Theor Chem Acc (2012) 131:1222
DOI 10.1007/s00214-012-1222-y

REGULAR ARTICLE

Methods of continuous translation of the origin of the current density revisited

P. Lazzeretti

Received: 9 March 2012 / Accepted: 8 April 2012 / Published online: 29 April 2012

Abstract Approaches to the calculation of magnetizability and nuclear magnetic shieldings in a molecule, based on continuous translation of the origin of the magnetic field-induced electronic current density, are reviewed. The connections among apparently unrelated philosophies (Geertsen propagator methods, Keith-Bader continuous set of gauge transformations, and analytical reformulation by Lazzeretti, Malagoli, and Zanasi) are emphasized, and a unitary theoretical scheme is given.

Keywords Molecular magnetic response · Magnetic field-induced current density · Continuous translation of the origin of the current density

1 Introduction

The van Vleck theory of magnetic susceptibilities [1] and the Ramsey approach to nuclear magnetic shielding [2–4] are based on the quantum mechanical Rayleigh–Schrödinger perturbation theory (RSPT). [5] The van Vleck–Ramsey (VR) method [1–4] can advantageously be reformulated via an equivalent approach, in terms of induced electronic current densities, allowing for "phenomenological" relationships that actually restate the validity of the laws of classical electrodynamics [6] in a quantum mechanical context. Magnetizability [1] $\xi_{\alpha\beta}$ and nuclear magnetic shielding [2–4] $\sigma^I_{\alpha\beta}$ can therefore be determined via the quantum mechanical electronic current densities $\mathbf{J}^{\mathbf{B}}$ and $\mathbf{J}^{\mathbf{m}_I}$, induced by an applied magnetic field with flux density $\mathbf{B}$ and by an intramolecular magnetic dipole moment $\mathbf{m}_I$ on nucleus I.

The theories of magnetic response [1–3] are gauge invariant in the limit of exact eigenfunctions to a model Hamiltonian. The conditions for gauge invariance of magnetic response properties calculated via optimal variational wavefunctions have been investigated by Epstein [7, 8] and Sambe [9] in connection with charge conservation [10]. Arrighini, Maestro, and Moccia (AMM) reported quantum mechanical sum rules for invariance in the gauge transformation that amounts to a translation of the origin of the coordinate system [11–13]. The AMM relationships, which also restate charge-current conservation [10] in integral form, as shown later on [14, 15], are exactly satisfied only in the ideal cases investigated by Epstein [7, 8] and Sambe [9]. In actual calculations employing a common gauge origin (CGO) and ordinary (gaugeless) basis sets, they are only approximately fulfilled. Numerical experience and simple theoretical considerations show that the quality of CGO calculations increases by improving basis set size and quality. Only in the limit of complete basis set would the AMM sum rules be numerically verified and calculated magnetic properties origin independent.

This state of affairs prompted the implementation of computational methods using gauge-including atomic orbitals (GIAO) [16][1], first introduced by London [17]. Computer packages available nowadays [18–20] adopt London orbitals for accurate calculation of magnetic properties including electronic correlation [21].

Dedicated to Professor Marco Antonio Chaer Nascimento and published as part of the special collection of articles celebrating his 65th birthday.

P. Lazzeretti (✉)
Dipartimento di Chimica dell'Università degli Studi di Modena e Reggio Emilia, Via Campi 183, 41124 Modena, Italy
e-mail: lazzeret@unimore.it

---

[1] This is the first reference in which the reinterpretation of the GIAO acronym for gauge-including-atomic-orbitals has been proposed, see footnote 6, p. 5047

A different solution of the gauge-origin problem for magnetizability and nuclear magnetic shielding was proposed by Geertsen [22–24]. In his treatment, the diamagnetic contributions to magnetic properties, evaluated as expectation values within the conventional RSPT approaches [2–4], are rewritten as polarization propagators. However, the Geertsen claim was later reconsidered, showing that his method provides only origin-independent average nuclear magnetic shieldings [25]. A computational scheme *à la* Geertseen has been employed by Smith et al. [26].

An approach referred to as CSGT (for continuous set of gauge transformations), which, at first sight, appears not linked to that of Geertsen, was put forward by Keith and Bader (KB) [27–29]. Within the computational scheme implemented by these authors, the diamagnetic contribution to the $\mathbf{J}^{\mathbf{B}}(\mathbf{r})$ current density vector field is formally annihilated at each point $\mathbf{r}$, by choosing that point as origin of the coordinate system. The procedure was reformulated in analytical form afterward and denominated "continuous transformation of the origin of the current density" (CTOCD), whereby the diamagnetic term is set to zero (DZ), in previous papers [25, 30], in which the reasons why the acronym CTOCD seems preferable to CSGT have been discussed. The denomination *ipsocentric* was suggested by Steiner and Fowler [31]. A large body of work is based on use of their methods for provision of interpretation of molecular magnetic response via orbital-contribution analysis [32–35], which can therefore be applied in a uniform way to both localized and delocalized description of the electronic structure. Thus, the advantages of the ipsocentric approach carry over into the description of integrated magnetic properties by a resolution into orbital components.

Analogous procedures, based on formal annihilation of the paramagnetic contribution to the current density, and indicated by CTOCD-PZ, have been proposed [36–38].

The central aim of this article is to give an updated, compact and self-contained, theoretical outline of CTOCD methods, discussing results scattered in different journals and illustrating in detail the connections with previous formulations, that of Geertsen in particular [22–24], which, as it were, has been reformulated allowing for Hermitian operators. The $\xi_{\alpha\beta}$ CTOCD-DZ and CTOCD-PZ magnetizabilities have been re-defined as tensors symmetrical in $\alpha \leftrightarrow \beta$, as physically required, and the relationships describing the change of $\xi_{\alpha\beta}$ in a translation of coordinate system have accordingly been modified. The paper is organized as follows. The conventional Rayleigh–Schrödinger approach to magnetic properties is summarized in Sect. 2. In Sect. 3, magnetizability and NMR shieldings are represented by second-rank tensors in terms of electron current densities induced by a static magnetic field and by a nuclear magnetic dipole. A comprehensive discussion of CTOCD is given in Sect. 4.

2 The Rayleigh–Schrödinger approach to magnetic response properties

Standard tensor formalism is employed throughout this paper, for example, the Einstein convention of implicit summation over two repeated Greek subscripts is in force. The notation adopted in previous references [15, 39, 40] is used. The SI system of units has been adopted.

Within the Born-Oppenheimer (BO) approximation, for a molecule with n electrons and N clamped nuclei, charge, mass, position, canonical, and angular momentum of the i-th electron are indicated, in the configuration space, by $-e, m_e, \mathbf{r}_i, \hat{\mathbf{p}}_i, \hat{\mathbf{l}}_i = \mathbf{r}_i \times \hat{\mathbf{p}}_i, \quad i = 1,2\ldots n$. Analogous quantities for nucleus I are $Z_I e$, M_I, $\mathbf{R}_I$, etc., for $I = 1,2\ldots N$. Capital letters denote total electronic operators, for example, $\hat{\mathbf{R}} = \sum_{i=1}^{n} \mathbf{r}_i, \hat{\mathbf{P}} = \sum_{i=1}^{n} \hat{\mathbf{p}}_i, \hat{\mathbf{L}} = \sum_{i=1}^{n} \hat{\mathbf{l}}_i$, etc. N' nuclei are endowed with an intrinsic magnetic dipole $\mathbf{m}_I = \gamma_I \hbar \mathbf{I}_I$, expressed via the magnetogyric ratio γ_I and spin $\hbar \mathbf{I}_I$ of nucleus I. Within the framework of the BO approximation, $\mathbf{m}_I$ is regarded as a mere phenomenological parameter.

The magnetic Hamiltonians describe the interaction of electrons with the intramolecular perturbation, that is, the intrinsic magnetic dipoles $\mathbf{m}_I$, via the vector potential $\sum_{I=1}^{N'} \mathbf{A}^{\mathbf{m}_I}$, and with an external, spatially uniform and time-independent magnetic field $\mathbf{B} = \nabla \times \mathbf{A}^{\mathbf{B}}$,

$$\mathbf{A} = \mathbf{A}^{\mathbf{B}} + \sum_{I=1}^{N'} \mathbf{A}^{\mathbf{m}_I}, \tag{1}$$

$$\mathbf{A}^{\mathbf{B}} = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \tag{2}$$

$$\mathbf{A}^{\mathbf{m}_I} = \frac{\mu_0}{4\pi} \frac{\mathbf{m}_I \times (\mathbf{r} - \mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|^3}. \tag{3}$$

within the constraint of Coulomb gauge

$$\nabla \cdot \mathbf{A} = 0, \tag{4}$$

explicitly satisfied by the vector potentials (1).

