave function is $U = \exp[-(\iota e/\hbar c) \Sigma_i \lambda(\mathbf{r}_i)]$. Both for exact eigenfunctions, and in the case of variational eigenfunctions belonging to a set of trial functions invariant to U,[1] the second-order energies,

$$W^{BB} = -\tfrac{1}{2} \chi_{\alpha\beta} B_\alpha B_\beta = W_d^{BB} + W_p^{BB}, \tag{7}$$

$$W^{\mu_I B} = \mu_{I\alpha} \sigma_{\alpha\beta}^I B_\beta = W_d^{\mu_I B} + W_p^{\mu_I B}, \tag{8}$$

are left invariant. This implies that a calculation of magnetic properties should fulfill constraints which can be expressed in the form of quantum mechanical sum rules. Denoting by

$$\mathbf{A}(\mathbf{r}) = \mathbf{A}^{\mathscr{E}}(\mathbf{r}) + \mathbf{A}^{\mu_I}(\mathbf{r}), \tag{9}$$

total vector potential at $\mathbf{r}$, the contributions to second-order interaction energy can be written

$$W_d^{BB} + W_d^{\mu_I B} = \frac{e^2}{2m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \mathbf{A}_i \cdot \mathbf{A}_i \right| a \right\rangle, \tag{10}$$

$$W_p^{BB} + W_p^{\mu_I B} = -\frac{e^2}{2m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}$$
$$\times \left[\left\langle a \left| \sum_{i=1}^{n} (A_\alpha p_\alpha)_i \right| j \right\rangle \left\langle j \left| \sum_{i=1}^{n} (A_\beta p_\beta)_i \right| a \right\rangle \right]. \tag{11}$$

In a gauge transformation (6) the diamagnetic contributions transform

$$W_d^{BB} \to W_d^{BB\prime} = W_d^{BB} + \Delta_d^{BB}, \tag{12}$$

$$W_d^{\mu_I B} \to W_d^{\mu_I B\prime} = W_d^{\mu_I B} + \Delta_d^{\mu_I B}, \tag{13}$$

where

$$W_d^{BB} = \frac{e^2}{2m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{A}_i^{\mathscr{E}} \right| a \right\rangle, \tag{14}$$

$$\Delta_d^{BB} = \frac{e^2}{2m_e c^2} \left[2 \left\langle a \left| \sum_{i=1}^{n} (\mathbf{A}^{\mathscr{E}} \cdot \nabla \lambda)_i \right| a \right\rangle \right.$$
$$\left. + \left\langle a \left| \sum_{i=1}^{n} (\nabla \lambda)_i^2 \right| a \right\rangle \right], \tag{15}$$

$$W_d^{\mu_I B} = \frac{e^2}{m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{A}_i^{\mu_I} \right| a \right\rangle, \tag{16}$$

$$\Delta_d^{\mu_I B} = \frac{e^2}{m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \mathbf{A}_i^{\mu_I} \cdot \nabla \lambda_i \right| a \right\rangle. \tag{17}$$

The paramagnetic contributions transform

$$W_p^{BB} \to W_p^{BB\prime} = W_p^{BB} + \Delta_p^{BB}, \tag{18}$$

$$W_p^{\mu_I B} \to W_p^{\mu_I B\prime} = W_p^{\mu_I B} + \Delta_p^{\mu_I B}, \tag{19}$$

where

$$W_p^{BB} = -\frac{e^2}{2m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R} \left[\left\langle a \left| \sum_{i=1}^{n} (\mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{p}_i) \right| j \right\rangle \right.$$
$$\left. \times \left\langle j \left| \sum_{i=1}^{n} (\mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{p}_i) \right| a \right\rangle \right], \tag{20}$$

$$\Delta_p^{BB} = -\frac{e^2}{2m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R} \left[\left\langle a \left| \sum_{i=1}^{n} (\mathbf{A}_i^{\mathscr{E}} \cdot \mathbf{p}_i) \right| j \right\rangle \right.$$
$$\left. \times \left\langle j \left| \sum_{i=1}^{n} (\nabla \lambda \cdot \mathbf{p})_i \right| a \right\rangle \right], \tag{21}$$

$$W_p^{\mu_I B} = -\frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left[\left\langle a\left|\sum_{i=1}^n (\mathbf{A}_i^{\mu_I} \cdot \mathbf{p}_i)\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (\mathbf{A}_i^{\mathscr{C}} \cdot \mathbf{p}_i)\right|a\right\rangle\right], \tag{22}$$

$$\Delta_p^{\mu_I B} = -\frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left[\left\langle a\left|\sum_{i=1}^n (\mathbf{A}_i^{\mu_I} \cdot \mathbf{p}_i)\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (\nabla\lambda \cdot \mathbf{p})_i\right|a\right\rangle\right]. \tag{23}$$

