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On CHF calculations of second-order magnetic properties using the method of continuous transformation of origin of the current density

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Summary. A fully analytical formulation is outlined for computing molecular magnetic susceptibilities and nuclear magnetic shieldings via a continuous change of origin of the electronic current density induced by an external magnetic field. The change of origin is described in terms of a (continuous) arbitrary shift function $\boldsymbol{d}(\boldsymbol{r})$. Coupled Hartree–Fock second-order magnetic properties of CH_4 and CO_2 molecules have been computed, using the special choice $\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{r}$ as generating function. A detailed analysis of results obtained with a variety of basis sets reveals that such a method is not as good as previously suggested. Large basis sets must be used to obtain accurate magnetic properties. On the other hand, all the components of theoretical nuclear magnetic shielding evaluated via this approach are independent of the origin of the vector potential. In general, theoretical magnetic susceptibilities depend linearly on the distance between different coordinate frames, but are origin independent for centre-symmetric molecules.

Key words: Coupled Hartree-Fock calculations – Second-order magnetic properties – Continuous transformation of origin of current density

1 Introduction

Recently Keith and Bader (KB) have developed novel approaches for computing molecular magnetic response properties via accurate determination of the three-dimensional electronic current density induced by external, uniform magnetic fields [1], first introducing the IGAIM (individual gauges for atoms in molecules) method [2] and subsequently the CSGT (continuous set of gauge transformations) and CSDGT (continuous set of damped gauge transformations) methods [3]. These techniques, formulated within the framework of coupled Hartree-Fock (CHF) perturbation theory [4], seem to give quite satisfactory results for magnetic susceptibility χ and nuclear magnetic shieldings σ^I, as documented by extended calculations on several molecular systems [2, 3].

The underlying idea of these procedures is that in practical situations the computed first-order molecular electron current density $\boldsymbol{J}^B(\boldsymbol{r})$ depends on the gauge origin [5], which can be chosen so as to obtain the best current density distribution for a given basis set. IGAIM uses a multiple set of gauge transformations to compute χ and σ^I as a sum of atomic contributions, which are in turn evaluated by choosing the nucleus position as gauge origin for $\boldsymbol{J}^B(\boldsymbol{r})$ within the basin of each atom. CSGT and CSDGT techniques use a different origin in real space for each point $\boldsymbol{r}$ where $\boldsymbol{J}^B(\boldsymbol{r})$ is to be computed, by introducing continuous shift functions $\boldsymbol{d}(\boldsymbol{r})$.

Within the philosophy of KB methods we have worked out [6] analytical computational schemes for molecular magnetic response properties, allowing for a continuous transformation of origin of the current density (accordingly we prefer the acronym CTOCD, as the KB transformation cannot be considered a change of gauge: the latter would imply also a simultaneous transformation of the vector potential entering the definition of the interaction energy in terms of $\boldsymbol{J}^B(\boldsymbol{r})$ [6]). These formulae, assuming the simple choice $\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{r}$, are completely general, and can be used also within *post* CHF approximations [6]. The computer code for matrix elements of some non Hermitian operators appearing in the CTOCD formulae has been easily implemented.

The main conclusions of our previous work were: (i) the exact $\boldsymbol{J}^B(\boldsymbol{r})$ is an invariant function, mapped onto itself in a general gauge transformation, but its mathematical form is affected by a change of gauge. In fact, within the CTOCD scheme, the diamagnetic contribution to the current density apparently disappears, but transformation of the paramagnetic contribution gives rise to another term equivalent to the former diamagnetic term, (ii) for $\boldsymbol{d}(\boldsymbol{r}) \equiv \boldsymbol{r}$, the theoretical magnetic properties in the KB method are in fact a sum of the conventional CHF paramagnetic term and a diamagnetic term in propagator form, (iii) the CTOCD method turns out to be equivalent to the Geertsen procedure [7], as far as average magnetic properties are concerned, (iv) within the CTOCD computational scheme all components of the σ^{I} tensor are origin independent, (v) for a given reference frame, the average theoretical magnetizability evaluated via Geertsen method does not depend on the origin of the vector potential. However, it depends linearly on an origin shift of the reference frame.

Nonetheless there is a fundamental point left unsolved in previous work [3, 6]. In order for the Geertsen method to yield accurate estimates of magnetic properties, using large basis sets is mandatory, for the computational approach relies on the assumption that some hypervirial theorems are fairly well satisfied. For instance, equivalence of dipole length and dipole velocity formalism is only insured in the limit of exact CHF wave functions. Therefore, owing to point (iii), the claim by KB that their procedure is capable of furnishing accurate theoretical magnetic properties, also when medium-size or relatively small basis sets are adopted, is apparently at variance with common experience [7].

The present work is mainly aimed at (i) outlining a general analytical formulation of the CTOCD method in terms of a continuous, but otherwise fully arbitrary, shift function; (ii) showing that the conclusions reached in Ref. [3] on the accuracy of the CSGT results are not legitimate, in that they are based on misunderstanding of the nature of the method. The reasons for this drawback are to be sought in the integration of *total* current density (instead of separate p and Δ contributions defined hereafter) performed by Keith and Bader [3], which disguises the inadequacy of their procedure for evaluating accurate diamagnetic contributions within the framework of medium-size basis sets. The analytical formulation of a general CTOCD method reported in the present note clearly pinpoints the causes of that misunderstanding.

In addition, a numerical test adopting a variety of cautiously chosen basis sets has been performed to analyze the accuracy of both paramagnetic and diamagnetic contributions to second-order magnetic properties of CH_4 and CO_2 molecules provided by conventional CHF and CTOCD approaches. In this case a function of the form $\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{r}$ is assumed.