The operator for the orbital magnetic dipole moment is related to the angular momentum operator with respect to the origin of the coordinate system, that is,

$$\hat{\mathbf{m}}_i = -\frac{e}{2m_e} \hat{\mathbf{l}}_i, \quad \hat{\mathbf{m}} = \sum_{i=1}^{n} \hat{\mathbf{m}}_i. \tag{5}$$

The operator for the magnetic field exerted by the electrons on nucleus I is

$$\hat{\mathbf{B}}_I^n = \sum_{i=1}^{n} \hat{\mathbf{B}}_I^i, \quad \hat{\mathbf{B}}_I^i = -\frac{e}{m_e} \hat{\mathbf{M}}_I^i, \tag{6}$$

introducing the operator

$$\hat{\mathbf{M}}_I^i = \frac{\mu_0}{4\pi}\frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r} - \mathbf{R}_I|^3} \times \hat{\mathbf{p}}_i = \frac{\mu_0}{4\pi}\frac{\hat{\mathbf{l}}_i(\mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|^3}, \qquad \hat{\mathbf{M}}_I^n = \sum_{i=1}^{n} \hat{\mathbf{M}}_I^i, \tag{7}$$

where $\hat{\mathbf{l}}_i(\mathbf{R}_I)$ is the angular momentum operator for electron i with respect to the origin at nucleus I. We also define the operators

$$\hat{\xi}^{\rm d}_{\alpha\beta} = -\frac{e^2}{4m_e}\sum_{i=1}^{n}\left(r_\gamma^2\delta_{\alpha\beta} - r_\alpha r_\beta\right)_i, \tag{8}$$

$$\hat{\sigma}^{{\rm d}I}_{\alpha\beta} = \frac{e}{2m_e c^2}\sum_{i=1}^{n}\left(r_{i\gamma}\hat{E}^i_{I_\gamma}\delta_{\alpha\beta} - r_{i\alpha}\hat{E}^i_{I_\beta}\right), \tag{9}$$

$$r_\gamma^2 \equiv r_\gamma r_\gamma \tag{10}$$

where $\hat{\mathbf{E}}_I^i$ denotes the multiplicative operator for the electric field of electron i on nucleus I,

$$\hat{\mathbf{E}}_I^i = \frac{1}{4\pi\epsilon_0} e \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}, \tag{11}$$

and

$$\mu_0\epsilon_0 c^2 = 1. \tag{12}$$

In this notation the VR Hamiltonians [1–3] are cast in the form

$$\hat{H}^{\mathbf{B}} = \frac{e}{m_e}\sum_{i=1}^{n}\mathbf{A}_i^{\mathbf{B}}\cdot\hat{\mathbf{p}}_i = -\hat{m}_\alpha B_\alpha, \tag{13}$$

$$\hat{H}^{\mathbf{m}_I} = \frac{e}{m_e}\sum_{i=1}^{n}\mathbf{A}_i^{\mathbf{m}_I}\cdot\hat{\mathbf{p}}_i = -\hat{B}^n_{I\alpha} m_{I_\alpha}, \tag{14}$$

$$\hat{H}^{\mathbf{BB}} = \frac{e^2}{2m_e}\sum_{i=1}^{n}\mathbf{A}_i^{\mathbf{B}}\cdot\mathbf{A}_i^{\mathbf{B}} = -\frac{1}{2}\hat{\xi}^{\rm d}_{\alpha\beta}B_\alpha B_\beta, \tag{15}$$

$$\hat{H}^{\mathbf{m}_I\mathbf{B}} = \frac{e^2}{m_e}\sum_{i=1}^{n}\mathbf{A}_i^{\mathbf{B}}\cdot\mathbf{A}_i^{\mathbf{m}_I} = \hat{\sigma}^{{\rm d}I}_{\alpha\beta} m_{I_\alpha} B_\beta. \tag{16}$$

The total electronic energy of a molecule, in the presence of external magnetic field **B** and intramolecular magnetic dipoles $\mathbf{m}_I$, is

$$W = W^{(0)} - \frac{1}{2}\xi_{\alpha\beta}B_\alpha B_\beta + \sigma^I_{\alpha\beta} m_{I_\alpha} B_\beta + \cdots, \tag{17}$$

where

$$\xi_{\alpha\beta} = -\left.\frac{\partial^2 W}{\partial B_\alpha \partial B_\beta}\right|_{\mathbf{B}\to\mathbf{0}} \tag{18}$$

is the magnetizability, and

$$\sigma^I_{\alpha\beta} = \left.\frac{\partial^2 W}{\partial m_{I_\alpha}\partial B_\beta}\right|_{\mathbf{m}_I,\mathbf{B}\to\mathbf{0}} \tag{19}$$

is the magnetic shielding at nucleus I. Within the Rayleigh–Schrödinger perturbation theory, the expressions for first- and second-order contributions to the electronic energy of a molecule in the reference electronic state $|a\rangle \equiv |\Psi_a^{(0)}\rangle$ are

$$W_a^{(1)} = \left\langle a\middle|\hat{H}^{(1)}\middle|a\right\rangle, \tag{20}$$

$$W_a^{(2)} = \left\langle a\middle|\hat{H}^{(2)}\middle|a\right\rangle - \frac{1}{\hbar}\sum_{j\neq a}\omega_{ja}^{-1}\left\langle a\middle|\hat{H}^{(1)}\middle|j\right\rangle\left\langle j\middle|\hat{H}^{(1)}\middle|a\right\rangle, \tag{21}$$

where $\hat{H}^{(1)} = \hat{H}^{\mathbf{B}} + \hat{H}^{\mathbf{m}_I}$ and the second-order Hamiltonians are specified by Eqs. (15) and (16). $\hat{H}^{(0)}$ is the BO unperturbed electronic Hamiltonian of a molecule, so that

$$\hat{H}^{(0)}|j\rangle = W_j^{(0)}|j\rangle,$$

and

$$\omega_{ja} = (W_j^{(0)} - W_a^{(0)})/\hbar$$

is a natural transition frequency for the excited state $|j\rangle \equiv |\Psi_j^{(0)}\rangle$.

Allowing for relationships (17), (20) and (21), for the Hellmann-Feynman theorem, and for the expression

$$\left\{\hat{A},\hat{B}\right\}_{-1} = \frac{2}{\hbar}\sum_{i\neq a}\omega_{ia}^{-1}\Re\left\{\left\langle a\middle|\hat{A}\middle|i\right\rangle\left\langle i\middle|\hat{B}\middle|a\right\rangle\right\} \equiv -\langle\langle A;B\rangle\rangle_{\omega=0}, \tag{22}$$

for the polarization propagator [41, 42], the magnetizability is evaluated as

$$\xi_{\alpha\beta} = \xi^{\rm d}_{\alpha\beta} + \xi^{\rm p}_{\alpha\beta}, \tag{23}$$

$$\xi^{\rm d}_{\alpha\beta} = \left\langle a\middle|\hat{\xi}^{\rm d}_{\alpha\beta}\middle|a\right\rangle, \tag{24}$$

$$\xi^{\rm p}_{\alpha\beta} = \left\{\hat{m}_\alpha, \hat{m}_\beta\right\}_{-1}, \tag{25}$$

and the magnetic shielding at nucleus I is

$$\sigma^I_{\alpha\beta} = \sigma^{{\rm d}I}_{\alpha\beta} + \sigma^{{\rm p}I}_{\alpha\beta}, \tag{26}$$

$$\sigma^{{\rm d}I}_{\alpha\beta} = \left\langle a\middle|\hat{\sigma}^{{\rm d}I}_{\alpha\beta}\middle|a\right\rangle, \tag{27}$$

$$\sigma^{{\rm p}I}_{\alpha\beta} = -\left\{\hat{B}^n_{I_\alpha}, \hat{m}_\beta\right\}_{-1}. \tag{28}$$

3 The electronic current density induced by a static magnetic field

Adopting the McWeeny normalization and allowing for his notation [43–45], the probability density matrix for an n-electron quantum state $|\Psi\rangle$ is defined by the relationship

$$\gamma(\mathbf{x};\mathbf{x}') = n\int \Psi(\mathbf{x},\mathbf{x}_2,\ldots\mathbf{x}_n)\Psi^*(\mathbf{x}',\mathbf{x}_2,\ldots\mathbf{x}_n)\,\mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n, \tag{29}$$

where $\mathbf{x}_i \equiv \mathbf{r}_i \otimes \eta_i$ is a space-spin coordinate, and $\mathrm{d}\mathbf{x}_i \equiv \mathrm{d}^3r_i \otimes \mathrm{d}\eta_i$. By integrating over the spin variable η, a spatial density matrix is obtained,

$$\gamma(\mathbf{r};\mathbf{r}') = \int_{\eta'=\eta} \gamma(\mathbf{x};\mathbf{x}')\mathrm{d}\eta. \tag{30}$$

The diagonal elements of the density matrix, Eq. (30),

$$\gamma(\mathbf{r}) = \gamma(\mathbf{r};\mathbf{r}), \tag{31}$$

give the electronic charge distribution of the state

$$\rho(\mathbf{r}) = -e\gamma(\mathbf{r}). \tag{32}$$

For the unperturbed reference state $\Psi_a^{(0)}$, the probability and charge density, Eqs. (31) and (32), become

$$\gamma^{(0)}(\mathbf{r}) = n\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n\,\Psi_a^{(0)}(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n)\Psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n), \tag{33}$$

$$\rho^{(0)}(\mathbf{r}) = -e\gamma^{(0)}(\mathbf{r}). \tag{34}$$

The probability current density is obtained from Eq. (30) for the density matrix,

$$\mathbf{j}(\mathbf{r}) = \frac{1}{m_e}\Re[\hat{\boldsymbol{\pi}}\gamma(\mathbf{r};\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}, \tag{35}$$

where $\Re$ takes the real part of the content within brackets. The operator for the electronic mechanical momentum in the presence of external magnetic field and intramolecular magnetic dipoles $\mathbf{m}_I$ at the nuclei is defined by

$$\hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} + e\left(\mathbf{A}^{\mathbf{B}} + \sum_{I=1}^{N'}\mathbf{A}^{\mathbf{m}_I}\right) \tag{36}$$

within the Gell-Mann minimal coupling principle [46]. The electronic current density is given by

$$\mathbf{J}(\mathbf{r}) = -e\mathbf{j}(\mathbf{r}). \tag{37}$$

The zero-order current density, see Eqs. (35) and (37), vanishes identically for a reality condition, if the reference state is an electronic singlet, which can always be expressed in real form.

