# Calculation of molecular magnetic properties within the Landau gauge

M. B. Ferraro and T. E. Herr
*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, 1428 Ciudad Universitaria, Pabellón I, Buenos Aires, Argentina*

P. Lazzeretti, M. Malagoli, and R. Zanasi
*Dipartimento di Chimica dell'Università degli Studi di Modena, Via Campi 183, 41100 Modena, Italy*
(Received 8 October 1991)

A theoretical procedure for calculating magnetic susceptibility and nuclear magnetic shieldings in molecules in the presence of a spatially uniform time-independent magnetic field, within the Landau gauge for the vector potential, is described. Sum rules for charge and current conservation and gauge invariance have been derived. A computational scheme based on the random-phase approximation has been used to calculate magnetic susceptibility and shielding tensors in the water molecule, adopting fairly flexible Gaussian basis sets of large size. The results show that very accurate molecular wave functions are needed to obtain paramagnetic contributions to the magnetic susceptibility of the same quality as those obtainable within the Coulomb gauge for the vector potential. The theoretical nuclear magnetic shielding tensors in the Landau gauge are characterized by the same quality as those in the Coulomb gauge.

PACS number(s): 31.90.+s, 35.20.My, 75.20.Ck

## I. INTRODUCTION

Theoretical determinations of magnetic properties of molecules in the presence of a time-independent and spatially uniform magnetic field are usually carried out within the Coulomb prescription [1] for the gauge of vector potential $\mathbf{A}$. Accordingly, the molecular Born-Oppenheimer Hamiltonian is written in terms of a divergenceless $\mathbf{A}^{\mathcal{C}}(\mathbf{r})=\frac{1}{2}\mathbf{B}\times\mathbf{r}$. The magnetic field $\mathbf{B}=\nabla\times\mathbf{A}^{\mathcal{C}}$ is invariant under a gauge transformation [1,2],

$$\mathbf{A}^{\mathcal{C}}\rightarrow\mathbf{A}^{\mathcal{C}}+\nabla\Lambda ,$$

where $\Lambda(\mathbf{r})$ is an arbitrary function of the position coordinate.

Under the change of gauge, the wave function $\psi$ and the Hamiltonian $h$ of a particle with charge $q$ undergo corresponding gauge transformations [2]:

$$\psi\rightarrow\psi'=\psi\exp\left[\frac{iq}{\hbar c}\Lambda\right] ,$$

$$h\rightarrow h'=\exp\left[\frac{iq}{\hbar c}\Lambda\right]h\exp\left[-\frac{iq}{\hbar c}\Lambda\right] ,$$

leaving invariant the Schrödinger equation $h\psi=\varepsilon\psi$ of the particle.

Hence, molecular magnetic properties evaluated via quantum-mechanical approaches must be gauge independent, which is a fundamental physical requirement. Whenever approximate methods are adopted, the degree to which the constraints for gauge invariance are satisfied provides a yardstick of accuracy for the computational scheme and a fundamental test of quality for the molecular wave function. In particular, if the algebraic approximation is used, the essential features of a basis set, i.e., optimum size, flexibility, degree of completeness, and ability to describe the magnetic perturbation, can be easily judged by analyzing appropriate sum rules [3,4].

In practice, the gauge transformations that have been studied so far amount merely to a change of origin of the coordinate system $\mathbf{r}'\rightarrow\mathbf{r}''=\mathbf{r}'+\mathbf{d}$, where $\mathbf{d}$ is an arbitrary vector, i.e., to a limited class of functions $\Lambda$, such that

$$\mathbf{A}^{\mathcal{C}''}=\mathbf{A}^{\mathcal{C}'}+\nabla\Lambda,\quad \Lambda\equiv\mathbf{d}\cdot\mathbf{A}^{\mathcal{C}'},\quad \mathbf{A}^{\mathcal{C}'}=\mathbf{A}^{\mathcal{C}}(\mathbf{r}-\mathbf{r}') .$$

Much more general choices for the gauge function $\Lambda$ can, of course, be made. A particularly interesting gauge transformation of vector potential has been devised by Landau [1,2,5], leading to a quite simple form for the Hamiltonian.

The present paper sets out to investigate the suitability of the Landau gauge as an alternative choice with respect to the customary Coulomb's gauge for calculating molecular magnetic properties. An essential aim is also that of obtaining a set of sum rules for gauge invariance of calculated magnetic properties which may serve as independent *a priori* criteria for the accuracy of molecular wave functions, i.e., when comparison with experimental data is difficult.

To this end, a series of basis sets of Gaussian functions have been considered for extended studies on the water molecule. Perturbed coupled Hartree-Fock (CHF) and random-phase-approximation (RPA) methods implemented in efficient computer programs [6–8] have been employed to calculate magnetic susceptibility and nuclear magnetic shielding tensors.

## II. MAGNETIC SUSCEPTIBILITY WITHIN THE LANDAU GAUGE

Within the Coulomb gauge, the transverse vector potential associated to spatially uniform, time-independent

 

magnetic field $B_\alpha$ is, using tensor notation [1],

$$A_\alpha^{\mathcal{C}} = \tfrac{1}{2}\epsilon_{\alpha\beta\gamma} B_\beta r_\gamma \tag{1}$$

(sum over repeated Greek indices is implied throughout this paper). The Landau gauge [1,2] is obtained introducing the gauge function

$$\Lambda = \tfrac{1}{2}(B_x yz + B_y zx + B_z xy) \tag{2}$$

and the gauge transformation (leaving $B_\alpha = \epsilon_{\alpha\beta\gamma}\nabla_\beta A_\gamma^{\mathcal{L}}$ invariant)

$$A_\alpha^{\mathcal{L}} = A_\alpha^{\mathcal{C}} + \nabla_\alpha \Lambda = B_\beta r_\gamma \ , \tag{3}$$

where $\alpha$, $\beta$, and $\gamma$ are an even cyclic permutation of $x$, $y$, and $z$. According to Eq. (3), also, the Landau vector potential is divergenceless, i.e.,

$$\nabla_\alpha A_\alpha^{\mathcal{L}} = 0 \ . \tag{4}$$

The Hamiltonian within the Coulomb gauge of an electron, with mass $m_e$, charge $-e$, position $\mathbf{r}$, and linear momentum $\mathbf{p}$,

$$h_{\mathcal{C}} = \frac{1}{2m_e}\left[p_\alpha + \frac{e}{c} A_\alpha^{\mathcal{C}}\right]^2 , \tag{5}$$

under the gauge transformation (3) becomes

$$h_{\mathcal{C}} \to h_{\mathcal{L}} = h_0 + h_{\mathcal{L}}^{(1)} + \tfrac{1}{2} h_{\mathcal{L}}^{(2)} \ , \tag{6}$$

where

$$h_0 = \frac{1}{2m_e} p_\alpha^2 \ , \tag{7}$$

$$h_{\mathcal{L}}^{(1)} = \frac{e}{m_e c} A_\alpha^{\mathcal{L}} p_\alpha = \frac{e}{m_e c}(B_y z p_x + B_z x p_y + B_x y p_z) \ , \tag{8}$$

$$h_{\mathcal{L}}^{(2)} = \frac{e^2}{m_e c^2} A_\alpha^{\mathcal{L}} A_\alpha^{\mathcal{L}} = \frac{e^2}{m_e c^2}(B_x^2 y^2 + B_y^2 z^2 + B_z^2 x^2) \ . \tag{9}$$

