Shielding polarizabilities via continuous transformation of the origin of the current density in the set of small molecules: H_2O_2, F_2, H_2C_2, H_2CO, NH_3, HCN, and HNC

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A procedure, based on a continuous transformation of the origin of the (quantum mechanical) current density that sets the diamagnetic contribution to zero (CTOCD-DZ) all over the molecular domain, is applied to determine shielding polarizabilities to first order in a perturbing electric field. In any calculations relying on the algebraic approximation, irrespective of size and quality of the (gaugeless) basis set employed, all the components of the CTOCD-DZ magnetic shielding polarizability are origin independent, and the constraints for charge and current conservation are exactly satisfied. The effects of a static uniform electric field on the nuclear magnetic resonance (NMR) shielding of H_2O_2, F_2, H_2C_2, H_2CO, NH_3, HCN, and HNC molecules have been investigated within the CTOCD-DZ method, and compared with the conventional results evaluated via the same basis sets, and with theoretical results taken from the literature. © *2000 American Institute of Physics.* [S0021-9606(00)30714-0]

I. INTRODUCTION

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

In fact, a static electric field induces polarization of the electronic charge distribution: the variation of molecular magnetic susceptibility and nuclear magnetic shielding 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 of a permanent dipole moment $\boldsymbol{\mu}_I$, the energy of a molecule in the singlet electronic state $|\psi_a\rangle$ is, employing Buckingham notation[1,2] to denote molecular tensors,

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

Nuclear magnetic shielding of a given nucleus I, in the presence of an external weak, homogeneous electric field **E** may be expanded via the equation[3]

$$\sigma^I_{\alpha\beta}(\mathbf{E}) = \sigma^I_{\alpha\beta} + \sigma^I_{\alpha\beta\gamma}E_\gamma + \tfrac{1}{2}\sigma^I_{\alpha\beta\gamma\delta}E_\gamma E_\delta + \cdots. \tag{2}$$

Therefore the third-rank tensors $\sigma^I_{\alpha\beta\gamma}$, describing non-

linear response of the electron cloud to first order in **E**, $\boldsymbol{\mu}_I$, and **B**, are sometimes referred to as shielding polarizabilities and hyperpolarizabilities.[4,5]

The number of independent tensor components depends on nuclear site symmetry; see an article by Raynes and Ratcliffe.[6] Several attempts at evaluating these quantities using various levels of accuracy have been reported. The first major application of Buckingham's theory has been to the study of intermolecular effects on nuclear shielding in gases.[7] Further studies deal with measurements of electric field in solids[8] and protonation shifts in amino acids.[9] Dykstra, Augspurger, and co-workers have carried out calculations for a wide range of nuclei in extended series of molecules.[5,10–12] Bishop and Cybulski adopted self-consistent field (SCF), second- and third-order Møller–Plesset (MP2, MP3), and linearized coupled cluster double excitation (L-CCD) methods for calculating the electric field dependence of nuclear shielding[4,13] and susceptibility.[14] Grayson and Raynes utilized random-phase approximation (RPA) within the framework of finite perturbation theory to estimate shielding polarizabilities.[15–17] An interesting analysis of the effects arising from an external charge on carbon, nitrogen, and oxygen shielding in amides has been reported by Hansen and co-workers.[18] The review by Raynes[19] is an excellent introduction to the subject.

SCF and multi-configuration self-consistent field (MCSCF) electric field dependence of magnetizability and nuclear magnetic shielding have been studied by Rizzo *et al.*[20–22] employing gauge-including atomic orbitals (GIAO) basis sets. The use of London orbitals guarantees invariance of theoretical estimates in a change of coordinate

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system, which is a basic requirement in the computation of magnetic properties.

Although faster convergence of procedures adopting GIAO basis sets seems to suggest that their use might be preferable in numerical studies,[23] CTOCD schemes for $\sigma_{\alpha\beta}^I$ are easier to implement at any level of accuracy[24] (even if their application has been limited so far to RPA), and become competitive provided that proper basis sets are employed.[25] They are nicely suited to satisfy the constraints of charge conservation by annihilation of either diamagnetic, or paramagnetic, contributions to the quantum mechanical electronic current density. This is actually achieved via continuous transformation of origin, according to CTOCD-DZ and continuous transformation of origin of current density-paramagnetic contribution set to zero (CTOCD-PZ) methods respectively, (Keith and Bader[26] have presented the idea of continuous transformation of origin by the first time).

The present article makes use of an extension of the CTOCD-DZ approach by annihilation of diamagnetic contributions to the electronic current density induced in the presence of both static homogeneous electric and magnetic fields.[27] The computations of CTOCD-DZ $\sigma_{\alpha\beta\gamma}^I$ nuclear shielding polarizabilities have been implemented in the SYSMO suite of computer programs,[28] employing a coupled Hartree–Fock (CHF) scheme within the algebraic approximation, via preliminary symmetrization of the non-Hermitian operators introduced in Ref. 27.

Corresponding calculations have been performed for the set of molecules H_2O_2, F_2, HCCH, H_2CO, NH_3, HCN, and HNC employing three basis sets of medium to large size. The results are compared with the conventional common origin (CO) CHF shielding polarizability, which are affected by the gauge dependence problem, and with other theoretical estimates from the literature. A few preliminary results have been previously reported.[29] Indeed, shielding polarizabilities evaluated within the CTOCD-DZ method are origin independent, and the constraints for charge and current conservation are exactly fulfilled, no matter the size of the basis set employed to perform the calculations. However, even if calculated results do not depend on the choice of the origin of coordinates, their accuracy is strongly affected by the quality of the basis set.

II. NUCLEAR MAGNETIC SHIELDING IN THE PRESENCE OF A STATIC ELECTRIC FIELD

We shall briefly review some definitions employed to compute nuclear magnetic shielding polarizabilities $\sigma_{\alpha\beta\gamma}^I$. A few basic statements of the practical features of implementing CTOCD for shielding polarizability calculations are eventually made.

In the presence of a static external electric field **E**, of a magnetic field **B**, and of an intrinsic magnetic moment $\boldsymbol{\mu}_I$ on nucleus I, the electronic Hamiltonian contains three first-order terms (Einstein summation over repeated Greek indices is implied throughout the article)

$$H^{\mathbf{E}} = eE_\alpha R_\alpha, \tag{3}$$

$$H^{\mathbf{B}} = \frac{e}{m_e c} \sum_{i=1}^n \mathbf{A}_i^{\mathbf{B}} \cdot \mathbf{p}_i = \frac{e}{2m_e c} B_\alpha L_\alpha, \tag{4}$$

$$H^{\boldsymbol{\mu}_I} = \frac{e}{m_e c} \sum_{i=1}^n \mathbf{A}_i^{\boldsymbol{\mu}_I} \cdot \mathbf{p}_i = \frac{e}{m_e c} M_{I\alpha}^n \mu_{I\alpha}, \tag{5}$$

and the second-order Hamiltonians are written

$$H^{\mathbf{BB}} = \frac{e^2}{2m_e c^2} \sum_{i=1}^n \mathbf{A}_i^{\mathbf{B}} \cdot \mathbf{A}_i^{\mathbf{B}} = \frac{e^2}{8m_e c^2} B_\alpha B_\beta$$
$$\times \sum_{i=1}^n (r^2 \delta_{\alpha\beta} - r_\alpha r_\beta)_i, \tag{6}$$

$$H^{\boldsymbol{\mu}_I \mathbf{B}} = \frac{e^2}{m_e c^2} \sum_{i=1}^n \mathbf{A}_i^{\mathbf{B}} \cdot \mathbf{A}_i^{\boldsymbol{\mu}_I}$$
$$= \frac{e}{2m_e c^2} \mu_{I\alpha} B_\beta \sum_{i=1}^n (r_{i\gamma} E_{I\gamma}^i \delta_{\alpha\beta} - r_{i\alpha} E_{I\beta}^i), \tag{7}$$

using the notation of previous articles.[30,31] The vector potentials are defined

$$\mathbf{A}^{\mathbf{B}} = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{r}_0), \quad \mathbf{A}^{\boldsymbol{\mu}_I} = \boldsymbol{\mu}_I \times \frac{\mathbf{r} - \mathbf{R}_I}{|\mathbf{r} - \mathbf{R}_I|^3}. \tag{8}$$

