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Magnetic properties of a molecule in non-uniform magnetic field*

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Summary. The potentials of the electromagnetic field in the Bloch gauge are used to obtain definitions for the multipole moment operators and for the operators expressing the electric and magnetic field of electrons acting on the nuclei of a molecule. Perturbation theory is employed to determine induced electronic moments and total electromagnetic field at the nuclei. A series of response tensors is defined to describe the contributions arising in non-uniform magnetic field and their origin dependence is studied.

Key words: Non-uniform magnetic field – Magnetic multipoles – Magnetic susceptibility – Nuclear magnetic shielding – Optical rotatory power – Vibrational circular dichroism

1 Introduction

A comprehensive theory is available to interpret the magnetic properties of a molecule in a spatially uniform, time-independent, magnetic field [1, 2] within the assumption of linear response. Non-linear effects arising in the presence of high intensity fields have also been examined [3, 4].

Phenomenologies observed in a molecule in the presence of periodic electromagnetic field associated with a monochromatic plane wave can be dealt with using suitable quantum mechanical approaches, e.g., propagator theory [5] and time-dependent perturbation theory [6, 7]. Within the quadrupole approximation, i.e., assuming that the magnetic field and the electric field gradient are uniform all over the molecular domain, a number of dynamic response tensors can be defined to rationalize the induced electromagnetic dipoles and fields [7]. To the next higher approximations, e.g., octupole and hexadecapole, one needs a convenient multipole expansion for the molecular interaction Hamiltonian. The problem of defining the set of electric multipole moments can be easily solved in the presence of static electric fields: it is customary to introduce electric multipoles traceless in any two tensor suffixes when static electric fields are studied [6].

* This paper is dedicated to Professor Werner Kutzelnigg on the occasion of his 60th birthday

According to Raab [8], this is no longer advisable for higher electric and magnetic multipoles in the case of time-dependent electromagnetic fields: the traceless moments beyond the quadrupole are unable to describe the general interaction Hamiltonian or even the classical radiation field [8]. As a matter of fact it is expedient to introduce a multipole expansion via proper definitions for the scalar and vector potentials, which explicitly appear in the interaction Hamiltonian.

The suitable form for the potentials has been first suggested by Bloch [9] and rediscovered from time to time [10–12]. Raab [8] has defined a set of magnetic susceptibilities, consistent with the interaction Hamiltonian a la Bloch, to describe the multipole moments induced in a molecule by non uniform time-dependent magnetic field.

So far, little attention has been payed to electronic magnetic multipoles in molecules, with a few noticeable exceptions [13–17]. Nonetheless, it has been emphasized that higher magnetic multipoles make small, but non-negligible contributions to the nuclear magnetic shielding and to NMR chemical shift [10]. At very large distance, the magnetic field arising from an electronic current density, is merely due to the magnetic dipole of the charge distribution. At closer distance, however, significant contributions arise from higher magnetic multipoles. Accordingly, the local field acting upon a probe, i.e. a nucleus carrying an intrinsic magnetic moment, will contain terms beyond the electronic magnetic dipole, leading to a "pseudo-contact" contribution to the nuclear magnetic shielding [17, 10]. Therefore an analysis of magnetic shielding relative to a given nucleus in terms of magnetic multipoles of neighbouring groups may help rationalize the role played by different domains of the electron distribution in determining NMR chemical shifts. In order to deal with the pseudo-contact term, Buckingham and Stiles [10] have reported equations which contain multipole magnetic susceptibilities.

The present paper sets out to extend Raab's method [8], reviewed in Sects. 2 and 3, and to define a set of Hermitian magnetic multipole operators and associated (mixed) multipole susceptibilities. Another essential aim is that of discussing contributions, which arise from non-uniform magnetic field, to the electric and magnetic fields at the nuclei, induced by the perturbed electron cloud, see Sects. 4 and 5. Similar formulae are developed to account for contributions from higher multipoles to the optical rotatory power in Sect. 5. The origin dependence of the response tensors is examined in Sect. 6. It is shown that, allowing for the Bloch normalization [9] for the operators appearing in the interaction Hamiltonian, several advantages of notation are gained. The gauge transformation leading to the Bloch potentials is outlined in the Appendix.

2 Molecule in non-uniform field

Let us consider a closed-shell molecule, i.e., a system symmetric under time-reversal, with n electrons and N nuclei. We denote by $-e, m_e, r_{i\alpha}$, $p_{i\alpha}$, $l_{i\alpha} = \varepsilon_{\alpha\beta\gamma} r_{i\beta} p_{i\gamma}$, for $i = 1, 2, \ldots, n$, charge, mass, position coordinates, linear, and angular momentum of the i-th electron. The analogous quantities for the I-th nucleus are $Z_I e$, M_I, $R_{I\alpha}$, etc. Sum over repeated Greek indices is implied all over the paper.