Therefore, under a gauge transformation (6) of the Coulomb vector potential, general conditions for invariance of magnetic susceptibility are obtained via the identities

$$\Delta_p^{BB} = -\Delta_d^{BB}, \quad \Delta_p^{\mu_I B} = -\Delta_d^{\mu_I B}, \tag{24}$$

in the form

$$(A_\alpha^{\mathscr{C}} p_\alpha, \nabla_\beta \lambda p_\beta)_{-1} = m_e\left\langle a\left|\sum_{i=1}^n (A_\alpha^{\mathscr{C}} \nabla_\alpha \lambda)_i\right|a\right\rangle, \tag{25}$$

$$(\nabla_\alpha \lambda p_\alpha, \nabla_\beta \lambda p_\beta)_{-1} = m_e\left\langle a\left|\sum_{i=1}^n (\nabla\lambda)_i^2\right|a\right\rangle, \tag{26}$$

$$(A_\alpha^{\mu_I} p_\alpha, \nabla_\beta \lambda p_\beta)_{-1} = m_e\left\langle a\left|\sum_{i=1}^n (A_\alpha^{\mu_I} \nabla_\alpha \lambda)_i\right|a\right\rangle, \tag{27}$$

where

$$(A_\alpha^{\mathscr{C}} p_\alpha, \nabla_\beta \lambda p_\beta)_{-1} = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^n (A_\alpha^{\mathscr{C}} p_\alpha)_i\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (\nabla_\beta \lambda p_\beta)_i\right|a\right\rangle\right), \tag{28}$$

$$(\nabla_\alpha \lambda p_\alpha, \nabla_\beta \lambda p_\beta)_{-1} = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^n (\nabla_\alpha \lambda p_\alpha)_i\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (\nabla_\beta \lambda p_\beta)_i\right|a\right\rangle\right), \tag{29}$$

$$(A_\alpha^{\mu_I} p_\alpha, \nabla_\beta \lambda p_\beta)_{-1} = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^n (A_\alpha^{\mu_I} p_\alpha)_i\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (\nabla_\beta \lambda p_\beta)_i\right|a\right\rangle\right). \tag{30}$$

The same formulas are established using the hypervirial theorem,[1] via the off-diagonal relation

$$\left\langle j\left|\sum_{i=1}^n (\nabla\lambda \cdot \mathbf{p})_i\right|a\right\rangle = im_e\omega_{ja}\left\langle j\left|\sum_{i=1}^n \lambda_i\right|a\right\rangle \tag{31}$$

and the operator equations

$$\frac{im_e}{\hbar}[H^{(0)},\lambda] = \nabla\lambda \cdot \mathbf{p}, \tag{32}$$

$$[\lambda,[\lambda,H^{(0)}]] = -\frac{\hbar^2}{m_e}(\nabla\lambda)^2. \tag{33}$$

These results can now be used to work out explicit conditions for invariance of molecular magnetic properties. The magnetic susceptibility tensor within the Coulomb gauge contains paramagnetic and diamagnetic contributions, compare for Eq. (7),

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^p + \chi_{\alpha\beta}^d, \tag{34}$$

$$\chi_{\alpha\beta}^{p\mathscr{C}} = \frac{e^2}{4m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}(\langle a|L_\alpha|j\rangle\langle j|L_\beta|a\rangle), \tag{35}$$

$$\chi_{\alpha\beta}^{d\mathscr{C}} = -\frac{e^2}{4m_e c^2}\left\langle a\left|\sum_{i=1}^n (r^2\delta_{\alpha\beta} - r_\alpha r_\beta)_i\right|a\right\rangle. \tag{36}$$

Analogously the paramagnetic and diamagnetic contributions to magnetic shielding of nucleus I carrying the intrinsic moment, compare for Eq. (8), are

$$\sigma_{\alpha\beta}^I = \sigma_{\alpha\beta}^{pI} + \sigma_{\alpha\beta}^{dI}, \tag{37}$$

$$\sigma_{\alpha\beta}^{pI} = -\frac{e^2}{2m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}(\langle a|M_{I\alpha}^n|j\rangle\langle j|\mathcal{L}_\beta|a\rangle), \tag{38}$$

$$\sigma_{\alpha\beta}^{dI} = \frac{e^2}{2m_e c}\left\langle a\left|\sum_{i=1}^n (r_{i\gamma}E_{I\gamma}^i\delta_{\alpha\beta} - r_{i\alpha}E_{I\beta}^i)\right|a\right\rangle. \tag{39}$$

III. SUM RULES FOR INVARIANCE IN A LANDAU TRANSFORMATION

The Landau transformation[9] is induced by the function

$$\lambda^{\mathscr{L}} = \tfrac{1}{2}(B_x yz + B_y zx + B_z xy), \tag{40}$$

and the Landau vector potential, compare for Eq. (6), has components $A_x^{\mathscr{L}} = A_z^{\mathscr{L}} = 0$, $A_y^{\mathscr{L}} = B_z x$, for a magnetic field in the z direction, $\mathbf{B} = \mathbf{e}_3 B_z$, whereas $A_x^{\mathscr{C}} = -\tfrac{1}{2}B_z y$, $A_y^{\mathscr{C}} = \tfrac{1}{2}B_z x$, $A_z^{\mathscr{C}} = 0$. The magnetic properties, in this gauge, are written[4–6]

$$\chi_{xx}^{d\mathscr{L}} = -\frac{e^2}{m_e c^2}\left\langle a\left|\sum_{i=1}^n y_i^2\right|a\right\rangle, \quad \chi_{xy}^{d\mathscr{L}} = 0,\dots \tag{41}$$

