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CTOCD-DZ shielding polarizabilities in a set of small molecules: N_2, H_2, HF, HCl, HCN and SH_2 ☆

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Abstract

A procedure based on formal annihilation of the diamagnetic contribution to the quantum mechanical electron current density, via a continuous transformation of its origin all over the molecular domain, CTOCD-DZ method, is applied for determining shielding polarizabilities to first-order in a perturbing electric field. Analytical expressions for the third-rank tensors have been implemented in the SYSMO suite of programs employing the coupled Hartree–Fock approach. In the limit of exact eigenfunctions to a model Hamiltonian, the CTOCD-DZ expressions reduce to conventional terms. In any calculation relying on the algebraic approximation, irrespective of size and quality of the (gaugeless) basis set employed, all the components of the magnetic shielding polarizabilities evaluated within these methods are origin independent. Test calculations have been carried out in N_2, H_2, HF, HCl, HCN and SH_2 compounds.

Keywords: Shielding polarizabilities; Hamiltonian; Coupled Hartree–Fock

1. Introduction

The presence of a time-independent electric field produces changes in the molecular second-rank tensors, i.e. the magnetic susceptibility $\chi_{\alpha\beta}$ and the magnetic shielding $\sigma^I_{\alpha\beta}$, of the Ith nucleus which are the usual response properties to the presence of an external magnetic field.

The application of a static electric field polarizes the electronic charge distribution and leads to changes in molecular magnetic susceptibility and nuclear magnetic shielding, which can be rationalized in terms of response tensors of higher rank [1,2].

In the presence of two external perturbations, i.e. the spatially uniform time-independent electric and magnetic fields **E** and **B**, and a permanent dipole moment $\boldsymbol{\mu}_I$, on nucleus I, the energy of the molecule, evaluated in the singlet electronic state $|\psi_a\rangle$ is, employing the Buckingham notation [1,2] to denote molecular tensors,

$$W_a = W_a^{(0)} - \mu_\alpha E_\alpha - \frac{1}{2}\alpha_{\alpha\beta}E_\alpha E_\beta + \cdots - \frac{1}{2}\chi_{\alpha\beta}B_\alpha B_\beta + \cdots + \sigma^I_{\alpha\beta}\mu_{I\alpha}B_\beta + \cdots - \frac{1}{2}\chi_{\alpha\beta\gamma}B_\alpha B_\beta E_\gamma + \cdots + \sigma^I_{\alpha\beta\gamma}\mu_{I\alpha}B_\beta E_\gamma + \cdots \quad (1)$$

Nuclear magnetic shielding of a chosen nucleus I, in the presence of an external weak, homogeneous

☆ Dedicated to Professor R. Gáspár on the occasion of his 80th year.

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electric field **E** may be expanded as [3]

$$\sigma^J_{\alpha\beta}(E) = \sigma^J_{\alpha\beta} + \sigma^J_{\alpha\beta\gamma}E_\gamma + \frac{1}{2}\sigma^J_{\alpha\beta\gamma\delta}E_\gamma E_\delta + \ldots \qquad (2)$$

The third-rank tensor $\sigma^J_{\alpha\beta\gamma}$ describes the non-linear response of the electron cloud to the first-order in **E**. These quantities are sometimes referred to as shielding polarizabilities [4–11].

Many groups have been active in this field recently. Augspurger and co-workers have carried out calculations for a wide range of nuclei in an extended series of molecules [7–10]. Cybulski and Bishop [11] employed MP3 and linearized coupled cluster to doubles (LCCD) plus finite field numerical differentiation calculations on N_2, HF, CO and H_2, and, very recently, Ågren et al. have calculated the MSCF cubic response [12]. Bishop and Cybulski also adopted SCF and MP2 methods for calculating the electric field dependence of magnetic nuclear shielding [6] and susceptibility [4]. The review by Raynes [13] is an excellent introduction to the subject. He pointed out that the effect of an electric field on the chemical shielding is invoked to explain experimental observations such as intermolecular interactions in gases, effects of solvent in liquids and intramolecular electric fields in solids.

SCF and MSCF electric field-dependence of the magnetizability and nuclear magnetic shielding have been studied by Rizzo et al. [5,14,15] within GIAO basis sets. The use of London orbitals guarantees invariance of theoretical estimates in a change of coordinate system, which is a basic requirement in the computation of magnetic response properties.

Although faster convergence of GIAO calculations might then be preferable in numerical studies [16], continuous transformation of the origin of the current density (CTOCD) schemes for $\chi_{\alpha\beta}$ and $\sigma^J_{\alpha\beta}$ are easier to implement at any level of accuracy [17–21] and become competitive, provided proper basis sets are employed [22]. They are well suited to satisfy the constraints of charge and current conservation by annihilation of either diamagnetic (CTOCD-DZ method) or paramagnetic (CTOCD-PZ method) contributions to electronic current density via continuous transformation of origin. (Keith and Bader [23] have presented the idea of continuous transformation of origin for the first time.).

The present paper makes a brief revision of the CTOCD-DZ method developed by Lazzeretti and Zanasi [24], via formal annihilation of diamagnetic contributions to the electronic current density induced in the presence of static homogeneous electric and magnetic fields. We have implemented the equations reported in Ref. [24], transforming the non-Hermitian operators into Hermitian ones and employing the coupled Hartree–Fock (CHF) approach to calculate origin-independent $\sigma^J_{\alpha\beta\gamma}$, nuclear shielding polarizabilities, for N_2 and the set of binary hydrides H_2, HF, HCl, HCN and SH_2. Indeed, shielding polarizability evaluated within this method is origin-independent and the constraints for charge and current conservation are exactly fulfilled, regardless of the size of the basis set employed to perform the calculations. Emphasis is placed in understanding the physical facts and testing the accuracy of the results. The results do not depend on the choice of the origin of coordinates. The accuracy of the results depends on the quality of the basis set. We compare our results with those of other authors, critically, and employ different basis sets described in Section 6.