If the analytic expressions for the spatial density functions, Eqs. (32) and (37), were known, the calculation of the electronic properties (23)–(25) and (26)–(28) of a molecule would be straightforward. The response tensors might be evaluated via phenomenological equations, formally identical to those applied in classical theory, see Eqs. (46)–(47) hereafter. In practice, however, the density functions, Eqs. (32) and (37), are evaluated from an electronic wavefunction $|\Psi\rangle$, which is usually given as a perturbation series in powers of some physically meaningful parameter. For instance, for a molecule in the presence of an external spatially uniform, time-independent magnetic field $\mathbf{B}$ and an intramolecular magnetic dipole $\mathbf{m}_I$ on nucleus I, the electronic wave function for the a reference state will be expressed in the general form

$$\Psi_a = \Psi_a^{(0)} + \boldsymbol{\Psi}_a^{\mathbf{B}}\cdot\mathbf{B} + \boldsymbol{\Psi}_a^{\mathbf{m}_I}\cdot\mathbf{m}_I + \cdots, \tag{38}$$

where $\boldsymbol{\Psi}_a^{\mathbf{B}}$ and $\boldsymbol{\Psi}_a^{\mathbf{m}_I}$ are axial vectors with three independent components, see Eqs. (39) and (40) hereafter.

Allowing for the Rayleigh–Schrödinger perturbation theory, see Sect. 2, we assume that a complete set $|\Psi_j^{(0)}\rangle \equiv |j\rangle$ of eigenstates to the unperturbed Hamiltonian $H^{(0)}$ is available, together with first-order perturbed functions,

$$\left|\Psi_a^{B_\alpha}\right\rangle = \frac{1}{\hbar}\sum_{j\neq a}\omega_{ja}^{-1}|j\rangle\langle j|\hat{m}_\alpha|a\rangle, \tag{39}$$

and

$$\left|\Psi_a^{m_{I_\alpha}}\right\rangle = \frac{1}{\hbar}\sum_{j\neq a}\omega_{ja}^{-1}|j\rangle\left\langle j|\hat{B}_{I_\alpha}^n|a\right\rangle. \tag{40}$$

Employing Eqs. (35)–(37), the first-order electronic current density induced by the external magnetic field can be written as a sum of paramagnetic and diamagnetic contributions,

$$\mathbf{J}^{\mathbf{B}} = \mathbf{J}_p^{\mathbf{B}} + \mathbf{J}_d^{\mathbf{B}}, \tag{41}$$

where

$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}) = -\frac{e^2}{2m_e}\mathbf{B}\times\mathbf{r}\gamma^{(0)}(\mathbf{r}), \tag{42}$$

is related to the probability density of the unperturbed molecule, see Eq. (34). Using Eq. (39), $\hat{p}_\alpha^* = -\hat{p}_\alpha$ and $\boldsymbol{\Psi}_a^{\mathbf{B}*} = -\boldsymbol{\Psi}_a^{\mathbf{B}}$, the paramagnetic contribution is given by

$$\begin{aligned}\mathbf{J}_p^{\mathbf{B}}(\mathbf{r}) = -\frac{ne}{m_e}\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \\ \times\Big[\mathbf{B}\cdot\boldsymbol{\Psi}_a^{\mathbf{B}*}(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n)\hat{\mathbf{p}}\Psi_a^{(0)}(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n) \\ +\Psi_a^{(0)*}(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n)\hat{\mathbf{p}}\mathbf{B}\cdot\boldsymbol{\Psi}_a^{\mathbf{B}}(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n)\Big].\end{aligned} \tag{43}$$

The terms of the vector potential, Eq. (36), involving nuclear magnetic dipoles give rise to the classical Larmor contributions, as discussed previously [15],

$$\mathbf{J}_d^{\mathbf{m}_I}(\mathbf{r}) = -\frac{e^2}{m_e}\mathbf{A}^{\mathbf{m}_I}\gamma^{(0)}(\mathbf{r}), \tag{44}$$

due to diamagnetic nuclear spin/electron orbit interaction discussed by Ramsey [47].

The paramagnetic spin-orbital contributions to the electronic current density induced by the nuclear magnetic dipole are obtained from Eqs. (35) and (36). Since $\Psi_a^{\mathbf{m}_I *} = -\Psi_a^{\mathbf{m}_I}$, the current density expression

$$\mathbf{J}_p^{\mathbf{m}_I}(\mathbf{r}) = -\frac{en}{m_e}\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times \Big[\mathbf{m}_I \cdot \boldsymbol{\Psi}_a^{\mathbf{m}_I *}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\,\hat{\mathbf{p}}\,\Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n) + \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\,\hat{\mathbf{p}}\,\boldsymbol{\Psi}_a^{\mathbf{m}_I}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n) \cdot \mathbf{m}_I\Big] \tag{45}$$

is found for the contribution due to paramagnetic spin-orbit interaction. The three-dimensional vector fields defined via Eqs. (43) and (45) have the direction of the $\hat{\mathbf{p}}$ vector.

The response properties introduced via Eqs. (17)–(19) are conveniently re-expressed via the induced current densities allowing for the relationships of classical electrodynamics [6]

$$W^{\mathbf{BB}} = -\frac{1}{2}\int \mathbf{A}^{\mathbf{B}} \cdot \mathbf{J}^{\mathbf{B}}\mathrm{d}^3 r, \tag{46}$$

$$W^{\mathbf{m}_I\mathbf{B}} = -\int \mathbf{A}^{\mathbf{m}_I} \cdot \mathbf{J}^{\mathbf{B}}\mathrm{d}^3 r = -\int \mathbf{A}^{\mathbf{B}} \cdot \mathbf{J}^{\mathbf{m}_I}\mathrm{d}^3 r, \tag{47}$$

which define the second-order contribution to the Rayleigh–Schrödinger electronic energy, Eq. (21).

The explicit expressions for the response tensors, obtained by differentiating the perturbed second-order energies (46), (47) as in Eqs. (18), (19), are identical to the relationships, Eqs. (23)–(26), from the Rayleigh–Schrödinger perturbation theory. Therefore, Eqs. (46) and (47) can be used as computational recipes alternative to Eqs. (23) and (26). Formulae rewritten in terms of current density tensors are obtained in the following.

3.1 Magnetizability and nuclear magnetic shielding tensors from electronic current density

The orbital magnetic dipole moment induced in the n electrons of a molecule by an external magnetic field with flux density $\mathbf{B}$ is evaluated assuming linear response,

$$\Delta\langle \hat{m}_\alpha \rangle = \xi_{\alpha\beta}B_\beta = -\frac{1}{2}\epsilon_{\alpha\beta\gamma}\int J_\beta^{\mathbf{B}}(\mathbf{r})r_\gamma\,\mathrm{d}^3 r. \tag{48}$$

The magnetic field induced at an observation point $\mathbf{R}$ is determined by the Biot-Savart law [6],

$$\Delta\big\langle B_\alpha^n(\mathbf{R})\big\rangle = -\sigma_{\alpha\beta}(\mathbf{R})B_\beta = \frac{\mu_0}{4\pi}\epsilon_{\alpha\beta\gamma}\int J_\beta^{\mathbf{B}}(\mathbf{r})\frac{R_\gamma - r_\gamma}{|\mathbf{R} - \mathbf{r}|^3}\,\mathrm{d}^3 r. \tag{49}$$

Introducing the current density tensor [25] via the derivative

$$\mathcal{J}_\alpha^{B_\beta}(\mathbf{r}) = \frac{\partial}{\partial B_\beta}J_\alpha^{\mathbf{B}}(\mathbf{r}), \tag{50}$$

with paramagnetic components

$$\mathcal{J}_{p_\alpha}^{B_\beta}(\mathbf{r}) = -\frac{ne}{m_e}\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n\Big[\Psi_a^{B_\beta *}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\hat{p}_\alpha\Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n) + \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\hat{p}_\alpha\Psi_a^{B_\beta}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\Big], \tag{51}$$

and diamagnetic components

$$\mathcal{J}_{d_\alpha}^{B_\beta}(\mathbf{r}) = -\frac{e^2}{2m_e}\epsilon_{\alpha\beta\gamma}r_\gamma\gamma^{(0)}(\mathbf{r}), \tag{52}$$

the magnetizability tensor is evaluated by (18) and (46)

$$\xi_{\alpha\beta} = \frac{1}{4}\int r_\gamma\left(\epsilon_{\alpha\gamma\delta}\mathcal{J}_\delta^{B_\beta} + \epsilon_{\beta\gamma\delta}\mathcal{J}_\delta^{B_\alpha}\right)\mathrm{d}^3 r, \tag{53}$$

and the shielding tensor at $\mathbf{R}$ is obtained as

$$\sigma_{\alpha\delta}(\mathbf{R}) = -\frac{\mu_0}{4\pi}\epsilon_{\alpha\beta\gamma}\int \frac{r_\beta - R_\beta}{|\mathbf{r} - \mathbf{R}|^3}\mathcal{J}_\gamma^{B_\delta}(\mathbf{r})\,\mathrm{d}^3 r. \tag{54}$$

If $\mathbf{R}$ coincides with the position $\mathbf{R}_I$ of the I-th nucleus, carrying an intrinsic magnetic dipole m_{I_α}, the quantity $\sigma_{\alpha\beta}(\mathbf{R}_I) \equiv \sigma_{\alpha\beta}^I$ defines the magnetic shielding tensor of that nucleus.

