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REGULAR ARTICLE

Response tensors for chiral discrimination in NMR spectroscopy

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Abstract Response tensors that may be used for rationalising chiral discrimination by nuclear magnetic resonance spectroscopy are selected relying on the criterion that the induced molecular electric moment and the induced magnetic field at a nucleus are invariant to a translation of the coordinate system.

1 Introduction

A chiral molecule and its mirror image cannot be distinguished by ordinary nuclear magnetic resonance (NMR) spectroscopy in disordered phase. A chiral potential may be sufficient to provide a chiral shift [1]. Thus parity-violating electroweak interactions yield contributions of opposite sign to nuclear magnetic shielding and nuclear spin–spin coupling in enantiomeric molecules [2–4], but the effects are very small and likely hard to detect experimentally according to some calculations [5–7].

Chiral discrimination has been attained by adding a chiral reagent or solvent [8,9] causing a change in the environment of the active nuclei [10]. In optical spectroscopies two enantiomeric forms are distinguished via circular dichroism [11] and differential scattering of left and right circularly polarised light [12].

Curie established that a system of two parallel electric and magnetic fields, **E** and **B**, has no left–right symmetry [13]. Group-theoretical aspects of the problem have been considered [14,15]. However, an NMR experiment in which a resonant nucleus is acted upon by an additional electric field can discriminate two enantiomers [16,17]. The third rank tensor $\sigma^I_{\alpha\beta\gamma}$ usually referred to as "polarisability of nuclear magnetic shielding", introduced to rationalise the effects of an electric field on chemical shift [18], is characterized by odd parity and can therefore account for shifts of the same magnitude but opposite sign expected for two optical antipodes of a chiral compound.

Assuming that the perturbing fields are time-independent and spatially uniform, the static $\sigma^I_{\alpha\beta\gamma}$ is sufficient to rationalise the phenomenology. As the application of a laser polarised in a reference plane could, in principle, give rise to an oscillating electric polarisation and chiral chemical shift [17], we enquire if other molecular properties should be considered in this case.

The frequency dependence of the shielding polarisability for a molecule in the presence of optical fields has been explicitly considered, also taking into account the precession of the probe nuclear magnetic dipole [17]. However, whereas $\sigma^I_{\alpha\beta\gamma}$ is origin independent in the static limit [19], the dynamic tensor is not uniquely defined, as it changes in a coordinate translation.

The present paper aims at analysing the origin dependence of this tensor in order to obtain invariant quantities. It is shown that other intrinsic molecular properties, which can be referred to as nuclear "mag-

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netoelectric hypershiedings" are, in principle, needed to define measurable origin-independent observables, e.g., the effective magnetic field at a nucleus, and the rotating electric dipole moment induced in the electron cloud [16,17].

2 Response tensors for chiral discrimination

For a molecule with n electrons and N nuclei, charge, mass, position with respect to an arbitrary origin, canonical, and angular momentum of the ith electron are indicated by $-e$, m_e, $\mathbf{r}_i$, $\mathbf{p}_i$, $\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$, $i = 1, 2, \ldots, n$. Analogous quantities for nucleus I are $Z_I e$, M_I, $\mathbf{R}_I$, etc. Capital letters are used for global electronic operators, e.g., $\hat{\mathbf{R}} = \sum_{i=1}^{n} \mathbf{r}_i$, $\hat{\mathbf{L}} = \sum_{i=1}^{n} \mathbf{l}_i$, etc. The Einstein convention of implicit summation over two repeated Greek subscripts is in force. $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita skew-symmetric unit tensor.

The electronic reference state $|a\rangle \equiv |\Psi_a^{(0)}\rangle$ and the excited states $|j\rangle \equiv |\Psi_j^{(0)}\rangle$ of the molecule are eigenfunctions of the unperturbed time-independent Hamiltonian $H^{(0)}$. The natural transition frequencies are indicated by ω_{ja}. SI units are employed.

The definition of electronic operators considered in the discussion is given hereafter. The electric and magnetic dipole, and electric quadrupole are respectively [19,20],

$$\hat{\mu}_\alpha = -e\hat{R}_\alpha, \tag{1}$$

$$\hat{m}_\alpha = -\frac{e}{2m_e}\hat{L}_\alpha, \tag{2}$$

$$\hat{\mu}_{\alpha\beta} = -\frac{e}{2}\sum_{i=1}^{n}\left(r_\alpha r_\beta\right)_i. \tag{3}$$

The electric field exerted on nucleus I by electron i is

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

and

$$\hat{\mathbf{E}}_I^n = \sum_{i=1}^{n}\hat{\mathbf{E}}_I^i \tag{5}$$

is the operator for the total field of n electrons. The operator for the total effective magnetic field on nucleus I in a molecule in the presence of an external homogeneous magnetic field with flux density $\mathbf{B}$ is

$$\hat{B}_{I\alpha} = B_\alpha + \hat{B}_{I\alpha}^{n\prime}. \tag{6}$$

The operator for the magnetic field of n electrons on nucleus I is

$$\hat{B}_{I\alpha}^{n\prime} = \hat{B}_{I\alpha}^{n} - \hat{\sigma}_{\alpha\beta}^{\mathrm{d}I} B_\beta \tag{7}$$

where

$$\hat{B}_{I\alpha}^{n} = -\frac{\mu_0}{4\pi}\frac{e}{m_e}\sum_{i=1}^{n}\frac{\mathbf{r}_i - \mathbf{R}_I}{\left|\mathbf{r}_i - \mathbf{R}_I\right|^3} \times \mathbf{p}_i. \tag{8}$$