2. Nuclear magnetic shielding in the presence of a static electric field

We shall briefly review some definitions to compute nuclear magnetic shielding in the presence of a static electric field, i.e. shielding polarizabilities, $\sigma^J_{\alpha\beta\gamma}$.

In the presence of static external electric field **E** and magnetic field **B** and an intrinsic magnetic moment $\boldsymbol{\mu}_I$, on nucleus I, the electronic first-order Hamiltonian contains three first-order terms

$$H^E = eE_\alpha R_\alpha, \qquad (3)$$

$$H^B = (e/m_e c)\sum_{i=1,n}\mathbf{A}^B_i\cdot\mathbf{p}_i = (e/2mc)B_\alpha L_\alpha, \qquad (4)$$

$$H^{\mu_I} = (e/m_e c)\sum_{i=1,n}\mathbf{A}^{\mu_I}_i\cdot\mathbf{p}_i = (e/mc)M^n_{I\alpha}\mu_{I\alpha} \qquad (5)$$

using the notation of Refs. [25,26]. The vector potentials $\mathbf{A}^B_i = \mathbf{A}^B(\mathbf{r}_i)$ and $\mathbf{A}^{\mu_I}_i = \mathbf{A}^{\mu_I}(\mathbf{r}_i)$ are

defined as

$$\mathbf{A}^B(\mathbf{r}) = \frac{1}{2}\mathbf{B}\times(\mathbf{r}-\mathbf{r}_0), \quad \mathbf{A}^{\mu I}(\mathbf{r}) = \frac{\mu_I \times (\mathbf{r}-\mathbf{R}_I)}{|\mathbf{r}-\mathbf{R}_I|^3}, \tag{6}$$

($\mathbf{r}_0$, the origin of the vector potential may be equal to **0**, without loss of generality).

The third-rank diamagnetic and paramagnetic contributions to electric field-dependent nuclear magnetic shielding, to first-order in **E** are

$$\sigma^I_{\alpha\beta\gamma} = \frac{\partial^3 W^{(3)}_{\tilde{a}}}{\partial\mu_{I\alpha}\,\partial B_\beta\,\partial E_\gamma} = \sigma^{I\mathrm{d}}_{\alpha\beta\gamma} + \sigma^{I\mathrm{p}}_{\alpha\beta\gamma}, \tag{7}$$

$$\sigma^{\mathrm{d}I}_{\alpha\beta\gamma} = -(e^2/2m_e c^2\hbar)\sum_{j\neq a} 2\omega_{ja}^{-1}\mathrm{Re} \times\left\{\langle a|\sum_{i=1,n}(r_i E^i_{I\gamma}\delta_{\alpha\beta} - r_{i\alpha}E^i_{I\beta})|j\rangle\langle j|R_\gamma|a\rangle\right\}, \tag{8}$$

$$\sigma^{\mathrm{p}I}_{\alpha\beta\gamma} = (e^3/2m_e^2c^2)\{M^n_{I\alpha}, L_\beta, R_\gamma\}_{-2} \tag{9}$$

In Eq. (9) we have employed the definition [26]

$$\{A,B,C\}_{-2} \equiv -4\mathrm{Tr}([\mathbf{F}^{(A)}(\mathbf{X}^{(B)}\,\Delta\mathbf{X}^{(C)} - \mathbf{X}^{(C)}\,\Delta\mathbf{X}^{(B)}] + [B,C,A] + [C,A,B]) \tag{10}$$

where $[B,C,A]$ and $[C,A,B]$ are permutations of the perturbators involved in the expression. Eq. (10) is a third-rank tensor written employing the McWeeney procedure [27] for the CHF approach. $\mathbf{F}^{(A)}$ represents the first-order perturbed Fock matrix, $\mathbf{X}^{(A)}$ matrices are computed only once to solve the first-order CHF problem for each perturbation, and $\mathbf{\Delta}_{pq}$ is the overlap matrix between the atomic orbitals, χ_p and χ_q, of an orthonormal basis set χ. In the actual calculations, employing non-orthogonal basis sets of Gaussian functions, it is customary to orthogonalize them according to the Löwdin procedure.

3. Electronic current density in the presence of static electric and magnetic fields

The third-order interaction energy contains contributions, which can be expressed in terms of the second-order electron current density vector $\mathbf{J^{BE}}$ induced by the fields,

$$W^{BBE} = -(1/2c)\int \mathbf{J}^{BE}\cdot\mathbf{A}^B\,\mathrm{d}r, \qquad W^{\mu_I BE} = -(1/c)\int \mathbf{A}^{\mu_I}\cdot\mathbf{J}^{BE}\,\mathrm{d}r \tag{11}$$

The expression for $\mathbf{J^{BE}}$ is derived via the general quantum mechanical definition [28], introducing the perturbation expansion for the current density and the a-state molecular wave-function (depending on n-electron space-spin coordinates χ_i), $\psi_a(\chi_1,\chi_2,\ldots\chi_n)$.

The first- and second-order electronic wave-functions necessary for further development are obtained from Rayleigh–Schrödinger perturbation theory (see Ref. [24] for details).

Diamagnetic and paramagnetic contributions to a third-rank current density tensor can be defined according to the following equations,

$$J^{BE}_\delta(\mathbf{r}) = B_\beta E_\gamma \vartheta^{B\beta E\gamma}_\delta(\mathbf{r}), \tag{12}$$

$$\vartheta^{B\beta E\gamma}_\delta(\mathbf{r}) = \vartheta^{B\beta E\gamma}_{\mathrm{d}\delta}(\mathbf{r}) + \vartheta^{B\beta E\gamma}_{\mathrm{p}\delta}(\mathbf{r}), \tag{13}$$

$$\vartheta^{B\beta E\gamma}_{\mathrm{d}\delta}(\mathbf{r}) = -(ne^2/2m_e c)\epsilon_{\delta\beta\nu}r_\nu\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times[\psi^{(0)}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\psi^{E\gamma *}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n) + \psi^{E\gamma}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\psi^{(0)*}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)], \tag{14}$$

$$\begin{aligned}\vartheta^{B\beta E\gamma}_{\mathrm{p}\delta}(\mathbf{r}) = -(ne/m_e)\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times[&\psi^{B\beta E\gamma *}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\delta\psi^{(0)}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\\ &+\psi^{E\gamma B\beta *}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\delta\psi^{(0)}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\\ &+\psi^{(0)*}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\delta\psi^{B\beta E\gamma}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\\ &+\psi^{(0)*}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\delta\psi^{E\gamma B\beta}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\\ &+\psi^{E\gamma *}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\delta\psi^{B\beta}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\\ &+\psi^{B\beta *}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\delta\psi^{E\gamma}_a(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)].\end{aligned} \tag{15}$$