3.2 Invariance of magnetizability, nuclear magnetic shielding and electronic current density in a gauge translation

In a gauge transformation of the vector potential (2),

$$\mathbf{A}^{\mathbf{B}} \rightarrow \mathbf{A}^{\mathbf{B}} + \nabla f, \tag{55}$$

induced by an arbitrary generating function $f(\mathbf{r})$ well-behaved for $\mathbf{r} \rightarrow \infty$, the interaction energy and the molecular properties (magnetizability, nuclear shieldings, and the induced current densities) are invariant for exact [12, 13, 15, 25, 40, 48–51] and optimal variational eigenfunctions [7]. Gauge invariance is related to charge-current conservation [7, 8, 10], as can immediately be seen. For instance, in the change of gauge (55) considered above, one gets an additional term on the r.h.s. of the second identity, Eq. (47), which is required to identically vanish for the energy to stay the same, that is,

$$\int \mathbf{J}^{\mathbf{m}_I} \cdot \nabla f \mathrm{d}^3 r = \int \nabla \cdot (f\mathbf{J}^{\mathbf{m}_I}) - \int f\nabla \cdot \mathbf{J}^{\mathbf{m}_I}. \tag{56}$$

In fact, owing to the Gauss theorem, the first volume integral on the r.h.s. of Eq. (56) is converted into a surface integral, vanishing due to the boundary conditions $\gamma^{(0)}(\mathbf{r}), \mathbf{J}_\alpha^{\mathbf{m}_I}(\mathbf{r}) \rightarrow 0$ for $\mathbf{r} \rightarrow \infty$. Therefore, the integral on the l.h.s. of Eq. (56), arising in the gauge transformation induced by the generating function f, vanishes, and the interaction energy (47) is invariant, if the continuity equation for the stationary state $\nabla \cdot \mathbf{J}^{\mathbf{m}_I} = 0$ is satisfied. As f is fully arbitrary, one finds in particular, for $f \equiv x, y, z$, the integral conservation condition

$$\int \mathrm{J}_\alpha^{\mathbf{m}_I} \mathrm{d}^3 r = \int \mathrm{d}^3 r \left(\mathrm{J}_{p\alpha}^{\mathbf{m}_I} + \mathrm{J}_{d\alpha}^{\mathbf{m}_I} \right) = \frac{e^2}{m_e^2} \left(\left\{ \hat{P}_\alpha, \hat{M}_{I_\beta}^n \right\}_{-1} - \frac{m_e}{ec^2} \epsilon_{\alpha\beta\gamma} \left\langle a \middle| \hat{E}_{I_\gamma}^n \middle| a \right\rangle \right) m_{I_\beta} = 0 \tag{57}$$

for the electronic current density induced by a nuclear magnetic dipole. The condition for charge-current conservation is expressed via the AMM sum rule [12, 13]

$$\left\{ \hat{P}_\alpha, \hat{M}_{I_\beta}^n \right\}_{-1} = \frac{m_e}{ec^2} \epsilon_{\alpha\beta\gamma} \left\langle a \middle| \hat{E}_{I_\gamma}^n \middle| a \right\rangle, \tag{58}$$

which is also a constraint for translational invariance of calculated magnetic shieldings, see Eqs. (76)–(77) hereafter.

The analogous integral constraint for conservation of the $\mathbf{J}^{\mathbf{B}}$ current density, Eq. (41), is obtained from Eqs. (42) and (43), relying on an equation similar to (56),

$$\int \mathrm{J}_\alpha^{\mathbf{B}} \mathrm{d}^3 r = \int \mathrm{d}^3 r \left(\mathrm{J}_{p\alpha}^{\mathbf{B}} + \mathrm{J}_{d\alpha}^{\mathbf{B}} \right) = \frac{e^2}{m_e^2} \left(\{ \hat{P}_\alpha, \hat{L}_\beta \}_{-1} - m_e \epsilon_{\alpha\beta\gamma} \langle a | \hat{R}_\gamma | a \rangle \right) B_\beta = 0. \tag{59}$$

This is satisfied by the AMM sum rule [11]

$$\{ \hat{P}_\alpha, \hat{L}_\beta \}_{-1} = m_e \epsilon_{\alpha\beta\gamma} \langle a | \hat{R}_\gamma | a \rangle, \tag{60}$$

which is also a condition for origin independence of calculated magnetizabilities [11, 15, 25, 40, 48–51], see Eqs. (74)–(75) hereafter. The Condon sum rule for rotational strengths within the dipole velocity formalism [52] is obtained from the more general Eq. (60) by putting $\alpha = \beta$.

In a change

$$\mathbf{r}' \to \mathbf{r}'' = \mathbf{r}' + \mathbf{d} \tag{61}$$

of the origin of coordinate system, which can be associated with the change of gauge

$$\mathbf{A}^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') \to \mathbf{A}^{\mathbf{B}}(\mathbf{r} - \mathbf{r}'') = \mathbf{A}^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') + \nabla[\mathbf{A}^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{d}], \tag{62}$$

the diamagnetic contribution (42) to the current density induced by the external magnetic field changes:

$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') \to \mathbf{J}_d^{\mathbf{B}}(\mathbf{r} - \mathbf{r}'') = \mathbf{J}_d^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') + \mathbf{J}_d^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}), \tag{63}$$

where

$$\mathbf{J}_d^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}) = -\frac{e^2}{2m_e} \mathbf{d} \times \mathbf{B} \gamma^{(0)}(\mathbf{r}). \tag{64}$$

The wavefunction $\boldsymbol{\Psi}_a^{\mathbf{B}}$ changes according to

$$\mathbf{B} \cdot \boldsymbol{\Psi}_a^{\mathbf{B}} \to \mathbf{B} \cdot \boldsymbol{\Psi}_a^{\mathbf{B}} + \mathbf{d} \times \mathbf{B} \cdot \boldsymbol{\Psi}_a^{\mathbf{d} \times \mathbf{B}}, \tag{65}$$

where

$$\left| \boldsymbol{\Psi}_a^{\mathbf{d} \times \mathbf{B}} \right\rangle = -\frac{e}{2m_e \hbar} \sum_{j \neq a} \omega_{ja}^{-1} |j\rangle \langle j | \hat{\mathbf{P}} | a \rangle, \tag{66}$$

therefore, the paramagnetic contribution to the current density induced by the external magnetic field, Eq. (43), transforms

$$\mathbf{J}_p^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') \to \mathbf{J}_p^{\mathbf{B}}(\mathbf{r} - \mathbf{r}'') = \mathbf{J}_p^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') + \mathbf{J}_p^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}), \tag{67}$$

where

$$\mathbf{J}_p^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}) = -\frac{ne}{m_e} \int \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_n \times \Big[\mathbf{d} \times \mathbf{B} \cdot \boldsymbol{\Psi}_a^{\mathbf{d} \times \mathbf{B} *}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n) \hat{\mathbf{p}} \Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n) + \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2 \ldots \mathbf{x}_n) \hat{\mathbf{p}} \mathbf{B} \cdot \boldsymbol{\Psi}_a^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n) \Big]. \tag{68}$$

Allowing for the Ehrenfest off-diagonal hypervirial relationship [7]

$$-\frac{i}{m_e} \omega_{ja}^{-1} \langle j | \hat{\mathbf{P}} | a \rangle = \langle j | \hat{\mathbf{R}} | a \rangle \tag{69}$$

one finds

$$\boldsymbol{\Psi}_a^{\mathbf{d} \times \mathbf{B}} = -\frac{ie}{2\hbar} \hat{\bar{\mathbf{R}}} \Psi_a^{(0)}, \quad \hat{\bar{\mathbf{R}}} = \hat{\mathbf{R}} - \langle a | \hat{\mathbf{R}} | a \rangle, \tag{70}$$

then

$$\mathbf{J}_p^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}) = -\mathbf{J}_d^{\mathbf{d} \times \mathbf{B}}(\mathbf{r}). \tag{71}$$

The conservation condition for $\mathbf{J}^{\mathbf{d} \times \mathbf{B}}(\mathbf{r})$, is obtained from Eqs. (64) and (68),

$$\int \mathrm{J}_\alpha^{\mathbf{d} \times \mathbf{B}} \mathrm{d}^3 r = \int \mathrm{d}^3 r \left(\mathrm{J}_{p\alpha}^{\mathbf{d} \times \mathbf{B}} + \mathrm{J}_{d\alpha}^{\mathbf{d} \times \mathbf{B}} \right) = -\frac{e^2}{2m_e^2} \epsilon_{\beta\gamma\delta} d_\gamma B_\delta \left(\{ \hat{P}_\alpha, \hat{P}_\beta \}_{-1} - m_e n \delta_{\alpha\beta} \right) = 0. \tag{72}$$

This is satisfied by the AMM sum rule [11]

$$\{ \hat{P}_\alpha, \hat{P}_\beta \}_{-1} = m_e n \delta_{\alpha\beta}, \tag{73}$$

which is the Thomas–Reiche–Kuhn (TRK) sum rule for oscillator strengths within the dipole velocity gauge, also providing a condition for origin independence of calculated magnetizabilities [11, 15, 25, 40, 48–51]. We emphasize that the Ehrenfest relationship (69) yields the basic condition for the existence of sum rules (58), (60), (73) and identities (70), (71).

In the gauge translation (62), the components of the magnetizability tensor change according to the relationships [11, 15, 40, 53]

$$\xi^{\mathrm{d}}_{\alpha\beta}(\mathbf{r}'') = \xi^{\mathrm{d}}_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{4m_e} \times \left[2\langle a|\hat{R}_\gamma(\mathbf{r}')|a\rangle\delta_{\alpha\beta}d_\gamma - d_\beta\langle a|\hat{R}_\alpha(\mathbf{r}')|a\rangle - d_\alpha\langle a|\hat{R}_\beta(\mathbf{r}')|a\rangle - n(d_\gamma d_\gamma\delta_{\alpha\beta} - d_\alpha d_\beta)\right], \quad (74)$$

$$\xi^{\mathrm{p}}_{\alpha\beta}(\mathbf{r}'') = \xi^{\mathrm{p}}_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{4m_e^2} \times \left[d_\delta\left(\epsilon_{\alpha\gamma\delta}\left\{\hat{P}_\gamma, \hat{L}_\beta(\mathbf{r}')\right\}_{-1} + \epsilon_{\beta\gamma\delta}\left\{\hat{P}_\gamma, \hat{L}_\alpha(\mathbf{r}')\right\}_{-1}\right) + d_\delta d_\mu \epsilon_{\alpha\gamma\delta}\epsilon_{\beta\lambda\mu}\{\hat{P}_\gamma, \hat{P}_\lambda\}_{-1}\right], \quad (75)$$

and the analogous change for the magnetic shielding tensor of nucleus *I* is given by [12, 13, 15, 25, 40, 48–51]

$$\sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}') - \frac{e}{2m_e c^2}\left(d_\gamma\left\langle a\left|\hat{E}^n_{I_\gamma}\right|a\right\rangle\delta_{\alpha\beta} - d_\alpha\left\langle a\left|\hat{E}^n_{I_\beta}\right|a\right\rangle\right), \quad (76)$$

$$\sigma^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{2m_e^2} d_\delta \epsilon_{\beta\gamma\delta}\left\{\hat{M}^n_{I_\alpha}, \hat{P}_\gamma\right\}_{-1}. \quad (77)$$

The total magnetizability, Eq. (23), is origin independent if the sum rules (60) and (73) are satisfied, and the condition for origin independence of nuclear magnetic shielding, Eq. (26), is given by the sum rule (58).