2 CTOCD–CHF analytical expressions

Using the notation of Refs. [6, 8], analytical expressions for the CTOCD second-order magnetic properties [6] within the case of a general variational wave function for the reference state are presented hereafter. The particular case of the CHF approximation is also discussed.

The interaction energies of the electron cloud of a molecule perturbed by an external magnetic field $\boldsymbol{B}$, and by an intramolecular permanent magnetic moment $\boldsymbol{\mu}_{\mathrm{I}}$ on nucleus I, can be written

$$W^{BB} = -\frac{1}{2c}\int \boldsymbol{J}^{B}\cdot\boldsymbol{A}^{B}\,\mathrm{d}\boldsymbol{r}, \qquad W^{\mu_{\mathrm{I}}B} = -\frac{1}{c}\int \boldsymbol{J}^{B}\cdot\boldsymbol{A}^{\mu_{\mathrm{I}}}\,\mathrm{d}\boldsymbol{r}. \tag{1}$$

Introducing a second-rank current density tensor via

$$J_{\alpha}^{B} = \mathscr{T}_{\alpha}^{B_{\beta}} B_{\beta}, \tag{2}$$

the magnetic properties are redefined as

$$\chi_{\alpha\delta} = -\frac{\partial^2 W^{BB}}{\partial B_{\alpha}\partial B_{\delta}} = \frac{1}{2c}\varepsilon_{\alpha\beta\gamma}\int (r_{\beta} - r_{0\beta})\mathscr{T}_{\gamma}^{B_{\delta}}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}, \tag{3}$$

$$\sigma_{\alpha\delta}^{\mathrm{I}} = \frac{\partial^2 W^{\mu_{\mathrm{I}}B}}{\partial \mu_{\mathrm{I}_{\alpha}}\partial B_{\delta}} = -\frac{1}{c}\varepsilon_{\alpha\beta\gamma}\int \frac{r_{\beta} - R_{\mathrm{I}\beta}}{|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{I}}|^3}\mathscr{J}_{\gamma}^{B_{\delta}}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}. \tag{4}$$

In a gauge transformation of the vector potential, the interaction energies (1) and the current density J_{α}^{B} defined in terms of exact eigenfunctions to a model Hamiltonian are left unchanged [6]. Let us now consider a change of coordinate frame affecting only the current density, i.e., which does not involve the vector potential. As a consequence of this transformation, $J_{\alpha}^{B}(\boldsymbol{r})$will be evaluated using a continuous transformation of origin.

Assuming an origin shift described by the continuous function $\boldsymbol{d} \equiv \boldsymbol{d}(\boldsymbol{r})$, satisfying the condition $[d_{\alpha}, r_{\beta}] = 0$, the general analytical expressions for second-order magnetic properties become

$$\begin{aligned}\chi_{\alpha\beta} = \frac{e^2}{4m_e^2c^2}\Bigg\{&(L_{\alpha}, L_{\beta})_{-1} - m_e\langle a\Bigg|\sum_{i=1}^{n}(r_{\gamma}r_{\gamma}\delta_{\alpha\beta} - r_{\alpha}r_{\beta})_i|a\rangle \\ &-\frac{1}{2}\varepsilon_{\beta\gamma\delta}\left[\left(\sum_{i=1}^{n}(d_{\gamma}l_{\alpha})_i, P_{\delta}\right)_{-1} + \left(P_{\delta}, \sum_{i=1}^{n}(d_{\gamma}l_{\alpha})_i\right)_{-1}\right] \\ &+ m_e\langle a\Bigg|\sum_{i=1}^{n}(d_{\gamma}r_{\gamma}\delta_{\alpha\beta} - d_{\alpha}r_{\beta})_i\Bigg|a\rangle\Bigg\},\end{aligned} \tag{5}$$

$$\begin{aligned}\sigma_{\alpha\beta}^{\mathrm{I}} = -\frac{e^2}{2m_e^2c^2}\Bigg\{&(M_{\mathrm{I}\alpha}^{n}, L_{\beta})_{-1} - m_e\langle a\Bigg|\sum_{i=1}^{n}(r_{i\gamma}E_{\mathrm{I}\gamma}^{i}\delta_{\alpha\beta} - r_{i\alpha}E_{\mathrm{I}\beta}^{i})\Bigg|a\rangle \\ &-\frac{1}{2}\varepsilon_{\beta\gamma\delta}\left[\left(\sum_{i=1}^{n}(d_{i\gamma}m_{\mathrm{I}\alpha}^{i}), P_{\delta}\right)_{-1} + \left(P_{\delta}, \sum_{i=1}^{n}(d_{i\gamma}m_{\mathrm{I}\alpha}^{i})\right)_{-1}\right] \\ &+ m_e\langle a\Bigg|\sum_{i=1}^{n}(d_{i\gamma}E_{\mathrm{I}\gamma}^{i}\delta_{\alpha\beta} - d_{i\alpha}E_{\mathrm{I}\beta}^{i})\Bigg|a\rangle\Bigg\}.\end{aligned} \tag{6}$$

In these equations, using a self-explanatory notation, q.v. Refs. [6, 8], $L_{\alpha} = \sum_i^n l_{i\alpha}$, $P_{\alpha} = \sum_i^n p_{i\alpha}$, $M_{\mathrm{I}\alpha}^{n} = \sum_i^n m_{\mathrm{I}\alpha}^{i}$, $m_{\mathrm{I}\alpha}^{i} = |\boldsymbol{r}_i - \boldsymbol{R}_{\mathrm{I}}|^{-3} l_{i\alpha}(\boldsymbol{R}_{\mathrm{I}}) = (1/e)\varepsilon_{\alpha\beta\gamma}E_{\mathrm{I}\beta}^{i}p_{i\gamma}$.