Gauge invariance of magnetic properties is associated with the continuity equation [29,30]. In a

gauge transformation of the vector potential

$$\mathbf{A}^{B'} \rightarrow \mathbf{A}^{B''} = \mathbf{A}^{B'} + \nabla f, \qquad \mathbf{A}^{B''} = \frac{1}{2}\mathbf{B}\times(\mathbf{r}-\mathbf{r}') \tag{16}$$

where $f = f(r)$ is an arbitrary function well-behaved for $r \rightarrow \infty$, the third-rank interaction energy, Eq. (11), and the response nuclear magnetic shielding, Eq. (7) are left-unchanged, provided the integral vanishes.

$$\int \mathbf{J}^{BE}\cdot\nabla f \, \mathrm{d}r = \int \nabla\cdot(\mathbf{J}^{BE} f)\mathrm{d}r - \int f\nabla\cdot\mathbf{J}^{BE} \, \mathrm{d}r \tag{17}$$

By applying the Gauss theorem, the first volume integral on the right-hand side is converted into a surface integral, and vanishes owing to the boundary conditions usually assumed for ψ_a and $\mathbf{J}^{\mathbf{BE}}$, i.e. ψ_a, $\mathbf{J}^{\mathbf{BE}} \rightarrow 0$ for $r \rightarrow \infty$. Thus the integral on the left-hand side vanishes if the continuity equation $\nabla\cdot\mathbf{J}^{BE} = 0$ is satisfied.

4. Transformation laws for the current density in a change of coordinate system

In the coordinate transformation

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d} \tag{18}$$

which can be described as a gauge transformation 16 with $f = (\mathbf{r}'' - \mathbf{r}')\cdot\mathbf{A}^{B'}$, the transformation law for the diamagnetic and paramagnetic contributions to the current density is [24]

$$\mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r}-\mathbf{r}'') = \mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_{\mathrm{d}}^{(r''-r')\times BE}(\mathbf{r}) \tag{19}$$

$$\mathbf{J}_{\mathrm{p}}^{BE}(\mathbf{r}-\mathbf{r}'') = \mathbf{J}_{\mathrm{p}}^{BE}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_{\mathrm{p}}^{(r''-r')\times BE}(\mathbf{r}), \tag{20}$$

where,

$$\begin{aligned}\mathbf{J}_{\mathrm{d}}^{(r''-r')\times BE}(\mathbf{r}) = & -(ne^2/2m_e c)(\mathbf{r}''-\mathbf{r}') \\ & \times \mathbf{B}\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n[\psi_a^{(0)}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\mathbf{E}\cdot\psi_a^{E*}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n) \\ & + \mathbf{E}\cdot\psi_a^{E}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)],\end{aligned} \tag{21}$$

and

$$\begin{aligned}\mathbf{J}_{\mathrm{p}}^{(r''-r')\times BE}(\mathbf{r}) = & -(ne/m_e)\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times\{[(\mathbf{r}''-\mathbf{r}') \\ & \times\mathbf{B}\cdot\psi_a^{(r''-r')\times BE*}\cdot\mathbf{E}\mathbf{p}\psi_a^{(0)} + \psi_a^{(0)*}(\mathbf{r}''-\mathbf{r}') \\ & \times\mathbf{B}\cdot\psi_a^{(r''-r')\times BE}\cdot\mathbf{E}] + [\mathbf{E}\cdot\psi_a^{E(r''-r')\times B*}\cdot(\mathbf{r}''-\mathbf{r}') \\ & \times\mathbf{B}\mathbf{p}\psi_a^{(0)} + \psi_a^{(0)}\mathbf{p}\mathbf{E}\cdot\psi_a^{E(r''-r')\times B}\cdot(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}] \\ & + [\mathbf{E}\cdot\psi_a^{E*}\mathbf{p}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\psi_a^{(r''-r')\times B} + (\mathbf{r}''-\mathbf{r}') \\ & \times\mathbf{B}\cdot\psi_a^{(r''-r')\times B*}\mathbf{p}\psi_a^{E}\cdot\mathbf{E}]\}.\end{aligned} \tag{22}$$

Using the hypervirial relationship [29]

$$\langle a|P_\alpha|j\rangle = -im_e\omega_{ja}\langle a|R_\alpha|j\rangle, \tag{23}$$

Lazzeretti and Zanasi [24] proved that

$$\mathbf{J}_{\mathrm{p}}^{(r''-r')\times BE}(\mathbf{r}) = -\mathbf{J}_{\mathrm{d}}^{(r''-r')\times BE}(\mathbf{r}) \tag{24}$$

so that

$$\begin{aligned}\mathbf{J}^{BE}(\mathbf{r}) &= \mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r}-\mathbf{r}'') + \mathbf{J}_{\mathrm{p}}^{BE}(\mathbf{r}-\mathbf{r}'') \\ &= \mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_{\mathrm{p}}^{BE}(\mathbf{r}-\mathbf{r}')\end{aligned} \tag{25}$$

is origin-independent for *exact* eigenfunctions to any model Hamiltonian. Within the exact CHF method, the current density $\mathbf{J}^{\mathbf{BE}}(\mathbf{r})$ is invariant in a coordinate transformation. In actual calculations, employing the algebraic approximation, this condition is only partially met, depending on the quality of the basis set.