The operator for the diamagnetic contribution is written

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

using $\epsilon_0\mu_0 c^2 = 1$. The expressions for first- and second-order perturbing Hamiltonians used within the time-dependent perturbation scheme [21] are

$$\hat{H}^{\mathbf{E}} = -\hat{\mu}_\alpha E_\alpha, \tag{10}$$

$$\hat{H}^{\mathbf{B}} = -\hat{m}_\alpha B_\alpha, \tag{11}$$

$$\hat{H}^{\boldsymbol{\mu}_I} = -\hat{B}_{I\alpha}^{n}\mu_{I\alpha}, \tag{12}$$

$$\hat{H}^{\boldsymbol{\mu}_I\mathbf{B}} = \hat{\sigma}_{\alpha\beta}^{\mathrm{d}I}\,\mu_{I\alpha}B_\beta. \tag{13}$$

Barred fluctuation operators are defined via

$$\overline{A} \equiv \hat{A} - \langle a|\hat{A}|a\rangle. \tag{14}$$

2.1 Linear response properties

In an NMR experiment a strong static field $\mathbf{B}^{(0)}$ in the z direction induces Larmor precession with frequency ω of a nuclear magnetic dipole $\boldsymbol{\mu}_I$. In order for resonance to occur, a small magnetic field $\mathbf{B}^{(1)}$ is applied at right angles to $\mathbf{B}^{(0)}$. The resonant pulsed field $\mathbf{B}^{(1)}$ rotates the bulk magnetisation of the precessing nuclei from the z direction to the xy plane so that there is a coherence in the phase of the precessing nuclei.

$\mathbf{B}^{(1)}$ is formally required to be circularly polarised and to rotate in synchronisation with the precession of $\boldsymbol{\mu}_I$ about $\mathbf{B}^{(0)}$ [22]. However, a linearly polarised field is used, since it can be regarded as the superimposition of two fields rotating in opposite directions [23]. Only the component having the same sense as the precession synchronises with the nuclear magnetic dipole, the other component is far from the resonance condition and has no effect. The total field acting on $\boldsymbol{\mu}_I$ is the vector sum $\mathbf{B}(\omega) = \mathbf{B}^{(0)} + \mathbf{B}^{(1)}(\omega)$. This perturbation is associated with a non uniform electric field $\mathbf{E}(\omega)$.

Time-dependent perturbation theory [21,24–26] and propagator approaches [27] can be applied to discuss the NMR experiment [20]. In general terms, the expectation value of the magnetic field induced at the position of nucleus I by the n-electron cloud of a molecule responding to an external electromagnetic field (represented as a monochromatic wave with any pulsation ω) is given by the expression

$$\begin{aligned}\Delta\langle \hat{B}^{n\prime}_{I\alpha}(\omega)\rangle = &-\left[\sigma^{\mathrm{p}I}_{\alpha\beta}(-\omega;\omega)+\sigma^{\mathrm{d}I}_{\alpha\beta}\right]B_\beta(\mathbf{0},t)\\ &-\sigma'^{\mathrm{p}I}_{\alpha\beta}(-\omega;\omega)\,\dot{B}_\beta(\mathbf{0},t)\,\omega^{-1}\\ &+\lambda^I_{\alpha\beta}(-\omega;\omega)\,E_\beta(\mathbf{0},t)\\ &+\lambda'^I_{\alpha\beta}(-\omega;\omega)\,\dot{E}_\beta(\mathbf{0},t)\,\omega^{-1}\\ &+\lambda^I_{\alpha,\beta\gamma}(-\omega;\omega)\,E_{\gamma\beta}(\mathbf{0},t)\\ &+\lambda'^I_{\alpha,\beta\gamma}(-\omega;\omega)\,\dot{E}_{\gamma\beta}(\mathbf{0},t)\,\omega^{-1}+\cdots\end{aligned}\tag{15}$$

where $E_\alpha(\mathbf{0},t)$, $E_{\alpha\beta}(\mathbf{0},t)\equiv\nabla_\alpha E_\beta(\mathbf{0},t)$, and $B_\alpha(\mathbf{0},t)$ are the oscillating electric field, the electric field gradient, and the magnetic field at the origin of the coordinate system. A dot denotes partial time derivative.

The contributions appearing on the r.h.s. of expression (15) are obtained within the quadrupole approximation to linear response [20]—which amounts to assuming spatially uniform magnetic field and electric field gradient over the molecular dimensions, by keeping terms up to the first spatial derivatives in the Taylor power expansion of the electromagnetic potentials within the Bloch gauge [28]. All the response tensors on the r.h.s. are needed to make the induced magnetic field $\Delta\langle\hat{B}^n_{I\alpha}(\omega)\rangle$ invariant in a translation of coordinate system [20], see Sect. (2.2).

Adopting the notation used by Orr and Ward [25] and Bishop [29] (OWB), the polarisation propagator [27] for two operators $\hat{A}$ and $\hat{B}$ is defined as

$$\langle\langle\hat{A};\hat{B}\rangle\rangle_\omega=-\sum_P\sum_{j\neq a}\frac{\langle a|\hat{A}|j\rangle\langle j|\hat{B}|a\rangle}{E^{(0)}_j-E^{(0)}_a-\hbar\omega_\sigma},\tag{16}$$

where $\sum_P$ indicates the sum over permutations of the pairs $(\hat{A}/-\omega_\sigma)$ and $(\hat{B}/\omega_1)$, and $\omega_\sigma=\omega_1\equiv\omega$. Therefore, the paramagnetic contributions to the nuclear magnetic shielding are

$$\begin{aligned}\sigma^{\mathrm{p}I}_{\alpha\beta}(-\omega;\omega)&=\Re\langle\langle\hat{B}^n_{I\alpha};\hat{m}_\beta\rangle\rangle_\omega\\&=-\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega^2_{ja}-\omega^2}\Re\left(\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\hat{m}_\beta|a\rangle\right),\end{aligned}\tag{17}$$

$$\begin{aligned}\sigma'^{\mathrm{p}I}_{\alpha\beta}(-\omega;\omega)&=-\Im\langle\langle\hat{B}^n_{I\alpha};\hat{m}_\beta\rangle\rangle_\omega\\&=\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega}{\omega^2_{ja}-\omega^2}\Im\left(\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\hat{m}_\beta|a\rangle\right),\end{aligned}\tag{18}$$

and the diamagnetic contribution is obtained as the expectation value of operator (9),

$$\sigma^{\mathrm{d}I}_{\alpha\beta}=\langle a|\hat{\sigma}^{\mathrm{d}I}_{\alpha\beta}|a\rangle.\tag{19}$$