4 Methods of continuous translation of the origin of the current density

Geertsen proposed to rewrite the diamagnetic contributions to total magnetic properties of the conventional theory [1, 2, 4] in propagator form [22–24]. The nice feature characterizing the Geertsen approach is that the calculated average magnetic shielding at a nucleus is origin independent, irrespective of size and quality of the gaugeless basis set retained within the algebraic approximation. Correlated and gauge-origin-independent Geertsen-type calculations of magnetic properties of triply bonded molecules [54, 55] and simple singly bonded molecules [56, 57] at the second-order polarization propagator approximation (SOPPA) [58] level have been reported.

Geertsen developed his approach via the commutators

$$A^{\mathbf{B}}_\alpha A^{\mathbf{B}}_\alpha = \frac{i}{4\hbar} B_\gamma B_\delta \epsilon_{\alpha\beta\gamma}[r_\alpha, r_\beta \hat{l}_\delta],$$
$$A^{\mathbf{B}}_\alpha A^{\mathbf{m}_I}_\alpha = \frac{i}{2\hbar} B_\gamma m_{I_\delta} \epsilon_{\alpha\beta\gamma}[r_\alpha, r_\beta \hat{M}_{I_\delta}]. \quad (78)$$

In the spirit of the Geertsen method, Smith et al. [26] proposed a sum-over-state expression for the diamagnetic contribution to the nuclear magnetic shielding tensor. They used the commutator

$$r_{0_\beta}\left[r_\alpha\nabla_\beta - r_\beta\nabla_\alpha, r_\gamma\right] = r_\alpha r_{0_\gamma} - r_\beta r_{0_\beta}\delta_{\alpha\gamma}, \quad (79)$$

see their Eqs. (23)–(25) for a gauge origin $\mathbf{r}_0$.

Slightly modifying the Geertsen formulation [22–24], it is expedient to introduce the Hermitian one-electron operators

$$\hat{u}_{\alpha\beta} = \frac{1}{2}(r_\alpha \hat{l}_\beta + \hat{l}_\beta r_\alpha), \quad (80)$$

$$\hat{t}_{I_{\alpha\beta}} = \frac{1}{2}(r_\alpha \hat{M}_{I_\beta} + \hat{M}_{I_\beta} r_\alpha), \quad (81)$$

so that

$$A^{\mathbf{B}}_\alpha A^{\mathbf{B}}_\alpha = \frac{i}{4\hbar} B_\gamma B_\delta \epsilon_{\alpha\beta\gamma}\left[r_\alpha, \hat{u}_{\beta\delta}\right], \quad (82)$$

$$A^{\mathbf{B}}_\alpha A^{\mathbf{m}_I}_\alpha = \frac{i}{2\hbar} B_\gamma m_{I_\delta} \epsilon_{\alpha\beta\gamma}\left[r_\alpha, \hat{t}_{I_{\beta\delta}}\right]. \quad (83)$$

Therefore, allowing for relationships (2), (3), (15), (16), (82) and (83), the *n*-electron operators for the diamagnetic contributions can be rewritten in the form

$$\hat{\xi}^{\Delta}_{\alpha\beta} = \frac{ie^2}{8m_e\hbar}\sum_{i=1}^{n}\left\{\epsilon_{\beta\gamma\delta}\left[r_\gamma, \hat{u}_{\delta\alpha}\right]_i + \epsilon_{\alpha\gamma\delta}\left[r_\gamma, \hat{u}_{\delta\beta}\right]_i\right\} = \frac{ie^2}{8m_e\hbar}\left\{\epsilon_{\beta\gamma\delta}\left[\hat{R}_\gamma, \hat{U}_{\delta\alpha}\right] + \epsilon_{\alpha\gamma\delta}\left[\hat{R}_\gamma, \hat{U}_{\delta\beta}\right]_i\right\}, \quad (84)$$

$$\hat{\sigma}^{\Delta I}_{\alpha\beta} = \frac{ie^2}{2m_e\hbar}\epsilon_{\beta\gamma\delta}\sum_{i=1}^{n}\left[r_\gamma, \hat{t}_{I_{\delta\alpha}}\right]_i = \frac{ie^2}{2m_e\hbar}\epsilon_{\beta\gamma\delta}\sum_{i=1}^{n}\left[\hat{R}_\gamma, \hat{T}_{I_{\delta\alpha}}\right], \quad (85)$$

where

$$\hat{U}_{\alpha\beta}(\mathbf{r}') = \sum_{i=1}^{n}\hat{u}_{i\alpha\beta}(\mathbf{r}') = \frac{1}{2}\sum_{i=1}^{n}\left[(r_{i\alpha} - r'_\alpha)\hat{l}_{i\beta}(\mathbf{r}') + \hat{l}_{i\beta}(\mathbf{r}')(r_{i\alpha} - r'_\alpha)\right], \quad (86)$$

is related to the Hermitian magnetic quadrupole operator [59]

$$\hat{m}_{\beta\alpha} = -\frac{e}{3m_e}\hat{U}_{\alpha\beta}, \quad (87)$$

and

$$\hat{T}^n_{I_{\alpha\beta}}(\mathbf{r}') = \sum_{i=1}^{n}\hat{t}_{I_{\alpha\beta}}(\mathbf{r}') = \frac{1}{2}\sum_{i=1}^{n}\left[(r_{i\alpha} - r'_\alpha)\hat{M}^i_{I_\beta} + \hat{M}^i_{I_\beta}(r_{i\alpha} - r'_\alpha)\right]. \quad (88)$$

Now, using the resolution of the identity

$$\sum_j |j\rangle\langle j| = I,$$

the hypervirial relationship (69), with $\langle a|\hat{P}_\alpha|a\rangle = 0$, and the expression (22) for the propagator, Δ contributions to magnetizability and nuclear magnetic shielding are obtained,

$$\xi^{\Delta}_{\alpha\beta} = \frac{e^2}{8m_e^2}\left(\epsilon_{\alpha\gamma\delta}\{\hat{P}_\gamma, \hat{U}_{\delta\beta}\}_{-1} + \epsilon_{\beta\gamma\delta}\{\hat{P}_\gamma, \hat{U}_{\delta\alpha}\}_{-1}\right), \tag{89}$$

$$\sigma^{\Delta I}_{\alpha\beta} = -\frac{e^2}{2m_e^2}\epsilon_{\beta\gamma\delta}\left\{\hat{P}_\gamma, \hat{T}^n_{I_{\delta\alpha}}\right\}_{-1}, \tag{90}$$

which reduce to the conventional diamagnetic terms, Eqs. (24) and (27), in the limit of exact eigenstates and optimal variational wavefunctions.

Within the computational procedure developed by KB [27, 28, 29], the current density induced in the electrons of a molecule by a spatially uniform static magnetic field is evaluated at every point of space assuming that the same point is also the origin of the coordinate system. Magnetic properties are then calculated by differentiating the relationships of classical electrodynamics, Eqs. (46) and (47), involving the current density, according to the definitions (18) and (19). The KB approach has been implemented developing a pointwise procedure [27–29].

We will now show that the procedure of Keith and Bader [27–29] is computationally equivalent to that of Geertsen [22–24] reformulated in Eqs. (80)–(90).

The total current density vector field induced in a molecule by an external magnetic field, Eq. (41), is a function of position $\mathbf{J}^{\mathbf{B}} = \mathbf{J}^{\mathbf{B}}(\mathbf{r})$, whose origin can arbitrarily be chosen in the case of exact and optimal variational wavefunctions [7]. In a change of coordinate system, Eq. (61), diamagnetic and paramagnetic contributions change according to Eqs. (63) and (67), but the total function should remain the same [14, 15], that is,

$$\begin{aligned}\mathbf{J}^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'') &= \mathbf{J}^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_d^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) + \mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r})\\ &= \mathbf{J}^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') \equiv \mathbf{J}^{\mathbf{B}}(\mathbf{r}).\end{aligned} \tag{91}$$

This notation implies that diamagnetic and paramagnetic components, which depend on the coordinate system, are evaluated corresponding to different origins.

Let us now consider continuous coordinate translations whereby either the diamagnetic or paramagnetic contributions to the total current density are systematically annihilated at every point $\mathbf{r}$, all over the domain of a molecule. These procedures were referred to as CTOCD-DZ and CTOCD-PZ, setting to zero either the diamagnetic or paramagnetic terms of the $\mathbf{J}^{\mathbf{B}}$ field.

The n-electron (diamagnetic) Larmor current density, $\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'')$ in Eq. (63), is formally killed within the CTOCD-DZ scheme for every point $\mathbf{r}$ by choosing that point as origin of the coordinate system [27–29], so that

$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') = -\mathbf{J}_d^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}). \tag{92}$$

Such a procedure amounts to killing everywhere the vector potential (2), appearing in the definition of the diamagnetic current density (42). However, it is impractical to regard this procedure as a continuous gauge transformation, as this would imply that also the second-order energies, Eq. (46) and second identity of Eq. (47), vanish. That's the reason why the denomination CTOCD seems preferable to CSGT.

