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***Ab initio* calculation of atomic contributions to the magnetic susceptibility by continuous transformation of the origin of the current density in HF, H₂O, NH₃, and CH₄ molecules**

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The conventional random phase approximation (RPA) of the polarization propagator theory and a computational method based on continuous transformation of origin for the current density (CTOCD) induced within the electron cloud by an external homogeneous, static magnetic field has been employed to calculate atomic contributions to magnetic susceptibilities. The diamagnetic part of the magnetic susceptibility is written in terms of the polarization propagator. Since the paramagnetic term may also be obtained from the propagator it is thus possible to compute both contributions at the same level of approximation. The evaluated average susceptibility is independent of the origin of the vector potential, but depends on the origin of the reference frame. The atomic contributions to the diamagnetic and paramagnetic parts of the magnetic susceptibility are derived by applying off-diagonal hypervirial relations which are exactly fulfilled if the state functions are *exact* eigenfunctions of a model Hamiltonian. The rationalization of the magnetic susceptibilities into atomic contributions is applied to some small molecules: HF, H₂O, NH₃ and CH₄, and the sum of these contributions is compared to the corresponding calculated total values and the experimental data for the molecular magnetic susceptibility for the same compounds. Computations are performed using basis sets of increasing quality. A series of sum rules for gauge independence of the computed results and charge-current conservation have been tested to document the accuracy of the calculation of magnetic properties. © 1999 American Institute of Physics. [S0021-9606(99)30321-4]

I. INTRODUCTION

The physical requirement of gauge invariance of molecular magnetic properties is only partially met in calculations involving the algebraic approximation, depending on the quality of the basis set. The coupled Hartree–Fock (CHF) procedure, which is origin independent in the limit of a complete basis set,¹ shows a considerable origin dependence even for extended basis sets.² The current density, $\mathbf{J}^{\mathbf{B}}(\mathbf{r})$, induced by an external magnetic field in the electron cloud of a molecule, is invariant under a gauge transformation for the exact solution of the Schrödinger equation. Within the algebraic approximation it is expected that estimates of increasing accuracy of $\mathbf{J}^{\mathbf{B}}(\mathbf{r})$ can be obtained for calculations corresponding to the origin of coordinates lying close to the point where the current density is to be evaluated. This is the aim of multiple-origin methods for magnetic properties.^{3–13} The IGLO^{3–7} and LORG^{8,9} approaches employ different origins for different orbitals in the Fock space. The DOGON^{10–12} and IGAIM¹³ techniques propose the use of multiple origins in real space.

Keith and Bader¹⁴ proposed the “continuous set of gauge transformations” (CSGT) in the calculation of second-order magnetic properties via numerical integration of expressions involving the current density. Their technique

presents some similarities to the Geertsen approach.¹⁵

A new procedure has been put forward to evaluate magnetic susceptibilities and nuclear magnetic shieldings within the framework of a continuous transformation of origin of current density (CTOCD), by providing a fully analytical formulation^{16,17} of the Keith and Bader technique.¹⁴

CTOCD magnetic susceptibilities are independent of the origin of the reference frame for center-symmetric molecules only¹⁶ and they do not depend on the origin of the potential vector.

The present work employs the polarization propagator theory and the technique proposed by Geertsen¹⁵ to write the diamagnetic part of the magnetic susceptibility in terms of the polarization propagator, χ^{Δ} . Application of the off-diagonal hypervirial relations,^{12,18,19} which are exactly fulfilled for the exact solution of the Hartree–Fock equation, allows the atomic contributions to the diamagnetic and paramagnetic parts of the average magnetic susceptibility to be successfully represented. The theoretical method applied to get these atomic contributions was originally developed by P. Lazzeretti,²⁰ and our RPA calculation of the CTOCD propagator is equivalent to the CHF implementation presented in Refs. 16,17. In this work all the calculations were performed by choosing the origin of the reference frame on the center-of-mass (c.m.) of each molecule.

The method breaks down the molecular magnetic susceptibility into atomic contributions and provides a theoretic

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cal scheme to sum these atomic contributions to recover Pascal's group increments²¹ for the magnetic susceptibility. Bader and Keith²² have shown how the electron charge and the current distributions might be used to determine the atomic and group contributions to magnetic response properties. They evaluated and reported on the calculation of atomic contributions to the magnetic susceptibilities of branched hydrocarbons, thus providing a further example of how the empirical additivity schemes of chemistry have a solid physical basis.

We discuss the quality of the wave functions by direct comparison between our additive results and total magnetic susceptibilities obtained by the conventional Coulomb calculation, and by inspection of the fulfillment of the virial sum rules. The calculated quantities depend linearly on the chosen origin for the reference frame, thus known hypervirial sum rules must be fulfilled to assure gauge invariance.

Our CTOCD results, evaluated in the random phase approximation,²³ CTOCD-RPA, verify: (i) calculated values of χ^Δ are less accurate than the corresponding χ^d , for the same basis sets; (ii) total magnetic susceptibility in the CTOCD-RPA scheme depends linearly on the origin of the reference frame.

In Sec. II we describe the magnetic susceptibility within the CTOCD-RPA method. In Sec. III we derive the atomic contributions to the average magnetic susceptibility. In Sec. IV we compare the molecular magnetic susceptibilities obtained by addition of atomic contributions, and the total CTOCD-RPA magnetic susceptibility, with the conventional Coulomb results for the total magnetic susceptibility. In addition we determine characteristic atomic susceptibilities for H, O, F, N, and C, by performing calculations in a set of small molecules HF, H₂O, NH₃, and CH₄, with basis sets of increasing quality.