Let us now consider a molecule with $n$ electrons and $N$ nuclei. We denote by $\mathbf{r}_i$, $\mathbf{p}_i$, and $\boldsymbol{l}_i = \mathbf{r}_i \times \mathbf{p}_i$, the position and linear and angular momentum of the $i$th electron and by $\mathbf{R}_I$ and $Z_I e$, the position and charge of the $I$th nucleus. The unperturbed Born-Oppenheimer Hamiltonian of the electrons is

$$H_0 = \sum_{i=1}^{n}\left[\frac{p_i^2}{2m_e} - e^2\sum_{I=1}^{N} Z_I |\mathbf{r}_i - \mathbf{R}_I|^{-1} + \frac{e^2}{2}\sum_{\substack{j=1 \\ j\neq i}}^{n} |\mathbf{r}_i - \mathbf{r}_j|^{-1}\right] + \frac{e^2}{2}\sum_{I=1}^{N}\sum_{\substack{J=1 \\ J\neq I}}^{N} Z_I Z_J |\mathbf{R}_I - \mathbf{R}_J|^{-1} \ , \tag{10}$$

with eigenfunctions $|j\rangle$. In the presence of the magnetic field $B_\alpha$, the first- and second-order Hamiltonians within the Landau gauge become

$$H_{\mathcal{L}}^{B} = \frac{e}{m_e c}\sum_{i=1}^{n} (A_\alpha^{\mathcal{L}} p_\alpha)_i \ , \tag{11}$$

$$H_{\mathcal{L}}^{BB} = \frac{e^2}{m_e c^2}\left[B_x^2 \sum_{i=1}^{n} y_i^2 + B_y^2 \sum_{i=1}^{n} z_i^2 + B_z^2 \sum_{i=1}^{n} x_i^2\right] , \tag{12}$$

so that the total Hamiltonian is

$$H_{\mathcal{L}} = H_0 + H_{\mathcal{L}}^{B} + \tfrac{1}{2} H_{\mathcal{L}}^{BB} \ . \tag{13}$$

In the reference state $|a\rangle$ the diamagnetic contribution to the magnetic susceptibility tensor [9] is

$$\chi_{xx}^{d\mathcal{L}} = -\frac{\partial^2}{\partial B_x^2}\langle a | \tfrac{1}{2} H_{\mathcal{L}}^{BB} | a \rangle = -\frac{e^2}{m_e c^2}\left\langle a \left| \sum_{i=1}^{n} y_i^2 \right| a \right\rangle ,$$

$$\chi_{xy}^{d\mathcal{L}} = 0 \ , \tag{14}$$

$$\cdots \ .$$

The other tensor components are obtained by cyclic permutation of the indices $x$, $y$, and $z$. It is worthy of notice that the off-diagonal components of the diamagnetic contribution are vanishing for any arbitrary coordinate system within the Landau gauge.

The paramagnetic contributions to the magnetic susceptibility tensor [9] are obtained from perturbation theory. They are

$$\chi_{xx}^{p\mathcal{L}} = \frac{e^2}{m_e^2 c^2 \hbar}\sum_{j(\neq a)} \frac{2}{\omega_{ja}} \mathrm{Re}\left[\left\langle a \left| \sum_{i=1}^{n} (y p_z)_i \right| j \right\rangle \left\langle j \left| \sum_{i=1}^{n} (y p_z)_i \right| a \right\rangle\right] ,$$

$$\chi_{xy}^{p\mathcal{L}} = \frac{e^2}{m_e^2 c^2 \hbar}\sum_{j(\neq a)} \frac{2}{\omega_{ja}} \mathrm{Re}\left[\left\langle a \left| \sum_{i=1}^{n} (y p_z)_i \right| j \right\rangle \left\langle j \left| \sum_{i=1}^{n} (z p_x)_i \right| a \right\rangle\right] , \tag{15}$$

$$\cdots \ ,$$

with cyclic permutation of the indices for the other tensor components. In these formulas $\hbar\omega_{ja} = E_j - E_a$ is the transition energy between the $|j\rangle$ excited state and the $|a\rangle$ reference state. The paramagnetic contribution is a symmetric tensor, as in the Coulomb gauge. Whereas the diamagnetic term (14) is always diagonal, the paramagnetic term (15) is diagonal only within its principal axis system.

As a consequence of the fact that the diamagnetic contribution (14) is diagonal, the off-diagonal components of the susceptibility tensor are paramagnetic, and, quite remarkably, they are origin independent within the Landau

gauge. From Eq. (15) one can realize that paramagnetic susceptibilities in the Landau gauge are simpler to calculate than in the Coulomb's gauge when a Gaussian basis set is used. In fact, operating with the canonical momentum $\mathbf{p}=-i\hbar\nabla$ on a given Gaussian, i.e., differentiating, gives rise to a linear combination of two Gaussians, which is very easy to handle, every type of integral appearing in Eq. (15) being eventually reducible to a sum of overlap integrals.

## III. NUCLEAR MAGNETIC SHIELDING IN THE LANDAU GAUGE

Let us suppose that nucleus $I$ carries an intrinsic magnetic dipole $\boldsymbol{\mu}_I$. The vector potential acting on electron $i$ due to such a nuclear dipole is

$$A_{i\alpha}^{\mu_I}=\frac{1}{e}\epsilon_{\alpha\beta\gamma}\mu_{I\beta}E_{I\gamma}^{i} , \tag{16}$$

where

$$E_{I\gamma}^{i}=e\frac{r_{i\gamma}-R_{I\gamma}}{|\mathbf{r}_i-\mathbf{R}_I|^3} \tag{17}$$

is the electric field of electron $i$ on nucleus $I$. In the presence of the nuclear magnetic dipole two extra terms enter Hamiltonian (13):

$$H^{\mu_I}=-\mu_{I\alpha}B_{I\alpha}^{n} \tag{18}$$

and

$$H_{\mathcal{L}}^{\mu_I B}=\frac{e^2}{m_e c^2}\sum_{i=1}^{n}(A_{\alpha}^{\mu_I}A_{\alpha}^{\mathcal{L}})_i , \tag{19}$$

where the operator for the magnetic field of electrons on nucleus $I$ in the absence of an external magnetic field is

$$B_{I\alpha}^{n}=-\frac{e}{m_e c}M_{I\alpha}^{n},\quad M_{I\alpha}^{n}=\frac{1}{e}\epsilon_{\alpha\beta\gamma}\sum_{i=1}^{n}E_{I\beta}^{i}p_{i\gamma} . \tag{20}$$

Within the Landau gauge for the vector potential, the diamagnetic contribution to the nuclear magnetic shielding [10] of nucleus $I$ becomes

$$\begin{aligned}\sigma_{xx}^{dI\mathcal{L}}&=\frac{\partial^2}{\partial\mu_{Ix}\partial B_x}\langle a|H_{\mathcal{L}}^{\mu_I B}|a\rangle\\&=\frac{e}{m_e c^2}\left\langle a\left|\sum_{i=1}^{n}y_i E_{Iy}^{i}\right|a\right\rangle ,\\\sigma_{yx}^{dI\mathcal{L}}&=\frac{\partial^2}{\partial\mu_{Iy}\partial B_x}\langle a|H_{\mathcal{L}}^{\mu_I B}|a\rangle\\&=-\frac{e}{m_e c^2}\left\langle a\left|\sum_{i=1}^{n}y_i E_{Ix}^{i}\right|a\right\rangle ,\\&\cdots .\end{aligned} \tag{21}$$

Other nonvanishing components are obtained by cyclic permutation of the indices $x$, $y$, and $z$. It is remarkable that, for any coordinate system,

$$\sigma_{xy}^{dI\mathcal{L}}=\sigma_{yz}^{dI\mathcal{L}}=\sigma_{zx}^{dI\mathcal{L}}=0 , \tag{22}$$

i.e., the diamagnetic contribution to the magnetic shielding tensor of nucleus $I$ in the Landau gauge is represented by a second-rank asymmetric tensor with six nonvanishing components in the absence of symmetry.