(The origin $\mathbf{r}_0$ is arbitrary. It equals **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 obtained via Eqs. (3)–(7), by differentiating with respect to electric and magnetic fields, and permanent magnetic moment:

$$\sigma_{\alpha\beta\gamma}^I = \frac{\partial^3 W_a^{(3)}}{\partial \mu_{I_\alpha} \partial B_\beta \partial E_\gamma} = \sigma_{\alpha\beta\gamma}^{\mathrm{d}I} + \sigma_{\alpha\beta\gamma}^{\mathrm{p}I}, \tag{9}$$

$$\sigma_{\alpha\beta\gamma}^{\mathrm{d}I} = -\frac{e^2}{2m_e c^2 \hbar} \sum_{j\neq a} \frac{2}{\omega_{ja}} \mathcal{R} \left[\langle a| \sum_{i=1}^n (r_{i\delta} E_{I\delta}^i \delta_{\alpha\beta} \right.$$
$$\left. - r_{i\alpha} E_{I\beta}^i)|j\rangle\langle j|R_\gamma|a\rangle \right], \tag{10}$$

$$\sigma_{\alpha\beta\gamma}^{\mathrm{p}I} = \frac{e^3}{2m_e^2 c^2} \{M_{I\alpha}^n, L_\beta, R_\gamma\}_{-2}. \tag{11}$$

In Eq. (11) the definition[32]

$$\{A,B,C\}_{-2} \equiv -4\,\mathrm{Tr}([\mathbf{F}^{(A)}(\mathbf{X}^{(B)}\mathbf{S}\mathbf{X}^{(C)} - \mathbf{X}^{(C)}\mathbf{S}\mathbf{X}^{(B)})]$$
$$+ [B,C,A] + [C,A,B]) \tag{12}$$

is employed, where $[B,C,A]$ and $[C,A,B]$ are permutations of the perturbators involved in the expression between square brackets. Equation (12) defines a third-rank tensor within the McWeeny notation[33] for the CHF approach. $\mathbf{F}^{(A)}$ represents the first-order perturbed Fock matrix; the perturbed density matrices are projected from $\mathbf{X}^{(A)}$, by solving

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the first-order CHF problem for each perturbation, and S_{pq} is the overlap matrix between atomic orbitals, χ_p and χ_q, of a basis set χ.

III. 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,

$$W^{\mathbf{BBE}} = -\frac{1}{2c}\int \mathbf{J^{BE}} \cdot \mathbf{A^B}\, d\mathbf{r}, \quad W^{\mu_I \mathbf{BE}} = -\frac{1}{c}\int \mathbf{A^{\mu_I}} \cdot \mathbf{J^{BE}}\, d\mathbf{r}. \tag{13}$$

To obtain the expression for $\mathbf{J^{BE}}$ via the general quantum mechanical definition,[34] the perturbation expansion for the current density and for the a-state molecular wave function (depending on n-electron space–spin coordinates $\mathbf{x}_i$) are needed.

The first- and second-order electronic wave functions are obtained from Rayleigh–Schrödinger perturbation theory (see Ref. 27 for details). Diamagnetic and paramagnetic contributions to a third-rank current density tensor are defined according to the relationships

$$J_\delta^{\mathbf{BE}}(\mathbf{r}) = B_\beta E_\gamma \mathcal{J}_\delta^{B_\beta E_\gamma}(\mathbf{r}), \tag{14}$$

$$\mathcal{J}_\delta^{B_\beta E_\gamma}(\mathbf{r}) = \mathcal{J}_{d\delta}^{B_\beta E_\gamma}(\mathbf{r}) + \mathcal{J}_{p\delta}^{B_\beta E_\gamma}(\mathbf{r}), \tag{15}$$

$$\mathcal{J}_{d\delta}^{B_\beta E_\gamma}(\mathbf{r}) = -\frac{ne^2}{2m_e c}\epsilon_{\delta\beta\nu}r_\nu \int d\mathbf{x}_2, \ldots d\mathbf{x}_n$$
$$\times [\Psi_a^{(0)}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)\Psi_a^{E_\gamma *}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)$$
$$+\Psi_a^{E_\gamma}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)\Psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)], \tag{16}$$

$$\mathcal{J}_{p\delta}^{B_\beta E_\gamma}(\mathbf{r}) = -\frac{ne}{m_e}\int d\mathbf{x}_2, \ldots d\mathbf{x}_n [\Psi_a^{B_\beta E_\gamma *}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)p_\delta \Psi_a^{(0)}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n) + \Psi_a^{E_\gamma B_\beta *}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)p_\delta \Psi_a^{(0)}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)$$
$$+\Psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)p_\delta \Psi_a^{B_\beta E_\gamma}(\mathbf{r},\mathbf{x}_2 \ldots \mathbf{x}_n) + \Psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)p_\delta \Psi_a^{E_\gamma B_\beta}(\mathbf{r},\mathbf{x}_2 \ldots \mathbf{x}_n)$$
$$+\Psi_a^{E_\gamma *}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)p_\delta \Psi_a^{B_\beta}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n) + \Psi_a^{B_\beta *}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)p_\delta \Psi_a^{E_\gamma}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)]. \tag{17}$$

Gauge invariance of magnetic properties is related to the continuity constraints.[35,36] In a gauge transformation of the vector potential

$$\mathbf{A^{B'}} \to \mathbf{A^{B''}} = \mathbf{A^{B'}} + \nabla f, \quad \mathbf{A^{B'}} = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{r'}), \tag{18}$$

where $f = f(\mathbf{r})$ is an arbitrary function well-behaved for $\mathbf{r} \to \infty$. The third-order interaction energy, Eq. (13) and all the response properties are left unchanged, provided that the integral,

$$\int \mathbf{J^{BE}} \cdot \nabla f\, d\mathbf{r} = \int \nabla \cdot (\mathbf{J^{BE}} f) d\mathbf{r} - \int f \nabla \cdot \mathbf{J^{BE}}\, d\mathbf{r}, \tag{19}$$

vanishes. Actually, 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 $\mathbf{J^{BE}}$, i.e., Ψ_a, $\mathbf{J^{BE}} \to \mathbf{0}$ for $\mathbf{r} \to \infty$. Thus the integral on the left-hand side vanishes if the continuity equation

$$\nabla \cdot \mathbf{J^{BE}} = 0 \tag{20}$$

is satisfied.