II. MAGNETIC SUSCEPTIBILITY WITHIN THE CONTINUOUS TRANSFORMATION OF THE CURRENT DENSITY IN THE RPA APPROACH, CTOCD-RPA

Within the commonly used notation,^{12,24,25} the magnetic susceptibility is defined as the sum of paramagnetic and diamagnetic contributions,

$$\chi_{\alpha\beta}^{\text{dc}}(\mathbf{r}') = -\frac{e^2}{4m_e c^2} \langle a | \sum_{i=1}^n (\mathbf{r}_i - \mathbf{r}')^2 \delta_{\alpha\beta} - (\mathbf{r}_i - \mathbf{r}')_\alpha \times (\mathbf{r}_i - \mathbf{r}')_\beta | a \rangle, \quad (1)$$

$$\chi_{\alpha\beta}^{\text{pc}}(\mathbf{r}') = \frac{e^2}{4m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \text{Re}(\langle a | L_\alpha(\mathbf{r}') | j \rangle \times \langle j | L_\beta(\mathbf{r}') | a \rangle), \quad (2)$$

where \mathbf{r}' stands for the origin of the vector potential. Geertsen¹⁵ has written both average contributions of (1) and (2), named χ^Δ and χ^p , in terms of the polarization propagator^{26,27}

$$\chi^p(\mathbf{r}') = -\frac{1}{3} \left(\frac{e}{2m_e c} \right)^2 \text{Tr} \langle \langle \mathbf{L}(\mathbf{r}'); \mathbf{L}(\mathbf{r}') \rangle \rangle_{E=0}, \quad (3)$$

$$\begin{aligned} \chi^\Delta(\mathbf{r}') &= -\frac{e^2}{6m_e c^2} \langle a | (\mathbf{r} - \mathbf{r}')^2 | a \rangle \\ &= -\frac{1}{3} \left(\frac{e}{2m_e c} \right)^2 \text{Tr} \langle \langle \mathbf{p}; \mathbf{G}' \rangle \rangle_{E=0}, \end{aligned} \quad (4)$$

where $|a\rangle$ represents the reference state, $\mathbf{L}(\mathbf{r}') = (\mathbf{r} - \mathbf{r}') \times \mathbf{p}$ is the angular momentum operator, the operator \mathbf{G}' is defined with respect to the origin \mathbf{r}'

$$\mathbf{G}' \equiv \mathbf{G}(\mathbf{r}') = (\mathbf{r} - \mathbf{r}') \times \mathbf{L}(\mathbf{r}') + (\mathbf{r} \times \mathbf{r}') \times \mathbf{p}, \quad (5)$$

and the propagator is given by

$$\begin{aligned} \langle \langle \mathbf{p}; \mathbf{G}' \rangle \rangle_{E=0} &\equiv \sum_{n \neq a} \frac{2}{(E_a - E_n)} (\langle a | \mathbf{P} | n \rangle \langle n | \mathbf{G}' | a \rangle) \\ &\equiv (\mathbf{P}, \mathbf{G}')_{-1}. \end{aligned} \quad (6)$$

The magnetic susceptibility must be invariant under a gauge transformation of the vector potential, e.g.,

$$\mathbf{A}' \rightarrow \mathbf{A}'' = \mathbf{A}' + \nabla \Lambda, \quad (7)$$

with $\mathbf{A}' = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{r}')$ and $\Lambda = \Lambda(r)$ an arbitrary function well behaved in the limit of $r \rightarrow \infty$.

In a change of origin

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}, \quad (8)$$

which can be considered as a gauge transformation (7)

$$\Lambda = -\frac{1}{2} (\mathbf{B} \times \mathbf{d}) \cdot (\mathbf{r} - \mathbf{r}'), \quad (9)$$

the invariance condition reads

$$\chi_{\alpha\beta}^\Delta(\mathbf{r}'') + \chi_{\alpha\beta}^p(\mathbf{r}'') = \chi_{\alpha\beta}^\Delta(\mathbf{r}') + \chi_{\alpha\beta}^p(\mathbf{r}'), \quad (10)$$

and the contributions to the magnetic susceptibilities transform as

$$\begin{aligned} \chi_{\alpha\beta}^\Delta(\mathbf{r}'') &= \chi_{\alpha\beta}^\Delta(\mathbf{r}') - \frac{e^2}{4m_e c^2} \epsilon_{\gamma\delta\beta} \left[d_\delta (P_\gamma, L_\alpha)_{-1} \right. \\ &\quad \left. - d_\delta d_\lambda \epsilon_{\alpha\lambda\mu} (P_\gamma, P_\mu)_{-1} + \hbar^{-1} d_\lambda \epsilon_{\alpha\lambda\mu} \right. \\ &\quad \times \sum_{j \neq a} \omega_{ja}^{-1} \left(\langle a | \sum_{i=1}^n (r_{i\delta} - r'_{i\delta}) p_{i\mu} | j \rangle \right. \\ &\quad \times \langle j | P_\gamma | a \rangle + \langle a | P_\gamma | j \rangle \\ &\quad \left. \left. \times \langle j | \sum_{i=1}^n (r_{i\delta} - r'_{i\delta}) p_{i\mu} | a \rangle \right) \right], \end{aligned} \quad (11)$$

and

$$\begin{aligned} \chi_{\alpha\beta}^p(\mathbf{r}'') &= \chi_{\alpha\beta}^p(\mathbf{r}') + \frac{e^2}{4m_e c^2} \{ d_\delta [\epsilon_{\alpha\gamma\delta} (P_\gamma, L_\beta)_{-1} \\ &\quad + \epsilon_{\beta\gamma\delta} (P_\gamma, L_\alpha)_{-1}] \\ &\quad + \epsilon_{\alpha\gamma\delta} \epsilon_{\beta\lambda\mu} d_\delta d_\mu (P_\gamma, P_\lambda)_{-1} \}. \end{aligned} \quad (12)$$

We can notice the exact cancellation of terms between the average diamagnetic susceptibility and the corresponding paramagnetic terms.