5. Advantage of the continuous transformation of the origin of the current density method

The CTOCD method for theoretical determination of hypermagnetizabilities and shielding polarizabilities is reported in detail in Ref. [24]. In this section we make only a very brief description of the theory involved in the formulation of CTOCD-DZ $\sigma^J_{\alpha\beta\gamma}$.

The scheme named CTOCD [17,18,20] proves that the transformed diamagnetic current density tensor, $\mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r}-\mathbf{r}'')$, can be formally annihilated in every point $\mathbf{r}$, all over the molecular domain, by considering the $\mathbf{d}$ shift in Eq. (18) as a function of $\mathbf{r}$, and choosing

$\mathbf{d}(\mathbf{r}) = \mathbf{r}$ in Eq. (19), that is setting $\mathbf{r}'' = \mathbf{r}'$ so that

$$\mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r} - \mathbf{r}') = -\mathbf{J}_{\mathrm{d}}^{(r-r')\times BE}(\mathbf{r}) \tag{26}$$

As the diamagnetic term is set to zero, the procedure is named CTOCD-DZ. Total current becomes completely paramagnetic in form, and contains two terms that are expressed within the original coordinates system as a function of $\mathbf{r}$, i.e.

$$J^{BE}(\mathbf{r}) = \mathbf{J}_{\mathrm{p}}^{BE}(\mathbf{r} - \mathbf{r}') + \mathbf{J}_{\mathrm{p}}^{(r-r')\times BE}(\mathbf{r}) \tag{27}$$

As the total current density is an invariant, comparison between Eqs. (25) and (27) necessarily implies that

$$\mathbf{J}_{\mathrm{p}}^{(r-r')\times BE}(\mathbf{r}) = \mathbf{J}_{\mathrm{d}}^{BE}(\mathbf{r} - \mathbf{r}') \tag{28}$$

for every $\mathbf{r}$, (provided that the hypervirial condition (23) holds). The formally annihilated diamagnetic contribution reappears as a new paramagnetic term. (See Ref. [24] for a detailed discussion about the new paramagnetic term along the direction of the external magnetic field.)

Employing Eq. (27) for the current density within expression (11) and right-hand side of Eq. (7), new definitions for total nuclear magnetic shielding are arrived at in the form

$$\sigma_{\alpha\beta\gamma}^{I} = \sigma_{\alpha\beta\gamma}^{\mathrm{p}I} + \sigma_{\alpha\beta\gamma}^{\Delta I} \tag{29}$$

where

$$\sigma_{\alpha\beta\gamma}^{\Delta I} = \frac{e^3}{2m_e^2c^2}\epsilon_{\beta\lambda\mu}\{P_\lambda, R_\gamma, T_{I\mu\alpha}^{n}\}_{-2} \tag{30}$$

and the definitions of the Hermitian operators T_I are

$$T_{I\alpha}^{n} = \frac{1}{2}\sum_{i=1,n}[(r_{i\alpha} - r'_\alpha)M_{I\beta}^{i}(\mathbf{r}') + M_{I\beta}^{i}(\mathbf{r}')(r_{i\alpha} - r'_\alpha)] \tag{31}$$

The CTOCD-DZ expression (30) reduce to the conventional $\sigma_{\alpha\beta\gamma}^{\mathrm{d}I}$, Eq. (8), if the hypervirial constraint (23) is satisfied, as it can be proven by direct substitution. $\sigma_{\alpha\beta\gamma}^{\Delta I}$ quantities are also symmetric in the $\alpha\beta$ indices in the Hartree–Fock limit. It has also been demonstrated [17] that the CTOCD-DZ approach is equivalent to the Geertsen approach [31–33], as far as average properties are concerned.

In a change of coordinate system (18), the contributions to the shielding polarizability transform

$$\sigma_{\alpha\beta\gamma}^{\mathrm{p}I}(\mathbf{r}'') = \sigma_{\alpha\beta\gamma}^{\mathrm{p}I}(\mathbf{r}') - \frac{e^3}{2m_e^2c^2}\epsilon_{\beta\lambda\mu}d_\lambda\{M_{I\alpha}^{n}, P_\mu, R_\gamma\}_{-2} \tag{32}$$

$$\sigma_{\alpha\beta\gamma}^{\Delta I}(\mathbf{r}'') = \sigma_{\alpha\beta\gamma}^{\Delta I}(\mathbf{r}') + \frac{e^3}{2m_e^2c^2}\epsilon_{\beta\lambda\mu}d_\lambda\{M_{I\alpha}^{n}, P_\mu, R_\gamma\}_{-2} \tag{33}$$

By comparing Eqs. (32) and (33) it can be noticed that the total CTOCD-DZ nuclear magnetic shielding polarizabilities are independent of the coordinate system, as there is exact cancellation between terms arising from variation of Δ and p components in any calculation employing the algebraic approximation, e.g. adopting gaugeless basis sets of arbitrary quality.

6. Results

A set of small molecules, N_2 and binary hydrides, H_2, HF, HCl, HCN and SH_2 has been considered in the present study. Zero-order molecular orbitals are expanded over atomic gaussian functions; three different basis sets have been employed to describe the CTOCD-DZ shielding polarizabilities of N_2, H_2, HF, and HCN. The first one, hereafter referred to as I, is taken from a compilation of Huzinaga [34] and is described in Ref. [35] as basis set IV, (11s7p3d1f)–[8s7p3d1f] for the heavy nucleus and (6s3p1d)–[5s3p1d] for the proton. Basis set II is a (12s14p5d)–[9s9p4d] set for the heavy nucleus and (5s5p)–[3s3p] set for the proton. The (s/p) substrate of basis set II was taken from van Duijneveldt's [36] compilation and polarized, adding to the set the electric field derivatives of an STO-3G basis suggested by Lazzeretti [37].

Basis set III is a (13s10p3d)–[6s5p3d] contraction for the heavy nucleus and a (8s3p)–[6s3p] set for the proton nucleus. The (s/p) substrate of basis set III was also taken from van Duijneveldt's tables [36] and the 3d polarization exponents are 0.51, 0.15 and 0.056 for nitrogen, 0.63, 0.21 and 0.07 for fluorine and 1.61, 0.43, 0.15 and 0.062 for carbon. The 3p set for hydrogen is 1.5, 0.4 and 0.1.