IV. TRANSFORMATION LAWS FOR THE CURRENT DENSITY IN A CHANGE OF COORDINATE SYSTEM

In the coordinate transformation

$$\mathbf{r'} \to \mathbf{r''} = \mathbf{r'} + \mathbf{d}, \tag{21}$$

which can be described as a gauge transformation, Eq. (18), where $f = (\mathbf{r''} - \mathbf{r'}) \cdot \mathbf{A}^{B'}$, the transformation law for the diamagnetic and paramagnetic contributions to the current density is[27]

$$\mathbf{J}_d^{\mathbf{BE}}(\mathbf{r} - \mathbf{r''}) = \mathbf{J}_d^{\mathbf{BE}}(\mathbf{r} - \mathbf{r'}) + \mathbf{J}_d^{(\mathbf{r''}-\mathbf{r'})\times\mathbf{BE}}(\mathbf{r}), \tag{22}$$

$$\mathbf{J}_p^{\mathbf{BE}}(\mathbf{r} - \mathbf{r''}) = \mathbf{J}_p^{\mathbf{BE}}(\mathbf{r} - \mathbf{r'}) + \mathbf{J}_p^{(\mathbf{r''}-\mathbf{r'})\times\mathbf{BE}}(\mathbf{r}), \tag{23}$$

where, compared to Eqs. (14)–(17),

$$\mathbf{J}_d^{(\mathbf{r''}-\mathbf{r'})\times\mathbf{BE}}(\mathbf{r}) = -\frac{ne^2}{2m_e c}(\mathbf{r''} - \mathbf{r'})$$
$$\times \mathbf{B}\int d\mathbf{x}_2 \ldots d\mathbf{x}_n [\Psi_a^{(0)}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)\mathbf{E}$$
$$\cdot \Psi_a^{\mathbf{E}*}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n) + \mathbf{E}$$
$$\cdot \Psi_a^{\mathbf{E}}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)\Psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2,\ldots \mathbf{x}_n)], \tag{24}$$

and

$$\mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}) = -\frac{ne}{m_e}\int d\mathbf{x}_2\dots d\mathbf{x}_n\{[(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\Psi_a^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{BE}*}\cdot\mathbf{Ep}\Psi_a^{(0)} + \Psi_a^{(0)*}\mathbf{p}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\Psi_a^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{BE}}\cdot\mathbf{E}]$$

$$+[\mathbf{E}\cdot\Psi_a^{\mathbf{E}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}*}\cdot(\mathbf{r}''-\mathbf{r}')\times\mathbf{Bp}\Psi_a^{(0)} + \Psi_a^{(0)*}\mathbf{pE}\cdot\Psi_a^{\mathbf{E}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}\cdot(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}]$$

$$+[\mathbf{E}\cdot\Psi_a^{\mathbf{E}*}\mathbf{p}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\Psi_a^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}} + (\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\Psi_a^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}*}\mathbf{p}\Psi_a^{\mathbf{E}}\cdot\mathbf{E}]\}. \tag{25}$$

Using the hypervirial relationship

$$\langle a|P_\alpha|j\rangle = -im_e\omega_{ja}\langle a|R_\alpha|j\rangle, \tag{26}$$

it is proved[27] that

$$\mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}) = -\mathbf{J}_d^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}), \tag{27}$$

so that

$$\mathbf{J}^{\mathbf{BE}}(\mathbf{r}) = \mathbf{J}_d^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}'') + \mathbf{J}_p^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}'') = \mathbf{J}_d^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_p^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}'), \tag{28}$$

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

V. CONTINUOUS TRANSFORMATION OF THE ORIGIN OF THE CURRENT DENSITY AND RELATED COMPUTATIONAL METHODS

The CTOCD method for theoretical determination of hypermagnetizabilities and shielding polarizabilities is reported in detail in Ref. 27. In this section only a brief description of the theory involved in the formulation of CTOCD-DZ nuclear shielding polarizabilities is presented.

Within the scheme named ''continuous transformation of origin of current density,'' see Refs. 24,37,38, the transformed diamagnetic current density tensor, $\mathbf{J}_d^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}'')$, can be formally annihilated in every point $\mathbf{r}$ of the molecular domain, by choosing that point as origin, which amounts to considering the $\mathbf{d}$ shift in Eq. (21) a function of $\mathbf{r}$. Therefore $\mathbf{d}(\mathbf{r})=\mathbf{r}$ is assumed in Eq. (22), by choosing $\mathbf{r}''=\mathbf{r}$, so that

$$\mathbf{J}_d^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}') = -\mathbf{J}_d^{(\mathbf{r}-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}). \tag{29}$$

As the diamagnetic term is set to zero, this procedure is conveniently indicated by the acronym CTOCD-DZ. The total current becomes formally paramagnetic, and contains two terms which are expressed within the original coordinate system as functions of $\mathbf{r}$, i.e.,

$$\mathbf{J}^{\mathbf{BE}}(\mathbf{r}) = \mathbf{J}_p^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}), \tag{30}$$

where, compared to Eq. (23),

$$\mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}) = [\mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r})]_{\mathbf{r}''=\mathbf{r}}, \tag{31}$$

that is, $\mathbf{r}''$ is put equal to $\mathbf{r}$ after operating with $\mathbf{p}$ in Eq. (25) for the transformed current density.

As total current density is an invariant, projected onto itself by any transformation (provided that the hypervirial

condition, Eq. (26), is obeyed), comparison between Eqs. (28) and (30) necessarily implies (which, however, is not useful as a calculation prescription) that

$$\mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{BE}}(\mathbf{r}) = \mathbf{J}_d^{\mathbf{BE}}(\mathbf{r}-\mathbf{r}'), \tag{32}$$

for every $\mathbf{r}$. In other words, the formally annihilated diamagnetic contribution reappears as a new ''paramagnetic'' term (see Ref. 27 for details).

By employing Eq. (30) for the current density within expressions (13) and right-hand side of Eq. (9), new definitions for total nuclear magnetic shielding are obtained in the form

$$\sigma_{\alpha\beta\gamma}^I = \sigma_{\alpha\beta\gamma}^{pI} + \sigma_{\alpha\beta\gamma}^{\Delta I}, \tag{33}$$

where

$$\sigma_{\alpha\beta\gamma}^{\Delta I} = \frac{e^3}{2m_e^2c^2}\epsilon_{\beta\lambda\mu}\{P_\lambda, R_\gamma, T_{I\mu\alpha}^n\}_{-2}, \tag{34}$$

and the Hermitian second-rank tensor operator $\mathbf{T}_I^n$,

$$T_{I\alpha\beta}^n = \frac{1}{2}\sum_{i=1}^n[(r_{i\alpha}-r_\alpha')M_{I\beta}^i + M_{I\alpha}^i(r_{i\beta}-r_\beta')], \tag{35}$$

has been defined. A non-Hermitian expression for the same operator had been previously introduced, see Eq. (73) of Ref. 27. In numerical implementations either definition can be employed. In any event the CTOCD-DZ scheme is very easy to code in a computer program, corresponding to any approximate computational technique presently adopted by quantum chemists. For instance, within the coupled Hartree–Fock, or equivalent random-phase approximation methods, the same basic algorithm is used to evaluate the paramagnetic p-contributions, Eq. (11), and the ''diamagnetic'' Δ-contributions, Eq. (34). The numerical procedure is essentially the same as that employed for electric hyperpolarizabilities, discussed in detail in Ref. 32, with minor variants related to the pure imaginary character of the operators describing the magnetic perturbations. It is also worth recalling that the CTOCD-DZ scheme can be applied to any desired level of accuracy, owing to the very general features of Eqs. (11) and (34). The MCSCF approximation is presently being developed within the framework of the DALTON program by Ligabue.[39]

The CTOCD-DZ expressions (34) reduce to the conventional diamagnetic contributions (10), if the hypervirial constraint, Eq. (26), is satisfied, as it can be proven by direct substitution. *Vice versa* the CTOCD-DZ formulas, established here by formally annihilating the diamagnetic contribution to the current density, can be alternatively derived

TABLE I. Specification of basis sets and SCF energy.