The expression for the total CTOCD-DZ current density contains two non-Larmor terms, both referred to the original coordinate system, that is,

$$\mathbf{J}^{\mathbf{B}}(\mathbf{r}) = \mathbf{J}_p^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}-\mathbf{r}'), \tag{93}$$

where, allowing for the CTOCD prescription $\mathbf{r}'' \equiv \mathbf{r}$ in Eq. (68), the second term on the r.h.s. is given by

$$\begin{aligned}\mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}-\mathbf{r}') = -\frac{ne}{m_e}\int & \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n\\ &\times\Big[(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\boldsymbol{\Psi}_a^{\mathbf{d}\times\mathbf{B}*}\hat{\mathbf{p}}\Psi_a^{(0)}\\ &+\Psi_a^{(0)*}\hat{\mathbf{p}}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\boldsymbol{\Psi}_a^{\mathbf{d}\times\mathbf{B}}\Big]_{\mathbf{r}''=\mathbf{r}}.\end{aligned} \tag{94}$$

This notation means that $\mathbf{r}''$ is put equal to $\mathbf{r}$ after operating with $\hat{\mathbf{p}}$. It is convenient to recast relationship (94) in tensor notation,

$$\begin{aligned}J_{p\alpha}^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}-\mathbf{r}') = -\frac{ne}{m_e}\epsilon_{\beta\gamma\delta}(r_\beta - r'_\beta)B_\gamma\int & \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n\\ &\times\left[\Psi_a^{(\mathbf{d}\times\mathbf{B})_\delta *}\hat{p}_\alpha\Psi_a^{(0)} + \Psi_a^{(0)*}\hat{p}_\alpha\Psi_a^{(\mathbf{d}\times\mathbf{B})_\delta}\right].\end{aligned} \tag{95}$$

The total quantum mechanical current density is an invariant quantity, mapped onto itself in a gauge transformation, in the ideal case of electronic wavefunctions satisfying hypervirial theorems, for example, optimal variational eigenfunctions [7]. In particular, it remains the same in a change of coordinate system, as recalled above. Then comparison between Eqs. (41) and (93) necessarily implies that the new, formally paramagnetic, term should be equivalent to the diamagnetic contribution in the conventional formulation, that is,

$$\mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) = \mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'), \tag{96}$$

for every $\mathbf{r}$. This relationship can be directly proven via Eqs. (42) and (94), using off-diagonal hypervirial relationships [15], for every plane perpendicular to $\mathbf{B}$, where the original diamagnetic flow takes place. However, it should be recalled that the formal replacement, according to Eq. (96) of the diamagnetic term described by Eq. (42) with a paramagnetic one in Eq. (93), introduces a spurious paramagnetic component along the inducing magnetic field in Eq. (94). Nonetheless, this quantity does not contribute to the diagonal components of response properties [15].

In a change of coordinate system (61), the transformation laws for (43) and (95) are, respectively,

$$J^{\mathbf{B}}_{p\alpha}(\mathbf{r}-\mathbf{r}'') = J^{\mathbf{B}}_{p\alpha}(\mathbf{r}-\mathbf{r}') - \frac{ne}{m_e}\epsilon_{\beta\gamma\delta}(r''_\beta - r'_\beta)B_\gamma \int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times \left[\Psi_a^{(\mathbf{d}\times\mathbf{B})_\delta *}\hat{p}_\alpha\Psi_a^{(0)} + \Psi_a^{(0)*}\hat{p}_\alpha\Psi_a^{(\mathbf{d}\times\mathbf{B})_\delta}\right], \tag{97}$$

and

$$J^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}_{p\alpha}(\mathbf{r}-\mathbf{r}'') = J^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}_{p\alpha}(\mathbf{r}-\mathbf{r}') + \frac{ne}{m_e}\epsilon_{\beta\gamma\delta}(r''_\beta - r'_\beta)B_\gamma \int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times \left[\Psi_a^{(\mathbf{d}\times\mathbf{B})_\delta *}\hat{p}_\alpha\Psi_a^{(0)} + \Psi_a^{(0)*}\hat{p}_\alpha\Psi_a^{(\mathbf{d}\times\mathbf{B})_\delta}\right]. \tag{98}$$

Two equal terms with opposite sign appear on the r.h.s of these equations, and then, the total CTOCD-DZ current, obtained by the algebraic sum of (97) and (98), is origin independent. Its origin independence is guaranteed also for approximate wavefunctions, whereas the property (41) expressed as a sum of conventional diamagnetic (42) and paramagnetic (43) contributions is invariant only in the ideal cases recalled above.

Within the analytical CTOCD-DZ procedure [25, 60–62], expressions for $\boldsymbol{\xi}$ and $\boldsymbol{\sigma}^I$ tensors are obtained from the second-order energies (46) and (47), substituting the current density, Eq. (93), and differentiating according to the definitions, Eqs. (18) and (19). The "diamagnetic" Δ-contributions are given by exactly the same relationships, Eqs. (89) and (90), arrived at via a modified Geertsen method. Therefore, the analytical CTOCD-DZ method [25, 30, 60–62] is fully equivalent to that of Geertsen [22–24] and to that implemented by Keith and Bader [27, 28], using the same philosophy to annihilate the diamagnetic current density term and numerical integration.

In a translation of origin $\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}$,

$$\hat{U}_{\alpha\beta}(\mathbf{r}'') = \hat{U}_{\alpha\beta}(\mathbf{r}') - d_\gamma\epsilon_{\beta\gamma\delta}\hat{V}_{\alpha\delta}(\mathbf{r}') - d_\alpha\hat{L}_\beta(\mathbf{r}') + d_\alpha d_\gamma\epsilon_{\beta\gamma\delta}\hat{P}_\delta, \tag{99}$$

$$\hat{T}^n_{I_{\alpha\beta}}(\mathbf{r}'') = \hat{T}^n_{I_{\alpha\beta}}(\mathbf{r}') - d_\alpha\hat{M}^n_{I_\beta}, \tag{100}$$

where the Hermitian virial tensor operator [7] $\hat{V}_{\alpha\beta}$ appearing in the transformation law, Eq. (99), for $\hat{U}_{\alpha\beta}$, see Eq. (86), is defined

$$\hat{V}_{\alpha\beta}(\mathbf{r}') = \frac{1}{2}\sum_{i=1}^{n}\left[(r_{i\alpha} - r'_\alpha)\hat{p}_{i\beta} + \hat{p}_{i\beta}(r_{i\alpha} - r'_\alpha)\right]. \tag{101}$$

Therefore, the changes of the diamagnetic CTOCD-DZ contributions are evaluated from

$$\begin{aligned}\xi^{\Delta}_{\alpha\beta}(\mathbf{r}'') = \xi^{\Delta}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{8m_e^2} &\times \Big[d_\delta\Big(\epsilon_{\alpha\gamma\delta}\Big\{\hat{L}_\beta(\mathbf{r}^{'}), \hat{P}_\gamma\Big\}_{-1} + \epsilon_{\beta\gamma\delta}\Big\{\hat{L}_\alpha(\mathbf{r}^{'}), \hat{P}_\gamma\Big\}_{-1}\Big) \\ &+ d_\lambda\left(\epsilon_{\alpha\gamma\delta}\epsilon_{\beta\lambda\mu} + \epsilon_{\beta\gamma\delta}\epsilon_{\alpha\lambda\mu}\right)\Big\{\hat{P}_\gamma, \hat{V}_{\delta\mu}(\mathbf{r}^{'})\Big\}_{-1} \\ &- d_\delta d_\lambda\left(\epsilon_{\alpha\gamma\delta}\epsilon_{\beta\lambda\mu} + \epsilon_{\beta\gamma\delta}\epsilon_{\alpha\lambda\mu}\right)\{\hat{P}_\mu, \hat{P}_\gamma\}_{-1}\Big],\end{aligned} \tag{102}$$

$$\sigma^{\Delta I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\Delta I}_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{2m_e^2}d_\delta\epsilon_{\beta\gamma\delta}\Big\{\hat{M}^n_{I_\alpha}, \hat{P}_\gamma\Big\}_{-1}. \tag{103}$$

On summing paramagnetic p and diamagnetic Δ contributions in Eqs. (77) and (103), full cancellation of equal terms linear in d_δ takes place on the r.h.s., then the total CTOCD-DZ shieldings $\sigma^I_{\alpha\beta} = \sigma^{\mathrm{p}I}_{\alpha\beta} + \sigma^{\Delta I}_{\alpha\beta}$ are origin independent. Terms depending on the square of the $\mathbf{d}$ shift, Eq. (61), in Eqs. (75) and (102) cancel out on summing, then total CTOCD-DZ magnetizabilities are origin independent if the AMM sum rule (60) and the additional constraint

$$\{\hat{L}_\alpha, \hat{P}_\beta\}_{-1} = \epsilon_{\alpha\gamma\epsilon}\{\hat{P}_\epsilon, \hat{V}_{\gamma\beta}\}_{-1} \tag{104}$$

are fulfilled.