Analogous relationships are obtained for the electric dipole and electric quadrupole magnetoelectric shielding at nucleus I [20,30,31],

$$\begin{aligned}\lambda^I_{\alpha\beta}(-\omega;\omega)&=-\Re\langle\langle\hat{B}^n_{I\alpha};\hat{\mu}_\beta\rangle\rangle_\omega\\&=\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega^2_{ja}-\omega^2}\Re\left(\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\hat{\mu}_\beta|a\rangle\right),\end{aligned}\tag{20}$$

$$\begin{aligned}\lambda'^I_{\alpha\beta}(-\omega;\omega)&=\Im\langle\langle\hat{B}^n_{I\alpha};\hat{\mu}_\beta\rangle\rangle_\omega\\&=-\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega}{\omega^2_{ja}-\omega^2}\Im\left(\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\hat{\mu}_\beta|a\rangle\right),\end{aligned}\tag{21}$$

$$\begin{aligned}\lambda^I_{\alpha,\beta\gamma}(-\omega;\omega)&=-\Re\langle\langle\hat{B}^n_{I\alpha};\hat{\mu}_{\beta\gamma}\rangle\rangle_\omega\\&=\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega^2_{ja}-\omega^2}\Re\left(\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\hat{\mu}_{\beta\gamma}|a\rangle\right),\end{aligned}\tag{22}$$

$$\begin{aligned}\lambda'^I_{\alpha,\beta\gamma}(-\omega;\omega)&=\Im\langle\langle\hat{B}^n_{I\alpha};\hat{\mu}_{\beta\gamma}\rangle\rangle_\omega\\&=-\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega}{\omega^2_{ja}-\omega^2}\Im\left(\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\hat{\mu}_{\beta\gamma}|a\rangle\right).\end{aligned}\tag{23}$$

The magnetoelectric shieldings (20) and (21), equivalent to the polarisabilities introduced by Buckingham [16],

$$\lambda^I_{\alpha\beta}\equiv-\xi^I_{\beta\alpha},\quad \lambda'^I_{\alpha\beta}\equiv-\xi'^I_{\beta\alpha},$$

appear also in the expression for the electric dipole induced by the permanent magnetic dipole at nucleus I [16,17,32],

$$\Delta\langle\mu_\alpha(\omega)\rangle=-\lambda^I_{\beta\alpha}(-\omega;\omega)\,\mu_{I\beta}-\lambda'^I_{\beta\alpha}(-\omega;\omega)\,\dot{\mu}_{I\beta}\,\omega^{-1}.\tag{24}$$

The orbital magnetic dipole induced by the nuclear dipole $\mu_{I\alpha}$ is [16,17,32]

$$\begin{aligned}\Delta\langle m_\beta(\omega)\rangle=&-\left[\sigma^{\mathrm{p}I}_{\alpha\beta}(-\omega;\omega)+\sigma^{\mathrm{d}I}_{\alpha\beta}\right]\mu_{I\alpha}\\&-\sigma'^{\mathrm{p}I}_{\alpha\beta}(-\omega;\omega)\,\dot{\mu}_{I\alpha}\,\omega^{-1}.\end{aligned}\tag{25}$$

$\sigma^{\mathrm{d}I}_{\alpha\beta}$, $\sigma^{\mathrm{p}I}_{\alpha\beta}$, and $\lambda'^I_{\alpha,\beta\gamma}$ are even under time reversal $\hat{T}$ and parity $\hat{P}$, $\sigma'^{\mathrm{p}I}_{\alpha\beta}$ and $\lambda^I_{\alpha,\beta\gamma}$ are odd under $\hat{T}$ and even under $\hat{P}$, $\lambda^I_{\alpha\beta}$ is odd under $\hat{T}$ and $\hat{P}$, $\lambda'^I_{\alpha\beta}$ is even under $\hat{T}$ and odd under $\hat{P}$. Thus $\sigma'^{\mathrm{p}I}_{\alpha\beta}$, $\lambda^I_{\alpha\beta}$, and $\lambda^I_{\alpha,\beta\gamma}$ are zero for a closed-shell molecule in the absence of magnetic field [16,17,20,32], but have a linear dependence on **B**. Full perturbation expressions for higher-rank tensors that explicitly account for **B** are considered in Sect. 3.

2.2 Transformation laws of linear-response properties in a change of coordinate system

In a translation of coordinates specified by an arbitrary shift **d** of the origin

$$\mathbf{r}'' = \mathbf{r}' + \mathbf{d}, \tag{26}$$

the relationships for the electric field, the quadrupole moment, and the magnetic dipole operators referred to the origin $\mathbf{r}''$ are, respectively,

$$E_\alpha(\mathbf{r}'', t) = E_\alpha(\mathbf{r}', t) + d_\beta E_{\beta\alpha}(t), \tag{27}$$

$$\overline{\hat{\mu}}_{\alpha\beta}(\mathbf{r}'') = \overline{\hat{\mu}}_{\alpha\beta}(\mathbf{r}') - \frac{1}{2}\overline{\hat{\mu}}_\alpha d_\beta - \frac{1}{2}\overline{\hat{\mu}}_\beta d_\alpha, \tag{28}$$

$$\hat{m}_\alpha(\mathbf{r}'') = \hat{m}_\alpha(\mathbf{r}') + \frac{e}{2m_e}\epsilon_{\alpha\beta\gamma} d_\beta \hat{P}_\gamma. \tag{29}$$