Geertsen found¹⁵ that it is very convenient to include an extra term $(-i\hbar\mathbf{r})$ in the definition of \mathbf{G}' (5)

$$\mathbf{G}' \rightarrow \mathbf{G}' - i\hbar\mathbf{r}, \quad (13)$$

to get a Hermitian operator. In this approach the diamagnetic average susceptibility, χ^Δ , is found by employing commutation relations valid for the exact wavefunction and propagators

$$\begin{aligned} \chi^\Delta(\mathbf{r}-\mathbf{r}') &= -\frac{1}{3} \left(\frac{e}{2m_e c} \right) \frac{i}{2\hbar} \langle a | [R_\alpha, G'_\alpha] | a \rangle \\ &= -\frac{1}{3} \left(\frac{e}{2m_e c} \right)^2 \text{Tr} \langle \langle \mathbf{p}; \mathbf{G}' \rangle \rangle_{E=0} \\ &= -\frac{1}{3} \left(\frac{e}{2m_e c} \right)^2 (P_\alpha, G'_\alpha)_{-1}, \end{aligned} \quad (14)$$

where sum over repeated indices is implied.

The inclusion of $(\mathbf{r} \times \mathbf{r}') \times \mathbf{p}$ in Eq. (5) makes no contribution to the commutator $[\mathbf{R}, \mathbf{G}']$ but its neglect produces a nonvanishing gauge error for noncomplete basis sets.¹⁵

The extra term $(-i\hbar\mathbf{r})$ in Eq. (13) makes no contribution to the commutator $[\mathbf{R}, \mathbf{G}']$, thereby permitting direct use of the RPA approach for Hermitian operators.^{26,27} Therefore, the diamagnetic traces (4) of the Geertsen approach coincide with the corresponding traces of the CTOCD formalism^{16,17}

$$\begin{aligned} \frac{1}{3} \chi_{\alpha\alpha}^\Delta &= \frac{1}{12} \frac{e^2}{m_e c^2 \hbar} \epsilon_{\alpha\beta\gamma} \sum_{j \neq \alpha} \omega_{ja}^{-1} \left(\langle a | \sum_{i=1}^n (r_{i\beta} \right. \\ &\quad \left. - r'_{i\beta}) l'_{i\gamma} | j \rangle \langle j | P_\alpha | a \rangle + \langle a | P_\alpha | j \rangle \right. \\ &\quad \left. \times \langle j | \sum_{i=1}^n (r_{i\beta} - r'_{i\beta}) l_{i\gamma} | a \rangle \right), \end{aligned} \quad (15)$$

where the nonHermitian character of the operator $(\mathbf{r}-\mathbf{r}') \times \mathbf{I}'$ in Eq. (15) has been taken into account.

By means of the off-diagonal hypervirial relation

$$\langle a | \mathbf{P} | j \rangle = -im_e \omega_{ja} \langle a | \mathbf{R} | j \rangle, \quad (16)$$

which holds for *exact* eigenfunctions of a model Hamiltonian, Eq. (15) may be rewritten as the expectation value of a commutator, which eventually gives the conventional diamagnetic term (1)

$$\begin{aligned} \chi_{\alpha\alpha}^\Delta &\equiv -\frac{e^2}{2m_e c^2} \frac{i}{2\hbar} \epsilon_{\alpha\beta\gamma} \langle a | \left[\sum_{i=1}^n (r_{i\alpha} - r'_{i\alpha}), \sum_{j=1}^n (r_{j\beta} \right. \\ &\quad \left. - r'_{j\beta}) l'_{j\gamma} \right] | a \rangle = \chi_{\alpha\alpha}^d. \end{aligned} \quad (17)$$

The magnetic properties obtained via the CTOCD method can be written as a sum of conventional paramagnetic terms, such as Eq. (2), plus a term which reduces to the conventional diamagnetic contribution in the Hartree–Fock limit.

The advantage of the CTOCD formalism is evident by realizing that the magnetic susceptibility can be recast in terms of integrals involving the second-rank electron current density tensor,¹⁶ $\mathcal{J}_\gamma^{B\beta}(r)$, a function of position \mathbf{r}

$$\chi_{\alpha\beta} = \frac{1}{2c} \epsilon_{\alpha\delta\gamma} \int (r_\delta - r'_\delta) \mathcal{J}_\gamma^{B\beta}(\mathbf{r}) d\mathbf{r}. \quad (18)$$

The *exact* electron current density $J_\gamma^B(r) = \mathcal{J}_\gamma^{B\beta}(r) B_\beta$ is invariant in a gauge transformation, e.g., in a change of coordinate system, although its analytical expression is usually changed in such a transformation.¹⁶ Lazzeretti *et al.*¹⁶ assumed, for each \mathbf{r} , that the point itself is used as origin of the coordinate system for calculating $\mathcal{J}_\gamma^{B\beta}(r)$, i.e., formally performing a continuous transformation of origin of the coordinate system in Eq. (18) and arrived at the analytical CTOCD closed formulas,

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^p + \chi_{\alpha\beta}^\Delta. \quad (19)$$

In the limit of exact electronic eigenfunctions to a model Hamiltonian, the equality $\chi_{\alpha\beta}^d = \chi_{\alpha\beta}^\Delta$ holds. In actual calculations these conditions will be only partially fulfilled, depending on the quality of the approximations retained within the computational scheme.

III. ATOMIC CTOCD–RPA CONTRIBUTIONS TO THE AVERAGE MAGNETIC SUSCEPTIBILITY

In order to derive the rationalization of the magnetic susceptibility into atomic contributions we employ the hypervirial relations

$$\begin{aligned} \langle a | \mathbf{R} | j \rangle &= \frac{i}{m_e \omega_{ja}} \langle a | \mathbf{P} | j \rangle \\ &= -\frac{1}{m_e \omega_{ja}^2} \langle a | \mathbf{F}_n^N | j \rangle \\ &= \frac{e}{m_e \omega_{ja}^2} \sum_{I=1}^N Z_I \langle a | \mathbf{E}_I^n | j \rangle, \end{aligned} \quad (20)$$

$$\langle a | \mathbf{L} | j \rangle = \frac{i}{\omega_{ja}} \langle a | \mathbf{K}_n^N | j \rangle, \quad (21)$$

for the *exact* states of the model Hamiltonian. In Eqs. (20) and (21) we used the definitions