In Eq. (61), the shift of origin is represented by an arbitrary constant vector $\mathbf{d}$. Within the CTOCD-PZ approach, a general transformation function $\mathbf{d} = \mathbf{d}(\mathbf{r})$ is sought, specifying the origin of the coordinate system in which the paramagnetic contributions to the current density is formally annihilated. This function is evaluated pointwise via the condition determined by Eq. (67). The l.h.s. of this relationship vanishes for

$$\mathbf{J}^{\mathbf{B}}_p(\mathbf{r}-\mathbf{r}') = -\mathbf{J}^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}_p(\mathbf{r}), \tag{105}$$

which gives the 3 × 3 system of linear equations

$$\mathbf{M}\mathbf{d} = \mathbf{T}, \tag{106}$$

where, allowing for Eqs. (66) and (67),

$$M_{\delta\beta} = \frac{ne}{m_e}\epsilon_{\alpha\beta\gamma}B_\gamma\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n \times \left[\Psi_a^{(\mathbf{d}\times\mathbf{B})_\alpha *}\hat{p}_\delta\Psi_a^{(0)} + \Psi_a^{(0)*}\hat{p}_\delta\Psi_a^{(\mathbf{d}\times\mathbf{B})_\alpha}\right], \tag{107}$$

and

$$T_\delta = -\frac{ne}{m_e}B_\alpha\int \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_n\left[\Psi_a^{B_\alpha *}\hat{p}_\delta\Psi_a^{(0)} + \Psi_a^{(0)*}\hat{p}_\delta\Psi_a^{B_\alpha}\right]. \tag{108}$$

The 3 × 3 **M** matrix defined by Eq. (107) is singular, for example, for $\mathbf{B} = B\epsilon_3$, its last column vanishes.

$$\mathbf{M} = \begin{pmatrix} M_{xx} & M_{xy} & 0 \\ M_{yx} & M_{yy} & 0 \\ M_{zx} & M_{zy} & 0 \end{pmatrix}. \tag{109}$$

In physical terms, the quantum mechanical paramagnetic current flowing in the direction of **B** cannot be annihilated [15]. Therefore, a 2 × 2 subsystem of Eq. (106),

$$\begin{pmatrix} M_{xx} & M_{xy} \\ M_{yx} & M_{yy} \end{pmatrix} \begin{pmatrix} d_x \\ d_y \end{pmatrix} = \begin{pmatrix} T_x \\ T_y \end{pmatrix}, \tag{110}$$

is solved, over a grid of points in real space, to determine the components

$$\begin{aligned} d_x &= \frac{T_x M_{yy} - T_y M_{xy}}{M_{xx} M_{yy} - M_{xy} M_{yx}}, \\ d_y &= \frac{T_y M_{xx} - T_x M_{yx}}{M_{xx} M_{yy} - M_{xy} M_{yx}} \end{aligned} \tag{111}$$

of the shift vector function that annihilates the paramagnetic current over planes perpendicular to **B**.

Thus, within the CTOCD-PZ scheme, the transverse current density contains only contributions that are formally diamagnetic,

$$\begin{aligned} \mathbf{J}^{\mathbf{B}}(\mathbf{r}) &= \mathbf{J}^{\mathbf{B}}_d(\mathbf{r}-\mathbf{r}') + \mathbf{J}^{\mathbf{d}\times\mathbf{B}}_d(\mathbf{r}-\mathbf{r}') \\ &= -\frac{e^2}{2m_e c}\mathbf{B} \times [\mathbf{r} - \mathbf{d}(\mathbf{r})]\gamma^{(0)}(\mathbf{r}). \end{aligned} \tag{112}$$

To show that the PZ current density, Eq. (112), is origin independent, it is sufficient to verify that the shift functions transform like a vector in a translation of coordinates, that is,

$$d_\alpha(\mathbf{r}-\mathbf{r}') - d_\alpha(\mathbf{r}-\mathbf{r}'') \equiv d'_\alpha - d''_\alpha = r''_\alpha - r'_\alpha \equiv s_\alpha, \tag{113}$$

see Fig. 1.

From the invariance constraint, Eqs. (91), and (105), the identity

$$\mathbf{J}^{\mathbf{d}\times\mathbf{B}}_d(\mathbf{r}-\mathbf{r}') = \mathbf{J}^{\mathbf{B}}_p(\mathbf{r}-\mathbf{r}') \tag{114}$$

is obtained. This relationship does not provide a recipe for calculating the shift functions in the approximate case but yields the definition of exact **d**(**r**),

$$\begin{aligned} d_x(\mathbf{r}) &= \frac{2m_e}{e^2}\left[\gamma^{(0)}(\mathbf{r})\right]^{-1}\mathcal{J}^{B_z}_{p_y}(\mathbf{r}), \\ d_y(\mathbf{r}) &= -\frac{2m_e}{e^2}\left[\gamma^{(0)}(\mathbf{r})\right]^{-1}\mathcal{J}^{B_z}_{p_x}(\mathbf{r}) \end{aligned} \tag{115}$$

using the paramagnetic contribution to the current density tensor, Eq. (51).

The Eqs. (109)–(111) are valid for cyclic permutations of x, y, z; therefore, the transverse PZ current density (112) is explicitly origin independent also for approximate electronic wavefunctions, since it depends on the difference $\mathbf{r} - \mathbf{d}(\mathbf{r})$ of two vectors whose origin can arbitrarily be chosen.

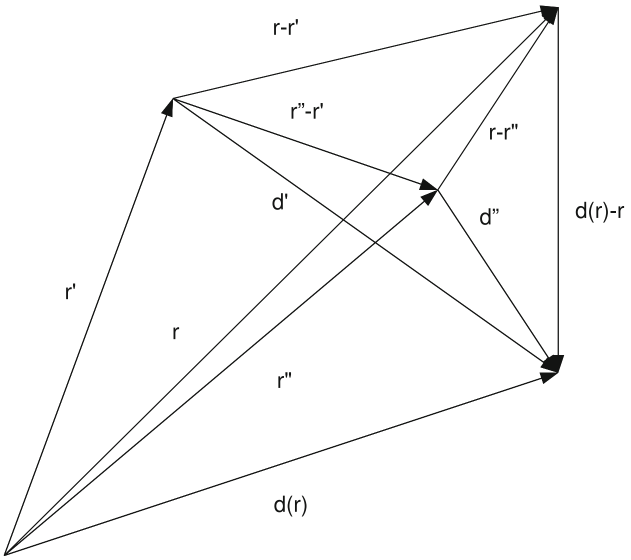

Fig. 1 Coordinate systems used in the CTOCD-PZ procedure. For every point **r**, the origin is translated to a point **d**(**r**), so that the paramagnetic contribution $\mathbf{J}^{\mathbf{B}}_p$ to the current density, evaluated with respect to the new origin, vanishes

The total CTOCD-PZ magnetizability is obtained by differentiating the second-order energy

$$\xi_{\alpha\beta} = \xi^{\mathrm{d}}_{\alpha\beta} + \xi^{\Pi}_{\alpha\beta} = -\frac{\partial^2}{\partial B_\alpha \partial B_\beta}\left(-\frac{1}{2}\int \mathbf{J}^{\mathbf{B}} \cdot \mathbf{A}^{\mathbf{B}} \mathrm{d}^3 r\right), \tag{116}$$

in which $\xi^{\mathrm{d}}_{\alpha\beta}$ is the conventional diamagnetic term (24) of the van Vleck theory [1], and the $\xi^{\Pi}_{\alpha\beta}$ term is obtained by numerical integration from the second addendum within brackets on the r.h.s. of Eq. (112). A formal expression is obtained,

$$\begin{aligned} \xi^{\Pi}_{\alpha\beta} &= \frac{e^2}{4m_e}\int \gamma^{(0)}(\mathbf{r}) \\ &\quad \times \left\{ d_\gamma(\mathbf{r}) r_\gamma \delta_{\alpha\beta} - \frac{1}{2}\left[d_\alpha(\mathbf{r}) r_\beta + r_\alpha d_\beta(\mathbf{r})\right] \right\} \mathrm{d}^3 r, \\ &= \frac{e^2}{4m_e}\left\langle a \left| \sum_{i=1}^{n} \left\{ d_\gamma(\mathbf{r}) r_\gamma \delta_{\alpha\beta} - \frac{1}{2}\left[d_\alpha(\mathbf{r}) r_\beta + r_\alpha d_\beta(\mathbf{r})\right] \right\}_i \right| a \right\rangle, \end{aligned} \tag{117}$$

replacing $\xi^{\mathrm{p}}_{\alpha\beta}$ of the canonical theory [1].

It is expedient to define a multiplicative operator

$$\hat{\mathbf{D}}(\mathbf{r}) = \sum_{i=1}^{n} \mathbf{d}_i(\mathbf{r})$$

for n electrons, with expectation value

$$\langle a|\hat{D}_\alpha|a\rangle = \left\langle a\left|\sum_{i=1}^{n} d_{i\alpha}\right|a\right\rangle, \tag{118}$$

then, denoting the origin shift in Eq. (61), $\mathbf{r}'' - \mathbf{r}' = \mathbf{s} = \mathbf{d}' - \mathbf{r}''$, as in Eq. (113), the change of the formally paramagnetic contribution (117) to the magnetizability is written

$$\begin{aligned}\xi^{\Pi}_{\alpha\beta}(\mathbf{r}'') = \xi^{\Pi}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{4m_e}\{ & s_\gamma(\langle a|\hat{R}_\gamma(\mathbf{r}')|a\rangle + \langle a|\hat{D}_\gamma(\mathbf{r}')|a\rangle)\delta_{\alpha\beta} \\ & -\frac{1}{2}[s_\alpha(\langle a|\hat{R}_\beta(\mathbf{r}')|a\rangle + \langle a|\hat{D}_\beta(\mathbf{r}')|a\rangle) \\ & + s_\beta(\langle a|\hat{R}_\alpha(\mathbf{r}')|a\rangle + \langle a|\hat{D}_\alpha(\mathbf{r}')|a\rangle)] \\ & - n(s_\gamma s_\gamma \delta_{\alpha\beta} - s_\alpha s_\beta)\}.\end{aligned} \tag{119}$$

Therefore, the condition for invariance of total CTOCD-PZ magnetizability is obtained by comparison with Eq. (74),

$$\langle a|\hat{R}_\alpha|a\rangle = \langle a|\hat{D}_\alpha|a\rangle, \tag{120}$$

valid for any coordinate system, since the operator $\hat{D}_\alpha$ transforms like a vector, according to Eq. (113). In particular, $\langle a|\hat{D}_\alpha(\mathbf{R}_e)|a\rangle = 0$ in the limit of a complete basis set calculation, if the origin of the coordinate system lies at $\mathbf{R}_e$, the electronic centroid: the *allocentric* [63] PZ procedure scatters the origin of the current density in such a way that the statistical average of the $d_\alpha(\mathbf{r})$ functions vanishes.