The paramagnetic contribution to the magnetic shielding [10] of nucleus $I$ is

$$\begin{aligned}\sigma_{xx}^{pI\mathcal{L}}&=-\frac{e^2}{m_e^2c^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}}\mathrm{Re}\left[\langle a|M_{Ix}^{n}|j\rangle\times\left\langle j\left|\sum_{i=1}^{n}(yp_z)_i\right|a\right\rangle\right] ,\\\sigma_{xy}^{pI\mathcal{L}}&=-\frac{e^2}{m_e^2c^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}}\mathrm{Re}\left[\langle a|M_{Ix}^{n}|j\rangle\times\left\langle j\left|\sum_{i=1}^{n}(zp_x)_i\right|a\right\rangle\right] ,\\&\cdots .\end{aligned} \tag{23}$$

This contribution is an asymmetric tensor with nine independent components in the absence of molecular symmetry. Similarly to the case of magnetic susceptibility, the off-diagonal components $\sigma_{xy}^{I\mathcal{L}}$, $\sigma_{yz}^{I\mathcal{L}}$, and $\sigma_{zx}^{I\mathcal{L}}$ are fully paramagnetic and origin independent.

## IV. CONNECTIONS BETWEEN MAGNETIC PROPERTIES IN LANDAU AND COULOMB GAUGES

Within the Coulomb gauge the diamagnetic contributions to the magnetic susceptibility and to the nuclear magnetic shielding tensors are [3,4]

$$\chi_{\alpha\beta}^{d\mathcal{C}}=-\frac{e^2}{4m_e c^2}\left\langle a\left|\sum_{i=1}^{n}(r_\gamma^2\delta_{\alpha\beta}-r_\alpha r_\beta)_i\right|a\right\rangle , \tag{24}$$

$$\sigma_{\alpha\beta}^{dI\mathcal{C}}=\frac{e}{2m_e c^2}\left\langle a\left|\sum_{i=1}^{n}(r_{i\gamma}E_{I\gamma}^{i}\delta_{\alpha\beta}-r_{i\alpha}E_{I\beta}^{i})\right|a\right\rangle . \tag{25}$$

Therefore, one can easily find, from Eqs. (14) and (21),

$$\begin{aligned}&\chi_{xx}^{d\mathcal{C}}=\tfrac{1}{4}(\chi_{xx}^{d\mathcal{L}}+\chi_{yy}^{d\mathcal{L}}) ,\\&\cdots ,\\&\chi_{\alpha\alpha}^{d\mathcal{C}}=\tfrac{1}{2}\chi_{\alpha\alpha}^{d\mathcal{L}} ,\\&\sigma_{xx}^{dI\mathcal{C}}=\tfrac{1}{2}(\sigma_{xx}^{dI\mathcal{L}}+\sigma_{yy}^{dI\mathcal{L}}) ,\\&\sigma_{yx}^{dI\mathcal{C}}=\tfrac{1}{2}\sigma_{yx}^{dI\mathcal{L}} ,\\&\cdots ,\\&\sigma_{\alpha\alpha}^{dI\mathcal{C}}=\sigma_{\alpha\alpha}^{dI\mathcal{L}} .\end{aligned} \tag{26}$$

In order to obtain the relationships between paramagnetic contributions within the different gauges, we consider the identity

$$\sum_{i=1}^{n}(xp_y)_i=\tfrac{1}{2}L_z+\tfrac{1}{2}\sum_{i=1}^{n}(xp_y+yp_x)_i,\quad L_z=\sum_{i=1}^{n}l_{iz} \tag{27}$$

and the commutator

$$\left[H_0, \sum_{i=1}^{n} (xy)_i\right] = -\frac{i\hbar}{m_e} \sum_{i=1}^{n} (xp_y + yp_x)_i \ . \tag{28}$$

For the off-diagonal matrix elements, one gets

$$\left\langle a \left| \sum_{i=1}^{n} (xp_y)_i \right| j \right\rangle = \tfrac{1}{2}\langle a|L_z|j\rangle - \frac{im_e}{2}\omega_{ja}\left\langle a \left| \sum_{i=1}^{n} (xy)_i \right| j \right\rangle , \tag{29}$$

$$\cdots \ .$$

By cyclic permutation of $x$, $y$ and $z$, the formulas for all tensor components are obtained. From the definitions of the paramagnetic contributions to the magnetic properties within the Coulomb gauge [3,4],

$$\chi_{\alpha\beta}^{p\mathcal{C}} = \frac{e^2}{4m_e^2c^2\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}} \mathrm{Re}(\langle a|L_\alpha|j\rangle\langle j|L_\beta|a\rangle) \ , \tag{30}$$

$$\sigma_{\alpha\beta}^{pI\mathcal{C}} = -\frac{e^2}{2m_e^2c^2\hbar} \times \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}} \mathrm{Re}(\langle a|M_{I\alpha}^n|j\rangle\langle j|L_\beta|a\rangle) \ , \tag{31}$$

and using formulas (29), one gets

$$\begin{aligned}
&\chi_{xx}^{p\mathcal{L}} = \chi_{xx}^{p\mathcal{C}} + \tfrac{1}{4}(\chi_{yy}^{d\mathcal{L}} - 3\chi_{xx}^{d\mathcal{L}}) \ , \\
&\chi_{xy}^{\mathcal{L}} \equiv \chi_{xy}^{p\mathcal{L}} = \chi_{xy}^{p\mathcal{C}} + \chi_{xy}^{d\mathcal{C}} \equiv \chi_{xy}^{\mathcal{C}} \ , \\
&\cdots \ , \\
&\chi_{\alpha\beta}^{p\mathcal{L}} + \chi_{\alpha\beta}^{d\mathcal{L}} \equiv \chi_{\alpha\beta}^{\mathcal{L}} = \chi_{\alpha\beta}^{\mathcal{C}} \equiv \chi_{\alpha\beta}^{p\mathcal{C}} + \chi_{\alpha\beta}^{d\mathcal{C}} \ ,
\end{aligned} \tag{32}$$

$$\begin{aligned}
&\sigma_{xx}^{pI\mathcal{L}} = \sigma_{xx}^{pI\mathcal{C}} + \tfrac{1}{2}(\sigma_{yy}^{dI\mathcal{L}} - \sigma_{xx}^{dI\mathcal{L}}) \ , \\
&\sigma_{xy}^{I\mathcal{L}} \equiv \sigma_{xy}^{pI\mathcal{L}} = \sigma_{xy}^{pI\mathcal{C}} + \sigma_{xy}^{dI\mathcal{C}} \equiv \sigma_{xy}^{I\mathcal{C}} \ , \\
&\sigma_{yx}^{pI\mathcal{L}} = \sigma_{yx}^{pI\mathcal{C}} - \sigma_{yx}^{dI\mathcal{C}} \ , \\
&\cdots \ , \\
&\sigma_{\alpha\beta}^{pI\mathcal{L}} + \sigma_{\alpha\beta}^{dI\mathcal{L}} \equiv \sigma_{\alpha\beta}^{I\mathcal{L}} = \sigma_{\alpha\beta}^{I\mathcal{C}} \equiv \sigma_{\alpha\beta}^{pI\mathcal{C}} + \sigma_{\alpha\beta}^{dI\mathcal{C}} \ .
\end{aligned} \tag{33}$$