$$\begin{aligned} \mathbf{F}_n^N &= \sum_{I=1}^N \sum_{i=1}^n \mathbf{F}_i^I; \quad \mathbf{F}_i^I = -e^2 Z_I \frac{(\mathbf{r}_i - \mathbf{R}_I)}{|\mathbf{r}_i - \mathbf{R}_I|^3}; \\ \mathbf{K}_n^N &= \sum_{I=1}^N \sum_{i=1}^n \mathbf{K}_i^I; \quad \mathbf{K}_i^I = -e^2 Z_I \frac{(\mathbf{r}_i - \mathbf{R}_I)}{|\mathbf{r}_i - \mathbf{R}_I|^3} \times (\mathbf{R}_I - \mathbf{r}'), \end{aligned} \quad (22)$$

for a system with n electrons in positions \mathbf{r}_i , N nuclei in positions \mathbf{R}_I and with charge Z_I . \mathbf{F}_n^N and \mathbf{K}_n^N are the force and the torque exerted by the n electrons on the nuclei. On applying Eqs. (20) and (21) we find the CTOCD–RPA average susceptibilities

$$\frac{1}{3} \chi_{\alpha\alpha}^\Delta(\mathbf{r}') = -\frac{1}{3} \left(\frac{e}{2m_e c^2} \right)^2 (F_{n\alpha}^N, G_\alpha)_{-2}, \quad (23)$$

within the “acceleration” gauge and

$$\frac{1}{3} \chi_{\alpha\alpha}^p(\mathbf{r}') = -\frac{1}{3} \left(\frac{e}{2m_e c^2} \right)^2 (K_{n\alpha}^N, L_\alpha)_{-2}, \quad (24)$$

TABLE I. Specification of basis sets and SCF energy.

Basis set	Contraction scheme		Number of GTOs	Number of CGTOs	SCF energy (au)
	GTO	CGTO			
HF					
I	(11s7p1d/8s3p)	[6s5p1d/6s3p]	55	42	-100.064 106 8
II	(13s8p4d/8s3p)	[8s6p4d/6s3p]	78	68	-100.068 777 9
III	(15s8p4d/10s3p)	uncontracted	82	82	-100.068 837 4
IV	(15s8p3d1f/10s2p1d)	uncontracted	98	98	-100.069 100 6
H ₂ O					
I	(11s7p2d/5s1p)	[6s5p2d/3s1p]	60	45	-76.052 283 23
II	(13s8p4d/8s3p)	[8s6p3d/6s3p]	85	70	-76.064 476 30
III	(15s8p4d/10s3p)	uncontracted	101	101	-76.065 283 39
IV	(15s8p4d1f/10s3p1d)	uncontracted	123	123	-76.065 797 99
CH ₄					
I	(11s7p2d/7s1p)	[5s3p2d/3s1p]	76	57	-40.213 017 22
II	(13s8p4d/8s3p)	[8s6p4d/6s3p]	129	110	-40.215 757 91
III	(15s8p4d/10s3p)	uncontracted	139	139	-40.215 809 53
IV	(15s8p4d1f/10s3p1d)	uncontracted	173	173	-40.215 886 85
NH ₃					
I	(11s7p2d/5s1p)	[6s5p1d/3s1p]	68	45	-56.214 716 21
II	(13s8p4d/8s3p)	[8s6p4d/6s3p]	112	95	-56.223 378 0
III	(15s8p4d/10s3p)	uncontracted	120	120	-56.223 350 9
IV	(15s8p4d1f/10s3p1d)	uncontracted	148	148	-56.223 533 6

within the mixed torque-angular momentum formalism, with

$$(F_{n\alpha}^N, G'_\alpha)_{-2} = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2} \text{Im} \langle a | F_{n\alpha}^N | j \rangle \langle j | G'_\alpha | a \rangle, \quad (25)$$

and

$$(K_{n\alpha}^N, L_\alpha)_{-2} = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2} \text{Im} \langle a | K_{n\alpha}^N | j \rangle \langle j | L_\alpha | a \rangle. \quad (26)$$

Equations (23) and (24) may be rewritten as sums of atomic contributions to the diamagnetic and paramagnetic parts of the CT OCD-RPA average susceptibilities, i.e.,

$$\mathbf{F}_n^N = \sum_{I=1}^N \left(\sum_{i=1}^n \mathbf{F}_i^I \right), \quad (27)$$

$$\mathbf{K}_n^N = \sum_{I=1}^N \left(\sum_{i=1}^n \mathbf{K}_i^I \right).$$

So, within the mixed torque-angular momentum, **K,L** formalism, for the paramagnetic contributions and the ‘‘acceleration’’ gauge, **G,F** formalism, for the diamagnetic contributions to the average susceptibility, we write

$$\chi^p(r') = \sum_{I=1}^N \chi^{pI}(r'),$$

$$\chi^{pI}(r') = \chi^{p(K_n^I, L)} = \frac{i}{6} \left(\frac{e}{m_e c} \right)^2 \frac{1}{\hbar} \sum_{j \neq a} \frac{1}{\omega_{ja}^2} \langle a | K_{n\alpha}^I(r') | j \rangle \times \langle j | L_\alpha(r') | a \rangle$$

$$= \frac{1}{6} \left(\frac{e}{m_e c} \right)^2 (K_{n\alpha}^I, L_\alpha)_{-2}, \quad (28)$$

and

$$\chi^\Delta(r') = \sum_{I=1}^N \chi^{\Delta I}(r'),$$

$$\chi^{\Delta I}(r') = \chi^{\Delta(F_n^I)} = \frac{i}{6} \left(\frac{e}{m_e c} \right)^2 \frac{1}{\hbar} \sum_{j \neq a} \frac{1}{\omega_{ja}^2} \langle a | F_{n\alpha}^I(r') | j \rangle \times \langle j | G_\alpha(r') | a \rangle$$

$$= \frac{1}{6} \left(\frac{e}{m_e c} \right)^2 (F_{n\alpha}^I, G'_\alpha)_{-2}, \quad (29)$$

and define the atomic contributions to the magnetic susceptibility

$$\chi^I(r') = \chi^{pI}(r') + \chi^{\Delta I}(r'). \quad (30)$$

TABLE II. Sum rules for charge-current conservation and gauge invariance of magnetic susceptibility of the HF molecule in au.^a