The integral condition for charge–current conservation [6] $\int J_\alpha^B \mathrm{d}\boldsymbol{r} = 0$, equivalent to the constraint for origin independence of magnetizability, becomes

$$\begin{aligned}&(P_\alpha, L_\beta)_{-1} - m_e \varepsilon_{\alpha\beta\gamma} \langle a | R_\gamma | a \rangle \\ &\quad - \frac{1}{2}\varepsilon_{\beta\gamma\delta}\left[\left(\sum_{i=1}^{n} (d_\gamma p_\alpha)_i, P_\delta\right)_{-1} + \left(P_\delta, \sum_{i=1}^{n} (d_\gamma p_\alpha)_i\right)_{-1}\right] \\ &\quad + m_e \varepsilon_{\alpha\beta\gamma} \left\langle a \left| \sum_{i=1}^{n} d_{i\gamma} \right| a \right\rangle = 0. \end{aligned} \tag{7}$$

By means of the off-diagonal hypervirial relation

$$\langle j | \boldsymbol{P} | a \rangle = \mathrm{i} m_e \omega_{ja} \langle j | \boldsymbol{R} | a \rangle, \tag{8}$$

it can be shown that, in the limit of a complete basis set, the second and third lines of Eqs. (5)–(7) cancel out, and the familiar expressions [9, 10] for magnetic properties are recovered.

By choosing $\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{r}$ one obtains simpler CTOCD expressions for second-order magnetic properties [6]. For magnetizability

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^{\mathrm{p}} + \chi_{\alpha\beta}^{\Delta}, \tag{9}$$

$$\chi_{\alpha\beta}^{\mathrm{p}} = \frac{e^2}{4m_e^2 c^2}(L_\alpha, L_\beta)_{-1}, \tag{10}$$

$$\chi_{\alpha\beta}^{\Delta} = -\frac{e^2}{8m_e^2 c^2}\varepsilon_{\beta\gamma\delta}\left[\left(\sum_{i=1}^{n} (r_\gamma l_\alpha)_i, P_\delta\right)_{-1} + \left(P_\delta, \sum_{i=1}^{n} (r_\gamma l_\alpha)_i\right)_{-1}\right], \tag{11}$$

and the condition for origin independence of magnetizability Eq. (7) can be written

$$(P_\alpha, L_\beta)_{-1} - \frac{1}{2}\varepsilon_{\beta\gamma\delta}\left[\left(\sum_{i=1}^{n} (r_\gamma p_\alpha)_i, P_\delta\right)_{-1} + \left(P_\delta, \sum_{i=1}^{n} (r_\gamma p_\alpha)_i\right)_{-1}\right] = 0. \tag{12}$$

For magnetic shielding of nucleus I,

$$\sigma_{\alpha\beta}^{\mathrm{I}} = \sigma_{\alpha\beta}^{\mathrm{pI}} + \sigma_{\alpha\beta}^{\Delta\mathrm{I}}, \tag{13}$$

$$\sigma_{\alpha\beta}^{\mathrm{pI}} = -\frac{e^2}{2m_e^2 c^2}(M_{\mathrm{I}\alpha}^{n}, L_\beta)_{-1}, \tag{14}$$

$$\sigma_{\alpha\beta}^{\Delta\mathrm{I}} = \frac{e^2}{4m_e^2 c^2}\varepsilon_{\beta\gamma\delta}\left[\left(\sum_{i=1}^{n} (r_{i\gamma} m_{\mathrm{I}\alpha}^{i}), P_\delta\right)_{-1} + \left(P_\delta, \sum_{i=1}^{n} (r_{i\gamma} m_{\mathrm{I}\alpha}^{i})\right)_{-1}\right]. \tag{15}$$

In these formulae the familiar paramagnetic terms [9, 10] (denoted by the superscript p) appear. The diamagnetic terms, written as expectation values in the conventional theory by van Vleck [9] and Ramsey [10], have been replaced by equivalent ones, carrying the superscript Δ. They have the same propagator form as the paramagnetic contributions. Therefore, within the CTOCD scheme, two different first-order wave functions are required to compute magnetic properties. In the limit of exact eigenfunctions to a model Hamiltonian, the Δ terms reduce to the conventional d diamagnetic contributions, as can be shown via off-diagonal hypervirial relations.

A similar argument holds for the current density $\boldsymbol{J}^B(\boldsymbol{r})$ within the CSGT method proposed by KB [3], i.e., the conventional diamagnetic contribution $\boldsymbol{J}_{\mathrm{d}}^B(\boldsymbol{r})$ is replaced by a Δ term arising from the transformation of the paramagnetic part [6]. Therefore both terms of the CSGT current density require knowledge of first-order wave functions: accurate determinations of the Δ contribution to the current density can be obtained only by means of large basis sets.