It may be useful to recall that in any calculation based on the algebraic approximation, Eqs. (26) are identically satisfied for any basis set. On the other hand, Eqs. (32) and (33), connecting the paramagnetic contributions within different gauges for the vector potential, are obeyed if and only if the off-diagonal relations (29) are satisfied, i.e., if the hypervirial theorem for the second moment operator holds [11]. For example, Eqs. (32) and (33) are valid for the exact $|a\rangle$ and $|j\rangle$ Hartree-Fock eigenstates [11]. If a finite basis set is employed according to the self-consistent-field scheme, the degree to which Eqs. (32) and (33) are fulfilled gives a measure of accuracy of the calculation, i.e., information on the quality of the basis set and its degree of completeness with respect to the operators involved. In particular, total magnetic properties are invariant under the gauge transformation (3), [see the last line of Eqs. (32) and (33)] only if the basis set is complete.

## V. ORIGIN DEPENDENCE OF THE MAGNETIC PROPERTIES IN THE LANDAU GAUGE

The theoretical total magnetic properties must to be independent of the origin of the coordinate system [9,10], i.e., the variation of the paramagnetic contributions should exactly cancel the corresponding variation of the diamagnetic contributions. An arbitrary shift $\mathbf{d}$ of origin

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d} \tag{34}$$

can be thought of as a gauge transformation of the Landau vector potential

$$A_\alpha^{\mathcal{L}'} \rightarrow A_\alpha^{\mathcal{L}''} = A_\alpha^{\mathcal{L}'} + \nabla_\alpha \mathcal{L} \ , \tag{35}$$

where

$$\mathcal{L} = B_y d_z x + B_z d_x y + B_x d_y z \ . \tag{36}$$

Accordingly, one finds for the magnetic susceptibility,

$$\begin{aligned}
&\chi_{xx}^{d\mathcal{L}}(\mathbf{r}'') = \chi_{xx}^{d\mathcal{L}}(\mathbf{r}') + \frac{e^2}{m_e c^2}\left[2\left\langle a \left| \sum_{i=1}^{n} (y_i - y') \right| a \right\rangle d_y - n d_y^2\right] \ , \\
&\chi_{xx}^{p\mathcal{L}}(\mathbf{r}'') = \chi_{xx}^{p\mathcal{L}}(\mathbf{r}') - \frac{e^2}{m_e^2c^2}[\,2(T_x, P_z)_{-1} d_y - (P_z, P_z)_{-1} d_y^2\,] \ , \\
&\chi_{xy}^{p\mathcal{L}}(\mathbf{r}'') = \chi_{xx}^{p\mathcal{L}}(\mathbf{r}') - \frac{e^2}{m_e^2c^2}[\,(T_x, P_x)_{-1} d_z + (T_y, P_z)_{-1} d_y - (P_z, P_x)_{-1} d_y d_z\,] \ , \\
&\cdots \ ,
\end{aligned} \tag{37}$$

and for the magnetic shielding of nucleus $I$,

$$\begin{aligned}
&\sigma_{xx}^{dI\mathcal{L}}(\mathbf{r}'') = \sigma_{xx}^{dI\mathcal{L}}(\mathbf{r}') - \frac{e}{m_e c^2}\langle a|E_{Iy}^n|a\rangle d_y \ , \\
&\sigma_{xx}^{pI\mathcal{L}}(\mathbf{r}'') = \sigma_{xx}^{pI\mathcal{L}}(\mathbf{r}') + \frac{e^2}{m_e^2c^2}(M_{Ix}^n, P_z)_{-1} d_y \ , \\
&\sigma_{yx}^{dI\mathcal{L}}(\mathbf{r}'') = \sigma_{yx}^{dI\mathcal{L}}(\mathbf{r}') + \frac{e}{m_e c^2}\langle a|E_{Ix}^n|a\rangle d_y \ , \\
&\sigma_{yx}^{pI\mathcal{L}}(\mathbf{r}'') = \sigma_{yx}^{pI\mathcal{L}}(\mathbf{r}') + \frac{e^2}{m_e^2c^2}(M_{Iy}^n, P_z)_{-1} d_y \ , \\
&\sigma_{xy}^{pI\mathcal{L}}(\mathbf{r}'') = \sigma_{xy}^{pI\mathcal{L}}(\mathbf{r}') + \frac{e^2}{m_e^2c^2}(M_{Ix}^n, P_x)_{-1} d_z \ , \\
&\cdots \ ,
\end{aligned} \tag{38}$$

where

$$P_\alpha = \sum_{i=1}^{n} p_{i\alpha}, \quad E_{I\alpha}^n = \sum_{i=1}^{n} E_{I\alpha}^i \ ,$$

and

$$(P_\alpha,P_\beta)_{-1}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}}\mathrm{Re}(\langle a|P_\alpha|j\rangle\langle j|P_\beta|a\rangle)\ , \tag{39}$$

$$(T_z,P_y)_{-1}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}}\times\mathrm{Re}\left[\left\langle a\left|\sum_{i=1}^{n}[(x-x')p_y]_i\right|j\right\rangle\times\langle j|P_y|a\rangle\right]\ , \tag{40}$$

$$(M^n_{I\alpha},P_\beta)_{-1}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}}\mathrm{Re}(\langle a|M^n_{I\alpha}|j\rangle\langle j|P_\beta|a\rangle)\ . \tag{41}$$

The conditions

$$\chi^{\mathcal{L}}_{\alpha\beta}(\mathbf{r}'')=\chi^{\mathcal{L}}_{\alpha\beta}(\mathbf{r}')\ ,$$
$$\sigma^{I\mathcal{L}}_{\alpha\beta}(\mathbf{r}'')=\sigma^{I\mathcal{L}}_{\alpha\beta}(\mathbf{r}')$$

for invariance of theoretical magnetic properties under a coordinate transformation imply that

$$(P_\alpha,P_\beta)_{-1}=m_e n\delta_{\alpha\beta}\ , \tag{42}$$

$$(P_z,T_x)_{-1}=m_e\left\langle a\left|\sum_{i=1}^{n}(y_i-y')\right|a\right\rangle\ , \tag{43}$$

$$(P_z,T_y)_{-1}=(T_x,P_x)_{-1}=0\ ,$$

$$(P_\alpha,M^n_{I\beta})_{-1}=\frac{m_e}{e}\epsilon_{\alpha\beta\gamma}\langle a|E^n_{I\gamma}|a\rangle\ . \tag{44}$$

These equations are directly obtained from (14), (15), (21), (23), (37), and (38). They are also directly obtained from the definitions (39)–(41) using simple off-diagonal hypervirial relations [4]. Equations (42) and (44) are the same as those obtained within the Coulomb gauge [3,4]; Eq. (43) is new. The hypervirial conditions under which (42)–(44) are satisfied are similar to those analyzed before in the case of Eqs. (32) and (33). In particular, they are obeyed by exact Hartree-Fock wave functions [11].