Basis set	I	(F _{nx} ^I , L _y) ₋₂	(K _{ny} ^I , P _x) ₋₂	⟨z⟩
I	F	-0.519	-0.623	
	H	0.340	0.765	
	Tot.	-0.179	0.141	0.091
II	F	-0.314	-0.777	
	H	0.341	0.898	
	Tot.	0.027	0.121	0.154
III	F	-0.300	-0.739	
	H	0.345	0.807	
	Tot.	0.045	0.068	0.102
IV	F	-0.292	-0.778	
	H	0.349	0.866	
	Tot.	0.056	0.088	0.102

^aCoordinates in bohr: H₁=(0, 0, 1.645 497), F=(0, 0, -0.087 302). All quantities are relative to center-of-mass.

TABLE III. Sum rules for charge–current conservation and gauge invariance of magnetic susceptibility of the H₂O molecule^a in au.

Basis set	<i>I</i>	$(F_{nx}^I, L_y)_{-2}$	$(F_{ny}^I, L_x)_{-2}$	$(F_{nz}^I, L_z)_{-2}$	$(F_{nz}^I, L_x)_{-2}$	$\langle z \rangle^b$	$(K_{ny}^I, P_x)_{-2}$	$(K_{nx}^I, P_y)_{-2}$	$(K_{nz}^I, P_x)_{-2}$	$(K_{nx}^I, P_z)_{-2}$
I	O ₁	0.518	-0.626	0.0	0.0		0.956	-0.985	0.0	0.0
	H ₁	-0.218	0.275	-0.312	0.394		-0.510	0.536	-0.740	0.890
	Tot.	0.081	-0.076	0.0	0.0	-0.162	-0.063	0.086	0.0	0.0
II	O ₁	0.395	-0.496	0.0	0.0		1.039	-1.036	0.0	0.0
	H ₁	-0.260	0.316	-0.366	0.442		-0.618	0.619	-0.897	1.033
	Tot.	-0.125	0.137	0.0	0.0	-0.193	-0.196	0.203	0.0	0.0
III	O ₁	0.371	-0.479	0.0	0.0		1.064	-1.055	0.0	0.0
	H ₁	-0.261	0.318	-0.367	0.443		-0.620	0.622	-0.901	1.041
	Tot.	-0.151	0.157	0.0	0.0	-0.197	-0.177	0.188	0.0	0.0
IV	O ₁	0.364	-0.473	0.0	0.0		1.068	-1.054	0.0	0.0
	H ₁	-0.265	0.319	-0.372	0.443		-0.629	0.622	-0.914	1.042
	Tot.	-0.166	0.165	0.0	0.0	-0.197	-0.190	0.190	0.0	0.0

^aAll quantities relative to center-of-mass; coordinates in bohr: H₁=(0, 1.431 53, -0.985 266), O₁=(0, 0, 0.124 114).

^b $\langle z \rangle$ is the only nonzero component of the dipolar moment.

It is interesting to check the origin dependence of CT OCD–RPA atomic contributions to the average magnetic susceptibility. In a change of origin (8) we find, after a little algebra from Eqs. (28) and (29), the relations

$$\begin{aligned} \chi_{\alpha\alpha}^{\text{pl}}(\mathbf{r}'') &= \chi_{\alpha\alpha}^{\text{pl}}(\mathbf{r}') + \left(\frac{e}{2m_e c}\right)^2 \{d_{\beta}\epsilon_{\alpha\beta\gamma}[(F_{n\gamma}^I, L_{\alpha})_{-2} \\ &+ (K_{n\alpha}^I, P_{\gamma})_{-2}] + d_{\gamma}^2(F_{n\beta}^I, P_{\beta})_{-2} \\ &- d_{\gamma}d_{\beta}(F_{n\gamma}^I, P_{\beta})_{-2}\}, \end{aligned} \quad (31)$$

$$\begin{aligned} \chi_{\alpha\alpha}^{\Delta I}(\mathbf{r}'') &= \chi_{\alpha\alpha}^{\Delta I}(\mathbf{r}') - \left(\frac{e}{2m_e c}\right)^2 \{2\epsilon_{\alpha\beta\gamma}d_{\beta}(F_{n\alpha}^I, L_{\gamma})_{-2} \\ &+ d_{\beta}^2(F_{n\alpha}^I, P_{\alpha})_{-2} - d_{\alpha}d_{\beta}(F_{n\alpha}^I, P_{\beta})_{-2}\} \\ &- \left(\frac{e}{2m_e c}\right)^2 (d_{\alpha}r'_{\beta} + d_{\beta}r'_{\alpha})(F_{n\alpha}^I, P_{\beta})_{-2}. \end{aligned} \quad (32)$$

The linear dependence on the origin of the reference frame appears in the last term of Eq. (32). Similar equations are valid for the total $\chi^p(r'')$ and $\chi^{\Delta}(r'')$, after replacing $F_{n\alpha}^I$ by $F_{n\alpha}^N$, and $K_{n\alpha}^I$ by $K_{n\alpha}^N$.