The barred dipole moment operator $\overline{\hat{\mu}}_\alpha$ is origin independent. Allowing for the expressions (27)–(29), and for the off-diagonal hypervirial relationship [33]

$$\frac{e}{m_e}\langle j|\hat{P}_\alpha|k\rangle = -i\,\omega_{jk}\,\langle j|\hat{\mu}_\alpha|k\rangle, \tag{30}$$

the transformation laws for the tensors appearing in Eq. (15) are obtained [19,20],

$$\sigma^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}'') + \sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}') + \sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}') - \frac{\omega}{2}\epsilon_{\beta\gamma\delta} d_\delta \lambda'^{I}_{\alpha\gamma}, \tag{31}$$

$$\sigma'^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}'') = \sigma'^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}') - \frac{\omega}{2}\epsilon_{\beta\gamma\delta} d_\gamma \lambda^{I}_{\alpha\delta}, \tag{32}$$

$$\lambda^{I}_{\alpha,\beta\gamma}(\mathbf{r}'') = \lambda^{I}_{\alpha,\beta\gamma}(\mathbf{r}') - \frac{1}{2}\lambda^{I}_{\alpha\gamma} d_\beta - \frac{1}{2}\lambda^{I}_{\alpha\beta} d_\gamma, \tag{33}$$

$$\lambda'^{I}_{\alpha,\beta\gamma}(\mathbf{r}'') = \lambda'^{I}_{\alpha,\beta\gamma}(\mathbf{r}') - \frac{1}{2}\lambda'^{I}_{\alpha\gamma} d_\beta - \frac{1}{2}\lambda'^{I}_{\alpha\beta} d_\gamma. \tag{34}$$

Then, using the Maxwell equation

$$\dot{B}_\alpha = -\epsilon_{\alpha\beta\gamma} E_{\beta\gamma}, \tag{35}$$

and the relationship for harmonic fields

$$\ddot{B}_\alpha = -\omega^2 B_\alpha, \tag{36}$$

it is seen that the expression (15) for the magnetic field induced at nucleus I is independent of the origin of the coordinate system, i.e.,

$$\Delta\langle \hat{B}^{n'}_{I\alpha}(\mathbf{r}'')\rangle = \Delta\langle \hat{B}^{n'}_{I\alpha}(\mathbf{r}')\rangle. \tag{37}$$

On the other hand, this result implies that all the tensors (17)–(23) are formally needed to define dynamic magnetic fields induced at the nuclei invariant to the passive transformation (26). Moreover, one can notice that time-dependent perturbation theory provides a direct clue to chiral discrimination via NMR through the magnetoelectric shielding tensors (20) and (21), although the latter seems too small for practical purposes, see Sect. 4. This approach reduces to the Ramsey formulation [34,35] allowing for time-independent perturbation theory in the limit $\omega \to 0$.

The magnetoelectric shieldings (20) and (21) and the induced dipole (24) are independent of the origin of the coordinate translations. The orbital magnetic dipole (25) induced by the magnetic moment of nucleus I changes in a coordinate translation. Using Eqs. (24), (31), (32), and

$$\ddot{\mu}_{I\alpha} = -\omega^2 \mu_{I\alpha}, \tag{38}$$

we obtain

$$\Delta\langle \hat{m}_\beta(\mathbf{r}'')\rangle = \Delta\langle \hat{m}_\beta(\mathbf{r}')\rangle + \frac{1}{2}\epsilon_{\beta\gamma\delta} d_\delta \frac{\partial}{\partial t}\Delta\langle \hat{\mu}_\gamma\rangle. \tag{39}$$

The origin dependence of the magnetic dipole moment in the presence of an oscillating electric dipole has been noticed by Buckingham and coworkers [36,37]. It is consistent with the definition of magnetic moment in classical mechanics, compare for Eq. (2), which is characterized by a similar transformation law.

3 Quadratic response to perturbing fields

The third-rank tensors needed to rationalise contributions quadratic in the external fields and intramolecular perturbations are expressed, within the quadratic response scheme [25,27,29], by

$$\langle\langle \hat{A}; \hat{B}, \hat{C}\rangle\rangle_{\omega_1,\omega_2} = \frac{1}{\hbar^2}\sum_P \sum_{j,k\neq a} \frac{\langle a|\hat{A}|j\rangle\langle j|\overline{\hat{C}}|k\rangle\langle k|\hat{B}|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)}, \tag{40}$$

where $\omega_\sigma = \omega_1 + \omega_2$, and $\sum_P$ means the sum over all permutations of the pairs $(\hat{A}/-\omega_\sigma)$, $(\hat{B}/\omega_1)$, $(\hat{C}/\omega_2)$. In the following we will assume that a field of frequency ω_1 and one of frequency ω_2 are applied to the molecular system.

The nuclear hypershielding accounting for quadratic response to external magnetic and electric fields, also referred to as dipole polarisability of nuclear magnetic shielding [17,18], is the sum of paramagnetic and diamagnetic contributions. Within the OWB notation [25,29] for the propagator [27],

$$\begin{aligned}\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}&(-\omega_\sigma;\omega_1,\omega_2)\\ &= -\langle\langle \hat{B}^n_{I\alpha};\hat{m}_\beta,\hat{\mu}_\gamma\rangle\rangle_{\omega_1,\omega_2}\\ &= -\frac{1}{\hbar^2}\sum_P\sum_{j,k\neq a}\frac{\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\overline{\hat{\mu}_\gamma}|k\rangle\langle k|\hat{m}_\beta|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)},\end{aligned}\tag{41}$$

where $\omega_\sigma = \omega_1+\omega_2$, and $\sum_P$ means the sum over all permutations of the pairs $(\hat{B}^n_{I\alpha}/-\omega_\sigma)$, $(\hat{m}_\beta/\omega_1)$, $(\hat{\mu}_\gamma/\omega_2)$.