For the HCl molecule we have employed basis set III with 3d exponents 1.7, 0.68 and 0.27 and for basis set IV, a (13s10p4d/8s3p1d)–[6s5p4d/6s3p1d] set,

Table 1
N_2 nuclear shielding constants (ppm) and CTOCD-DZ shielding polarizabilities (ppm a.u.) for basis sets I–III ($\sigma_{\alpha\beta\delta} = \sigma^{\Delta}_{\alpha\beta\delta} + \sigma^{p}_{\alpha\beta\delta}$; the z-axis is in the direction of the bond, the gauge origin is at the nitrogen nucleus)

Basis set	Nitrogen nucleus						
	I	II	III		I	II	III
σ_{Av}	−120.8	−118.91	−124.74	σ^{d}_{zzz}	−47.52	−47.52	−48.15
σ^{d}_{xxz}	−7.11	−7.08	−7.03	σ^{Δ}_{zzz}	−46.39	−49.02	−21.84
σ^{Δ}_{xxz}	−0.88	−2.94	−2.93	σ^{p}_{zzz}	0.00	0.00	0.00
σ^{p}_{xxz}	−1571.96	−1535.87	−1544.38	σ_{zzz}	−46.39	−49.02	−21.84
σ_{xxz}	−1572.84	−1538.81	−1547.31	A_z	1064.02	1042.21	1038.82
[5]	σ_{Av}		−109.4	A_z	1047.0		
[6]	σ_{Av}		−111.38	A_z	1051.7		

with (s/p) substrate also taken from van Duijneveldt's tables [36], 3d polarization exponents, 10.455, 2.81, 1.0 and 0.41 on chlorine, and 3p polarization exponents, 4.22, 1.27 and 0.47 on hydrogen.

Finally, we have employed basis set V for SH_2, a large (20s19p10d/6s5p)–[9s8p4d/3s3p] set reported by Sadlej [38,39] and added to the set the electric field derivatives of an STO-3G basis suggested by Lazzeretti [37]. The electric field derivatives introduced on basis sets II and V, following Lazzeretti's receipt [37], are suitable because we are dealing with two simultaneous perturbations on the molecule, electric and magnetic fields, and the basis set must be suitable enough to produce good values for both nuclear magnetic shielding and shielding polarizabilities.

The calculations reported in this work have been carried out within the SYSMO suite of computer programs [40], modified by us to implement a new CHF section to describe the CTOCD-DZ shielding polarizabilities.

A description of the effect of a uniform electric field on the nuclear shielding was given by Buckingham [3]. The change in the main shielding, after averaging over all molecular orientations in the NMR external magnetic field, keeping the electric field fixed relative to the molecule, is

$$\sigma^{I}_{Av} = -A^{I}_{\gamma}E_{\gamma} - B^{I}_{\gamma\delta}E_{\gamma}E_{\delta} \tag{34}$$

where Einstein summation is implied. The shielding polarizabilities are related to the A^{I}_{γ} values by

$$A^{I}_{\gamma} = -(1/3)\sigma^{I}_{\alpha\alpha\gamma} \tag{35}$$

The number of non-vanishing elements $\sigma^{I}_{\alpha\beta}$ and $\sigma^{I}_{\alpha\beta\gamma}$, for a given nucleus depends on the local "on-site" symmetry at the position of the nucleus [41]. Two types of site symmetry are exhibited by the nuclei of the molecules given above: $C_{\infty v}$ for N_2, H_2, HF, HCl, and HCN and C_S for SH_2. We have defined the *yz*-plane as the plane of symmetry for C_S.

In Tables 1–6 we report $\sigma^{I}_{Av}$and all those $\sigma^{I}_{\alpha\beta\gamma}$

Table 2
H_2 nuclear shielding constants (ppm) and CTOCD-DZ shielding polarizabilities (ppm a.u.) for basis sets I–III ($\sigma_{\alpha\beta\gamma} = \sigma^{\Delta}_{\alpha\beta\gamma} + \sigma^{p}_{\alpha\beta\gamma}$; the z-axis is in the direction of the bond, the gauge origin is at the hydrogen nucleus)

Basis set	Hydrogen nucleus						
	I	II	III		I	II	III
σ_{Av}	26.70	26.70	26.72	σ^{d}_{zzz}	−32.28	−32.39	−32.33
σ^{d}_{xxz}	−14.52	−14.45	−14.52	σ^{Δ}_{zzz}	−31.24	−32.77	−23.81
σ^{Δ}_{xxz}	−7.08	−9.08	−5.46	σ^{p}_{zzz}	0.00	0.00	0.00
σ^{p}_{xxz}	−44.78	−44.38	−43.16	σ_{zzz}	−31.24	−32.77	−23.81
σ_{xxz}	−51.86	−53.46	−48.62	A_z	44.98	46.56	40.35
[47]	A_z	41.2			[13]	A_z (MP2)	A_z (SCF)
					[13]	49.4	50.45

Table 3
HF nuclear shielding constants (in ppm) and CTOCD-DZ shielding polarizabilities (ppm a.u.) for basis sets I–III ($\sigma_{\alpha\beta\gamma} = \sigma^{\Delta}_{\alpha\beta\gamma} + \sigma^{p}_{\alpha\beta\gamma}$; the *z*-axis is in the direction of the bond from the fluorine to the hydrogen nucleus, the gauge origin is taken at the nucleus whose shielding and shielding polarizabilities are evaluated)