From Rayleigh–Schrödinger perturbation theory the first-order wave functions are

$$|\Psi^{L}\rangle = -\frac{e}{2m_e c\hbar}\sum_{j\neq a}|j\rangle\langle j|\boldsymbol{L}|a\rangle\omega_{ja}^{-1}, \tag{16}$$

$$|\Psi^{P}\rangle = -\frac{e}{2m_e c\hbar}\sum_{j\neq a}|j\rangle\langle j|\boldsymbol{P}|a\rangle\omega_{ja}^{-1}, \tag{17}$$

and, within the CHF approximation, the magnetic properties of a molecule with closed shell electronic structure become

$$\chi^{\mathrm{p}}_{\alpha\beta} = -\frac{2e}{m_e c}\sum_{i=1}^{\mathrm{occ}}\langle\phi_i^o|l_\alpha|\phi_i^{l_\beta}\rangle = -\frac{e}{m_e c}\mathrm{Tr}\,\boldsymbol{H}^{l_\alpha}\boldsymbol{R}^{l_\beta}, \tag{18}$$

$$\begin{aligned}\chi^{\Delta}_{\alpha\beta} &= \frac{e}{m_e c}\varepsilon_{\beta\gamma\delta}\sum_{i=1}^{\mathrm{occ}}(\langle\phi_i^o|r_\gamma l_\alpha|\phi_i^{\mathrm{p}_\delta}\rangle + \langle\phi_i^{\mathrm{p}_\delta}|r_\gamma l_\alpha|\phi_i^o\rangle)\\ &= \frac{e}{m_e c}\varepsilon_{\beta\gamma\delta}\mathrm{Tr}\,\boldsymbol{H}^{r_\gamma l_\alpha}\boldsymbol{R}^{\mathrm{p}_\delta},\end{aligned} \tag{19}$$

$$\sigma^{\mathrm{pI}}_{\alpha\beta} = \frac{4e}{m_e c}\sum_{i=1}^{\mathrm{occ}}\langle\phi_i^o|m_{\mathrm{I}\alpha}|\phi_i^{l_\beta}\rangle = \frac{2e}{m_e c}\mathrm{Tr}\,\boldsymbol{H}^{m_{\mathrm{I}\alpha}}\boldsymbol{R}^{l_\beta}, \tag{20}$$

$$\begin{aligned}\sigma^{\Delta\mathrm{I}}_{\alpha\beta} &= -\frac{2e}{m_e c}\varepsilon_{\beta\gamma\delta}\sum_{i=1}^{\mathrm{occ}}(\langle\phi_i^o|r_\gamma m_{\mathrm{I}\alpha}|\phi_i^{\mathrm{p}_\delta}\rangle + \langle\phi_i^{\mathrm{p}_\delta}|r_\gamma m_{\mathrm{I}\alpha}|\phi_i^o\rangle)\\ &= -\frac{2e}{m_e c}\varepsilon_{\beta\gamma\delta}\mathrm{Tr}\,\boldsymbol{H}^{r_\gamma m_{\mathrm{I}\alpha}}\boldsymbol{R}^{\mathrm{p}_\delta},\end{aligned} \tag{21}$$

where $\boldsymbol{R}^l$ and $\boldsymbol{R}^P$ are first-order density matrices, $\boldsymbol{H}^l$, $\boldsymbol{H}^{rl}$, $\boldsymbol{H}^{m_{\mathrm{I}}}$ and $\boldsymbol{H}^{rm_{\mathrm{I}}}$ are matrices of atomic integrals of the one electron operators $\boldsymbol{l}$, $\boldsymbol{rl}$, $\boldsymbol{m}_{\mathrm{I}}$ and $\boldsymbol{rm}_{\mathrm{I}}$ respectively. The calculation of these matrix elements, and of similar quantities relative to operator $\boldsymbol{rp}$ appearing in sum rule (12), can be easily coded within the framework of current quantum chemistry programs.

3 Test calculations

The accuracy of theoretical magnetizability and nuclear magnetic shieldings obtained within the CTOCD–CHF approach for CH_4 and CO_2 molecules is analyzed in this section. These species have been chosen for the following reasons: (i) owing to their small size, an extended series of calculations can be performed to estimate the Hartree–Fock limit for p and Δ contributions and the degree of quality of results furnished by smaller basis sets, (ii) due to high symmetry, only a few tensor components are sufficient to convey full information on the reliability of theoretical magnetic properties, (iii) as CH_4 is a saturated molecule and CO_2 has a π-electron system and lone pairs, their magnetic properties are affected by electron correlation to a different extent, (iv) as intermolecular interactions can be considered negligible for these species, discrepancies between experimental results and theoretical CHF estimates can be mainly rationalized in terms of electron correlation effects and vibrational contributions.

The experimental molecular geometries, see footnotes to Tables 1 and 2, have been used. Seven Gaussian basis sets of increasing size and quality have been considered. They span a large domain, ranging from small, split-valence plus polarization basis sets to large, uncontracted sets augmented by several polarization functions. This selection has been carefully made to monitor the quality of theoretical results, and to analyze different trends for p and Δ contributions, attempting to assess the relative quality of these quantities and the actual accuracy of their sum, i.e., of total properties. We believe that a careful investigation of the trend of the Δ terms is of paramount importance in order to compare the relative accuracy of conventional CHF and CTOCD–CSGT methods. As a matter of fact, a yardstick for quadratic properties, e.g. the diagonal components of magnetic susceptibility, is provided by variational principles [11, 12], but, owing to their cross structure, the quality of the diamagnetic Δ terms can be judged only indirectly (for instance, by examining sum rules), as no variational condition for them has been described so far.

For the sake of comparison, two basis sets, similar to those used in CSGT calculations by KB [3], have been retained in the present study.

Basis set I is a standard 6-31G**/6-31G* (CH_4/CO_2). Usual exponents for polarization functions have been adopted, namely 0.8 for *d*-type functions on C and O, and 1.1 for *p*-type functions on H [13].

Basis set II, 6-311 + + G(2*d*,2*p*)/6-311 + *G*(2*d*) (CH_4/CO_2), has been taken from Refs. [14–16]. The exponents for polarization functions have been chosen according to the "even scaling rule" [17]: $\alpha_1 = \frac{1}{2}\alpha$ and $\alpha_2 = 2\alpha$, where $\alpha = 0.626$ for C, $\alpha = 1.292$ for O and $\alpha = 0.75$ for H. We guess that this basis set is equivalent to the "small" basis set used by KB [3].