The constraints for invariance are very general quantum-mechanical relationships—for instance, Eq. (42) is the Thomas-Reiche-Kuhn sum rule [12] within the dipole velocity formalism. They also restate commutation formulas, conditions for current conservation, hypervirial theorems, etc. [3,4,11].

## VI. OUTLINES OF CALCULATION

A series of Gaussian basis sets of increasing quality has been examined in the present study. The main features of these basis sets are available in Table I. Basis set I is obtained from the 6-31G basis [13], *polarized* according to a recipe previously discussed [6,7]. Basis set II, taken from Ref. [14], is especially designed to calculate near-Hartree-Fock dipole polarizabilities in the length gauge. It has been examined here in view of the fact that, according to Eqs. (15), a good representation of the dipole length operator is also needed to get accurate Landau paramagnetic susceptibilities.

Basis set III is constructed from the $(11s7p/5s)$ substrate from van Duijneveldt's tables [15], by adding two sets of $3d$ functions with exponents 1.218 79 and 0.361 02 on oxygen and one set of $2p$ functions with exponent 1.16 to hydrogen. Basis set IV adopts the $(13s8p/8s)$ substrate from the same tables [15]; the exponents for the $3d$ functions on oxygen are 2.516 91, 0.755 41, and 0.277 62; the exponents for the $2p$ functions on hydrogen are 3.568 and 0.830.

In basis set V the same $(13s8p/8s)$ substrate has been augmented by two diffuse $s$ functions on oxygen, with exponents 0.076 666 and 0.030 666, to improve the description of the tail regions of the molecular domain. These functions are expected to yield significant contributions to the transition matrix of the dipole length operator. The $3d$ exponents for oxygen are 4.0, 1.218 87, 0.361 02, and 0.1; the $2p$ exponents for hydrogen are 1.5, 0.4, and 0.1. Basis set VI is the same as V, with one set of $4f$ on oxygen, with exponent 0.41 and one set of $3d$ functions on hydrogen, with exponent 0.235.

The overall quality of the Gaussian basis sets can be judged from the self-consistent-field (SCF) energies reported in Table I. Supplementary information can be obtained from Ref. [8], where wave function V has been used to calculate a number of properties. The second-order magnetic tensors and sum rule (43) have been calculated via the SYSMO suite of computer programs [6–8], implementing an RPA section designed for the Landau gauge.

From the results displayed in Table II, one can see that the dipole-velocity Thomas-Reiche-Kuhn sum rule (42) is satisfied almost exactly by basis sets V and VI, quite good

TABLE I. Specification of basis sets and SCF energy. GTO stands for Gaussian-type orbitals; CGTO for contracted Gaussian-type orbitals.

| Basis set | Contraction scheme GTO | CGTO | Number of GTO | Number of CGTO's | SCF energy (a.u.) |
|---|---|---|---|---|---|
| I | $(13s13p4d/4s4p)$ | $[4s4p2d/2s2p]$ | 108 | 44 | −76.028 242 83 |
| II | $(10s6p4d/6s4p)$ | $[5s3p2d/3s2p]$ | 88 | 44 | −76.054 459 28 |
| III | $(11s7p2d/5s1p)$ | $[6s5p2d/3s1p]$ | 60 | 45 | −76.055 997 00 |
| IV | $(13s8p3d/8s2p)$ | $[8s6p3d/6s2p]$ | 83 | 68 | −76.064 541 66 |
| V | $(15s8p4d/10s3p)$ | Uncontracted | 101 | 101 | −76.065 283 39 |
| VI | $(15s8p4d1f/10s3p1d)$ | Uncontracted | 123 | 123 | −76.065 797 96 |

TABLE II. Sum rules [coordinates in bohr: $d(H_1)=(0,1.431\,53,-0.985\,27)$, $d(O)=(0,0,0.124\,14)$] for charge and current conservation and gauge invariance of magnetic susceptibility (a.u.).

| Basis set | $\langle z \rangle$ | $(T_x,P_y)_{-1}$ | $(T_y,P_x)_{-1}$ | $(P_x,P_x)_{-1}$ | $(P_y,P_y)_{-1}$ | $(P_z,P_z)_{-1}$ | $\frac{1}{3}(P_\alpha,P_\alpha)_{-1}$ |
|---|---|---|---|---|---|---|---|
| I | −0.226 13 | 0.060 73 | 0.061 99 | 8.765 | 9.064 | 8.968 | 8.933 |
| II | −0.196 17 | −0.020 87 | −0.299 88 | 7.828 | 8.192 | 8.078 | 8.033 |
| III | −0.187 56 | 0.034 80 | 0.038 81 | 9.113 | 9.356 | 9.278 | 9.249 |
| IV | −0.193 22 | 0.025 89 | −0.027 79 | 9.731 | 9.883 | 9.844 | 9.819 |
| V | −0.196 95 | 0.030 41 | −0.025 21 | 9.862 | 10.003 | 9.970 | 9.945 |
| VI | −0.196 93 | −0.000 73 | −0.164 10 | 9.942 | 9.990 | 9.972 | 9.968 |

values having already been obtained via basis set IV. On the other hand, constraint (43) is much more difficult to fulfill allowing for the basis sets retained here. In the case of basis sets I and III, the sign of the theoretical predictions is wrong. Even the results yielded by very large basis sets are far from being fully satisfactory. In fact, whereas some of the conditions $(T_\alpha,P_\beta)_{-1}=0$ are satisfied by symmetry, the conditions $(T_y,P_x)_{-1}=\langle z \rangle$ and $(T_x,P_y)_{-1}=0$ are fulfilled with good accuracy only via basis set VI.

This means that sum rule (43) is a quite severe probe of accuracy for molecular wave functions. In particular, as can be realized from definition (40), the basis set ought to be suitable to represent both dipole length and velocity operators at the same time, which may be difficult to obtain via ordinary Gaussian basis sets. In fact, it is worth noticing that Sadlej basis sets [14], especially developed to calculate near-Hartree-Fock electric polarizabilities, i.e., to represent the position operator fairly accurately, give the right sign, even if their extension is smaller than that of basis sets IV–VI. From these findings one infers that *ad hoc* basis sets are to be constructed by carefully tailoring the exponents of the polarization functions in order for sum rule (43) to be fulfilled to a reasonable extent. It seems to be mandatory to include $4f$ functions on heavy atoms and $3d$ functions on hydrogen for a basis set to guarantee accurate simultaneous representation of length and velocity operators.

The sum rules for charge conservation and origin independence of the nuclear magnetic shieldings are reported in Table III. The theoretical expectation value of the electric fields at oxygen, $\langle \mathbf{E}^n_O \rangle$, and hydrogen, $\langle \mathbf{E}^n_H \rangle$, is little affected by basis-set quality, as can be achieved by inspection of Table III, but, as expected, tensors $(\mathbf{M}^n_H,\mathbf{P})_{-1}$ and $(\mathbf{M}^n_O,\mathbf{P})_{-1}$ are much more dependent on the number of polarization functions and their exponents. We can see that sum rule (44) is poorly obeyed by basis sets of lower quality and only basis sets V and VI provide accurate results for oxygen. For hydrogen, basis set IV already seems to be fairly adequate to guarantee a good degree of origin independence. This is due to the fact that the Gaussian sets we have taken into account are, in general, more suitable to describe the electronic environment of hydrogen than of oxygen.