Basis set	Contraction scheme		Number of GTOs	Number of CGTOs	SCF energy (hartree)
	GTO	CGTO			
H_2O_2					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	140	70	$-150.821\,934\,8$
II	$(14s14p5d/5s5p)$	$[9s9p4d/3s3p]$	212	144	$-150.829\,016\,5$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	162	154	$-150.842\,632\,3$
F_2					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	104	52	$-198.742\,211\,6$
II	$(14s14p5d/5s5p)$	$[9s9p4d/3s3p]$	172	120	$-198.754\,667\,4$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	120	114	$-198.770\,274\,4$
HCCH					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	140	70	$-76.832\,201\,7$
II	$(14s14p5d/5s5p)$	$[9s9p4d/3s3p]$	212	144	$-76.844\,809\,1$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	162	154	$-76.854\,284\,8$
H_2CO					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	140	70	$-113.900\,842\,1$
II	$(14s14p5d/5s5p)$	$[9s9p4d/3s3p]$	212	144	$-113.907\,731\,0$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	162	154	$-113.919\,806\,5$
NH_3					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	106	53	$-56.212\,873\,2$
II	$(14s14p5d/5s5p)$	$[9s9p4d/3s3p]$	146	96	$-56.216\,874\,0$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	123	117	$-56.223\,393\,3$
HCN					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	122	61	$-92.896\,904\,8$
II	$(14s14p5d/5s5p)$	$[9s9p4d/3s3p]$	192	132	$-92.906\,492\,3$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	141	134	$-92.916\,180\,0$
HNC					
I	$(10s6p4d/6s4p)$	$[5s3p2d/3s2p]$	122	61	$-92.880\,801\,8$
III	$(11s7p3d1f/6s3p1d)$	$[8s7p3d1f/5s3p1d]$	141	134	$-92.899\,071\,9$

from Eq. (10), by means of commutation relationships.[24,37,40] Corresponding to the origin of the coordinate system on the nucleus in question, $\sigma^{dI}_{\alpha\beta\gamma}$ is symmetric in the $\alpha\beta$ indices, as it is the case for $\sigma^{\Delta I}_{\alpha\beta\gamma}$, provided that the hypervirial constraint Eq. (26) is satisfied. It has also been demonstrated[24] that the CTOCD-DZ approach is equivalent to the Geertsen approach,[41–43] as far as average properties are concerned.

In a change of coordinate system, Eq. (18), the contributions to the shielding polarizability change according to the relationships

$$\sigma^{pI}_{\alpha\beta\gamma}(\mathbf{r}'') = \sigma^{pI}_{\alpha\beta\gamma}(\mathbf{r}') - \frac{e^3}{2m_e^2c^2}\epsilon_{\beta\lambda\mu}d_\lambda\{M^n_{I\alpha},P_\mu,R_\gamma\}_{-2},$$
(36)

$$\sigma^{\Delta I}_{\alpha\beta\gamma}(\mathbf{r}'') = \sigma^{\Delta I}_{\alpha\beta\gamma}(\mathbf{r}') + \frac{e^3}{2m_e^2c^2}\epsilon_{\beta\lambda\mu}d_\lambda\{M^n_{I\alpha},P_\mu,R_\gamma\}_{-2}.$$
(37)

By comparing Eqs. (36) and (37), exact cancellation between terms arising from variations of Δ- and p-contributions is noticed, so that total CTOCD-DZ nuclear magnetic shielding polarizabilities are independent of the origin of the coordinate system, in any calculation employing the algebraic approximation, i.e., adopting gaugeless basis sets of arbitrary quality and extension. However the accuracy of the results heavily depends on size and flexibility of the basis set. For instance, only for a wave function of very good quality is the

diamagnetic CTOCD-DZ contribution symmetric in the first two indices (for the coordinate origin on the nucleus).

VI. RESULTS

A set of small molecules, H_2O_2, F_2, H_2C_2, H_2CO, NH_3, HCN, and HNC has been considered in the present study. Zero-order molecular orbitals are expanded over atomic Gaussian functions.

Three different basis sets, described in Table I, where corresponding SCF energies are also reported, have been employed to evaluate CTOCD-DZ CHF and conventional CO CHF shielding polarizabilities. The first one, hereafter referred to as I, is an $ad\ hoc$ basis set, developed by Sadlej to evaluate near Hartree–Fock electric dipole polarizabilities within the dipole length gauge.[44] Basis set II has been constructed according to the contraction scheme $(14s14p5d/5s5p)\rightarrow[9s9p4d/3s3p]$ adopting the $9s/5p$ substratum from the van Duijneveldt report[45] and the polarization set from a well known recipe by Sadlej and co-workers.[46,47] According to previous numerical experience,[48] the inclusion of diffuse polarization functions is mandatory to account for the effect of the external electric field. In fact the numerical accuracy of shielding polarizabilities depends essentially on reliable description of charge distribution in the tail regions of the molecule. To this end, the Sadlej procedure[46,47] was found very well suited.

Basis set III, a $(11s7p3d1f/6s3p1d)-[8s7p3d1f/$

TABLE II. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for H_2O_2 molecule.[a]

Basis	Hydrogen [b]			Oxygen [b]		
	I	II	III	I	II	III
σ_{xxx}^{d}	−37.63	−37.44	−37.54	−4.54	−4.65	−4.44
σ_{xxx}^{Δ}	−35.68	−33.96	−35.20	−1.42	−4.24	−4.14
σ_{xxx}^{p}	−20.72	−23.45	−21.02	−973.74	−1075.0	−1000.8
σ_{xxx}^{d+p}	−58.35	−60.89	−58.56	−978.28	−1079.7	−1005.2
$\sigma_{xxx}^{\Delta+p}$	−56.40	−57.41	−56.22	−974.94	−1079.3	−1004.9
σ_{yyx}^{d}	−15.52	−15.37	−15.43	9.16	9.83	9.37
σ_{yyx}^{Δ}	−17.77	−14.37	−14.68	8.06	10.91	7.93
σ_{yyx}^{p}	−92.12	−94.96	−91.69	733.59	738.10	744.44
σ_{yyx}^{d+p}	−107.64	−110.33	−107.12	742.75	747.93	753.81
$\sigma_{yyx}^{\Delta+p}$	−109.89	−109.33	−106.37	741.65	749.01	752.37
σ_{zzx}^{d}	−18.90	−18.99	−18.94	0.43	0.46	0.41
σ_{zzx}^{Δ}	−20.09	−16.88	−17.69	2.87	1.56	0.18
σ_{zzx}^{p}	−46.38	−50.47	−46.79	−278.85	−314.87	−282.80
σ_{zzx}^{d+p}	−65.28	−69.46	−65.73	−278.42	−314.41	−282.39
$\sigma_{zzx}^{\Delta+p}$	−66.47	−67.35	−64.48	−275.98	−313.31	−282.62
σ_{xxy}^{d}	−16.26	−16.30	−16.21	−32.64	−32.37	−32.26
σ_{xxy}^{Δ}	−14.75	−16.00	−15.17	−31.41	−30.77	−29.21
σ_{xxy}^{p}	−217.87	−213.03	−210.91	−7824.0	−7898.3	−7802.1
σ_{xxy}^{d+p}	−234.13	−229.33	−227.12	−7856.4	−7930.7	−7834.3
$\sigma_{xxy}^{\Delta+p}$	−232.62	−229.03	−226.08	−7855.4	−7929.1	−7831.3
σ_{yyy}^{d}	−31.56	−31.50	−31.54	4.82	4.19	4.37
σ_{yyy}^{Δ}	−37.33	−33.27	−31.14	−11.97	2.34	1.69
σ_{yyy}^{p}	−0.18	−7.53	−8.66	174.90	177.25	170.65
σ_{yyy}^{d+p}	−31.74	−39.03	−40.20	179.72	181.44	175.02
$\sigma_{yyy}^{\Delta+p}$	−37.51	−40.80	−39.80	162.93	179.59	172.34
σ_{zzy}^{d}	−18.92	−18.92	−18.84	−33.17	−32.76	−32.68
σ_{zzy}^{Δ}	−19.32	−17.21	−18.09	−33.18	−31.63	−29.97
σ_{zzy}^{p}	−72.50	−71.62	−68.91	−4525.8	−4534.1	−4533.1
σ_{zzy}^{d+p}	−91.42	−90.54	−87.75	−4559.0	−4566.9	−4565.8
$\sigma_{zzy}^{\Delta+p}$	−91.82	−88.83	−87.00	−4559.0	−4565.7	−4563.1
σ_{xxz}^{d}	−9.37	−9.18	−9.22	3.11	3.88	3.23
σ_{xxz}^{Δ}	−8.54	−5.77	−7.58	10.63	7.75	4.06
σ_{xxz}^{p}	−15.86	−15.68	−14.83	161.42	217.14	203.27
σ_{xxz}^{d+p}	−25.23	−24.86	−24.05	164.53	221.02	206.50
$\sigma_{xxz}^{\Delta+p}$	−24.40	−21.45	−22.41	172.25	224.89	207.33
σ_{yyz}^{d}	−7.30	−7.01	−7.18	4.32	4.60	4.36
σ_{yyz}^{Δ}	−6.63	−4.83	−6.23	6.65	6.82	4.32
σ_{yyz}^{p}	−52.66	−53.94	−51.10	407.61	415.55	415.18
σ_{yyz}^{d+p}	−59.96	−60.95	−58.28	411.93	420.15	419.54
$\sigma_{yyz}^{\Delta+p}$	−59.29	−58.77	−57.33	414.26	422.37	419.50
σ_{zzz}^{d}	−17.18	−16.57	−16.97	4.72	4.92	4.98
σ_{zzz}^{Δ}	−11.65	−13.38	−15.42	7.59	6.33	5.02
σ_{zzz}^{p}	−8.68	−6.73	−3.84	83.71	86.64	83.05
σ_{zzz}^{d+p}	−25.86	−23.33	−20.81	88.43	91.56	88.03
$\sigma_{zzz}^{\Delta+p}$	−20.33	−20.11	−19.26	91.30	92.97	88.07
A_{x}^{d+p}	77.09	80.23	77.14	171.3	215.4	177.9
$A_{x}^{\Delta+p}$	77.59	78.03	75.69	169.8	214.5	178.4
A_{y}^{d+p}	119.1	119.6	118.4	4078.6	4105.4	4075.0
$A_{y}^{\Delta+p}$	120.65	119.6	117.6	4083.8	4105.1	4074.0
A_{z}^{d+p}	37.02	36.38	34.38	221.63	244.3	238.0
$A_{z}^{\Delta+p}$	34.67	33.44	33.00	225.94	246.7	238.3