The contraction scheme (11*s*7*p*2*d*/5*s*2*p*) → [6*s*4*p*1*d*/3*s*1*p*] has been employed to construct basis set III from van Duijneveldt *sp* substrate [18], adding to both C and H two polarization functions contracted to one according to Huzinaga [19] and Dunning [20] recipes. The exponents of polarization functions have been optimized to maximize the average value of the χ^{p} tensor. In the case of CH_4 they are 2.2 for *d*-type functions on C and 1.2 for *p*-type functions on H. In the case of CO_2 they are 1.0 and 2.2 for *d*-type functions on C and O respectively.

Basis set IV is a [6*s*4*p*2*d*/3*s*2*p*], obtained from III by allowing the polarization functions to vary freely. Basis set V is constructed from (11*s*7*p*4*d*/5*s*3*p*) primitive set of Gaussians, adopting the same *sp* substrate from van Duijneveldt [18] and expanding the polarization functions of basis set III over four *d*-type functions for C and O, and three *p*-type functions for H [19, 20]. Basis set VI is an uncontracted (13*s*8*p*4*d*/8*s*3*p*), where the *sp* substrate is from van Duijneveldt [18] and the exponents of polarization functions are: 2.7, 0.9, 0.3 and 0.1 for *d*-type functions on O, 1.8, 0.6, 0.2 and 0.07 for *d*-type functions on C, and 1.8, 0.6 and 0.2 for *p*-type functions on H. This basis set should be similar to the "large" basis set of KB [3].

Basis set VII is an uncontracted (13*s*10*p*5*d*2*f*/8*s*4*p*1*d*) where, according to the suggestions of Refs. [21, 22] the *sp* van Duijeneveldt substrate has been augmented by two tight even-tempered *p* functions with exponents 3694.5 and 859.6 for O, 1512.9 and 355.1 for C. For H one tight *p* function with exponent 6.269 has been added to the Dunning set [23] 2.292, 0.838 and 0.292. The exponents of *d* functions are 10.962, 3.775, 1.300, 0.444 and 0.152 for O, 5.262, 1.848, 0.649, 0.228 and 0.08 for C, 1.057 for H. Those of *f* functions are 2.666 and 0.895 for O, 1.419 and 0.485 for C.

The results are reported in Tables 1–4. Theoretical magnetizability and nuclear magnetic shielding tensors obtained for CH_4 are shown in Table 1; magnetizability,

Table 1. Single-origin CHF and CTOCD–CHF magnetic properties of CH_4 molecule[a]

Basis →	I	II	III	IV	V	VI	VII	Expt.
$\chi^{d}(C)$	− 316.8	− 317.7	− 318.0	− 317.8	− 317.7	− 317.6	− 317.6	− 299 ± 9[b]
$X^{\Delta}(C)$	− 196.4	− 301.6	− 310.0	− 313.8	− 316.5	− 316.5	− 315.8	− 299 ± 9[b]
$\chi^{p}(C)$	76.1	102.1	103.1	104.0	104.9	104.9	105.1	104.2 ± 0.1[c]
$\chi^{d+p}(C)$	− 240.7	− 215.6	− 214.8	− 213.8	− 212.8	− 212.7	− 212.5	−195±9[d], −210[e]
$\chi^{\Delta+p}$	− 120.3	− 199.6	− 206.9	− 209.8	− 211.6	− 211.7	− 210.7	−195±9[d], −210[e]
$\sigma^{dC}(C)$	296.2	296.2	296.3	296.3	296.3	296.3	296.3	
$\sigma^{\Delta C}(C)$	101.7	170.0	172.1	173.5	290.1	291.3	295.9	
$\sigma^{pC}(C)$	− 87.0	− 99.6	− 98.8	− 100.3	− 102.0	− 102.2	− 102.8	
$\sigma^{d+pC}(C)$	209.1	196.7	197.5	196.0	194.3	194.1	193.5	195.1[f], 195.15[g]
$\sigma^{\Delta+pC}$	14.7	70.5	73.3	73.1	188.1	189.1	193.1	195.1[f], 195.15[g]
$\sigma^{dH}_{Av}(H)$	87.5	87.5	87.4	87.5	87.5	87.5	87.5	
$\sigma^{dH}_{xy}(H)$	− 19.8	− 19.8	− 19.8	− 19.8	− 19.8	− 19.8	− 19.8	
$\sigma^{\Delta H}_{Av}(H)$	60.6	79.2	78.5	78.9	86.5	86.4	87.3	
$\sigma^{\Delta H}_{xy}(H)$	− 12.2	− 16.7	− 16.5	− 16.8	− 19.8	− 19.8	− 19.8	
$\sigma^{pH}_{Av}(H)$	− 36.7	− 49.2	− 49.1	− 49.2	− 55.7	− 55.7	− 56.1	− 56.45[h]
$\sigma^{pH}_{xy}(H)$	13.2	19.6	19.8	19.8	23.0	23.0	23.1	
$\sigma^{d+pH}_{Av}(H)$	50.8	38.3	38.3	38.3	31.7	31.8	31.4	30.611±0.024[i], 30.72[j]
$\sigma^{d+pH}_{xy}(H)$	− 6.6	− 0.1	0.0	− 0.0	3.2	3.1	3.3	
$\sigma^{\Delta+pH}_{Av}$	23.9	30.1	29.3	29.7	30.7	30.6	31.2	30.611±0.024[i], 30.72[j]
$\sigma^{\Delta+pH}_{xy}$	1.0	3.0	3.3	3.0	3.2	3.2	3.3	