To guarantee the gauge invariance in

$$\frac{1}{3}\chi_{\alpha\alpha}^{(F,K)} = \frac{1}{3}\chi_{\alpha\alpha}^{\Delta(F,G')} + \frac{1}{3}\chi_{\alpha\alpha}^{p(K,L)}, \quad (33)$$

the conditions which must hold are

$$(L_{\alpha}, F_{n\gamma}^N)_{-2} = (K_{n\alpha}^N, P_{\gamma})_{-2} = m_e \epsilon_{\alpha\beta\gamma} \langle a | R_{\beta} | a \rangle. \quad (34)$$

These sum rules may also be obtained using off-diagonal hypervirial relations²⁵ obeyed by the exact Hartree–Fock wavefunction.¹⁹ Supposing that the gauge invariance condition

$$\chi^I(\mathbf{r}'') = \chi^I(\mathbf{r}'), \quad (35)$$

TABLE IV. Sum rules for charge–current conservation and gauge invariance of magnetic susceptibility of the NH₃ molecule in au.^a

Basis	<i>I</i>	$(F_{nx}^I, L_y)_{-2}$	$(F_{ny}^I, L_x)_{-2}$	$(F_{nz}^I, L_z)_{-2}$	$(F_{nz}^I, L_y)_{-2}$	$(F_{nz}^I, L_x)_{-2}$	$\langle z \rangle^b$	$(K_{ny}^I, P_x)_{-2}$	$(K_{nx}^I, P_y)_{-2}$	$(K_{ny}^I, P_z)_{-2}$	$(K_{nz}^I, P_y)_{-2}$
I	N ₁	0.489	-0.489	0.0	0.0	0.0	0.0	0.946	-0.946	0.0	0.0
	H ₁	-0.207	0.267	0.803	-0.614	0.0	0.0	-0.310	0.466	-1.250	1.396
	H ₂	-0.253	0.225	-0.401	0.307	-0.695	0.532	-0.427	0.349	0.625	-0.698
	Tot.	-0.228	0.153	0.0	0.0	0.0	0.0	-0.236	-0.218	0.218	0.0
II	N ₁	0.511	-0.511	0.0	0.0	0.0	0.0	0.945	-0.945	0.0	0.0
	H ₁	-0.231	0.285	0.865	-0.688	0.0	0.0	-0.294	0.492	-1.344	1.472
	H ₂	-0.271	0.244	-0.433	0.344	-0.749	0.596	-0.442	0.343	0.672	-0.736
	Tot.	-0.263	0.263	0.0	0.0	0.0	0.0	-0.246	-0.233	0.233	0.0
III	N ₁	0.562	-0.562	0.0	0.0	0.0	0.0	0.926	-0.926	0.0	0.0
	H ₁	-0.231	0.281	0.857	-0.684	0.0	0.0	-0.293	0.489	-1.342	1.464
	H ₂	-0.268	0.243	-0.428	0.342	-0.742	0.592	-0.440	0.342	0.671	-0.732
	Tot.	-0.206	0.206	0.0	0.0	0.0	0.0	-0.246	-0.247	0.247	0.0
IV	N ₁	0.563	-0.563	0.0	0.0	0.0	0.0	0.926	-0.926	0.0	0.0
	H ₁	-0.233	0.281	0.859	-0.689	0.0	0.0	-0.291	0.491	-1.354	1.469
	H ₂	-0.269	0.245	-0.430	0.344	-0.744	0.597	-0.441	0.341	0.680	-0.734
	Tot.	-0.208	0.208	0.0	0.0	0.0	0.0	-0.245	-0.248	0.248	0.0

^aAll values are relative to the center-of-mass; coordinates in bohr: N₁=(0, 0, 0.127 799), H₁=(1.770 998, 0, -0.591 964), H₂=(−0.885 499, 1.533 729, −0.591 964).

^b $\langle z \rangle$ is the only nonzero component of the dipolar moment.

TABLE V. Sum rules for charge–current conservation and gauge invariance of magnetic susceptibility of the CH₄ molecule^a in au.

Basis set	<i>I</i>	$(F_{nx}^I, L_y)_{-2}$	$(F_{nx}^I, L_z)_{-2}$	$(K_{ny}^I, P_x)_{-2}$	$(K_{nz}^I, P_x)_{-2}$
I	C ₁	0.0	0.0	0.0	0.0
	H ₁	0.596	-0.843	0.714	-1.010
	Tot.	0.0	0.0	0.0	0.0
II	C ₁	0.0	0.0	0.0	0.0
	H ₁	0.823	-1.165	1.120	-1.584
	Tot.	0.0	0.0	0.0	0.0
III	C ₁	0.0	0.0	0.0	0.0
	H ₁	0.823	-1.165	1.113	-1.575
	Tot.	0.0	0.0	0.0	0.0
IV	C ₁	0.0	0.0	0.0	0.0
	H ₁	0.827	-1.170	1.118	-1.581
	Tot.	0.0	0.0	0.0	0.0

^aCoordinates in bohr: C₁=(0,0,0), H₁=(0,1.683 396,1.190 341). The dipolar moment is exactly 0.0 by symmetry.

also holds for the atomic contribution, a new “atomic” sum rule

$$(L_{\alpha}, F_{n\gamma}^I)_{-2} = (K_{n\alpha}^I, P_{\gamma})_{-2}, \quad (36)$$

would be satisfied.

IV. RESULTS AND DISCUSSION

A set of small molecules: HF, H₂O, NH₃, and CH₄ has been considered in the present study. The aim of this work is to determine atomic susceptibilities for H, O, F, N, and C, giving a theoretical background for the experimental Pascal’s constants.²¹

Molecular geometries adopted in the calculation are informed in previous papers.^{24,28–32} Gaussian basis sets employed are specified in Table I. The (*s/p*) substrates for each basis set, I–IV, for all the molecules were taken from van Duijneveldt tables.³³ For atoms heavier than hydrogen two diffuse *s* functions have been added to build up larger basis sets (II to IV), in order to improve the description of the

outer regions of the molecular domain. The overall quality of these basis sets can be judged from the self-consistent (SCF) energies reported in Table I. Supplementary information can be obtained from Refs. 29,30, where the same basis sets have been used to calculate molecular magnetic properties in the Landau gauge^{34,35} and in the presence of a nonuniform magnetic field.³⁶

The calculations reported in this work have been carried out with the SYSMO computer programs,^{24,28} modified by us to implement a new RPA section for the CTOCD–RPA diamagnetic part, both for atomic contributions and total average magnetic susceptibilities.