(other tensor components are obtained by cyclic permutation of the indices x, y, and z). Off-diagonal diamagnetic components vanish for any coordinate system in the Landau gauge. The paramagnetic contribution is

$$\chi_{xx}^{p\mathscr{L}} = \frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left[\left\langle a\left|\sum_{i=1}^n (yp_z)_i\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (yp_z)_i\right|a\right\rangle\right],$$

$$\chi_{xy}^{p\mathscr{L}} = \frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left[\left\langle a\left|\sum_{i=1}^n (yp_z)_i\right|j\right\rangle \right.$$

$$\left. \times \left\langle j\left|\sum_{i=1}^n (zp_x)_i\right|a\right\rangle\right]. \tag{42}$$

The diamagnetic contribution to nuclear shielding is

$$\sigma_{xx}^{dI\mathscr{L}} = \frac{e}{m_e c^2} \left\langle a \left| \sum_{i=1}^{n} y_i E_{Iy}^i \right| a \right\rangle,$$

$$\sigma_{yx}^{dI\mathscr{L}} = -\frac{e}{m_e c^2} \left\langle a \left| \sum_{i=1}^{n} y_i E_{Ix}^i \right| a \right\rangle, \tag{43}$$

etc. For any coordinate system, $\sigma_{xy}^{dI\mathscr{L}} = \sigma_{yz}^{dI\mathscr{L}} = \sigma_{zx}^{dI\mathscr{L}} = 0$. The paramagnetic contribution is

$$\sigma_{xx}^{pI\mathscr{L}} = -\frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}}$$

$$\times \mathscr{R} \left[\langle a | M_{Ix}^n | j \rangle \left\langle j \left| \sum_{i=1}^{n} (yp_z)_i \right| a \right\rangle \right],$$

$$\sigma_{xy}^{pI\mathscr{L}} = -\frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \tag{44}$$

$$\times \mathscr{R} \left[\langle a | M_{Ix}^n | j \rangle \left\langle j \left| \sum_{i=1}^{n} (zp_x)_i \right| a \right\rangle \right],$$

etc. The conditions for invariance

$$\chi_{\alpha\beta}^{\mathscr{L}} = \chi_{\alpha\beta}^{\mathscr{C}}, \tag{45}$$

$$\sigma_{\alpha\beta}^{I\mathscr{L}} = \sigma_{\alpha\beta}^{I\mathscr{C}}, \tag{46}$$

imply, according to Eqs. (25)–(30), that the sum rules for susceptibilities,

$$(L_x, \dot{\mathscr{V}}_{yz})_{-1} = \frac{m_e}{2} \left\langle a \left| \sum_{i=1}^{n} (y_i^2 - z_i^2) \right| a \right\rangle, \tag{47}$$

$$(L_x, \dot{\mathscr{V}}_{zx})_{-1} + (L_y, \dot{\mathscr{V}}_{yz})_{-1} = 0, \tag{48}$$

$$(\dot{\mathscr{V}}_{yz}, \dot{\mathscr{V}}_{yz})_{-1} = \frac{m_e}{4} \left\langle a \left| \sum_{i=1}^{n} (y_i^2 + z_i^2) \right| a \right\rangle,$$

$$(\dot{\mathscr{V}}_{yz}, \dot{\mathscr{V}}_{zx})_{-1} = \frac{m_e}{4} \left\langle a \left| \sum_{i=1}^{n} (xy)_i \right| a \right\rangle, \tag{49}$$

and for nuclear shielding,

$$(M_{Ix}^n, \dot{\mathscr{V}}_{yz})_{-1} = \frac{m_e}{2e} \left\langle a \left| \sum_{i=1}^{n} (y_i E_{Iy}^i - z_i E_{Iz}^i) \right| a \right\rangle,$$

$$(M_{Ix}^n, \dot{\mathscr{V}}_{zx})_{-1} = \frac{m_e}{2e} \left\langle a \left| \sum_{i=1}^{n} x_i E_{Iy}^i \right| a \right\rangle, \tag{50}$$

$$(M_{Iy}^n, \dot{\mathscr{V}}_{yz})_{-1} = -\frac{m_e}{2e} \left\langle a \left| \sum_{i=1}^{n} y_i E_{Ix}^i \right| a \right\rangle,$$

must be fulfilled (other tensor components are obtained by cyclic permutation of the indices x, y, and z). In these equations the off-diagonal hypervirial relation

$$\langle j | \mathscr{V}_{\alpha\beta} | a \rangle = \frac{im_e}{2} \omega_{ja} \left\langle j \left| \sum_{i=1}^{n} (r_\alpha r_\beta)_i \right| a \right\rangle, \tag{51}$$

for the virial operator, compare for Refs. 1 and 10,

$$\mathscr{V}_{\alpha\beta} = \frac{1}{2} \sum_{i=1}^{n} (r_\alpha p_\beta + p_\alpha r_\beta)_i$$

$$= \frac{im_e}{2\hbar} \left[H^{(0)}, \sum_{i=1}^{n} (r_\alpha r_\beta)_i \right]$$

$$= \sum_{i=1}^{n} (r_\alpha p_\beta)_i - \frac{1}{2} \epsilon_{\alpha\beta\gamma} L_\gamma - \frac{i\hbar n}{2} \delta_{\alpha\beta}, \tag{52}$$

has been introduced (other symbols have the same meaning as in Refs. 4–6), so that, for instance

$$(L_x, \dot{\mathscr{V}}_{yz})_{-1} = \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}(\langle a | L_x | j \rangle \langle j | \dot{\mathscr{V}}_{yz} | a \rangle), \tag{53}$$

etc. Sum rules for other components are obtained by cyclic permutations of the indices.