The diamagnetic contributions to the magnetic susceptibility within the Landau prescription for the gauge of the vector potential [see the first line of Eqs. (26)], are expected to be roughly two times larger than the corresponding quantities in the Coulomb gauge. In fact, the theoretical values for the latter, calculated via basis set V [8], $\chi^d_{xx}=-183.360$, $\chi^d_{yy}=-161.983$, $\chi^d_{zz}=-171.435$, show that, at least in the case of water, the diamagnetic contribution is not highly anisotropic; therefore, for the diamagnetic contributions within the Landau gauge, one expects $\chi^{d\mathcal{L}}_{xx}\approx 2\chi^{d\mathcal{C}}_{xx}$, etc., which holds exactly for the trace of the tensor [see the third line of Eqs. (26)]. From the condition for gauge invariance of total magnetic susceptibility [see the last line of Eqs. (32)], paramagnetic contributions within the Landau gauge much larger than the corresponding ones within the Coulomb gauge are also achieved [see also the first of Eqs. (32)]. Accordingly, total magnetic susceptibilities within the Landau gauge are the difference between two large numbers. Now, the diamagnetic contributions are merely expectation values over the unperturbed wave function and are usually rather accurate even for relatively small basis sets. The paramagnetic contributions, however, are much more dependent on the quality of the basis sets. As a consequence, for a given basis set, paramagnetic contributions and total susceptibilities in the Landau gauge are expected to be generally worse than those in the Coulomb gauge.

TABLE III. Sum rules [coordinates in bohr: $d(H)\equiv d(H_1)=(0,1.43\,153,-0.985\,27)$] for charge and current conservation and gauge invariance of nuclear magnetic shieldings (a.u.).

| Basis set | $\langle E^n_{Hy} \rangle$ | $(M^n_{Hz},P_x)_{-1}$ | $(M^n_{Hx},P_z)_{-1}$ | $\langle E^n_{Hz} \rangle$ | $\langle M^n_{Hx},P_y)_{-1}$ | $(M^n_{Hy},P_x)_{-1}$ | $\langle E^n_{Oz} \rangle$ | $(M^n_{Ox},P_y)_{-1}$ | $(M^n_{Oy},P_x)_{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| I | −2.057 00 | 1.785 87 | −1.823 61 | 1.503 89 | −1.344 89 | 1.316 57 | −0.376 42 | 0.181 33 | −0.114 39 |
| II | −2.041 54 | 1.469 12 | −1.502 05 | 1.489 13 | −1.114 62 | 1.043 75 | −0.302 17 | −0.397 83 | 0.503 15 |
| III | −2.026 60 | 1.757 43 | −1.767 37 | 1.477 84 | −1.321 66 | 1.271 43 | −0.346 72 | 0.174 71 | −0.423 40 |
| IV | −2.049 65 | 1.954 16 | −1.964 58 | 1.497 27 | −1.457 23 | 1.428 93 | −0.370 20 | 0.312 85 | −0.411 97 |
| V | −2.055 40 | 1.990 72 | −2.003 13 | 1.501 23 | −1.486 18 | 1.458 82 | −0.373 27 | 0.360 80 | −0.377 88 |
| VI | −2.056 25 | 2.018 33 | −2.022 77 | 1.501 61 | −1.485 49 | 1.473 65 | −0.373 55 | 0.359 91 | −0.360 91 |

TABLE IV. Magnetic susceptibility of $H_2O$ in ppm (a.u.).

| Basis set | $\chi^d_{xx}$ | $\chi^p_{xx}$ | $\chi_{xx}$ | $\chi^d_{yy}$ | $\chi^p_{yy}$ | $\chi_{yy}$ | $\chi^d_{zz}$ | $\chi^p_{zz}$ | $\chi_{zz}$ | $\chi^d_{av}$ | $\chi^p_{av}$ | $\chi_{av}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | −385.542 | 171.721 | −213.821 | −342.992 | 91.741 | −251.251 | −292.124 | 70.199 | −221.925 | −340.219 | 111.221 | −228.999 |
| II | −386.911 | 203.893 | −183.018 | −349.330 | 116.139 | −233.191 | −299.767 | 97.148 | −202.349 | −345.336 | 139.150 | −206.186 |
| III | −384.676 | 196.095 | −188.581 | −346.038 | 114.960 | −231.078 | −297.519 | 97.574 | −199.945 | −342.744 | 136.210 | −206.535 |
| IV | −384.993 | 209.567 | −175.426 | −346.937 | 123.191 | −223.746 | −299.253 | 108.574 | −190.679 | −343.728 | 147.111 | −196.617 |
| V | −385.625 | 212.509 | −173.116 | −347.816 | 127.674 | −220.142 | −300.115 | 113.603 | −186.512 | −344.519 | 151.262 | −193.257 |
| VI[b] | −385.913 | 221.705 | −164.208 | −348.691 | 181.022 | −167.669 | −298.800 | 134.627 | −164.173 | −344.468 | 179.118 | −165.350 |
| LZ[c] | −183.360 | 26.473 | −156.887 | −161.983 | 7.485 | −154.498 | −171.435 | 14.166 | −157.269 | −172.259 | 16.042 | −156.217 |
| Expt.[d] | | | −154±20 | | | −136±18 | | | −151±22 | | | |
| Expt.[e] | | | −150±22 | | | −137±22 | | | −150±28 | | | |

[a]The conversion factor from ppm (a.u.) per molecule to usual ppm (cgs) per mole is $8.923\,887\,8\times10^{-2}$.
[b]Paramagnetic susceptibilities in the Coulomb gauge from the same basis set: $\chi^p_{xx}=26.318$ ppm (a.u.), $\chi^p_{yy}=7.588$ ppm (a.u.), $\chi^p_{zz}=14.357$ ppm (a.u.).
[c]Theoretical susceptibility in the Coulomb gauge from Ref. [8].
[d]Experimental values from Ref. [16].
[e]Experimental values from Ref. [17].

TABLE V. Magnetic shielding at proton $H_1$ in ppm from basis sets I, II, III, IV, and V.