The Hartree–Fock (HF) accuracy of the calculations can be judged from the results of various sum rules reported in previous calculations in the same set of compounds.^{29–31,37} Here we only included the sum rules presented in Eqs. (34) and (36), which are necessary to assure the conservation of current density and gauge invariance for the CTOCD–RPA susceptibilities in the force-torque formalism. Tables II, III, IV, and V, for HF, H₂O, NH₃, and CH₄, report the value for the operator **R**, the dipolar moment, and the atomic partitions of quantities $(\mathbf{F}, \mathbf{P})_{-2}$, $(\mathbf{F}, \mathbf{L})_{-2}$ and $(\mathbf{K}, \mathbf{P})_{-2}$, appearing in the translational invariance sum rule (34).

R_{β} becomes closer to $(K_{n\alpha}^N, P_{\gamma})_{-2}$ when improved basis sets are used. The quantities $(F_{n\alpha}^N, L_{\gamma})_{-2}$ do not satisfy sum rule (34) as well as $(K_{n\alpha}^N, P_{\gamma})_{-2}$ do. This feature is attributed to the fact that the force and the torque operators weigh the electron density differently.^{24,37} It has been shown³⁷ that the full **K, K** formalism to express the paramagnetic contribution to the magnetic susceptibility is the best alternative choice when the conventional **L, L** formalism is not used. As it was shown previously,^{24,38} the force operator is more difficult to be well represented than the **K** one because of the obvious difficulties to mimic their \mathbf{r}^{-3} dependence using CGTOs functions whose algebraic part contains only positive powers of *r*.

TABLE VI. Atomic contributions to magnetic susceptibility of the HF in PPM au per molecule.^a

Basis set	Nucleus	$\chi_{Av}^{p(L,L)}$	χ_{Av}^d	$\chi_{Av}^{p(K_n^I, L)}$	$\chi_{Av}^{\Delta(F_n^I)}$	χ_{Av}^C	χ_{Av}^I
I	F			0.402	-101.219		-100.817
	H			4.960	-4.757		0.203
	Tot.	5.215	-121.803	5.362	-105.976	-116.588	-100.614
II	F			0.243	-117.879		-117.636
	H			4.973	-6.208		-1.235
	Tot.	5.222	-121.780	5.217	-124.087	-116.558	-118.870
III	F			0.246	-118.259		-118.013
	H			4.973	-6.208		-1.235
	Tot.	5.221	-121.780	5.219	-124.466	-116.559	-119.247
IV	F			0.248	-117.880		-117.632
	H			5.046	-6.432		-1.386
	Tot.	5.259	-121.775	5.294	-124.312	-116.516	-119.018

^aThe conversion factor from ppm au per molecule to usual ppm cgs per mole is $8.923\ 8878 \times 10^{-2}$. Magnetic susceptibility in the Coulomb gauge, χ_{Av}^C , is reported in column 7. Total CTOCD–RPA magnetic susceptibility [Eq. (33)] and its partition into atomic contributions, χ_{Av}^I , are reported in column 8. Experimental magnetic susceptibility is -115.4 ± 1 ppm au quoted in Ref. 40.

TABLE VII. Atomic contributions to magnetic susceptibility of H₂O in PPM au per molecule.^a

Basis set	Nucleus <i>I</i>	$\chi_{Av}^{p(L,L)}$	χ_{Av}^d	$\chi_{Av}^{p(K_n^I, L)}$	$\chi_{Av}^{\Delta(F_n^I)}$	χ_{Av}^C	χ_{Av}^I
I	O			0.630	-124.882		-124.252
	H			6.638	-6.983		-0.345
	Tot.	14.708	-171.440	13.905	-138.847	-156.732	-124.942
II	O			0.491	-149.758		-149.267
	H			7.656	-11.129		-3.473
	Tot.	16.006	-171.953	15.804	-172.016	-155.947	-156.212
III	O			0.469	-149.982		-149.513
	H			7.680	-11.231		-3.551
	Tot.	16.042	-172.259	15.829	-172.444	-156.217	-156.615
IV	O			0.461	-150.123		-149.662
	H			7.729	-11.429		-3.700
	Tot.	16.085	-172.234	15.920	-172.981	-156.149	-157.061

^aThe conversion factor from ppm au per molecule to usual ppm cgs per mole is $8.923\,8878 \times 10^{-2}$. Magnetic susceptibility in the Coulomb gauge, χ_{Av}^C , is reported in column 7. Total CTOCD-RPA magnetic susceptibility [Eq. (33)] and its partition into atomic contributions, χ_{Av}^I , are reported in column 8. Experimental magnetic susceptibility is -147 ± 20 ppm au quoted in Ref. 41.

Tables II–V also show that the gauge independence of the atomic contributions to the magnetic susceptibility is reasonably satisfied for basis sets III and IV.

Bader and Keith considered that the definition of an atomic contribution must be origin independent if theory must recover transferability of group contributions.²² The behavior of condition (35) is then a measure of that transferability. The CTOCD-RPA method applied here to describe the atomic contributions to magnetic susceptibility is not an origin independent theory. Condition (34) is a virial sum rule exactly obeyed in the Hartree-Fock limit. Condition (36) is the atomic partition of condition (34). This is the reason why its fulfillment cannot be better than that evidenced by virial sum rule (34).

In Tables VI–IX the average CTOCD-RPA atomic magnetic susceptibilities for H, O, F, N, and C, are expressed

by Eq. (30). Total CTOCD-RPA average molecular magnetic susceptibilities are reported as “Tot.” entry in the last column. They are compared with the traditional Coulomb results (obtained as the sum of columns 3, Eq. (1), and 4, Eq. (2), of the same tables). Total CTOCD-RPA-average molecular magnetic susceptibilities reported in these tables have been obtained employing Eq. (33), and verify the additivity of the atomic contributions, Eq. (30), informed in the last column of those tables. The CTOCD-RPA diamagnetic contributions, $\chi^{\Delta I}$, depend on the choice of the basis set. By inspection of these tables we see that total χ^{Δ} approximate the traditional Coulomb results, χ^d , evaluated as expectation values in the reference state for the three most extended basis sets. All values reported in these tables are calculated taking the origin of coordinates in the center-of-mass (c.m.).