IV. RESULTS AND DISCUSSION

In previous papers[5,6] magnetic properties have been evaluated *ab initio* for HF, H_2O, NH_3, and CH_4 molecules, within the random-phase approximation (RPA), using Gaussian basis sets of increasing extension and flexibility.

The quality of theoretical magnetic susceptibilities and nuclear shieldings in the Landau gauge was established by direct comparison with corresponding quantities in the Coulomb gauge.[5,6] Moreover, quite general yardsticks of accuracy for first-order perturbed wave functions, relying on Thomas–Reiche–Kuhn sum rules and other constraints for origin independence of theoretical magnetic properties, were used in extended numerical tests.[5,6]

Much more specific criteria for assessing the overall quality of theoretical values in the Landau gauge is provided by Eqs. (47)–(50). According to these constraints, a given basis set should, at the same time, yield accurate representations of $\mathscr{V}_{\alpha\beta}$, the virial operator (52), and of $M_{I\alpha}^n$, the operator for the magnetic field of electrons on nucleus I. The former, defined via position and linear momentum, weighs the electron cloud in the tail regions of molecular domain, the latter, owing to $|\mathbf{r} - \mathbf{R}_I|^{-3}$ factor, samples charge distribution in the environment of the nuclei. It is quite difficult to meet both these requirements with a Gaussian basis set; "steep," as well as diffuse polarization functions should be necessarily included. Therefore, results reported in Tables I–XV provide additional fairly complete information on the ability of electronic wave functions adopted in previous studies to predict magnetic properties within the Landau gauge.[5,6]

For each molecule, four tables, showing theoretical estimates of sum rules (47), (49), and (50) respectively for hydrogen and heavy atom shieldings, are reported in the present study [for all the molecules of the series examined here constraint (48) is satisfied by symmetry]. For HF, NH_3, and CH_4, basis sets I–IV are the same as in Ref. 6. Similarly, for H_2O, basis sets I–IV are those of Ref. 5. The same molecular geometries have been employed here.

Numerical results relative to sum rule (47) for susceptibility evaluated assuming the origin on a hydrogen nucleus, compare for Tables I, V, IX, and XIII demonstrate that basis sets of high quality are necessary to guarantee gauge invariance in a Landau transformation. Less accurate estimates were obtained for HF, where the discrepancies between left

TABLE I. Invariance condition (47) for magnetic susceptibility of the HF molecule.[a]

Basis set	$2(L_y, V_{zx})_{-1}$	$\langle z^2 - x^2 \rangle$
I	−437.4	−491.8
II	−484.4	−492.9
III	−482.7	−493.1
IV	−482.9	−493.1

[a]In atomic units, a.u. Nonvanishing components evaluated with the origin on the hydrogen nucleus (0,0,0.164 550) bohr, $(L_y, V_{yz})_{-1} = -(L_y, V_{zx})_{-1}$, $(L_y, V_{xy})_{-1} = (L_x, V_{zx})_{-1} = (L_x, V_{xy})_{-1} = (L_z, V_{xy})_{-1} = 0$ by symmetry.

TABLE III. Invariance condition (50) for nuclear magnetic shielding of hydrogen in the HF molecule.[a]

Basis set	$2(M_{Hy}^n, V_{zx})_{-1}$	$\langle zE_z - xE_x \rangle$
I	179.6	192.9
II	206.7	193.1
III	194.6	193.1
IV	194.7	193.1

[a]Nonvanishing components evaluated with origin on hydrogen nucleus, (0,0,0.164 550) bohr, $(M_{Hz}^n, V_{xy})_{-1} = 0$, $(M_{Hx}^n, V_{zx})_{-1} = (M_{Hx}^n, V_{yx})_{-1} = (M_{Hy}^n, V_{xy})_{-1} = (M_{Hy}^n, V_{yz})_{-1} = (M_{Hz}^n, V_{yz})_{-1} = (M_{Hz}^n, V_{zx})_{-1} = 0$, $(M_{Hx}^n, V_{yz})_{-1} = -(M_{Hy}^n, V_{zx})_{-1}$ by symmetry.

and right-hand sides of Eq. (47) are ≈10%. On the other hand, the same constraint (47) is very accurately fulfilled for basis sets IV of NH_3 and CH_4, and almost exactly satisfied for basis set VI of H_2O. This trend is confirmed by numerical tests for sum rule (49) (relative to origin on hydrogen nucleus) involving two virial operators $\mathscr{V}_{\alpha\beta}$ compare for Tables II, VI, X and XIV. Possibly, an even more severe probe for wave function accuracy is furnished by this constraint for magnetic susceptibilities, particularly in the case of HF, see Table II. This may imply that the basis sets adopted in the present work are better suited to represent angular momentum operator L_α than virial tensor operator $\mathscr{V}_{\alpha\beta}$. Accordingly, the Hartree–Fock electronic wave functions adopted in the present study could still be improved to insure a higher degree of invariance in a transformation to the Landau gauge.