Third- and fourth-rank nuclear magnetoelectric hypershieldings are defined,

$$\begin{aligned}\lambda'^{I}_{\alpha\beta\gamma}&(-\omega_\sigma;\omega_1,\omega_2)\\ &= i\langle\langle \hat{B}^n_{I\alpha};\hat{\mu}_\beta,\hat{\mu}_\gamma\rangle\rangle_{\omega_1,\omega_2}\\ &= \frac{i}{\hbar^2}\sum_P\sum_{j,k\neq a}\frac{\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\overline{\hat{\mu}_\gamma}|k\rangle\langle k|\hat{\mu}_\beta|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)},\end{aligned}\tag{42}$$

where $\omega_\sigma = \omega_1+\omega_2$, and $\sum_P$ means the sum over all permutations of the pairs $(\hat{B}^n_{I\alpha}/-\omega_\sigma)$, $(\hat{\mu}_\beta/\omega_1)$, $(\hat{\mu}_\gamma/\omega_2)$, and

$$\begin{aligned}\lambda'^{I}_{\alpha,\beta\gamma,\delta}&(-\omega_\sigma;\omega_1,\omega_2)\\ &= i\langle\langle \hat{B}^n_{I\alpha};\hat{\mu}_{\beta\gamma},\hat{\mu}_\delta\rangle\rangle_{\omega_1,\omega_2}\\ &= \frac{i}{\hbar^2}\sum_P\sum_{j,k\neq a}\frac{\langle a|\hat{B}^n_{I\alpha}|j\rangle\langle j|\overline{\hat{\mu}_\delta}|k\rangle\langle k|\hat{\mu}_{\beta\gamma}|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)},\end{aligned}\tag{43}$$

where $\sum_P$ means the sum over all permutations of the pairs $(\hat{B}^n_{I\alpha}/-\omega_\sigma)$, $(\hat{\mu}_{\beta\gamma}/\omega_1)$, $(\hat{\mu}_\delta/\omega_2)$. We also introduce the frequency dependent diamagnetic contribution to the magnetic shielding polarisability,

$$\begin{aligned}\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}(-\omega;\omega) &= -\Re\langle\langle \hat{\sigma}^{\mathrm{d}I}_{\alpha\beta};\hat{\mu}_\gamma\rangle\rangle_\omega\\ &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\Re\left(\langle a|\hat{\sigma}^{\mathrm{d}I}_{\alpha\beta}|j\rangle\langle j|\hat{\mu}_\gamma|a\rangle\right),\end{aligned}\tag{44}$$

and the dynamic nuclear electric shielding

$$\begin{aligned}\gamma^I_{\alpha\beta}(-\omega;\omega) &= \Re\langle\langle \hat{E}^n_{I\alpha};\hat{\mu}_\beta\rangle\rangle_\omega\\ &= -\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\Re\left(\langle a|\hat{E}^n_{I\alpha}|j\rangle\langle j|\hat{\mu}_\beta|a\rangle\right).\end{aligned}\tag{45}$$

A few possible experiments are discussed, for measuring the magnetic field at a nucleus and the electric dipole moment induced in the electron cloud, imposing their invariance to a transformation of coordinates, as in the case of linear response examined in Sect. 2.1. This symmetry criterion enables us to select molecular response tensors that can be used for chiral discrimination.

3.1 Magnetic field induced at a nucleus

Let us consider the expression

$$\begin{aligned}\Delta\langle\hat{B}^{n\prime}_{I\alpha}(\omega)\rangle &= -\left[\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}(-\omega;\omega,0)+\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}(0;0)\right]B_\beta(\mathbf{0},t)E^{(0)}_\gamma\\ &\quad+\lambda'^{I}_{\alpha\beta\gamma}(-\omega;\omega,0)\,\omega^{-1}\dot{E}_\beta(\mathbf{0},t)E^{(0)}_\gamma\\ &\quad+\lambda'^{I}_{\alpha,\beta\delta,\gamma}(-\omega;\omega,0)\,\omega^{-1}\dot{E}_{\delta\beta}(\mathbf{0},t)E^{(0)}_\gamma+\cdots\end{aligned}\tag{46}$$

for the magnetic field at nucleus I of a molecule in the presence of a static, uniform electric field $E^{(0)}_\alpha$, induced by electronic response to an electromagnetic field with pulsation ω. For simplicity, contributions linear in the perturbing fields are omitted in this formula and in similar relationships for the induced electric dipole, e.g., Eq. (54). Within the quadrupole approximation, the electric field gradient $E_{\alpha\beta}(\mathbf{0},t)\equiv E_{\alpha\beta}$ and the magnetic field $B_\alpha(\mathbf{0},t)\equiv B_\alpha$ at the origin of the coordinate system are supposed spatially uniform.

In a coordinate transformation, by using Eqs. (26)–(30), the commutator

$$\left[\hat{B}^n_{I\alpha},\hat{\mu}_\beta\right] = \frac{ie\hbar}{m_ec^2}\epsilon_{\alpha\beta\gamma}\hat{E}^n_{I\gamma},\tag{47}$$

and the definitions (41)–(45), we obtain

$$\begin{aligned}\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}&\left(-\omega;\omega,0|\mathbf{r}''\right)\\ &= \sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(-\omega;\omega,0|\mathbf{r}'\right)+\frac{\omega}{2}\epsilon_{\beta\lambda\mu}d_\lambda\,\lambda'^{I}_{\alpha\mu\gamma}(-\omega;\omega,0)\\ &\quad-\frac{e}{2m_ec^2}\left[\gamma^I_{\delta\gamma}(0;0)\,\delta_{\alpha\beta}d_\delta-\gamma^I_{\beta\gamma}(0;0)\,d_\alpha\right],\end{aligned}\tag{48}$$