[a]Coordinates in bohr: H_1: (1.589 4421; 1.688 577; 0.864 51); O_1: (0; 1.411 439; −0.054 032), H_2: (−1.589 4421; −1.688 577; 0.864 51); O_2: (0; −1.411 439; −0.054 032).
[b]The gauge origin is taken on the H_1 nucleus.
[c]The gauge origin is taken on the O_1 nucleus.

$5s3p1d$], is the same as basis set *IV* employed in Ref. 49 retaining the s/p set from Huzinaga.[50]

The calculations of shielding polarizabilities reported in this work have been carried out by means of the SYSMO suite of computer programs.[28] The results are reported in Tables II to VIII.

A discussion of the effect of a uniform electric field on the nuclear magnetic 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, can be rationalized via the relationship

$$\sigma_{Av}^{I} = -A_{\gamma}^{I} E_{\gamma} - B_{\gamma\delta}^{I} E_{\gamma} E_{\delta}. \tag{38}$$

The shielding polarizabilities are related to the A_{γ}^{I} vector by

$$A_{\gamma}^{I} = -\tfrac{1}{3} \sigma_{\alpha\alpha\gamma}^{I}. \tag{39}$$

For a given nucleus, the number of nonvanishing elements $\sigma_{\alpha\alpha\gamma}^{I}$ depends on the local symmetry of the nucleus.[6] The site-symmetries employed for the nuclei of the molecules given above are: C_1 for H_2O_2; C_{2v} for F_2, H_2C_2, HCN, and HNC, and C_S for H_2CO and NH_3 molecules.

In Tables II–VIII the nonvanishing $\sigma_{\alpha\alpha\gamma}^{I}$ components which contribute to the average shielding in Eq. (38) have been reported. The nuclear geometries employed by Cybulski and Bishop[51] have been retained in the present study. They are specified in the tables. The A_{γ}^{I} values in Eq. (39), obtained via the CTOCD-DZ approach Eq. (33), as well as the conventional CO method, Eq. (9), have been compared with corresponding data taken from the literature. With the exception of the H_2O_2 molecule, theoretical values from other sources have been transformed to the coordinate system adopted here to make proper comparison. All the results are expressed in ppm a.u.

H_2O_2

Table II displays the results of nuclear shielding polarizabilities for hydrogen and oxygen nuclei of hydrogen peroxide. Cybulski and Bishop reported the corresponding conventional calculations,[51] by employing large basis sets to minimize the gauge origin problem. The comparison between the present calculations and those of Ref. 51 is left aside because, although the nuclear geometry employed there is identical to ours, a different coordinates frame, with the C_2 axis coincident with the z-direction, is chosen in the present investigations. Then, the CHF-CTOCD-DZ results are discussed comparing them with the conventional CO results evaluated via the same basis sets in this work. $\sigma_{\alpha\beta\gamma}^{\Delta I}$ results are fairly close to $\sigma_{\alpha\beta\gamma}^{dI}$ in spite of the fact that the size of the three basis sets employed here is smaller than in previous calculations. This is an indication of near Hartree–Fock quality, since both results would be identical if the hypervirial constraint Eq. (26) were exactly satisfied. It should be recalled that Ref. 51 reports CO-CHF as well as correlated calculations at different levels of accuracy, e.g., MP2, MP3, and L-CCD, showing that, especially for the oxygen nucleus, the shielding polarizability is very sensitive to electron correlation.

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TABLE III. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for F_2 molecule. [a]

Basis	Fluorine [b]			
	I	II	III	Ref. 51[c]
σ^d_{xxz}	-38.13	-37.42	-37.55	
σ^Δ_{xxz}	-34.33	-33.59	-29.86	
σ^p_{xxz}	$-18\,014.1$	$-17\,723.7$	$-17\,626.4$	
σ^{d+p}_{xxz}	$-18\,052.2$	$-17\,761.1$	$-17\,663.9$	$-17\,753.6$
$\sigma^{\Delta+p}_{xxz}$	$-18\,048.4$	$-17\,757.3$	$-17\,656.3$	
σ^d_{zzz}	-0.99	-1.55	-0.73	
σ^Δ_{zzz}	-19.33	-3.12	-4.67	
σ^p_{zzz}	0.00	0.00	0.00	
σ^{d+p}_{zzz}	-0.99	-1.55	-0.73	-0.6
$\sigma^{\Delta+p}_{zzz}$	-19.33	-3.12	-4.67	
A^{d+p}_z	$12\,035.1$	$11\,841.3$	$11\,776.2$	$11\,836.0$
$A^{\Delta+p}_z$	$12\,038.7$	$11\,839.2$	$11\,772.4$	

[a]Coordinates in bohr: F_1: $(0;0;1.334)$.
[b]The gauge origin is taken on the F_1 nucleus.
[c]CHF approximation.

F_2

The results displayed in Table III show insufficient convergence for the σ^I_{zzz} component, whereas $\sigma^I_{xxz}=\sigma^I_{yyz}$ values are similar to the CHF results of Cybulski and Bishop.[51] In fact the $\sigma^{\Delta I}_{zzz}$ results are rather different from the conventional σ^{dI}_{zzz} for the basis sets chosen in this work, which clearly indicates that the quality of the wave function should be substantially improved for accurate description of response of F_2 to both electric and magnetic perturbations. In addition, Cybulski and Bishop showed[51] that the fluorine shielding polarizabilities are very sensitive to the electron correlation, and that, in any event, F_2 is a difficult case which deserves additional studies.

H_2C_2

The results for this molecule are shown in Table IV. A number of $\sigma^{\Delta I}_{zzz}$ estimates are fairly close to σ^{dI}_{zzz}, and also total σ^I_{zzz} are quite similar to the CHF results reported by Cybulski and Bishop.[51] On the other hand, the $\sigma^{\Delta I}_{xxz}=\sigma^{\Delta I}_{yyz}$ values are very different from the corresponding σ^{dI}_{xxz} values. As a consequence, total CTOCD-DZ proton shielding polarizabilities are rather different from those of other authors quoted in the same table. At any rate, in the case of the carbon nucleus, the paramagnetic contributions are three orders-of-magnitude larger than the diamagnetic d- and Δ-terms, which makes less evident the insufficient accuracy of CTOCD-DZ results arising from some inadequacies of the basis set, e.g., lack of flexibility.