Constraint (50) for magnetic shieldings was checked assuming the origin on the nucleus in question, see Tables III, VII, XI, and XV for hydrogen and Tables IV, VIII, and XII for the heavy atoms. In the case of carbon shieldings, corresponding sum rule becomes the trivial identity 0=0, exactly fulfilled by symmetry for some tensor components, or virtually satisfied (e.g., to three significant figures) for other components. Accordingly the relative table is not reported.

Theoretical values calculated via Eq. (50) for hydrogen are quite good, and possibly close to the Hartree–Fock limit, as can be achieved by inspection. These findings confirm the conclusions, reached in Refs. 5 and 6, that a procedure based on Landau gauge is viable and well suited for accurate a priori determinations of proton magnetic shielding.

Quite different judgments are arrived at by considering theoretical results in Tables IV, VIII, and XII for sum rules checking gauge invariance of the heavy atoms. In the case of fluorine, compare for Table IV, magnitude and sign of right and left-hand sides of Eq. (50) calculated in the present work

are different. For oxygen and nitrogen magnetic shielding similar discrepancies can be observed in Tables VIII and XII. A similar drawback is usually encountered in evaluating the $(M_{I\alpha}^n, P_\beta)_{-1}$ tensor in analyzing origin dependence of nuclear magnetic shieldings of heavy atoms within the Coulomb gauge.[4–6] Accordingly, a possible explanation for this partial failure may be partially ascribed to lack of steep p functions in the basis sets retained for heavy atoms. In other words, in order to fulfill sum rule (50), one could add other sets of p Gaussian functions with high exponents to heavy nucleus basis, possibly forming an even tempered set.

V. CONCLUSIONS

A series of sum rules for gauge invariance of electronic second-order energy terms in a Landau gauge transformation has been worked out. According to a well-known connection between gauge invariance and the continuity equation,[2] the degree to which these constraints are fulfilled provides physical information on the reliability of a calculation of magnetic properties, i.e., charge and current conservation in the presence of magnetic field. These sum rules can be rewritten as hypervirial theorems,[1] which hold exactly for optimum variational wave functions obtained via sets of trial functions invariant to the unitary transformation induced by the Landau change of gauge. Within the algebraic approximation, i.e., expanding the trial functions over a basis set, the constraints for gauge invariance are only approximately obeyed, depending on the quality of the set, i.e., its completeness with respect to various operators involved. Accordingly, the results obtained analyzing the sum rules are useful to sample a given basis set, and furnish clear indications to improve it. In addition, they help understand the conditions

TABLE II. Invariance condition (49) for magnetic susceptibility of the HF molecule.[a]

Basis set	$4(V_{xy}, V_{xy})_{-1}$	$\langle x^2 + y^2 \rangle$	$4(V_{zx}, V_{zx})_{-1}$	$\langle z^2 + x^2 \rangle$
I	120.1	437.7	1536.3	1913.2
II	143.5	450.6	1741.4	1929.3
III	384.5	449.8	1856.0	1929.2
IV	385.0	450.1	1858.3	1929.5

[a]In atomic units, a.u. Nonvanishing components evaluated with the origin on the hydrogen nucleus, (0,0,0.164 550) bohr, $(V_{yz}, V_{yz})_{-1} = (V_{zx}, V_{zx})_{-1}$, $(V_{yx}, V_{zx})_{-1} = (V_{yz}, V_{zx})_{-1} = (V_{xy}, V_{yz})_{-1} = 0$ by symmetry.

TABLE IV. Invariance condition (50) for nuclear magnetic shielding of fluorine in the HF molecule.[a]

Basis set	$2(M_{Fy}^n, V_{zx})_{-1}$	$\langle zE_z - xE_x \rangle$
I	−61.6	0.2
II	−17.5	1.0
III	−3.0	1.2
IV	−10.0	1.2

[a]Nonvanishing components evaluated with origin on fluorine nucleus, (0,0, −0.087 30) bohr, $(M_{Fx}^n, V_{yz})_{-1} = -(M_{Fy}^n, V_{zx})_{-1}$, and other components vanish by symmetry.