| Component | $\sigma^d$ (c.m.) | $\sigma^p$ (c.m.) | $\sigma^d$ ($H_1$) | $\sigma^p$ ($H_1$) | $\sigma$ (c.m.) | $\sigma$ ($H_1$) |
|---|---|---|---|---|---|---|
| | | | Basis set I | | | |
| *xx* | −1.526 | 23.609 | 155.281 | −115.406 | 22.083 | 39.875 |
| *yy* | 26.319 | 9.383 | 105.224 | −59.693 | 35.702 | 45.531 |
| *zz* | 46.310 | −10.752 | 46.310 | −10.752 | 35.558 | 35.558 |
| *yz* | 0.0 | −5.314 | 0.0 | −5.314 | −5.314 | −5.314 |
| *zy* | −29.431 | 14.746 | 78.493 | −78.953 | −14.685 | −0.46 |
| *Av* | 23.701 | 7.413 | 102.271 | −61.950 | 31.114 | 40.321 |
| $\Delta\sigma$ | 33.914 | −27.248 | −83.943 | 76.798 | 6.666 | −7.145 |
| | | | Basis set II | | | |
| *xx* | −0.094 | 18.950 | 155.493 | −95.549 | 18.856 | 59.944 |
| *yy* | 26.843 | 8.606 | 104.966 | −46.169 | 35.449 | 58.797 |
| *zz* | 46.331 | −10.975 | 46.331 | −10.975 | 35.356 | 35.356 |
| *yz* | 0.0 | −5.808 | 0.0 | −5.808 | −5.808 | −5.808 |
| *zy* | −28.822 | 15.396 | 78.263 | 15.396 | −13.426 | 93.659 |
| *Av* | 24.36 | 5.527 | 102.263 | −50.897 | 29.887 | 51.366 |
| $\Delta\sigma$ | 32.956 | −24.753 | −83.898 | 59.884 | 8.203 | −24.014 |
| | | | Basis set III | | | |
| *xx* | 1.022 | 16.615 | 155.542 | −118.085 | 17.637 | 37.457 |
| *yy* | 27.389 | 4.557 | 104.935 | −62.128 | 31.946 | 42.807 |
| *zz* | 46.326 | −9.176 | 46.326 | −9.176 | 37.15 | 37.15 |
| *yz* | 0.0 | −4.553 | 0.0 | −4.553 | −4.553 | −4.553 |
| *zy* | −27.903 | 9.1 | 78.447 | −83.084 | −18.803 | −4.637 |
| *Av* | 24.912 | 3.999 | 102.267 | −63.130 | 28.911 | 39.137 |
| $\Delta\sigma$ | 32.120 | −19.762 | −83.912 | 80.930 | 12.358 | −2.982 |
| | | | Basis set IV | | | |
| *xx* | −0.610 | 21.426 | 155.663 | −128.292 | 20.816 | 27.371 |
| *yy* | 26.537 | 8.107 | 105.080 | −66.868 | 34.644 | 38.212 |
| *zz* | 46.434 | −12.751 | 46.434 | −12.751 | 33.683 | 33.683 |
| *yz* | 0.0 | −7.023 | 0.0 | −7.023 | −7.023 | −7.023 |
| *zy* | −29.129 | 13.268 | 78.428 | −89.252 | −15.861 | −10.824 |
| *Av* | 24.120 | 5.594 | 102.392 | −69.304 | 29.714 | 33.088 |
| $\Delta\sigma$ | 33.470 | −27.517 | −83.937 | 84.829 | 5.953 | 0.892 |
| | | | Basis set V | | | |
| *xx* | −0.994 | 21.982 | 155.691 | −130.719 | 20.988 | 24.972 |
| *yy* | 26.314 | 8.188 | 105.079 | −68.352 | 34.502 | 36.727 |
| *zz* | 46.417 | −12.755 | 46.417 | −12.755 | 33.662 | 33.662 |
| *yz* | 0.0 | −6.810 | 0.0 | −6.810 | −6.810 | −6.810 |
| *zy* | −29.388 | 12.922 | 78.452 | −91.525 | −16.466 | −13.073 |
| *Av* | 23.912 | 5.805 | 102.395 | −70.609 | 29.717 | 31.786 |
| $\Delta\sigma$ | 33.757 | −27.840 | −83.968 | 86.781 | 5.917 | 2.813 |

TABLE VI. Magnetic shielding at proton $H_1$ in ppm from basis set VI and comparison with previous theoretical and experimental results.

| | Component | $\sigma^d$ (c.m.) | $\sigma^p$ (c.m.) | $\sigma^d(H_1)$ | $\sigma^p(H_1)$ | $\sigma$ (c.m.) | $\sigma(H_1)$ |
|---|---|---|---|---|---|---|---|
| | $xx$ | −1.004 | 22.245 | 155.727 | −131.970 | 21.241 | 23.757 |
| | $yy$ | 26.353 | 10.582 | 105.158 | −66.754 | 36.935 | 38.404 |
| | $zz$ | 46.326 | −14.538 | 46.326 | −14.538 | 31.788 | 31.788 |
| | $yz$ | 0.0 | −8.457 | 0.0 | −8.457 | −8.457 | −8.457 |
| | $zy$ | −29.473 | 18.433 | 78.399 | −87.445 | −11.040 | −9.046 |
| | $Av$ | 23.892 | 6.096 | 102.403 | −71.087 | 29.988 | 31.316 |
| | $\Delta\sigma$ | 33.652 | −30.952 | −84.116 | 84.824 | 2.700 | 0.708 |
| Expt.[a] | $Av$ | | | 102.4 | −71.80 | 30.2 | 30.2 |
| Calc.[b] | $Av$ | 23.912 | 5.968 | 102.395 | − 70.526 | 29.880 | 31.869 |
| | $\Delta\sigma$ | −1.801 | 1.052 | −2.012 | 1.978 | −0.749 | −0.034 |

[a]Experimental values from Refs. [18] and [19].
[b]GTO calculations from Ref. [8].

The results reported in Table IV largely confirm these expectations. The diamagnetic contributions in the Landau gauge are fairly independent of basis-set quality and are roughly two times larger than in the Coulomb gauge. Landau paramagnetic susceptibilities are also much larger, roughly one order of magnitude, and extremely dependent on basis-set quality: It can be observed that, even for the largest basis sets V and VI, the results have not fully converged. As a matter of fact, total Landau magnetic susceptibilities are usually less accurate than

TABLE VII. Magnetic shielding at oxygen O in ppm from basis sets I–V. Coordinates in bohr: $d(O)=(0,0,0.124\,14)$.

| Component | $\sigma^d$ (c.m.) | $\sigma^p$ (c.m.) | $\sigma^d(O)$ | $\sigma^p(O)$ | $\sigma$ (c.m.) | $\sigma(O)$ |
|---|---|---|---|---|---|---|
| | | | Basis set I | | | |
| $xx$ | 416.988 | −102.988 | 416.988 | −102.988 | 314.000 | 314.000 |
| $yy$ | 413.921 | −35.596 | 416.410 | −36.353 | 378.324 | 380.057 |
| $zz$ | 414.174 | −119.794 | 414.174 | −119.794 | 294.380 | 294.380 |
| $Av$ | 415.027 | −86.126 | 415.857 | −86.378 | 328.901 | 329.478 |
| $\Delta\sigma$ | −1.280 | −50.502 | −2.525 | −51.124 | −51.782 | −52.649 |
| | | | Basis set II | | | |
| $xx$ | 417.395 | −108.118 | 417.395 | −108.118 | 309.277 | 309.277 |
| $yy$ | 416.351 | −66.660 | 416.388 | −63.335 | 349.691 | 353.053 |
| $zz$ | 413.749 | −92.637 | 413.749 | −92.637 | 321.112 | 321.112 |
| $Av$ | 415.832 | −89.138 | 415.844 | −88.030 | 326.694 | 327.814 |
| $\Delta\sigma$ | −3.124 | −5.248 | −3.143 | −6.910 | −8.372 | −10.053 |
| | | | Basis set III | | | |
| $xx$ | 417.253 | −118.678 | 417.253 | −118.678 | 298.575 | 298.575 |
| $yy$ | 414.226 | −77.406 | 416.520 | −80.202 | 336.820 | 336.318 |
| $zz$ | 414.331 | −104.161 | 414.331 | −104.161 | 310.170 | 310.170 |
| $Av$ | 415.270 | −100.082 | 416.034 | −101.013 | 315.188 | 315.021 |
| $\Delta\sigma$ | −1.408 | −6.119 | −2.555 | −4.721 | −7.527 | −7.276 |
| | | | Basis set IV | | | |
| $xx$ | 417.633 | −112.190 | 417.633 | −112.190 | 305.443 | 305.443 |
| $yy$ | 414.128 | −60.667 | 416.754 | −62.736 | 353.458 | 353.838 |
| $zz$ | 413.872 | −107.163 | 413.872 | −107.163 | 306.709 | 306.709 |
| $Av$ | 415.211 | −93.340 | 416.026 | −94.030 | 321.871 | 321.997 |
| $\Delta\sigma$ | −2.008 | −20.734 | −3.231 | −19.700 | −22.742 | −22.931 |
| | | | Basis set V | | | |
| $xx$ | 417.104 | −109.943 | 417.104 | −109.943 | 307.161 | 307.161 |
| $yy$ | 412.736 | −49.783 | 415.204 | −52.281 | 362.953 | 326.923 |
| $zz$ | 415.739 | −112.965 | 415.739 | −112.965 | 302.774 | 302.774 |
| $Av$ | 415.193 | −90.897 | 416.016 | −91.729 | 324.296 | 324.287 |
| $\Delta\sigma$ | −0.819 | −33.102 | −0.415 | −31.853 | −32.283 | −32.268 |