In spite of the large differences in the total susceptibility

TABLE VIII. Atomic contributions to magnetic susceptibility of NH₃ in PPM au per molecule.^a

Basis set	Nucleus <i>I</i>	$\chi_{Av}^{p(L,L)}$	χ_{Av}^d	$\chi_{Av}^{p(K_n^I, L)}$	$\chi_{Av}^{\Delta(F_n^I)}$	χ_{Av}^C	χ_{Av}^I
I	N ₁			0.554	-214.944		-214.390
	H ₁			12.388	-17.150		-4.762
	Tot.	37.872	-235.370	37.717	-266.395	-197.498	-228.678
II	N ₁			0.580	-169.403		-168.823
	H ₁			13.562	-19.646		-6.084
	Tot.	41.391	-235.827	41.264	-228.341	-194.437	-187.077
III	N ₁			0.637	-177.224		-176.587
	H ₁			13.452	-19.647		-6.195
	Tot.	41.507	-235.973	40.993	-236.163	-194.468	-195.170
IV	N ₁			0.639	-177.398		-176.759
	H ₁			13.516	-19.777		-6.261
	Tot.	41.590	-235.955	41.188	-236.730	-194.365	-195.542

^aThe conversion factor from ppm au per molecule to usual ppm cgs per mole is $8.923\,8878 \times 10^{-2}$. Magnetic susceptibility in the Coulomb gauge, χ_{Av}^C , is reported in column 7. Total CTOCD-RPA magnetic susceptibility [Eq. (33)] and its partition into atomic contributions, χ_{Av}^I , are reported in column 8. Experimental magnetic susceptibility is -183 ± 9 ppm au quoted in Ref. 41.

TABLE IX. Atomic contributions to magnetic susceptibility of CH₄ in PPM au per molecule.^a

Basis set	Nucleus <i>I</i>	$\chi_{Av}^{p(L,L)}$	χ_{Av}^d	$\chi_{Av}^{p(K_n^L)}$	$\chi_{Av}^{\Delta(F_n^L)}$	χ_{Av}^C	χ_{Av}^I
I	C ₁			0.0	-127.798		-127.798
	H ₁			18.895	-19.907		-1.012
	Tot.	80.161	-317.930	75.579	-207.427	-237.769	-131.848
II	C ₁			0.0	-171.633		-171.633
	H ₁			26.098	-34.699		-8.601
	Tot.	104.601	-317.582	104.392	-310.428	-212.981	-206.036
III	C ₁			0.0	-177.009		-177.009
	H ₁			26.098	-34.688		-8.590
	Tot.	104.589	-317.575	104.391	-315.762	-212.986	-211.371
IV	C ₁			0.0	-177.220		-177.220
	H ₁			26.218	-34.924		-8.706
	Tot.	104.962	-317.561	104.870	-316.916	-212.599	-212.046

^aThe conversion factor from ppm au per molecule to usual ppm cgs per mole is $8.923\,8878 \times 10^{-2}$. Magnetic susceptibility in the Coulomb gauge, χ_{Av}^C , is reported in column 7. Total CTOCD-RPA magnetic susceptibility [Eq. (33)] and its partition into atomic contributions, χ_{Av}^I , are reported in column 8. Experimental magnetic susceptibility is -195 ± 9 ppm au quoted in Ref. 41.

of HF, H₂O, NH₃, and CH₄, the hydrogen contribution exhibits an interesting pattern: It increases its absolute value as the electronegativity of the heavy atom diminishes, $\chi_X^H = -1.4, -3.7, -6.0, -8.7$ ppm au, for $X = \text{HF}, \text{H}_2\text{O}, \text{NH}_3$, and CH₄, respectively. This is a reasonable behavior, since we would expect a larger negative contribution, the larger the density of the electron cloud around the hydrogen atom.

The contribution of heavy atoms is (ppm au): $\chi^F = -118$ in HF; $\chi^O = -150$ in H₂O; $\chi^N = -177$ in NH₃; $\chi^C = -177$ in CH₄. A direct comparison of these theoretical results with the experimentally derived parameters of Refs. 21 and 39 is not possible. In fact Ref. 21 considers a large class of compounds but the corresponding Pascal constants give incorrect molecular susceptibilities unless correction factors are introduced.

From the comparison between Coulomb, total CTOCD-RPA magnetic susceptibilities given in Tables VI-IX (columns 7 and 8), and the experimental measures, it may be considered that the theory presented in this work is quite appealing, as it provides a natural way of breaking down the molecular magnetic susceptibilities into atomic near gauge-independent terms. It is important to point out that the quality of the calculations is not judged by direct comparison between theoretical values and experimental data because the electronic correlation is not included in the approach. Instead, total magnetic susceptibilities are compared with Coulomb results, calculated also at the Hartree-Fock level, and the quality of the calculations, as the gauge invariance of the atomic contributions are assured by the fulfillment of the hypervirial conditions informed in Tables II-V.

The results are linearly dependent on the choice of the origin of the reference frame and the constraint (34) must be satisfied to assure gauge independence. The CTOCD method gives total susceptibilities results independent of the choice of the origin of the vector potential but the use of the "force formalism" to provide diamagnetic CTOCD-RPA atomic contributions relaxes that CTOCD characteristic and requires the fulfillment of the hypervirial condition (36). The diamag-

netic, χ^d and χ^Δ contributions, *vide infra* do not satisfy any variational principle.²⁴ The accuracy of the diamagnetic CTOCD-RPA contributions to magnetic susceptibility depends on the quality of the basis set and, both contributions, diamagnetic and paramagnetic, are calculated in the same level of approximation. The next step is to perform similar calculations in hydrocarbons and substituted hydrocarbons to get groups magnetic susceptibilities, i.e., -CH₂, -CH₃, -CHO, -NH₂, etc., that might be used to predict molecular magnetic susceptibilities in larger systems.

The choice of the small size molecules HF, H₂O, NH₃, and CH₄, is appropriated to present the breakdown of the magnetic susceptibility into atomic contributions, because the main emphasis is placed in understanding physical facts and testing the accuracy of the computational scheme.

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