$$\begin{aligned}\lambda'^{I}_{\alpha,\beta\delta,\gamma}&\left(-\omega;\omega,0|\mathbf{r}''\right)\\ &= \lambda'^{I}_{\alpha,\beta\delta,\gamma}\left(-\omega;\omega,0|\mathbf{r}'\right)-\frac{1}{2}\lambda'^{I}_{\alpha\beta\gamma}(-\omega;\omega,0)\,d_\delta\\ &\quad-\frac{1}{2}\lambda'^{I}_{\alpha\delta\gamma}(-\omega;\omega,0)\,d_\beta,\end{aligned}\tag{49}$$

$$\begin{aligned}\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}&\left(-\omega;\omega|\mathbf{r}''\right)\\ &= \sigma^{\mathrm{d}I}_{\alpha\beta\gamma}\left(-\omega;\omega|\mathbf{r}'\right)+\frac{e}{2m_ec^2}\left[\gamma^I_{\delta\gamma}(-\omega;\omega)\,\delta_{\alpha\beta}d_\delta\right.\\ &\quad\left.-\gamma^I_{\beta\gamma}(-\omega;\omega)\,d_\alpha\right].\end{aligned}\tag{50}$$

Therefore, for any two arbitrary origins, and for $\omega = 0$ in Eq. (50), which is the case to consider for the diamagnetic contribution in the presence of a static, uniform electric field $E^{(0)}_\alpha$, exact cancellation of terms occurs and the same magnetic field (46) is obtained, as for Eq. (37). This result implies that all the tensors (41)–(44) should be considered in order to evaluate origin-independent magnetic field induced at a nucleus within the quadrupole approximation.

In an NMR experiment, the pulsation ω in Eq. (46) corresponds to the Larmor frequency. However, this relationship is formally valid for an arbitrary ω. Buckingham and Fischer suggested that application of a laser could in principle give rise to a chiral chemical shift, see Sect. 5.2 of Ref. [17]. For a liquid, they examined the isotropic average $\overline{\sigma^{(1)}}^I$ defined via Eq. (62) hereafter. Assuming that $B_z^{(0)}$ is the static magnetic field of the NMR spectrometer, an experimental set-up could employ a laser polarised in the xy plane. The laser fields considered by Buckingham and Fischer [17] are $B_x(\omega)$ and $E_y(-\omega)$, then the sum of the frequency arguments of the response tensors, e.g., $\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\,(0;\omega,-\omega)$ and $\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}$ $(\omega;-\omega)$, vanishes as in optical rectification. A contribution to the static magnetic field is needed, as any frequency dependence in $\Delta\langle\hat{B}^{n\prime}_{Iz}\rangle$ would mean that the magnetic field induced at the nucleus averages to zero over the course of the NMR experiment [17]. Therefore, see Eq. (38) of Ref. [17], a contribution

$$\Delta\langle\hat{B}^{n\prime}_{Iz}(0)\rangle = -\overline{\sigma^{(1)}}^I\left[B_x(\omega)E_y(-\omega) - B_y(\omega)E_x(-\omega)\right] \tag{51}$$

is obtained for an isotropic medium. In the present context this result is arrived at via relationships (46) and (62) by considering the $\pm\omega$ components of the impinging radiation and only the static response that they determine. The effects of the electric field gradient and of the time-derivatives appearing in Eq. (46) are not examined in relationship (51) [17].

However, the laser induced chiral chemical shift is likely to be so small that probably cannot be observed in the laboratory. Moreover, the induced field (51) is origin dependent, so that one can ask if an expression involving other response tensors can be found which is translationally invariant.

In a transformation of coordinates, by using Eqs. (26)–(30), (47), and including all the tensors required within the quadrupole approximation, see definitions (41)–(45), we obtain

$$\begin{aligned}&\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(0;\omega,-\omega|\mathbf{r}''\right)\\&\quad=\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(0;\omega,-\omega|\mathbf{r}'\right)+\frac{\omega}{2}\epsilon_{\beta\lambda\mu}d_\lambda\,\lambda'^I_{\alpha\mu\gamma}\left(0;\omega,-\omega\right)\\&\qquad-\frac{e}{2m_ec^2}\left[\gamma^I_{\delta\gamma}\left(\omega;-\omega\right)\delta_{\alpha\beta}d_\delta-\gamma^I_{\beta\gamma}\left(\omega;-\omega\right)d_\alpha\right],\end{aligned} \tag{52}$$

$$\begin{aligned}&\lambda'^I_{\alpha,\beta\delta,\gamma}\left(0;\omega,-\omega|\mathbf{r}''\right)\\&\quad=\lambda'^I_{\alpha,\beta\delta,\gamma}\left(0;\omega,-\omega|\mathbf{r}'\right)-\frac{1}{2}\lambda'^I_{\alpha\beta\gamma}\left(0;\omega,-\omega\right)d_\delta\\&\qquad-\frac{1}{2}\lambda'^I_{\alpha\delta\gamma}\left(0;\omega,-\omega\right)d_\beta.\end{aligned} \tag{53}$$

We have not been able to obtain an invariant expression analogous to (46) for the the induced field $\Delta\langle\hat{B}^{n\prime}_{I\alpha}(0)\rangle$ via Eqs. (50), (52), and (53).