[a] Nuclear coordinates in bohr: C = (0, 0, 0), H = (1.190341, 1.190341, 1.190341).
Magnetizability in cgs ppm a.u.; the conversion factor from cgs ppm a.u. per molecule to ppm cgs emu per mole is 8.9238878×10^{-2} $cm^3\,mol^{-1}$. To convert to ppm SI units, further multiply by 10 (1 $J\,T^{-2}\,mol^{-1}$ = 0.1 cgs emu mol^{-1}).
Nuclear magnetic shielding in p.p.m. Gauge origin in parentheses

[b] Estimated in Ref. [28] using total χ values from Ref. [30]

[c] From Ref. [28]

[d] From Ref. [30]

[e] From Ref. [29]

[f] From Ref. [26]

[g] From Ref. [31]; estimated rovibrational correction − 3.3 and − 3.56 ppm, equilibrium $\sigma_e^C = 198.7$ ppm [26]

[h] From Ref. [32]

[i] From Ref. [33]

[j] From Ref. [34]

^{13}C and ^{17}O magnetic shielding tensors for CO_2 are displayed in Tables 2–4. For a given magnetic property, each total theoretical value is obtained (i) as a sum of the conventional diamagnetic and paramagnetic term (i.e., single-origin CHF value indicated with subscript d + p in the tables), (ii) as a sum of the Δ "diamagnetic" contribution, see Eqs. (11) and (15), and conventional p paramagnetic terms (i.e., CTOCD–CHF value indicated with subscript Δ + p). An entry between parentheses specifies the gauge origin for origin dependent quantities, no entry means that the corresponding quantity is translationally invariant (compare for the

Table 2. Single-origin CHF and CTOCD–CHF magnetizability of CO_2 molecule[a]

Basis →	I	II	III	IV	V	VI	VII	Expt.
$\Delta\chi^{d}(C)$	− 1080.2	− 1075.2	− 1073.5	− 1072.9	− 1075.7	− 1075.7	− 1076.2	− 1072 ± 22[b]
$\chi^{d}_{Av}(C)$	− 1008.1	− 1011.0	− 1012.7	− 1012.1	− 1010.5	− 1010.6	− 1010.5	− 994 ± 22[b]
$\Delta\chi^{\Delta}(C)$	− 756.8	− 959.5	− 979.0	− 975.3	− 1075.8	− 1074.7	− 1076.6	− 1072 ± 22[b]
$\chi^{\Delta}_{Av}(C)$	− 656.3	− 859.5	− 894.1	− 899.0	− 997.5	− 1005.6	− 1010.1	− 994 ± 22[b]
$\Delta\chi^{p}(C)$	718.7	973.0	1015.9	1018.6	1126.8	1125.9	1136.6	
$\chi^{p}_{Av}(C)$	479.2	648.7	677.2	679.1	751.2	750.6	757.7	
$\Delta\chi^{d+p}(C)$	− 361.4	− 102.2	− 56.7	− 54.3	51.1	50.2	60.4	69.8 ± 2[c], 68[d]
$\chi^{d+p}_{Av}(C)$	− 529.0	− 362.3	− 335.5	− 333.0	− 259.3	− 260.0	− 252.7	− 235[e], − 244[f]
$\Delta\chi^{\Delta+p}$	− 38.0	13.5	36.9	43.3	51.0	51.2	60.0	69.8 ± 2[c], 68[d]
$\chi^{\Delta+p}_{Av}$	− 177.1	− 210.9	− 216.9	− 220.0	− 246.3	− 255.0	− 252.3	− 235[e], − 244[f]

[a] Nuclear coordinates in bohr: C = (0, 0, 0), O = (0, 0, 2.1944).
In cgs ppm a.u.; for conversion factors to cgs emu and SI units see Table 1.
$\Delta\chi = \chi_{\perp} - \chi_{\parallel}$. For the paramagnetic component $\Delta\chi^{p} = \chi^{p}_{\perp}$, $\chi^{p}_{\parallel} = 0$.
Gauge origin in parentheses

[b] From Ref. [35]

[c] From Ref. [36]

[d] From Ref. [37]

[e] From Ref. [38]

[f] From Ref. [37]

Table 3. Single-origin CHF and CTOCD–CHF ^{13}C magnetic shielding in CO_2 molecule[a]

Basis →	I	II	III	IV	V	VI	VII	Expt.
$\Delta\sigma^{dC}(C)$	155.9	155.0	155.3	155.4	156.2	156.2	156.7	
$\sigma^{dC}_{Av}(C)$	386.8	387.0	386.9	386.9	387.1	387.1	387.2	
$\Delta\sigma^{\Delta C}(C)$	113.2	138.0	141.7	143.0	154.7	154.4	156.5	
$\sigma^{\Delta C}_{Av}(C)$	153.7	236.2	225.3	227.0	376.3	378.9	386.5	
$\Delta\sigma^{pC}(C)$	− 410.1	− 474.3	− 480.6	− 479.2	− 499.0	− 499.4	− 505.6	
$\sigma^{pC}_{Av}(C)$	− 273.4	− 316.2	− 320.4	− 319.4	− 332.6	− 332.9	− 337.1	
$\Delta\sigma^{d+pC}(C)$	− 254.3	− 318.3	− 325.2	− 323.8	− 342.7	− 343.1	− 348.9	
$\sigma^{d+pC}_{Av}(C)$	113.4	70.8	66.5	67.5	54.4	54.2	50.1	58.8[b]
$\Delta\sigma^{\Delta+pC}$	− 297.0	− 336.3	− 338.9	− 336.2	− 344.3	− 345.0	− 349.1	
$\sigma^{\Delta+pC}_{Av}$	− 119.7	− 80.0	− 95.1	− 92.4	43.6	45.9	49.4	58.8[b]