It should also be reminded that compensation of spurious terms of different sign can take place in CTOCD-DZ calculations, making the results less diamagnetic than corresponding CO values.[37]

H_2CO

The results for hydrogen, carbon, and oxygen nuclei of formaldehyde are reported in Table V, where comparison with CHF predictions of Cybulski and Bishop,[51] Grayson and Raynes,[15,52] and Augspurger et al.[10] is also made. The estimates from other articles have been transformed to the coordinate system specified in footnote ''a'' to this table. Theoretical CO and CTOCD-DZ A^H_α vector components obtained from hydrogen shielding polarizabilities provided by basis sets II and III lie within the range of values reported by other authors, see Refs. 51,52. In any event, the comparison between zzx and zzy components of $\sigma^{\Delta H}$ and σ^{dH} tensors clearly indicates that the basis set needs to be improved to account for the case in which the additional electric field

TABLE IV. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for HCCH molecule.[a]

Basis	Hydrogen [b,c]				Carbon [d,e]			
	I	II	III	Ref. 51[f]	I	II	III	Ref. 51[f]
σ^d_{xxz}	-32.10	-31.95	-31.97		-5.74	-5.63	-5.70	
σ^Δ_{xxz}	-16.59	-14.00	-13.73		4.91	3.05	3.70	
σ^p_{xxz}	-39.86	-41.70	-41.88		-1025.44	-1082.90	-1101.47	
σ^{d+p}_{xxz}	-71.96	-73.65	-73.85	-74.1	-1031.18	-1088.53	-1107.17	-1106.7
$\sigma^{\Delta+p}_{xxz}$	-56.45	-55.70	-55.61		-1020.5	-1079.85	-1097.7	
σ^d_{zzz}	-59.64	-60.04	-60.27		-56.36	-56.67	-56.65	
σ^Δ_{zzz}	-59.08	-58.94	-55.78		-60.71	-57.52	-54.56	
σ^p_{zzz}	0.00	0.00	0.00		0.00	0.00	0.00	
σ^{d+p}_{zzz}	-59.64	-60.04	-60.27	-59.9	-56.36	-56.67	-56.65	-56.5
$\sigma^{\Delta+p}_{zzz}$	-59.08	-58.94	-55.78		-60.71	-57.52	-54.56	
A^{d+p}_z	67.85	69.11	69.32	69.4	706.25	744.58	756.95	756.6
$A^{\Delta+p}_z$	57.33	56.78	55.67		700.56	739.07	750.00	

[a]Coordinates in bohr: H_1: $(0;0;3.139\,78)$, C_1: $(0;0;1.136\,67)$.
[b]The gauge origin is taken on the H_1 nucleus.
[c]$A^{H_1}_z= 70.1$ (Ref. 52), 69.1 (Ref. 20), 67.2 (Ref. 10).
[d]The gauge origin is taken on the C_1 nucleus.
[e]$A^{C_1}_z= 750.7$ (Ref. 17), 756.2 (Ref. 20), 733.9 (Ref. 10).
[f]CHF approximation.

TABLE V. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for H_2CO molecule.[a]

				Hydrogen $H_1^{b,c,d}$					
Basis	I	II	III	Ref. 51[i]		I	II	III	Ref. 51[i]
σ_{xxx}^{d}	-38.11	-38.07	-38.08		σ_{xxy}^{d}	11.32	10.75	10.78	
σ_{xxx}^{Δ}	-36.34	-35.01	-35.76		σ_{xxy}^{Δ}	7.41	11.58	9.60	
σ_{xxx}^{p}	29.12	29.13	30.10		σ_{xxy}^{p}	-3.52	-7.01	-6.51	
σ_{xxx}^{d+p}	-8.99	-8.94	-7.98		σ_{xxy}^{d+p}	7.80	3.74	4.27	
$\sigma_{xxx}^{\Delta+p}$	-7.22	-5.88	-5.66		$\sigma_{xxy}^{\Delta+p}$	3.89	4.57	3.09	
σ_{yyx}^{d}	-16.00	-15.91	-15.83		σ_{yyy}^{d}	35.15	34.29	34.64	
σ_{yyx}^{Δ}	-20.01	-18.07	-15.00		σ_{yyy}^{Δ}	31.65	33.75	33.19	
σ_{yyx}^{p}	32.80	35.28	33.45		σ_{yyy}^{p}	-43.93	-49.06	-48.82	
σ_{yyx}^{d+p}	16.80	19.37	17.62		σ_{yyy}^{d+p}	-8.78	-14.77	-14.18	
$\sigma_{yyx}^{\Delta+p}$	12.79	17.21	18.45		$\sigma_{yyy}^{\Delta+p}$	-12.28	-15.31	-15.63	
σ_{zzx}^{d}	-20.04	-19.59	-20.00		σ_{zzy}^{d}	11.88	11.23	11.41	
σ_{zzx}^{Δ}	-11.83	-10.39	-10.21		σ_{zzy}^{Δ}	-1.09	0.28	0.32	
σ_{zzx}^{p}	-13.60	-15.25	-15.07		σ_{zzy}^{p}	10.47	6.90	6.93	
σ_{zzx}^{d+p}	-33.64	-34.84	-35.07		σ_{zzy}^{d+p}	22.35	18.13	18.34	
$\sigma_{zzx}^{\Delta+p}$	-25.43	-25.64	-25.28		$\sigma_{zzy}^{\Delta+p}$	9.38	7.18	7.25	
A_{x}^{d+p}	8.61	8.14	8.48	5.2	A_{y}^{d+p}	-7.12	-2.37	-2.81	3.9
$A_{x}^{\Delta+p}$	6.62	4.77	4.16		$A_{y}^{\Delta+p}$	-0.33	1.18	1.76	

	Carbon[e,g,h]				Oxygen[f,g,h]			
Basis	I	II	III	Ref. 51[i]	I	II	III	Ref. 51[i]
σ_{xxy}^{d}	17.51	16.58	17.13		-34.78	-35.49	-35.07	
σ_{xxy}^{Δ}	10.11	15.80	15.42		-41.28	-37.40	-32.24	
σ_{xxy}^{p}	-397.87	-346.50	-338.97		-5940.0	-6164.5	-6240.0	
σ_{xxy}^{d+p}	-380.36	-329.92	-321.84	-279.4	-5974.8	-6200.0	-6275.1	-6040.4
$\sigma_{xxy}^{\Delta+p}$	-387.76	-330.70	-323.55		-5981.3	-6201.9	-6272.2	
σ_{yyy}^{d}	21.27	20.63	20.56		-50.22	-51.16	-50.81	
σ_{yyy}^{Δ}	24.41	20.24	19.47		-61.44	-53.71	-50.39	
σ_{yyy}^{p}	2502.9	2553.1	2562.3		$-14\,231.6$	$-14\,462.6$	$-14\,459.8$	
σ_{yyy}^{d+p}	2524.2	2573.7	2582.9	2558.0	$-14\,180.8$	$-14\,513.8$	$-14\,510.6$	-13892.0
$\sigma_{yyy}^{\Delta+p}$	2527.3	2573.3	2581.8		$-14\,170.2$	$-14\,516.3$	$-14\,510.2$	
σ_{zzy}^{d}	-17.62	-18.13	-17.79		-0.21	-1.14	-0.60	
σ_{zzy}^{Δ}	-17.89	-21.78	-21.22		-9.12	-2.24	-1.24	
σ_{zzy}^{p}	-11.86	5.66	4.54		47.37	24.79	51.75	
σ_{zzy}^{d+p}	-29.48	-12.47	-13.25	-19.2	47.16	23.65	51.15	93.1
$\sigma_{zzy}^{\Delta+p}$	-29.75	-16.12	-16.68		38.25	22.55	50.51	
A_{y}^{d+p}	-704.8	-743.8	-749.3	-753.1	6702.8	6896.7	6911.5	6613.1
$A_{y}^{\Delta+p}$	-703.3	-742.2	-747.2		6704.4	6898.6	6910.8	