3.2 Induced electric dipole moment

Let us consider the expression

$$\begin{aligned}\Delta\langle\hat{\mu}_\gamma(\omega)\rangle=&-\left[\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(0;\omega,-\omega\right)+\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}\left(\omega;-\omega\right)\right]\mu_{I\alpha}\,B_\beta(\mathbf{0},t)\\&+\lambda'^I_{\alpha\beta\gamma}\left(0;\omega,-\omega\right)\,\mu_{I\alpha}\,\dot{E}_\beta(\mathbf{0},t)\,\omega^{-1}\\&+\lambda'^I_{\alpha,\beta\delta,\gamma}\left(0;\omega,-\omega\right)\,\mu_{I\alpha}\,\dot{E}_{\delta\beta}(\mathbf{0},t)\,\omega^{-1}+\cdots\end{aligned} \tag{54}$$

for the induced electric dipole moment. The relationships (50), (52), and (53) describe the change of the response tensors on the r.h.s. of (54). Therefore, for any two arbitrary origins, exact cancellation of terms occurs and the same electric dipole

$$\Delta\langle\hat{\mu}_\alpha(\mathbf{r}'')\rangle=\Delta\langle\hat{\mu}_\alpha(\mathbf{r}')\rangle, \tag{55}$$

is obtained. This result indicates that all the tensors (41)–(44) should be considered to evaluate an origin-independent induced electric dipole within the quadrupole approximation.

One can also consider the expression

$$\begin{aligned}&\Delta\langle\hat{\mu}_\gamma(2\omega)\rangle\\&\quad=-\left[\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(\omega;\omega,-2\omega\right)+\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}\left(2\omega;-2\omega\right)\right]\mu_{I\alpha}\,B_\beta(\mathbf{0},t)\\&\qquad+\lambda'^I_{\alpha\beta\gamma}\left(\omega;\omega,-2\omega\right)\,\mu_{I\alpha}\,\dot{E}_\beta(\mathbf{0},t)\,\omega^{-1}\\&\qquad+\lambda'^I_{\alpha,\beta\delta,\gamma}\left(\omega;\omega,-2\omega\right)\,\mu_{I\alpha}\,\dot{E}_{\delta\beta}(\mathbf{0},t)\,\omega^{-1}+\cdots\end{aligned} \tag{56}$$

In a coordinate transformation, by using Eqs. (26)–(30), (47), and the definitions (41)–(45), we obtain

$$\begin{aligned}&\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(\omega;\omega,-2\omega|\mathbf{r}''\right)\\&\quad=\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(\omega;\omega,-2\omega|\mathbf{r}'\right)+\frac{\omega}{2}\epsilon_{\beta\lambda\mu}d_\lambda\,\lambda'^I_{\alpha\mu\gamma}\left(\omega;\omega,-2\omega\right)\\&\qquad-\frac{e}{2m_ec^2}\left[\gamma^I_{\delta\gamma}\left(2\omega;-2\omega\right)\delta_{\alpha\beta}d_\delta-\gamma^I_{\beta\gamma}\left(2\omega;-2\omega\right)d_\alpha\right],\end{aligned} \tag{57}$$

$$\lambda'^{I}_{\alpha,\beta\delta,\gamma}\left(\omega;\omega,-2\omega|\mathbf{r}''\right) = \lambda'^{I}_{\alpha,\beta\delta,\gamma}\left(\omega;\omega,-2\omega|\mathbf{r}'\right) - \frac{1}{2}\lambda'^{I}_{\alpha\beta\gamma}\left(\omega;\omega,-2\omega\right) d_\delta - \frac{1}{2}\lambda'^{I}_{\alpha\delta\gamma}\left(\omega;\omega,-2\omega\right) d_\beta. \quad (58)$$

Therefore, for any two arbitrary origins, allowing for Eq. (50) with $\omega \to 2\omega$, exact cancellation of terms occurs, and the same electric dipole $\Delta\langle\hat{\mu}_\alpha(\mathbf{r}'')\rangle = \Delta\langle\hat{\mu}_\alpha(\mathbf{r}')\rangle$ is obtained also in this case. This result indicates that all the tensors (41)–(44) should be considered to evaluate an origin-independent induced electric dipole within the quadrupole approximation.

Buckingham and Fischer suggested that a rotating chiral electric polarisation, induced by the precessing nuclear magnetization, could be observed experimentally, see Sect. 5.1 of Ref. [17]. As the precessing magnetic moment of the nucleus has a component orthogonal to the field $B_z^{(0)}$ of the magnet, a laser is not needed. A capacitor is used to detect the induced rf-voltage. The frequency argument for the response tensors in this case is $(\omega; 0, -\omega)$. Therefore we consider the expression

$$\Delta\langle\hat{\mu}_\gamma(\omega)\rangle = -\left[\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}(\omega;0,-\omega) + \sigma^{\mathrm{d}I}_{\alpha\beta\gamma}(\omega;-\omega)\right]\mu_{I\alpha}B^{(0)}_\beta + \cdots \quad (59)$$

for the induced electric dipole moment. In a transformation of coordinates, by using Eqs. (26)–(30), (41), (44), (45), and (47), we obtain

$$\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(0;\omega,-\omega|\mathbf{r}''\right) = \sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(0;\omega,-\omega|\mathbf{r}'\right) - \frac{e}{2m_ec^2}\left[\gamma^I_{\delta\gamma}\left(\omega;-\omega\right)\delta_{\alpha\beta}d_\delta - \gamma^I_{\beta\gamma}\left(\omega;-\omega\right)d_\alpha\right]. \quad (60)$$

Then, allowing for the corresponding change (50) of the diamagnetic term, the induced electric dipole (59) is origin independent. The pulsation ω in relationships (59)–(60) is that of nuclear precession. It is much smaller than the optical frequency formally assumed in Eqs. (48), (51), and (54). Therefore one can safely drop the frequency dependence in a calculation of the induced electric dipole (59).