TABLE VIII. Magnetic shielding at oxygen O in ppm from basis set VI and comparison with previous theoretical and experimental results.

| | Component | $\sigma^d$ (c.m.) | $\sigma^p$ (c.m.) | $\sigma^d$(O) | $\sigma^p$(O) | $\sigma$ (c.m.) | $\sigma$(O) |
|---|---|---|---|---|---|---|---|
| | $xx$ | 417.758 | −112.054 | 417.758 | −112.054 | 305.704 | 305.704 |
| | $yy$ | 414.213 | −45.751 | 416.679 | −48.138 | 368.462 | 368.541 |
| | $zz$ | 413.617 | −106.286 | 413.617 | −106.826 | 307.331 | 307.331 |
| | $Av$ | 415.196 | −88.030 | 416.018 | −88.826 | 327.166 | 327.192 |
| | $\Delta\sigma$ | −2.368 | −27.384 | −3.602 | −26.190 | −29.752 | −29.792 |
| Expt.[a] | $Av$ | | | | | 334±15 | |
| Calc.[b] | $Av$ | 415.193 | −88.066 | 416.016 | −88.878 | 327.127 | 327.138 |
| | $\Delta\sigma$ | 0.820 | −23.569 | −0.414 | −22.352 | −22.749 | −22.766 |

[a]Experimental values from Ref. [18].
[b]GTO calculations from Ref. [8].

corresponding quantities in the Coulomb gauge [8], which have virtually attained the Hartree-Fock limit and are close to the experimental values reported for $\chi_{xx}$ and $\chi_{zz}$.

On the other hand, as can be expected by inspection of Eqs. (26) and (33), the accuracy of theoretical nuclear magnetic shieldings furnished by a given basis set should be comparable within Coulomb and Landau gauges, at least in the case of diagonal components. In fact, from the fourth line of Eq. (26), we observe that the diamagnetic contributions should have comparable magnitude—in particular, the trace of the tensor must be the same within the different gauges [see the last line of Eqs. (26)]. Therefore, from the gauge invariance for total values [see the last line of Eqs. (33)], one could predict that similar quality could be obtained for the paramagnetic contributions in the Coulomb and Landau gauges. The results from the present calculation do in fact support this hypothesis. The paramagnetic contributions to the nuclear magnetic shieldings of hydrogen and oxygen (see Tables V–VIII) are continuously improving from basis set I to VI. The theoretical predictions from basis sets V and VI are very close to those obtained in our best previous calculations of the same quantities in the Coulomb gauge [8], using angular momentum and torque formalisms. Accordingly, we believe that the present estimates are of near-Hartree-Fock quality. Comparison with the available experimental average nuclear shieldings (see Tables VI and VIII) also confirms the very good quality of the calculated values.

## VII. CONCLUSIONS

These findings are a piece of evidence showing that accurate paramagnetic susceptibilities in the Landau gauge are obtainable only by means of very large Gaussian basis sets, including $4f$ polarization functions on heavy atoms and $3d$ functions on hydrogen, carefully constructed for this quantity. Together with sum rule (43), Landau paramagnetic susceptibilities provide an extremely severe test on the quality of molecular wave functions and their ability to represent magnetic perturbations.

In ordinary calculations aimed at predicting accurate magnetic susceptibilities, it is advisable to adopt the Coulomb gauge for the vector potential. The opposite may be true in the case of nuclear magnetic shielding within the Landau gauge, owing to the advantages in evaluating integrals over a Gaussian basis discussed in Sec. II. As a matter of fact, nuclear magnetic shielding calculated via Gaussian basis sets is characterized by comparable accuracy within the Coulomb and Landau gauges.

## ACKNOWLEDGMENTS

Generous allocation of computer resources provided by SEYCAD, Armada Argentina, and the CICAIA of the University of Modena and financial support for the present research from the Argentinian CONICET, the Italian CNR (Progetto Finalizzato Sistemi Informatici e Calcolo Parallelo), and the Italian Ministry of Public Education are gratefully acknowledged.

[1] L. Landau and E. Lifshitz, *Théorie de Champs,* 3rd ed. (Mir, Moscow, 1970).
[2] L. Landau and E. Lifshitz, *Mécanique Quantique* (Mir, Moscow, 1966).
[3] P. Lazzeretti and R. Zanasi, Phys. Rev. A **32**, 2607 (1985).
[4] P. Lazzeretti, Adv. Chem. Phys. **75**, 507 (1987).
[5] F. Bloch, in *W. Heisenberg und die Physik unserer Zeit* (Vieweg, Braunschweig, 1961).
[6] P. Lazzeretti and R. Zanasi, J. Chem. Phys. **84**, 3916 (1986).
[7] P. Lazzeretti and R. Zanasi, J. Chem. Phys. **85**, 5932 (1986).
[8] P. Lazzeretti and R. Zanasi, Phys. Rev. A **33**, 3727 (1986).
[9] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).
[10] J. A. Pople, W. G. Schneider, and H. T. Bernstein, *High Resolution Nuclear Magnetic Resonance Spectroscopy* (McGraw-Hill, New York, 1959).
[11] S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974).
[12] H. A. Bethe and E. W. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).
[13] W. J. Hehre, L. Radom, P. von R. Schleyer, and J. A. Po-

ple, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
[14] A. J. Sadlej, Collect. Czech. Chem. Commun. **53**, 1995 (1988).
[15] F. B. van Duijneveldt, IBM Res. Rep. RJ 945 (1971).
[16] H. Taft and B. P. Dayley, J. Chem. Phys. **51**, 1002 (1969).
[17] W. H. Flygare, Chem. Rev. **74**, 653 (1974).
[18] C. J. Jameson, in *Nuclear Magnetic Resonance,* Vol. 2 of *Specialist Periodical Reports* (Royal Chemical Society, London, 1983).
[19] P. Lazzeretti and R. Zanasi, J. Chem. Phys. **68**, 1523 (1978).