Basis set	Hydrogen			Fluorine		
	I	II	III	I	II	III
σ_{Av}	29.36	30.65	31.54	414.85	412.23	414.19
σ^{d}_{xxz}	−14.20	−13.57	−14.35	10.03	10.73	9.85
σ^{Δ}_{xxz}	−4.55	−1.19	−2.31	7.87	13.30	6.21
σ^{p}_{xxz}	−88.39	−96.19	−94.60	874.80	862.73	882.52
σ_{xxz}	−92.94	−97.38	−96.91	882.67	876.03	888.73
σ^{d}_{zzz}	−32.90	−32.50	−33.01	1.31	2.42	1.11
σ^{Δ}_{zzz}	−29.87	−23.34	−22.91	6.17	8.56	6.02
σ^{p}_{zzz}	0.0	0.00	0.00	0.0	0.00	0.00
σ_{zzz}	−29.87	−23.34	−22.91	6.17	8.56	6.02
A_z	71.92	72.70	72.24	−590.5	−586.87	−594.49
[10]	A_z		81.5	[44]	σ_{Av}	415.18
[43]	A_z		83.5		A_z	−585.5
[13]	A_z	SCF	79.42	[13]	A_z (SCF)	−597.1
	A_z	MP2	79.08		A_z (MP2)	−490.2

elements that contribute to the main shielding in Eq. (34). The σ^{I}_{Av} values are included only for completeness and they are compared with calculations of other authors and with experimental data when they are available. The A^{I}_{γ} values, Eq. (35) for the CTOCD-DZ approach are given and compared with other authors' calculations taken from the literature. The explicit conformation employed to make the calculations is given in the same tables. The corresponding geometries were optimized employing a 6-31G** basis set at the SCF level implemented in GUASSIAN 94 programs [42]. Other authors' values have been transformed to our conformations if they have employed any other one, i.e. the positive direction of the *z*-axis.

Table 4
HCl nuclear shielding constants (ppm) and CTOCD-DZ shielding polarizabilities (ppm a.u.) for basis sets III and IV ($\sigma_{\alpha\beta\gamma} = \sigma^{\Delta}_{\alpha\beta\gamma} + \sigma^{p}_{\alpha\beta\gamma}$; the *z*-axis is in the direction of the bond from the hydrogen to the chlorine nucleus, the gauge origin is taken at the nucleus whose shielding and shielding polarizabilities are evaluated)

Basis set	Hydrogen		Fluorine	
	III	IV	III	IV
σ_{Av}			952.90	940.80
σ^{d}_{xxz}	29.81	30.90	−10.64	−10.68
σ^{Δ}_{xxz}	11.80	22.19	−2.58	−3.27
σ^{p}_{xxz}	102.05	88.42	−2689.40	−3317.03
σ_{xxz}	113.85	110.61	−2691.98	−3320.30
σ^{d}_{zzz}	56.75	54.62	−0.01	0.22
σ^{Δ}_{zzz}	37.64	54.20	−5.78	1.47
σ^{p}_{zzz}	0.0	0.0	0.0	0.0
σ_{zzz}	37.64	54.20	−5.78	1.47
A_z	−88.45	−91.80	1796.58	2213.04
[47]	A_z	−101.9	[44] σ_{Av}	956.14
[43]	A_z	−117.9	A_z	1149.8

6.1. N_2 molecule

Table 1 summarizes the results of the nuclear magnetic shielding and its polarizabilities for the nitrogen nucleus in N_2. The molecule was placed along the *z*-axis.

The $\sigma^{\Delta I}_{\alpha\beta\gamma}$ values, Eq. (30), are compared with the $\sigma^{dI}_{\alpha\beta\gamma}$, Eq. (8), for each basis set. Basis set I and II produce very good agreement between those quantities for the *zzz* component, i.e. both electric and magnetic fields along the bond direction. When the magnetic field, **B**, is perpendicular to the electric field $\mathbf{E} = \mathbf{E}e_z$, the basis sets are not suitable enough to get confident CTOCD-DZ diamagnetic contributions to the shielding polarizabilities. We are not near the Hartree–Fock limit. On comparing the A^{N}_{z} values with those of Bishop and Cybulski [6], 1057.1 ppm a.u. and those of Rizzo et al. [5],

Table 5
HCN nuclear shielding constants (in ppm) and CTOCD-DZ shielding polarizabilities (ppm a.u.) for basis sets I–III ($\sigma_{\alpha\beta\gamma} = \sigma^{\Delta}_{\alpha\beta\gamma} + \sigma^{p}_{\alpha\beta\gamma}$; the *z*-axis is in the direction of the bond from the hydrogen to the nitrogen nucleus, the gauge origin is taken at the nucleus whose shielding and shielding polarizabilities are evaluated)

Basis set	Hydrogen			Carbon			Nitrogen		
	I	II	III	I	II	III	I	II	III
σ_{Av}	29.75	30.26	31.93	76.92	78.64	79.74	−36.77	−36.5	−37.27
σ^{d}_{xxz}	27.10	26.91	27.11	1.16	0.89	1.09	−9.81	−10.09	−9.61
σ^{Δ}_{xxz}	12.33	13.34	13.87	0.58	6.36	3.72	−3.11	−5.32	−3.62
σ^{p}_{xxz}	32.23	30.45	27.63	598.50	586.82	573.49	−2733.50	−2704.2	−2775.5
σ_{xxz}	44.56	43.79	41.50	599.08	592.98	577.21	−2736.61	−2709.5	−2779.1
σ^{d}_{zzz}	50.55	50.37	50.76	43.47	43.26	43.87	−55.76	−55.84	−55.95
σ^{Δ}_{zzz}	48.52	50.22	49.12	43.02	45.56	44.25	−54.86	−56.59	−24.73
σ^{p}_{zzz}	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.0	0.0
σ_{zzz}	48.52	50.22	49.12	43.02	45.56	44.25	−54.86	−56.59	−24.73
A_z	−45.88	−45.93	−44.04	−413.73	−410.51	−399.56	1842.69	1825.2	1860.99
[46]	56.6 (SCF)	−53.5 (MP3)	[46]	440.4 (SCF)	442.3 (MP3)	[46]	1943.1 (SCF)	1662.7 (MP3)	
A_z	51.1 (MP2)	−52.8 (LCCD)	A_z	−436.2 (MP2)	−449.4 (LCCD)	A_z	1480.1 (MP2)	1549.0 (LCCD)	
[5]	σ_{Av}	29.2	[46]	σ_{Av}	[5] 71.1	[45] 75.74	[5]	σ_{Av}	−50.4
	A_z	−55.9		A_z	−440.2	−428.6		A_z	1949.1