[a]Coordinates in bohr: H_1: (1.766 9143; $-$2.250 1629;0), C_1: (0;$-$1.150 5432;0), H_2: ($-$1.766 9143; $-$2.250 1629;0), O_1: (0;1.144 1778;0).
[b]The gauge origin is taken on the H_1 nucleus.
[c]$A_z^{H_1}$ is zero by symmetry.
[d]$A_x^{H_1} = 8.9$, $A_y^{H_1} = 10.1$ (Ref. 52).
[e]The gauge origin is taken on C_1 nucleus.
[f]The gauge origin is taken on O_1 nucleus.
[g]$A_y^{C_1}$ and $A_y^{O_1}$ are the only nonzero components for those nuclei.
[h]$A_y^{C_1} = -769$, $A_y^{O_1} = 6555.3$ (Ref. 15); $A_y^{C_1} = -697.4$, $A_y^{O_1} = 7019.0$ (Ref. 15).
[i]CHF approximation.

lies in the xy plane of the molecule, whereas the nuclear magnetic moment and the magnetic field are both normal to that plane. For carbon and oxygen nuclei CO and CTOCD-DZ results arrived at in the present study are sufficiently close to one other for the three basis sets employed here. Some discrepancies with previous predictions of Ref. 51 can be observed for the xxy component of carbon and the zzy component of oxygen nuclei.

NH$_3$

The results are reported in Table VI; values taken from the literature have been rotated to the coordinate system adopted here. CO and CTOCD-DZ shielding polarizabilities show that the lower size basis sets I and II employed in the present calculation are sufficient to get reliable predictions. Satisfactory agreement with other authors is also observed.

TABLE VI. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for NH_3 molecule.[a]

				Hydrogen H_1[b,c,d]					
Basis	I	II	III	Ref. 51[h]		I	II	III	Ref. 51[h]
σ_{xxx}^{d}	9.52	8.72	9.19		σ_{xxy}^{d}	−18.16	−18.07	−18.19	
σ_{xxx}^{Δ}	6.33	4.62	7.44		σ_{xxy}^{Δ}	−18.51	−16.80	−16.80	
σ_{xxx}^{p}	7.79	9.01	5.26		σ_{xxy}^{p}	−74.99	−76.48	−75.41	
σ_{xxx}^{d+p}	17.31	17.73	14.45		σ_{xxy}^{d+p}	−93.15	−94.55	−93.60	
$\sigma_{xxx}^{\Delta+p}$	14.12	13.63	12.66		$\sigma_{xxy}^{\Delta+p}$	−93.50	−93.28	−92.21	
σ_{yyx}^{d}	6.20	5.84	5.94		σ_{yyy}^{d}	−42.28	−42.12	−42.07	
σ_{yyx}^{Δ}	3.43	−0.05	3.89		σ_{yyy}^{Δ}	−40.83	−38.59	−38.82	
σ_{yyx}^{p}	20.43	17.81	18.03		σ_{yyy}^{p}	−0.73	0.21	0.43	
σ_{yyx}^{d+p}	26.63	23.65	23.97		σ_{yyy}^{d+p}	−43.01	−41.91	−41.64	
$\sigma_{yyx}^{\Delta+p}$	23.86	17.76	21.92		$\sigma_{yyy}^{\Delta+p}$	−41.56	−38.38	−38.39	
σ_{zzx}^{d}	3.63	2.81	3.24		$\sigma_{zz,y}^{d}$	−21.06	−20.90	−20.96	
σ_{zzx}^{Δ}	−1.58	−0.72	2.78		$\sigma_{zz,y}^{\Delta}$	−24.57	−21.52	−20.34	
σ_{zzx}^{p}	36.31	35.30	30.46		$\sigma_{zz,y}^{p}$	−88.38	−90.41	−89.15	
σ_{zzx}^{d+p}	39.94	38.11	33.70		$\sigma_{zz,y}^{d+p}$	−109.44	−111.31	−110.11	
$\sigma_{zzx}^{\Delta+p}$	34.73	34.58	33.24		$\sigma_{zz,y}^{\Delta+p}$	−112.95	−111.93	−109.49	
A_{x}^{d+p}	−27.96	−26.50	−24.04	−19.1	A_{y}^{d+p}	81.87	82.59	81.78	82.1
$A_{x}^{\Delta+p}$	−24.24	−21.99	−22.59		$A_{y}^{\Delta+p}$	82.67	81.20	80.03	

				Nitrogen[e,f,g]					
Basis	I	II	III	Ref. 51[h]		I	II	III	Ref. 51[h]
σ_{xxx}^{d}	−5.45	−5.81	−6.01		σ_{yyy}^{d}	−5.60	−5.65	−5.65	
σ_{xxx}^{Δ}	−8.85	−7.17	−6.17		σ_{yyy}^{Δ}	−0.48	−3.24	−3.19	
σ_{xxx}^{p}	−69.77	−70.06	−77.25		σ_{yyy}^{p}	−140.5	−154.4	−158.2	
σ_{xxx}^{d+p}	−75.22	−75.16	−83.26	−82.9	σ_{yyy}^{d+p}	−146.1	−160.9	−163.8	−162.3
$\sigma_{xxx}^{\Delta+p}$	−78.62	−77.23	−83.42		$\sigma_{yyy}^{\Delta+p}$	−141.0	−157.6	−161.4	
σ_{yyx}^{d}	−4.07	−5.47	−4.62		A_{x}^{d+p}	51.81	76.98	74.59	64.4
σ_{yyx}^{Δ}	−15.68	−11.01	−5.48		$A_{x}^{\Delta+p}$	60.67	81.36	75.07	
σ_{yyx}^{p}	−36.03	−72.42	−65.41						
σ_{yyx}^{d+p}	−40.10	−77.89	−70.25	−55.1					
$\sigma_{yyx}^{\Delta+p}$	−51.70	−83.43	−70.89						

[a]Coordinates in bohr: N_1: (0.127 993 37;0;0), H_1: (−0.591 964 363;1.770 9799;0), H_2: (−0.591 964 363; −0.885 499;1.533 729 25), H_3: (−0.591 964 363;−0.885 499;−1.533 729 25).
[b]The gauge origin is taken at the H_1 nucleus.
[c]$A_z^{H_1}$ is zero by symmetry.
[d]$A_x^{H_1} = −21.0$, $A_y^{H_1} = 82.1$ (Refs. 16,53).
[e]The gauge origin is taken on the N_1 nucleus.
[f]$A_y^{N_1}$ and $A_z^{N_1}$ are zero by symmetry.
[g]$A_x^{N_1} = 87.7$ (Ref. 15).
[h]CHF approximation.

HCN

The results for shielding polarizabilities and for the **A** vectors of hydrogen, carbon, and nitrogen nuclei are shown in Table VII and compared with those from other sources.[17,20,51] A failure similar to that observed for the formaldehyde molecule is evident when the electric field lies in the direction of the bond, whereas the magnetic field and the nuclear magnetic moment are both perpendicular to it: the Δ-values do not converge to the conventional diamagnetic d-terms. Therefore, for the hydrogen nucleus, the $A_z^{\Delta+p}$ values are very different from A_z^{d+p} obtained in this study and by other authors. Accordingly, the basis set needs to be conveniently enlarged to achieve better convergence.