[a] In ppm $\Delta\sigma = \sigma_\perp - \sigma_\parallel$. For the paramagnetic component $\sigma^p_\parallel = 0$, $\Delta\sigma^p = \sigma^p_\perp$. Gauge origin in parentheses

[b] From Refs. [26, 31]; estimated rovibrational correction − 1.5 ppm, equilibrium value $\sigma^C_e = 60.3$ [26]

Table 4. Single-origin CHF and CTOCD–CHF ^{17}O magnetic shielding in CO_2 molecule[a]

Basis →	I	II	II	IV	V	VI	VII	Expt.
$\Delta\sigma^{dO}(O)$	91.4	91.4	90.7	90.8	91.5	91.5	92.0	
$\sigma^{dO}_{Av}(O)$	475.3	475.7	475.8	475.8	475.9	475.9	475.9	
$\Delta\sigma^{\Delta O}(O)$	63.1	83.3	70.8	77.0	91.3	91.5	92.0	
$\sigma^{\Delta O}_{Av}(O)$	160.6	284.1	295.0	295.6	467.6	465.2	475.2	
$\Delta\sigma^{pO}(O)$	− 321.2	− 355.3	− 389.0	− 387.9	− 378.2	− 378.8	− 382.2	
$\sigma^{pO}_{Av}(O)$	− 214.2	− 236.8	− 259.3	− 258.6	− 252.2	− 252.5	− 254.8	
$\Delta\sigma^{d+pO}(O)$	− 229.9	− 263.9	− 298.3	− 297.1	− 286.7	− 287.3	− 290.1	
$\sigma^{d+pO}_{Av}(O)$	261.1	238.9	216.5	217.2	223.8	223.4	221.2	243.4[b]
$\Delta\sigma^{\Delta+pO}$	− 258.1	− 271.3	− 318.1	− 310.8	− 286.9	− 287.3	− 290.2	
$\sigma^{\Delta+pO}_{Av}$	− 53.6	47.2	35.7	37.0	215.4	212.6	220.4	243.4[b]

[a] In ppm $\Delta\sigma = \sigma_\perp - \sigma_\parallel$. For the paramagnetic component $\sigma^p_\parallel = 0$, $\Delta\sigma^p = \sigma^p_\perp$. Gauge origin in parentheses

[b] From Refs. [39], derived assuming an absolute shielding constant of − 42.3 ± 17.2 ppm for CO

case of CTOCD nuclear magnetic shielding [6]). For the molecular systems considered here, and in general for molecules having a vanishing dipole moment, also the CTOCD magnetizability is origin independent, as relation (12) is exactly fulfilled by symmetry.

As regards theoretical magnetizabilities, it can be observed that, improving the basis set, the conventional diamagnetic and paramagnetic contributions show their characteristic trend, namely the former does not change appreciably and the latter increases, as expected from variational principles [11, 12] for a quadratic quantity. Accordingly, total single-origin CHF results approach the Hartree–Fock (HF) limit from below. This limit value has been virtually reached via basis set VII for both molecules. In addition, $\chi = -212.5$ cgs ppm a.u. and $\chi^p = 105.1$ cgs ppm a.u. evaluated for CH_4, compare quite nicely with the experimental data. For CO_2 the best single-origin result is 9–18 cgs ppm a.u. lower than the experimental one: correlation effects are expected to play an important role in this molecule.

For CH_4 we obtained a limit value of the CTOCD–CHF magnetizability, see basis sets V–VII, which is very close to the conventional one. In the case of CO_2 only basis set VII gives comparable results.

The magnetizabilities evaluated via basis sets II and VI can be compared with those reported by KB [3] to assess the practical equivalence of CTOCD and CSGT methods, i.e., of analytical and numerical integration procedures. For CH_4 slight differences are found, compare, for instance, -199.6 cgs ppm a.u. from basis set II in the present work with their -192 cgs ppm a.u., and our -211.7 cgs ppm a.u. from basis set VI with their -210 cgs ppm a.u.. These small differences might be due to slightly different molecular geometries and/or exponents of polarization functions (little discrepancies of the same magnitude are found also between conventional CHF results). In the case of CO_2 our total CTOCD magnetizabilities are rather different from those reported by KB, compare our -210.9 cgs ppm a.u. with their -235 cgs ppm a.u. for basis set II, and our -255.0 cgs ppm a.u. with their -245 cgs ppm a.u. for basis set VI, as these values are obtained in a different way. As shown by Keith and Bader in Ref. [25], their average CSGT magnetizability from 6-311 + G(2*d*) basis set, -235 cgs ppm a.u. (identical to the experimental one), was obtained by summing the conventional CHF value, -291 cgs ppm a.u., for $\chi_{\parallel}$ and the CSGT estimate, -207 cgs ppm a.u., for $\chi_{\perp}$ (this value is in very good agreement with our -206.4 cgs ppm a.u. for $\chi_{\perp}^{\Delta+\mathrm{p}}$).

It is worth noticing that *total* CTOCD–CHF magnetizabilities yielded by intermediate basis sets, II–IV for CH_4 and II–V for CO_2, are apparently in better agreement with the experimental data than corresponding conventional CHF predictions. Similar findings led KB to the erroneous conclusion [3] that CTOCD method is more accurate than CHF (in fact, one can observe that their CSGT estimates for magnetic susceptibilities obtained via the larger basis set lie systematically between experimental and conventional data, and that the smaller basis set often yields CSGT magnetizabilities in better agreement with the experimental value).

This misconception arises from their use of integration of total current density to work out magnetic properties (instead of separate p and Δ contributions): their computational technique hides the intrinsic lack of accuracy, due to incomplete cancellation of errors affecting p and Δ terms to a different extent.