TABLE V. Invariance condition (47) for magnetic susceptibility of the H_2O molecule.[a]

Basis set	$2(L_z,V_{xy})_{-1}$	$\langle x^2-y^2\rangle$	$2(L_y,V_{zx})_{-1}$	$\langle z^2-x^2\rangle$	$2(L_x,V_{yz})_{-1}$	$\langle y^2-z^2\rangle$	$2(L_y,V_{xy})_{-1}$	$\langle yz\rangle$
I	339.1	394.9	−164.5	−181.4	−185.5	−213.5	214.3	244.6
II	311.9	392.8	−138.5	−182.0	−179.1	−210.8	185.3	245.4
III	344.5	391.6	−171.5	−181.8	−187.8	−209.8	224.7	246.2
IV	379.9	392.4	−180.5	−181.6	−205.4	−210.8	238.8	245.5
V	385.1	392.3	−183.1	−181.3	−208.0	−210.9	242.3	245.4
VI	390.2	392.8	−181.9	−182.1	−209.3	−210.7	244.0	245.4

[a]In a.u. Nonvanishing components evaluated with origin on hydrogen nucleus, (0,1.431 53,−0.985 266) bohr, $(L_x,V_{zx})_{-1}=(L_x,V_{xy})_{-1}=0$ by symmetry.

TABLE VI. Invariance condition (49) for magnetic susceptibility of the H_2O molecule.[a]

Basis set	$4(V_{xy},V_{xy})_{-1}$	$\langle x^2+y^2\rangle$	$4(V_{zx},V_{zx})_{-1}$	$\langle z^2+x^2\rangle$	$4(V_{yz},V_{yz})_{-1}$	$\langle y^2+z^2\rangle$	$4(V_{xy},V_{zx})_{-1}$	$\langle yz\rangle$
I	1307.6	1768.9	758.5	1128.3	1964.6	2313.0	−341.7	−366.9
II	1350.9	1777.9	738.4	1145.4	1901.0	2323.9	−287.1	−368.1
III	1325.5	1774.6	775.6	1145.1	1980.4	2320.0	−356.2	−369.3
IV	1595.1	1775.7	895.8	1143.3	2229.2	2320.4	−370.2	−368.2
V	1632.4	1777.0	919.8	1144.2	2263.0	2321.0	−375.3	−368.0
VI	1737.2	1776.0	1095.1	1143.8	2293.5	2322.1	−368.1	−368.0

[a]In a.u. Nonvanishing components evaluated with origin on hydrogen nucleus, (0,1.431 53,−0.985 266) a.u., $(V_{zx},V_{yz})_{-1}=(V_{xy},V_{yz})_{-1}=0$, $\langle xy\rangle=\langle xz\rangle=0$ by symmetry.

TABLE VII. Invariance condition (50) for hydrogen magnetic shielding in the H_2O molecule.[a]

Basis set	$2(M_{Hz}^n,V_{xy})_{-1}$	$\langle xE_x-yE_y\rangle$	$2(M_{Hy}^n,V_{zx})_{-1}$	$\langle zE_z-xE_x\rangle$	$2(M_{Hx}^n,V_{yz})_{-1}$	$\langle yE_y-zE_z\rangle$	$2(M_{Hy}^n,V_{xy})_{-1}$	$\langle zE_y\rangle$	$2(M_{Hz}^n,V_{zx})_{-1}$
I	−98.8	−109.0	55.8	58.9	44.3	50.1	−72.6	−78.5	78.1
II	−78.8	−109.2	42.7	58.6	35.7	50.5	−54.3	−78.3	59.5
III	−111.0	−109.1	60.8	58.5	43.1	50.6	−77.6	−78.5	86.0
IV	−110.4	−109.2	62.4	58.7	48.5	50.6	−79.8	−78.4	87.2
V	−112.9	−109.3	63.9	58.7	49.5	50.6	−82.3	−78.5	90.0
VI	−111.0	−109.4	60.1	58.8	50.6	50.6	−79.8	−78.4	80.8

[a]Nonvanishing components evaluated with the origin on the hydrogen nucleus, (0,1.431 53,−0.985 266) bohr, $\langle yE_z\rangle=\langle zE_y\rangle$, $(M_{Hx}^n,V_{zx})_{-1}=(M_{Hx}^n,V_{xy})_{-1}=(M_{Hy}^n,V_{yz})_{-1}=(M_{Hz}^n,V_{yz})_{-1}=0$ by symmetry. In the HF limit $2(M_{Hy}^n,V_{xy})_{-1}=\langle yE_z\rangle=-2(M_{Hz}^n,V_{zx})_{-1}$.

TABLE VIII. Invariance condition (50) for oxygen magnetic shielding in the H_2O molecule.[a]

Basis set	$2(M_{Oz}^n,V_{xy})_{-1}$	$\langle xE_x-yE_y\rangle$	$2(M_{Oy}^n,V_{zx})_{-1}$	$\langle zE_z-xE_x\rangle$	$2(M_{Ox}^n,V_{yz})_{-1}$	$\langle yE_y-zE_z\rangle$
I	19.1	−2.8	−32.4	2.2	−23.3	0.6
II	−24.5	−3.6	25.0	2.6	−8.8	1.0
III	−55.8	−3.1	58.0	2.2	21.6	0.9
IV	3.5	−3.8	22.0	2.7	−5.6	1.1
V	18.4	−3.8	4.7	2.7	−6.2	1.1
VI	5.2	−4.1	−2.9	3.1	−1.8	1.1

[a]Nonvanishing components evaluated with the origin on the oxygen nucleus, (0,0,0.124 144) bohr, $\langle yE_z\rangle=\langle zE_y\rangle=\langle xE_z\rangle=\langle zE_x\rangle=\langle xE_y\rangle=\langle yE_x\rangle=0$, $(M_{Ox}^n,V_{zx})_{-1}=(M_{Oy}^n,V_{zy})_{-1}=(M_{Oy}^n,V_{zy})_{-1}=(M_{Oz}^n,V_{zy})_{-1}=0$ by symmetry. In the HF limit $2(M_{Oy}^n,V_{yx})_{-1}=\langle yE_z\rangle=-2(M_{Oz}^n,V_{zx})_{-1}$.