HNC

Shielding polarizabilities of H, N and C nuclei of hydrogen isocyanide arrived at via basis sets I and III are given in

Table VIII. Also in the case of this molecule the CTOCD-DZ Δ-values do not converge to the conventional diamagnetic contribution for all of three nuclei. Since the paramagnetic contributions to the response tensor of carbon and nitrogen nuclei are three orders-of-magnitude larger than the diamagnetic ones, the lack of accuracy of the CTOCD-DZ results is only evident for proton shielding. In addition, as observed by Bishop and Cybulski,[51] the shielding polarizability of hydrogen isocyanide is heavily affected by electron correlation.

VII. CONCLUSIONS

For all the nuclei of the compounds examined in the present study a satisfactory agreement between the A_γ^I components evaluated via the CTOCD-DZ and the CO-CHF procedures was found. With some exception, the numerical values provided by the latter also agree with corresponding estimates from the literature.

TABLE VII. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for HCN molecule.[a]

Basis	Hydrogen[b,c]				Carbon[d,e]				Nitrogen[f,g]			
	I	II	III	Ref. 49[h]	I	II	III	Ref. 49[h]	I	II	III	Ref. 49[h]
σ_{xxz}^{d}	27.63	26.91	27.10		1.46	0.89	1.16		-9.46	-10.09	-9.81	
σ_{xxz}^{Δ}	12.92	13.34	12.33		4.73	6.36	7.06		-10.74	-5.32	-3.11	
σ_{xxz}^{p}	34.36	30.45	32.23		528.8	586.8	598.5		-2592.4	-2704.2	-2733.5	
σ_{xxz}^{d+p}	61.99	57.36	59.33	58.9	530.3	587.7	599.7	638.2	-2601.9	-2714.3	-2743.3	-2886.2
$\sigma_{xxz}^{\Delta+p}$	47.28	43.79	44.56		533.5	593.2	605.6		-2603.1	-2709.5	-2736.6	
σ_{zzz}^{d}	50.69	50.37	50.55		43.94	43.26	43.47		-55.05	-55.84	-55.76	
σ_{zzz}^{Δ}	46.65	50.22	48.52		49.29	45.56	43.02		-65.93	-56.59	-54.86	
σ_{zzz}^{p}	0.00	0.00	0.00		0.00	0.00	0.00		0.00	0.00	0.00	
σ_{zzz}^{d+p}	50.69	50.37	50.55	51.9	43.94	43.26	43.47	44.9	-55.05	-55.84	-55.76	-57.0
$\sigma_{zzz}^{\Delta+p}$	46.65	50.22	48.52		49.29	45.56	43.02		-65.93	-56.59	-54.86	
A_{z}^{d+p}	-58.22	-55.03	-56.40	-56.6	-368.18	-406.22	-414.29	-440.4	1752.9	1828.1	1847.5	1943.1
$A_{z}^{\Delta+p}$	-47.07	-45.93	-45.88		-372.12	-410.65	-418.07		1757.4	1825.2	1842.7	

[a]Coordinates in bohr: H_1:(0;0;-3.32487), C_1:(0;0;-1.132362), N_1:(0;0;0.81655).
[b]The gauge origin is taken at the H_1 nucleus.
[c]$A_z^{H_1} = -54.9$ (Ref. 52), -55.9 (Ref. 20), -54.1 (Ref. 10).
[d]The gauge origin is taken at C_1 nucleus.
[e]$A_z^{C_1} = -428.6$ (Ref. 17), -422.6 (Ref. 20).
[f]The gauge origin is taken on the N_1 nucleus.
[g]$A_z^{N_1} = 1949.1$ (Ref. 20), 1910.1 (Ref. 10).
[h]CHF approximation.

These results are easily understood recalling that basis sets of much smaller size than those adopted by other authors have been retained here in the attempt at developing computational tools suitable to handle molecules of larger size.

The indications clearly emerging from this numerical test are that (i) the accuracy of the results critically depends on the quality of the basis set, for both CTOCD-DZ and CO procedures. (ii) The diamagnetic $\sigma_{\alpha\beta\gamma}^{dI}$ values are much less dependent on the quality of the basis set than the corresponding CTOCD-DZ Δ-terms. This is related to the fact that only two first-order perturbed wave functions are needed to evaluate the former, whereas three perturbations are involved in the sum-over-states formula, Eq. (34) defining the latter. (iii) Sometimes some cancellation of terms can arise between ''diamagnetic'' CTOCD-DZ Δ- and conventional paramagnetic contributions, which makes the comparison of total CTOCD-DZ shielding polarizabilities with corresponding CO estimates really mandatory. The drawbacks observed in the CTOCD-DZ calculations of nuclear magnetic shielding in the absence of electric field document the insufficient reliability of theoretical results obtained via basis set of reduced size, despite the apparently better agreement with experimental data.[37] Similar shortcomings can occur for shielding polarizabilities, as found in this study. (iv) The use

TABLE VIII. CTOCD-DZ shielding polarizabilities (in ppm a.u.) for HNC molecule.[a]

Basis	Hydrogen[b]			Carbon[c]			Nitrogen[d]		
	I	III	Ref. 51[e]	I	III	Ref. 51	I	III	Ref. 51[e]
σ_{xxz}^{d}	29.69	29.67		-5.78	-5.68		6.25	6.44	
σ_{xxz}^{Δ}	14.47	13.60		-6.63	3.76		-0.42	-1.64	
σ_{xxz}^{p}	11.99	14.67		-1221.5	-1296.6		1287.8	1394.0	
σ_{xxz}^{d+p}	41.68	44.3	45.2	-1227.3	-1302.3	-1302.3	1294.0	1400.4	1401.9
$\sigma_{xxz}^{\Delta+p}$	26.46	28.27		-1228.1	-1292.8		1287.4	1392.4	
σ_{zzz}^{d}	54.48	54.52		-39.36	-39.27		44.86	44.77	
σ_{zzz}^{Δ}	55.60	52.28		-46.09	-37.38		51.54	44.55	
σ_{zzz}^{p}	0.00	0.00		0.00	0.00		0.00	0.00	
σ_{zzz}^{d+p}	54.48	54.52	54.6	-39.36	-39.27	-44.2	44.86	44.77	44.77
$\sigma_{zzz}^{\Delta+p}$	55.60	52.28		-46.09	-37.38		51.54	44.55	
A_{z}^{d+p}	-45.95	-47.73	-48.3	831.3	881.3	-885.1	-877.6	-948.5	-949.5
$A_{z}^{\Delta+p}$	-36.17	-36.27		834.1	874.4		-875.4	-943.1	

[a]Coordinates in bohr: H: (0;0;$-0.908\,4981$), C: (0;0;$-2.786\,1281$), N: (0;0;1.292\,0919).
[b]The gauge origin is taken on the hydrogen nucleus.
[c]The gauge origin is taken on the carbon nucleus.
[d]The gauge origin is taken on the nitrogen nucleus.
[e]CHF approximation.

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of the Sadlej's polarization recipe[46] seems quite effective in a number of cases to account for the electric perturbation. Accordingly, quite useful basis sets of reasonable dimension can be constructed by Sadlej-polarizing the basis sets customarily adopted in the calculation of second-order magnetic properties. This recipe turns out to be quite effective in many instances; it provides a reliable compromise between computational cost and accuracy of theoretical determinations, and is probably useful for theoretical evaluations of CTOCD-DZ shielding polarizabilities of larger molecular systems.

Eventually, it should be borne in mind that the CTOCD-DZ approach to nuclear magnetic shielding and shielding polarizabilities provides results independent of a gauge translation, and guarantees at the same time that the related continuity constraint, Eq. (20), is exactly fulfilled. The price to pay, however, is that the basis set to be used in a CTOCD-DZ calculation should be larger than GIAO basis sets. In any event, the use of GIAOs, while ensuring invariance of calculated results in a translation of coordinates, does not imply that the continuity equation is satisfied.

ACKNOWLEDGMENTS

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