3.3 Oscillating chiral magnetization

An electrostatic field $E^{(0)}_\alpha$ will induce an orbital magnetic dipole moment due to the precessing nuclear dipole moment [17]. The frequency argument in this case is $(\omega; -\omega, 0)$, i.e.,

$$\Delta\langle\hat{m}_\beta(\omega)\rangle = -\left[\sigma^{\mathrm{p}I}_{\alpha\beta\gamma}\left(\omega;-\omega,0\right) + \sigma^{\mathrm{d}I}_{\alpha\beta\gamma}\left(0;0\right)\right]\mu_{I\alpha}E^{(0)}_\gamma + \cdots \quad (61)$$

The transformation laws for the shielding polarisability on the r.h.s of (61) are obtained by $\omega \leftrightarrow -\omega$ in Eq. (48) and by Eq. (50) for $\omega = 0$. Allowing for these equations we could not prove origin independence of the induced magnetic dipole (61), without considering the time derivative of the induced electric dipole. The transformation law contains terms that can be related to it, as in Eq. (39).

4 Isotropic tensors for chiral discrimination

The magnetoelectric shielding $\lambda'^{I}_{\alpha\beta}(-\omega;\omega)$ has equal but opposite value for D and L enantiomers [16,17,19]. Its mean value vanishes for achiral molecules. The estimated magnitude for $CH_3CH(OH)C_6H_5$ is small, i.e., $\lambda^I_{\alpha\alpha}B_z/\lambda'^{I}_{\beta\beta} \approx 10^4$ for $B_z \approx 10\,\mathrm{T}$ [16]. Calculated values of off-diagonal components for non chiral systems, water [38], methane [39], and ammonia [40], are actually small. Chiral effects from quadratic response are more likely to be observed. Estimates of quantities that could be detected experimentally have been reported [17].

For an isotropic medium, it is expedient to introduce molecular averages [16,17,41]

$$\overline{\sigma^{(1)}}^I = \frac{1}{6}\left(\sigma^{\mathrm{p}I}_{\alpha\beta\gamma} + \sigma^{\mathrm{d}I}_{\alpha\beta\gamma}\right)\epsilon_{\alpha\beta\gamma}, \quad (62)$$

$$\overline{\lambda'^{(1)}}^I = \frac{1}{6}\lambda'^{I}_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}, \quad (63)$$

$$\overline{\Lambda'_{(1)}}^I = \frac{1}{15}\left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right)\lambda'^{I}_{\alpha,\beta\gamma,\delta}, \quad (64)$$

$$\overline{\Lambda'_{(2)}}^I = \frac{1}{30}\left(4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}\right)\lambda'^{I}_{\alpha,\beta\gamma,\delta}. \quad (65)$$

then, for instance, the magnetic field (46) induced at nucleus I is written in terms of isotropic tensors having the same frequency labels,

$$\Delta\langle\hat{B}^{n'}_{I\alpha}(\omega)\rangle = -\overline{\sigma^{(1)}}^I\epsilon_{\alpha\beta\gamma}B_\beta(\mathbf{0},t)E^{(0)}_\gamma + \overline{\lambda'^{(1)}}^I\epsilon_{\alpha\beta\gamma}\,\omega^{-1}\dot{E}_\beta(\mathbf{0},t)E^{(0)}_\gamma + \overline{\Lambda'_{(1)}}^I\left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right) \times \omega^{-1}\dot{E}_{\delta\beta}(\mathbf{0},t)E^{(0)}_\gamma + \cdots \quad (66)$$

We note that the diamagnetic contribution to the average value (62) vanishes if the origin of the coordinate system is taken at the position of nucleus I, since, in this case, the tensor $\sigma^{\mathrm{d}I}_{\alpha\beta\gamma}$ is symmetric in the first two indices.

The induced electric dipole (54), with the same frequency labels, becomes

$$\Delta\langle\hat{\mu}_\gamma(\omega)\rangle = -\overline{\sigma^{(1)}}^{I}\epsilon_{\alpha\beta\gamma}\,\mu_{I\alpha}\,B_\beta(\mathbf{0},t) + \overline{\lambda'^{(1)}}^{I}\epsilon_{\alpha\beta\gamma}\,\mu_{I\alpha}\,\dot{E}_\beta(\mathbf{0},t)\,\omega^{-1} + \overline{\Lambda'_{(1)}}^{I}\left(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}\right) \times\ \mu_{I\alpha}\,\dot{E}_{\delta\beta}(\mathbf{0},t)\,\omega^{-1}+\cdots \tag{67}$$

Terms depending on $\overline{\lambda'^{(1)}}^{I}$ in (66) and (67) contribute to the same amount for both D and L enantiomers, whereas those depending on $\overline{\sigma^{(1)}}^{I}$, $\overline{\Lambda'_{(1)}}^{I}$, and $\overline{\Lambda'_{(2)}}^{I}$ have equal but opposite values, and may be considered for chiral discrimination.

Within an isotropic medium, the expression for rotating induced electric dipole (59),

$$\Delta\langle\hat{\mu}_\gamma(\omega)\rangle = -\overline{\sigma^{(1)}}^{I}\epsilon_{\alpha\beta\gamma}\,\mu_{I\alpha}\,B_\beta(\mathbf{0},t), \tag{68}$$

is origin independent.

5 Concluding remarks

Response tensors that can be considered for chiral discrimination via NMR spectroscopy have been examined. The magnitude of some effects which could be experimentally detectable is essentially determined by the polarisability of nuclear magnetic shielding. This is described by a third-rank tensor that is invariant to coordinate translation in the static limit. The corresponding frequency dependent tensor varies in a coordinate transformation, and other tensors, which could be referred to as polarisabilities of nuclear magnetoelectric shieldings, or magnetoelectric hypershieldings, have been considered. Any dispersion effects related to nuclear magnetoelectric hypershieldings are likely to be small for the radio frequencies appropriate to NMR, however, they are formally required to ensure origin independence of (a) the induced electric polarisation and (b) the magnetic field induced at the nuclei. The rotating chiral electric polarisation induced by a precessing nuclear moment is origin independent, and could experimentally be observed, as suggested by Buckingham and Fischer [17].

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