Table 6
SH_2 nuclear shielding constants (in ppm) and CTOCD-DZ shielding polarizabilities (in ppm a.u.) for basis sets V ($\sigma_{\alpha\beta\gamma} = \sigma^{\Delta}_{\alpha\beta\gamma} + \sigma^{p}_{\alpha\beta\gamma}$; the sulfur nucleus is on the *z*-axis and the hydrogen nuclei are in the *yz*-plane, the gauge origin is taken at the nucleus whose shielding and shielding polarizabilities are evaluated)

Hydrogen				Sulfur	
σ_{Av}	32.35			σ_{Av}	731.58
σ^{d}_{xxy}	−23.71	σ^{d}_{xxz}	17.54	σ^{d}_{xxz}	−12.82
σ^{Δ}_{xxy}	−19.33	σ^{Δ}_{xxz}	13.53	σ^{Δ}_{xxz}	−17.33
σ^{p}_{xxy}	−71.19	σ^{p}_{xxz}	64.25	σ^{p}_{xxz}	−207.46
σ_{xxy}	−90.52	σ_{xxz}	77.78	σ_{xxz}	−224.79
σ^{d}_{yyy}	−53.05	σ^{d}_{yyz}	15.73	σ^{d}_{yyz}	−3.48
σ^{Δ}_{yyy}	−47.14	σ^{Δ}_{yyz}	9.24	σ^{Δ}_{yyz}	−14.43
σ^{p}_{yyy}	−10.53	σ^{p}_{yyz}	57.13	σ^{p}_{yyz}	−347.28
σ_{yyy}	−57.67	σ_{yyz}	66.37	σ_{yyz}	−361.71
σ^{d}_{zzy}	−21.62	σ^{d}_{zzz}	43.05	σ^{d}_{zzz}	−8.40
σ^{Δ}_{zzy}	−18.38	σ^{Δ}_{zzz}	32.88	σ^{Δ}_{zzz}	−8.84
σ^{p}_{zzy}	−70.35	σ^{p}_{zzz}	10.94	σ^{p}_{zzz}	−1045.08
σ_{zzy}	−88.73	σ_{zzz}	43.82	σ_{zzz}	−1053.92
A_y	78.97	A_z	−62.66	A_z	−546.81
[43]	σ_{Av}	32.69	[44]	A_z	−534.1
$A_y = 78.01$		$A_z = -74.0$		σ_{Av}	731.89

1047.0 ppm a.u., the quality of the wave function is not evidenced because the diamagnetic contributions to the shielding polarizability is very small in comparison with the paramagnetic one, and so the *xxz* and *yyz* contributions to A^{N}_{z} do not depend very much on $\sigma^{\Delta I}_{\alpha\alpha\gamma}$. In spite of this the cited authors included electron correlation in their results, and we are making all the calculations at SCF level. The CTOCD-DZ A^{N}_{z} values are in good agreement with their results. The σ^{N}_{Av} values, −118.91 to −124.74 ppm, are similar in magnitude to the nitrogen magnetic shielding calculated by Rizzo [5] and by Bishop and Cybulski [6]. All those calculated nuclear magnetic shieldings are far from −61.6 ppm [48]. This behavior indicates that correlation effects are very important for describing properly the nuclear shielding in the N_2 molecule.

6.2. H_2 molecule

Table 2 reports the hydrogen magnetic shielding and its polarizabilities in H_2. In this case, the better convergence between $\sigma^{\Delta I}_{\alpha\beta\gamma}$ and $\sigma^{dI}_{\alpha\beta\gamma}$ is again for the *zzz* component. The best results for CTOCD-DZ A^{H}_{z} quantities correspond to basis set II, which includes the electric field derivatives of an STO-3G set introduced by Lazzeretti [37]. 44.98, 40.35 and 46.56 ppm a.u. for basis set II make a very good comparison with those values reviewed by Raynes, 49.4 (MP2) and 50.45 ppm a.u. (SCF) [13].

6.3. HF molecule

The nuclear magnetic shielding and its polarizabilities for hydrogen and fluorine nuclei in HF are shown in Table 3. The nuclear shielding constants evaluated employing basis sets I, II, and III are in very good agreement with experiment for both nuclei: $\sigma^{H}_{exp} = 28.57$ ppm [49] and $\sigma^{F}_{exp} = 410.0$ ppm. [50]. The quality of the shielding polarizabilities is better for the fluorine than for the proton nucleus for the three basis sets. CTOCD-DZ A^{H}_{z}, 72.7 and 72.24 ppm a.u., show a very good behavior by comparison with the results of Grayson and Raynes [43] and Augspurger et al. [10] and with those reviewed by Raynes [13] at SCF, 79.42 and MP2 level, 79.08 ppm a.u.

CTOCD-DZ A^{F}_{z}, −586.9 to −594.5 ppm a.u. is excellent by comparison with the results of Grayson et al. [44], and those values reviewed by Raynes [13] for SCF, −597.1 and MP2, −490.2 ppm a.u., employing large basis sets including 5f-type functions.

6.4. HCl molecule

For this hydride we employed two basis sets, those described above as basis sets III and IV, to evaluate the proton and the chlorine shielding and their shielding polarizabilities. The calculated chlorine magnetic shielding is close to the experimental result, 952 ppm, taken from Ref. [51]. The computational cost of basis set IV is notably larger than that of basis set III, and the comparison between $\sigma^{\Delta I}_{\alpha\beta\gamma}$ and $\sigma^{dI}_{\alpha\beta\gamma}$ show the corresponding improvement. The A^{Cl}_{z} and A^{H}_{z} are not very close to other authors' results. From the analysis of both contributions, diamagnetic (traditional and CTOCD-DZ) and paramagnetic, we see that the difference is because of the paramagnetic contribution and not the CTOCD-DZ approach. In particular, for the chlorine nucleus, this inaccuracy is more evident. We consider that the basis set must be greatly improved in order to reproduce the correct results for chlorine.