In order to clarify this point it is expedient to recall that *the same* χ^{p} contribution is evaluated both in ordinary CHF and CTOCD schemes, and that the CHF expectation value for the χ^{d} contribution is accurate. Therefore one has to analyze the trend of computed χ^{Δ} tensors versus the quality of basis sets. In the limit of a complete set of expansion the hypervirial relation (8) holds and χ^{Δ} tensor is equal to χ^{d}. From our calculations it can be observed that the components of χ^{Δ} usually approach the corresponding χ^{d} terms from above, as basis set improves.

Total CTOCD magnetizability is obtained as a sum of Δ and p contribution. Both of them are hard to compute accurately, as they depend on the quality of first-order perturbed wave functions, see Eqs. (9), (18) and (19). In addition, they are differently affected by basis set characteristics. Actually it is evident that, for a given basis set, χ^{Δ} is less accurate than χ^{p}, i.e., the percent deviation from the HF limit is much larger for the former than for the latter. Therefore cancellation of errors in the sum for total magnetizability takes place to a different extent for different basis sets. As a result, the CTOCD–CHF magnetizability approaches the HF limit from above for both molecules (a similar behaviour has been already observed by Geertsen [7] for the average magnetizability). Therefore, recalling the trend of paramagnetic magnetizabilities, the actual HF limit should lie somewhere in between conventional CHF and CTOCD results, i.e., − 217.7: − 212.7 cgs ppm a.u. from basis set VI for CH_4 and − 252.3: − 252.7 cgs ppm a.u. for the average magnetizability from basis set VII of CO_2. These values compare quite nicely with the limit magnetizabilities recently reported by Ruud et al. [24], i.e., − 213 cgs ppm a.u. for CH_4 and − 252 cgs ppm a.u. for CO_2.

Paradoxically enough, CTOCD–CHF estimates provided by smaller basis sets are *apparently* in better agreement with experiment than corresponding single-origin CHF values, which is merely due to the inaccuracy of the Δ contribution and to the aforementioned spurious cancellation of errors: *as a matter of fact, the CTOCD–CHF magnetic susceptibilities from basis sets I–IV for methane, and from basis sets I–V for carbon dioxide, are less accurate than conventional CHF.*

As regards nuclear magnetic shieldings of heavy atoms one can observe that CTOCD–CHF results are quite poor, and only basis set VII gives ^{13}C and ^{17}O magnetic shieldings comparable with the conventional ones: since accurate first-order wave functions are obtained only adopting very large basis sets, it turns out that CTOCD results from intermediate basis sets are far from being accurate. The use of compact p and d functions suggested by Refs. [21, 22] improves significantly the theoretical values of nuclear magnetic shieldings.

Therefore we can safely conclude that, for a given basis set, also nuclear magnetic shieldings from ordinary CHF approach are more accurate than those evaluated via the CTOCD procedure, at least for the choice $\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{r}$.

Surprisingly enough, IGAIM and CSDGT ^{13}C magnetic shieldings reported by KB [3] seem to compare very well with experimental data, which is difficult to justify, as contributions arising from correlation and rovibrational effects are not accounted for by these authors. In fact a more accurate analysis of experimental data shows that for CH_4 the experimental value 195.1 ppm becomes 198.7 ppm, after rovibrational correction [26], 3.6 ppm larger than the KB estimate [3], and in good agreement with an accurate value, 201.5 ppm, recently obtained by Gauss [27] accounting for correlation effects via a GIAO-MBPT(2) method. Analogously, ^{13}C magnetic shielding in CO_2 becomes 60.3 ppm after rovibrational correction, close to the correlated GIAO-MBPT(2) value, 63.5 ppm [27]. In these cases at least, it does not seem that IGAIM and CSDGT methods provide nuclear magnetic shieldings more accurate than conventional ones obtained assuming the origin of the gauge on the nucleus in question.

As a matter of fact, nuclear magnetic shielding is essentially determined by density current flowing in a close environment of the nucleus, as the contribution of $\boldsymbol{J}^B(\boldsymbol{r})$ decreases with the square of the distance of each point $\boldsymbol{r}$ from the nucleus itself. Accordingly, discrepancies among IGAIM, CSDGT and conventional CHF results for magnetic shielding are not expected to be large in general.

Within the CSDGT method, all of the four terms entering Eqs. (5) and (6) need to be evaluated, i.e., two expectation values and two terms involving first-order wave functions (16) and (17), which require large basis sets for accurate calculations.

4 Conclusion

Considering Eqs. (5) and (6) it is easy to see that by choosing $\boldsymbol{d}(\boldsymbol{r}) = \boldsymbol{r}$ one cannot generally expect accurate results, as two first-order wave functions are involved. A better solution would be possibly obtained looking for a $\boldsymbol{d}(\boldsymbol{r})$ which made the sum of first and third term on the r.h.s. of Eqs. (5) and (6) vanish. One could alternatively try minimizing the sum, in order to reduce the contribution from perturbed wave functions as much as possible. In principle there are no reasons to expect that such $\boldsymbol{d}(\boldsymbol{r})$ should have the same form for both magnetic properties and for every basis set. Moreover, as angular momentum is not the total time derivative of another observable, there is no $\boldsymbol{X}$ operator connected via off-diagonal hypervirial relation to angular momentum, i.e., $\langle j|\boldsymbol{L}|a\rangle \neq i\omega_{ja}\langle j|\boldsymbol{X}|a\rangle$ [8]. Thus exact cancellation of first and third term on right side of Eqs. (5) and (6) does not seem possible in general. On the other hand, one might look for a $\boldsymbol{d}(\boldsymbol{r})$ which minimizes the contribution due to perturbed wave functions within the magnetizability functional (5).

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