The Π contribution to the magnetic shielding at nucleus I is obtained by differentiating the second-order energy (47), from the second addendum within brackets on the r.h.s. of Eq. (112). Using numerical integration, it becomes

$$\begin{aligned}\sigma^{\Pi I}_{\alpha\beta} &= -\frac{e}{2m_e c^2}\int \gamma^{(0)}(\mathbf{r})\left[d_\gamma(\mathbf{r})\hat{E}_{I_\gamma}(\mathbf{r})\delta_{\alpha\beta} - d_\alpha(\mathbf{r})\hat{E}_{I_\beta}(\mathbf{r})\right]\mathrm{d}^3 r \\ &= -\frac{e}{2m_e c^2}\left\langle a\left|\sum_{i=1}^{n}\left(d_{i\gamma}\hat{E}^i_{I_\gamma}\delta_{\alpha\beta} - d_{i\alpha}\hat{E}^i_{I_\beta}\right)\right|a\right\rangle.\end{aligned} \tag{121}$$

The change in the Π contributions to the nuclear magnetic shieldings in the translation (61) of the origin of the coordinate system is

$$\begin{aligned}\sigma^{\Pi I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\Pi I}_{\alpha\beta}(\mathbf{r}') \\ + \frac{e}{2m_e c^2}\left(s_\gamma\left\langle a\left|\hat{E}^n_{I_\gamma}\right|a\right\rangle\delta_{\alpha\beta} - s_\alpha\left\langle a\left|\hat{E}^n_{I_\beta}\right|a\right\rangle\right),\end{aligned} \tag{122}$$

then there is complete cancellation with the corresponding change in Eq. (76), and the total CTOCD-PZ shielding is origin independent irrespective of basis set size and quality.

Calculations of magnetizability and nuclear magnetic shielding in molecules employing the CTOCD-PZ approach have been reported [37, 38, 64–66].

5 Concluding remarks and outlook

A review and new perspectives are presented on the connections among various methods of calculation of molecular magnetic response properties, all constructed with the aim of finessing the troublesome gauge-origin problem that plagued calculations of these types in the latter half of the twentieth century. The analytical formulation of CTOCD-DZ procedures, based on the ipsocentric choice of origin that formally annihilates the diamagnetic contribution to magnetic field-induced quantum mechanical current density, provides a compact and unitary theoretical framework, showing the equivalence of apparently unrelated work of different authors. CTOCD-PZ methods, formally destroying the paramagnetic contribution to the electronic current density via a systematic allocentric choice of origin, have only been implemented at numerical level: an analytical formulation of the PZ philosophy has not so far been reported. Attempts at developing CTOCD-PZ algorithms via closed-form equations would seem theoretically interesting, as well as able to be used for practical purposes.

Whereas current computational techniques based on gauge-including atomic orbitals meet the requirement of translational invariance of calculated magnetic properties, they do not necessarily guarantee current/charge conservation. On the other hand, CTOCD schemes account for the fundamental identity between these constraints, which are expressed by the same quantum mechanical sum rules.

References

1. van Vleck JH (1932) The theory of electric and magnetic susceptibilities. Oxford University Press, Oxford
2. Ramsey NF (1950) Phys Rev 78:699
3. Ramsey NF (1951) Phys Rev 83:540
4. Ramsey NF (1952) Phys Rev 86:243
5. Hirschfelder JO, Byers-Brown W, Epstein ST (1964) Adv Quantum Chem 1:255 (references therein)
6. Jackson JD (1999) Classical electrodynamics. 3rd edn. Wiley, New York, pp 175–178
7. Epstein ST (1974) The variation method in quantum chemistry. Academic Press, New York
8. Epstein ST (1973) J Chem Phys 58:1592
9. Sambe H (1973) J Chem Phys 59:555
10. Landau LD, Lifshitz EM (1979) The classical theory of fields, 4th revised english edition. Pergamon Press, Oxford
11. Arrighini GP, Maestro M, Moccia R (1968) J Chem Phys 49:882
12. Arrighini GP, Maestro M, Moccia R (1970) J Chem Phys 52:6411

13. Arrighini G, Maestro M, Moccia R (1970) Chem Phys Lett 7:351
14. Lazzeretti P, Malagoli M, Zanasi R (1991) Chem Phys 150:173
15. Lazzeretti P (2003) Electric and magnetic properties of molecules. In: Handbook of molecular physics and quantum chemistry, vol 3, Part 1, Chapter 3. Wiley, Chichester, pp 53–145
16. Hansen AE, Bouman TD (1985) J Chem Phys 82:5035
17. London F (1937) J Phys Radium 8:397 (7ème Série)
18. DALTON (2008) An electronic structure program, release 2.0, 2005 (http://www.kjemi.uio.no/software/dalton/)
19. Frisch MJ, Trucks GW et al (2003) Gaussian 2003, revision B.05. Gaussian, Inc., Pittsburgh
20. Stanton JF, Gauss J, Harding ME, Szalay PG (2010) CFOUR, coupled-cluster techniques for computational chemistry (http://www.cfour.de)
21. Gauss J (2002) J Chem Phys 116:4773
22. Geertsen J (1989) J Chem Phys 90:4892
23. Geertsen J (1991) Chem Phys Lett 179:479
24. Geertsen J (1992) Chem Phys Lett 188:326
25. Lazzeretti P, Malagoli M, Zanasi R (1994) Chem Phys Lett 220:299
26. Smith CM, Amos RD, Handy NC (1992) Mol Phys 77:381
27. Keith TA, Bader RFW (1993) Chem Phys Lett 210:223
28. Keith TA, Bader RFW (1993) J Chem Phys 99:3669
29. Keith TA, Bader RFW (1996) Can J Chem 74:185
30. Coriani S, Lazzeretti P, Malagoli M, Zanasi R (1994) Theor Chim Acta 89:181
31. Steiner E, Fowler PW (2001) J Phys Chem A 105:9553
32. Steiner E, Fowler PW (2001) J Chem Soc Chem Comm 2220
33. Steiner E, Fowler PW, Havenith RWA (2002) J Phys Chem A 106:7048
34. Steiner E, Soncini A, Fowler PW (2006) J Phys Chem A 110:12882
35. Steiner E, Fowler PW (2004) Phys Chem Chem Phys 6:261
36. Zanasi R, Lazzeretti P, Malagoli M, Piccinini F (1995) J Chem Phys 102:7150
37. Zanasi R (1996) J Chem Phys 105:1460
38. Lazzeretti P, Zanasi R (1996) Int J Quantum Chem 60:249
39. Lazzeretti P (1989) Chem Phys 134:269
40. Lazzeretti P (1987) Adv Chem Phys 75:507
41. Linderberg J, Öhrn Y (1973) Propagators in quantum chemistry. Academic Press, London
42. Olsen J, Jorgensen P (1985) J Chem Phys 82:3235
43. McWeeny R (1962) Phys Rev 126:1028
44. McWeeny R (1969) Quantum mechanics: methods and basic applications. Pergamon Press, Oxford
45. McWeeny R (1989) Methods of molecular quantum mechanics. Academic Press, London
46. Gell-Mann M (1956) Nuovo Cimento Suppl IV:848
47. Ramsey NF (1953) Phys Rev 91:303
48. Lazzeretti P, Zanasi R (1980) J Chem Phys 72:6768
49. Lazzeretti P, Zanasi R (1977) Int J Quantum Chem 12:93
50. Lazzeretti P, Malagoli M, Zanasi R (1991) Chem Phys 150:173
51. Lazzeretti P (2000) Ring currents. In: Emsley JW, Feeney J, Sutcliffe LH (eds) Progress in nuclear magnetic resonance spectroscopy, vol 36, Elsevier, Amsterdam, pp 1–88
52. Condon EU (1937) Rev Mod Phys 9:432
53. Lazzeretti P, Zanasi R, Cadioli B (1977) J Chem Phys 67:382
54. Sauer SPA, Oddershede J (1993) Correlated and Gauge invariant calculations of nuclear shielding constants, volume 386 of NATO ASI series C. Kluwer, Dordrecht
55. Sauer SPA, Paidarová I, Oddershede J (1994) Mol Phys 81:87
56. Sauer SPA, Oddershede J (1993) Correlated and gauge invariant calculations of nuclear shielding constants. In: Tossell JA (eds) Nuclear magnetic shieldings and molecular structure, volume 386 of NATO ASI series C, Kluwer, Dordrecht, pp 351–365
57. Sauer SPA, Paidarová I, Oddershede J (1994) Theor Chim Acta 88:351
58. Sauer SPA (2011) Molecular electromagnetism: a computational chemistry approach. Oxford University Press, Oxford
59. Faglioni F, Ligabue A, Pelloni S, Soncini A, Lazzeretti P (2004) Chem Phys 304:289
60. Ligabue A, Sauer SPA, Lazzeretti P (2003) J Chem Phys 118:6830
61. Ligabue A, Sauer SPA, Lazzeretti P (2007) J Chem Phys 126:154111
62. Cuesta IG, Marin JS, de Meras AS, Pawlowski F, Lazzeretti P (2010) Phys Chem Chem Phys 12:6163
63. Lazzeretti P (2004) Phys Chem Chem Phys 6:217
64. Ligabue A, Pincelli U, Lazzeretti P, Zanasi R (1999) J Am Chem Soc 121:5513
65. Lazzeretti P, Malagoli M, Zanasi R (1995) J Chem Phys 102:9619
66. Pelloni S, Lazzeretti P (2008) J Chem Phys 128:194305