TABLE IX. Invariance condition (47) for magnetic susceptibility of the NH_3 molecule.[a]

Basis set	$2(L_z,V_{xy})_{-1}$	$\langle x^2-y^2 \rangle$	$2(L_y,V_{zx})_{-1}$	$\langle z^2-x^2 \rangle$	$2(L_x,V_{yz})_{-1}$	$\langle y^2-z^2 \rangle$	$2(L_x,V_{xy})_{-1}$	$\langle zx \rangle$
I	−517.1	−556.7	465.0	527.9	34.5	28.8	168.4	177.7
II	−556.0	−556.7	511.6	523.9	36.1	32.9	178.2	178.4
III	−555.9	−556.7	515.0	524.0	34.3	32.8	178.3	178.3
IV	−554.7	−556.7	519.6	524.3	32.7	32.4	177.9	178.4

[a]In a.u. Nonvanishing components evaluated with origin on hydrogen nucleus, $(-0.885\,50, 1.533\,73, -0.591\,96)$ bohr, $(L_x,V_{zx})_{-1}=(L_y,V_{xy})_{-1}=0$, $\langle xy \rangle = \langle yz \rangle = 0$ by symmetry.

TABLE X. Invariance condition (49) for magnetic susceptibility of the NH_3 molecule.[a]

Basis set	$4(V_{xy},V_{xy})_{-1}$	$\langle x^2+y^2 \rangle$	$4(V_{zx},V_{zx})_{-1}$	$\langle z^2+x^2 \rangle$	$4(V_{yz},V_{yz})_{-1}$	$\langle y^2+z^2 \rangle$	$4(V_{yz},V_{xy})_{-1}$	$\langle zx \rangle$
I	2333.6	2658.2	2291.6	2744.5	793.0	1074.3	236.2	266.6
II	2561.2	2661.8	2582.1	2760.4	939.0	1090.2	265.8	267.5
III	2599.1	2662.6	2643.5	2760.9	995.4	1090.7	266.8	267.5
IV	2633.8	2663.3	2714.5	2760.5	1057.7	1090.3	267.3	267.6

[a]In a.u. Nonvanishing components evaluated with the origin on hydrogen nucleus, $(-1.771\,00, 0.0, -0.591\,96)$ bohr, $(V_{yz},V_{zx})_{-1}=(V_{zx},V_{yz})_{-1}=0$, $\langle xy \rangle=0$ by symmetry.

TABLE XI. Invariance condition (50) for hydrogen magnetic shielding in the NH_3 molecule.[a]

Basis set	$2(M_{Hz}^n,V_{xy})_{-1}$	$\langle xE_x-yE_y \rangle$	$2(M_{Hy}^n,V_{zx})_{-1}$	$\langle zE_z-xE_x \rangle$	$2(M_{Hx}^n,V_{yz})_{-1}$	$\langle yE_y-zE_z \rangle$	$2(M_{Hx}^n,V_{xy})_{-1}$	$\langle xE_z \rangle$	$2(M_{Hz}^n,V_{yz})_{-1}$
I	118.1	123.8	−100.2	−108.0	−18.0	−15.8	43.4	45.5	−47.4
II	127.9	124.0	−109.1	−108.4	−17.1	−15.6	45.8	45.3	−48.9
III	128.2	124.0	−109.5	−108.4	−17.1	−15.6	46.1	45.3	−48.6
IV	125.8	123.9	−108.9	−108.4	−16.0	−15.5	45.8	45.3	−46.4

[a]Nonvanishing components evaluated with origin on hydrogen nucleus, $(-1.771\,00, 0.0, -0.591\,96)$ a.u., $(M_{Hx}^n,V_{zx})_{-1}=(M_{Hy}^n,V_{xy})_{-1}=(M_{Hy}^n,V_{yz})_{-1}=(M_{Hz}^n,V_{zx})_{-1}=0$ by symmetry. In the HF limit $2(M_{Hx}^n,V_{xy})_{-1}=\langle xE_z \rangle=\langle zE_x \rangle=-2(M_{Hz}^n,V_{yz})_{-1}$.

TABLE XII. Invariance condition (50) for nitrogen magnetic shielding in the NH_3 molecule.[a]

Basis set	$2(M_{Ny}^n,V_{zx})_{-1}$	$\langle zE_z-xE_x \rangle$	$2(M_{Nx}^n,V_{yz})_{-1}$	$\langle yE_y-zE_z \rangle$	$2(M_{Nx}^n,V_{xy})_{-1}$	$\langle xE_z \rangle$
I	28.4	−3.7	−28.4	3.7	−9.2	0.0
II	−1.1	−4.4	1.1	4.4	−2.3	0.0
III	2.9	−4.4	−2.9	4.4	0.2	0.0
IV	0.2	−4.6	−0.1	4.6	0.4	0.0

[a]Nonvanishing components evaluated with origin on nitrogen nucleus, $(0,0,0.127\,80)$ bohr, $2(M_{Nz}^n,V_{xy})_{-1}=-0.01$, only for basis set IV.