6.5. HCN molecule

We have evaluated the magnetic shielding constant and the shielding polarizabilities of hydrogen, carbon and nitrogen nuclei in HCN for basis sets I–III. The corresponding results are reported in Table 5. The calculated nuclear shielding constants evaluated with the same basis sets are close to the values calculated by other authors for hydrogen and carbon nuclei. All values are in very good agreement with the experimental data for carbon ($\sigma^{C}_{exp} = 82.1$ ppm, from Ref. [52]), but our $\sigma^{N}_{Av} \approx -37$ ppm and the nitrogen magnetic shielding evaluated by Rizzo [5], -50.5 ppm, are far from the experimental $\sigma^{N}_{exp} = -20.1$ ppm [48]. The comparison between the behavior of $\sigma^{\Delta I}_{\alpha\beta\gamma}$ for the different nuclei shows that the best quality is exhibited by the carbon nucleus, and the most difficult case is the hydrogen nucleus, when the magnetic field is perpendicular to the electric field. The A^{H}_{z} values are very good in comparison with other authors' calculations. It must be noted that the paramagnetic contribution to the shielding polarizability is larger than the diamagnetic one when the external magnetic field is perpendicular to the external electric field. Hence, it is more important to have a very good description of the paramagnetic contribution. For the nitrogen nucleus the σ^{pI}_{xxz} contribution is three orders larger than σ^{dI}_{xxz}. The general behavior of A^{H}_{z}, A^{C}_{z} and A^{N}_{z} is excellent in comparison with those results of Augspurger and Dykstra [8], Grayson and Raynes [45] and Rizzo et al. [5]. The authors cited above have employed larger basis sets than those that we have reported, and the calculations in Refs. [8,5] include electron correlation. We have included also in Table 5 very recent calculations of Cybulski and Bishop [46] employing the SCF, MP2, MP3 and LCCD methods level. Their results show that the shielding polarizabilities of hydrogen and carbon are not very much dependent on the inclusion of electron correlation, they are of the same order of our CTOCD-DZ A^{I}_{γ}. Different electron-correlated approximations differ greatly on the A^{N}_{γ} [46], nearly about 10% for the different levels informed by those authors. Our results are similar to their SCF results.

6.6. SH_2 molecule

The results from hydrogen and sulfur are shown in Table 6. In this molecule, the sulfur atom is placed on the *z*-axis and the two hydrogen nuclei lie on the *yz*-plane. We report on only one of those protons because they are equivalent. We have employed a very large basis set to describe the nuclear magnetic shielding and their shielding polarizabilities, basis set V, with 81 contracted functions. The results are excellent. The hydrogen magnetic shielding is in good agreement with the experimental data, $\sigma^{H}_{exp} = 30.54$ ppm [53]. The agreement between $\sigma^{\Delta I}_{\alpha\beta\gamma}$ and $\sigma^{dI}_{\alpha\beta\gamma}$ is excellent for all the components informed and for both the nuclei. The comparison of total CTOCD-DZ A^{I}_{γ} with results taken from other work indicates that the accuracy of our SCF results is also excellent. To compare our A^{H}_{γ} values with those of Grayson and Raynes [43], we transformed their coordinate system to ours, because they considered the *z*-axis in the *X–H* direction, and we have the two protons on the *yz*-plane in equivalent positions at both sides of the *z*-axis.

7. Conclusions

For all the nuclei treated here, we have a good fit between our CTOCD-DZ A^{I}_{γ}, and those taken from other work. It must be noted that we have made our calculations at the SCF level. We have included neither electron correlation nor vibrational corrections. The results of Rizzo et al. [5] for N_2 and HCN have been obtained employing multi configuration self-consistent field calculations and finite-field strengths of the external electric field. In spite of the fact that they defined active spaces and had a considerable computational cost in their calculations, our results are in similar quality, employing only medium-size basis sets.

The results taken from the work of Grayson and Raynes [43] have also been carried out employing the finite-field method at the SCF level.

Our calculations do not include vibrational corrections. Bishop and Cybulski [6] have computed them for nuclear magnetic shielding and shielding polarizabilities.

We have reported the $\sigma^{\Delta I}_{\alpha\beta\gamma}$ and the $\sigma^{dI}_{\alpha\beta\gamma}$ values because they must be identical in the Hartree–Fock limit. The $\sigma^{\Delta I}_{\alpha\beta\gamma}$ values depend very much on the quality of the basis set while the $\sigma^{dI}_{\alpha\beta\gamma}$ values are

almost independent of that quality. The reason is that the $\sigma^{dI}_{\alpha\beta\gamma}$ evaluation requires the calculation of the first-order electric field perturbed density matrix, but it is necessary to compute three first-order CHF perturbations to get $\sigma^{\Delta I}_{\alpha\beta\gamma}$ values. The $\sigma^{\Delta I}_{\alpha\beta\gamma}$ must be improved by extending the size of the basis set. Basis sets of medium size have been employed in all calculations of the present article.

The goal of the CTOCD-DZ method is to provide nuclear magnetic shieldings and shielding polarizabilities, which are origin-independent, i.e total shielding polarizabilities that are origin-independent in calculations employing any finite basis set. In the limit of exact eigenfunctions of a model Hamiltonian, e.g. within the exact Hartree–Fock limit, $(\sigma^{\Delta I}_{\alpha\beta\gamma} + \sigma^{pI}_{\alpha\beta\gamma})$ and $(\sigma^{dI}_{\alpha\beta\gamma} + \sigma^{pI}_{\alpha\beta\gamma})$ must be identical. Both contributions to the shielding polarizabilities, $\sigma^{\Delta I}_{\alpha\beta\gamma}$ and $\sigma^{pI}_{\alpha\beta\gamma}$ are calculated within the same approximation. The accuracy of the shielding polarizabilities computed within the CTOCD-DZ approach is affected by the quality of the basis set, but they are origin-independent for any (gaugeless) basis set, because the constraints for charge and current conservation are exactly satisfied.

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