TABLE XIII. Invariance condition (47) for magnetic susceptibility in the CH_4 molecule.[a]

Basis set	$2(L_z,V_{xy})_{-1}$	$\langle x^2-y^2 \rangle$	$2(L_y,V_{zx})_{-1}$	$\langle z^2-x^2 \rangle$	$2(L_y,V_{xy})_{-1}$	$\langle yz \rangle$
I	466.6	503.0	−239.2	−251.5	−330.0	−355.7
II	499.4	503.0	−252.8	−251.5	−353.1	−355.7
III	500.7	503.0	−253.5	−251.5	−354.1	−355.7
IV	501.7	503.0	−251.5	−251.5	−354.7	−355.7

[a]In a.u. Nonvanishing components evaluated with the origin on the hydrogen nucleus, $(0,1.683\,396,1.190\,341)$ bohr, $(L_x,V_{zx})_{-1}=(L_x,V_{xy})_{-1}=0$, $\langle xy \rangle=\langle xz \rangle=0$, $(L_y,V_{zx})_{-1}=(L_x,V_{yz})_{-1}$ by symmetry.

TABLE XIV. Invariance condition (49) for magnetic susceptibility of the CH_4 molecule.[a]

Basis set	$4(V_{xy},V_{xy})_{-1}$	$\langle x^2+y^2\rangle$	$4(V_{zx},V_{zx})_{-1}$	$\langle z^2+x^2\rangle$	$4(V_{yz},V_{yz})_{-1}$	$\langle y^2+z^2\rangle$	$4(V_{xy},V_{xz})_{-1}$	$\langle yz\rangle$
I	2501.0	2774.7	1826.4	2020.2	3155.9	3529.2	507.4	533.5
II	2682.2	2779.4	1929.0	2024.9	3389.7	3533.9	536.3	533.5
III	2686.1	2779.3	1931.7	2024.8	3395.8	3533.9	537.8	533.5
IV	2747.3	2779.3	2002.8	2024.8	3499.8	3533.8	533.5	533.5

[a]Nonvanishing components evaluated with the origin on hydrogen nucleus, (0,1.683 396 3,1.190 340 9) a.u., $(V_{zx},V_{yz})_{-1}=(V_{xy},V_{yz})_{-1}=0$, $\langle xy\rangle=\langle zx\rangle$ by symmetry.

TABLE XV. Invariance condition (50) for hydrogen magnetic shielding in the CH_4 molecule.[a]

Basis set	$2(M^n_{Hz},V_{xy})_{-1}$	$\langle xE_x-yE_y\rangle$	$2(M^n_{Hy},V_{zx})_{-1}$	$\langle zE_z-xE_x\rangle$	$2(M^n_{Hx},V_{yz})_{-1}$	$\langle yE_y-zE_z\rangle$	$2(M^n_{Hy},V_{xy})_{-1}$	$\langle yE_z\rangle$	$2(M^n_{Hz},V_{zx})_{-1}$
I	−74.3	−79.2	38.0	39.6	38.0	39.6	52.5	56.0	−56.0
II	−79.8	−79.3	40.3	39.6	40.3	39.6	56.5	56.0	−57.0
III	−80.3	−79.3	40.5	39.6	40.5	39.6	56.7	56.0	−57.3
IV	−79.7	−79.3	39.8	39.6	39.8	39.6	56.4	56.0	−56.3

[a]Nonvanishing components evaluated with the origin on hydrogen nucleus, (0,1.683 396,1.190 341) bohr, $(M^n_{Hx},V_{zx})_{-1}=(M^n_{Hx},V_{xy})_{-1}=(M^n_{Hy},V_{yz})_{-1}=(M^n_{Hz},V_{yz})_{-1}=0$ by symmetry; $2(M^n_{Hy},V_{xy})_{-1}=\langle yE_z\rangle=\langle zE_y\rangle=-2(M^n_{Hz},V_{zx})_{-1}=0$ in the HF limit.

that are to be fulfilled to guarantee that, starting from an accurate wave function, the gauge transformed wave function is also a good one.

Extended Gaussian basis sets have been adopted for HF, H_2O, NH_3, and CH_4 molecules. The calculations show that the sum rules examined in this work yield extremely severe tests of accuracy for SCF wave functions; the basis set must contain diffuse polarization functions to satisfy constraints (47)–(49) (see text), i.e., an accurate representation of the virial tensor operator should be provided to ensure invariant magnetic susceptibilities.

This requirement is comparably easier to fulfill than that necessary for invariance of magnetic shielding, compare for sum rules (50). In this case, in addition to guaranteeing a reliable representation of the virial operator, the basis set for heavy nuclei must also be enriched with steep polarization functions to accurately represent the operator for magnetic field of electrons on the nucleus in question.

ACKNOWLEDGMENTS

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