In the presence of an external electromagnetic field, which, for simplicity, is represented by a monochromatic wave of frequency ω, the spinless interaction

Hamiltonian for the electrons, within the Born–Oppenheimer approximation, is:

$$H = H_0 + V, \qquad V = H^{(1)} + H^{(2)}, \tag{1}$$

$$V = \sum_{i=1}^{n} \left[\frac{e}{2m_e c} \mathbf{A}_i \cdot \mathbf{p}_i + \frac{e}{2m_e c} \mathbf{p}_i \cdot \mathbf{A}_i + \frac{e^2}{2m_e c^2} A_i^2 - e\phi_i \right], \tag{2}$$

$$H_0 = \sum_{i=1}^{n} \left[\frac{p_i^2}{2m_e} - \sum_{I=1}^{N} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{j \neq i}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] + \frac{1}{2} \sum_{I}^{N} \sum_{J \neq I}^{N} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \tag{3}$$

In order to get a multipole expansion of the interaction Hamiltonian, we introduce the potentials of the electromagnetic field according to Bloch [9], see Appendix (we simplify the notation in this section, omitting the $\mathscr{B}$ index):

$$A(\mathbf{r}, t)_\alpha = \varepsilon_{\beta\alpha\gamma} r_\beta \left[\tfrac{1}{2} B(\mathbf{0}, t)_\gamma + \tfrac{1}{3} r_\delta B(\mathbf{0}, t)_{\delta\gamma} + \tfrac{1}{8} r_\delta r_\varepsilon B(\mathbf{0}, t)_{\varepsilon\delta\gamma} + \ldots \right], \tag{4}$$

$$\phi(\mathbf{r}, t) = -r_\alpha \left[E(\mathbf{0}, t)_\alpha + \tfrac{1}{2} r_\beta E(\mathbf{0}, t)_{\beta\alpha} + \tfrac{1}{6} r_\beta r_\gamma E(\mathbf{0}, t)_{\gamma\beta\alpha} + \ldots \right]. \tag{5}$$

The charge density and the current density operators for the electrons are defined, respectively:

$$\bar{\rho}(\mathbf{r}) = -e \sum_{i=1}^{n} \delta(\mathbf{r} - \mathbf{r}_i), \tag{6}$$

$$\bar{\mathbf{J}}(\mathbf{r}) = -\frac{e}{2m_e} \sum_{i=1}^{n} [\mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{p}_i], \tag{7}$$

and the first-order Hamiltonian of a charge distribution is then given the form [9]:

$$\begin{aligned} H^{(1)} &= \int d\tau \bar{\rho} \phi - \frac{1}{c} \int d\tau (\bar{\mathbf{J}} \cdot \mathbf{A}) \\ &= -\sum_{k=0}^{\infty} [E(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha} \mu_{\alpha \alpha_1 \alpha_2 \ldots \alpha_k} \\ &\quad + B(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha} m_{\alpha \alpha_1 \alpha_2 \ldots \alpha_k}], \end{aligned} \tag{8}$$

where the Hermitian tensor operators of rank $k + 1$ for the electric and magnetic multipole moments are defined according to Bloch [9]. The electric multipole moments of the electron distribution are:

$$\mu_\alpha = -e \sum_{i=1}^{n} r_{i\alpha},$$

$$\mu_{\alpha\beta} = -\frac{e}{2} \sum_{i=1}^{n} (r_\alpha r_\beta)_i,$$

$$\mu_{\alpha\beta\gamma} = -\frac{e}{6} \sum_{i=1}^{n} (r_\alpha r_\beta r_\gamma)_i,$$

$$\ldots$$

$$\begin{aligned} \mu_{\alpha\alpha_1 \ldots \alpha_k} &= -\frac{e}{(k+1)!} \sum_{i=1}^{n} (r_\alpha r_{\alpha_1} \ldots r_{\alpha_k})_i \\ &= -\frac{\partial H^{(1)}}{\partial E_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha}}, \end{aligned} \tag{9}$$

and the magnetic multipole moments, omitting contributions from electron spin, are:

$$m_\alpha = -\frac{e}{2m_e c}\sum_{i=1}^{n} l_{i\alpha},$$

$$m_{\alpha\beta} = -\frac{e}{6m_e c}\sum_{i=1}^{n} (l_\alpha r_\beta + r_\beta l_\alpha)_i,$$

$$m_{\alpha\beta\gamma} = -\frac{e}{16m_e c}\sum_{i=1}^{n} (l_\alpha r_\beta r_\gamma + r_\beta r_\gamma l_\alpha)_i,$$

$$\ldots$$

$$m_{\alpha\alpha_1\ldots\alpha_k} = -\frac{k+1}{(k+2)!}\frac{e}{2m_e c}\sum_{i=1}^{n} (l_\alpha r_{\alpha_1}\ldots r_{\alpha_k} + r_{\alpha_1}\ldots r_{\alpha_k} l_\alpha)_i$$
$$= -\frac{\partial H^{(1)}}{\partial B_{\alpha_k\alpha_{k-1}\ldots\alpha_1\alpha}}. \tag{10}$$

It is easily shown that, whenever two tensor indices are repeated:

$$m_{\alpha\alpha} = 0 = m_{\alpha\alpha\beta\ldots}, \tag{11}$$

etc. The electronic magnetic multipoles (10) are *unperturbed* or *permanent* moment operators. In the presence of a vector potential $\mathbf{A}(\mathbf{r}, t)$, the canonical momentum is replaced by the mechanical momentum:

$$\mathbf{P} = \sum_{i=1}^{n} \mathbf{p}_i \rightarrow \boldsymbol{\Pi} = \sum_{i=1}^{n} \boldsymbol{\pi}_i, \qquad \boldsymbol{\pi}_i = \mathbf{p}_i + \frac{e}{c}\mathbf{A}_i, \tag{12}$$

and the angular momentum becomes:

$$\mathbf{L}' = \mathbf{L} + \frac{e}{c}\sum_{i=1}^{n} \mathbf{r}_i \times \mathbf{A}_i, \qquad \mathbf{L} = \sum_{i=1}^{n} \mathbf{l}_i. \tag{13}$$

According to Eqs. (4), (10) and (13), within the Bloch gauge [9] for the vector potential, the operators for perturbed magnetic multipole moments become:

$$m'_\alpha = m_\alpha + \bar{\chi}^{d}_{\alpha\beta} B(\mathbf{0}, t)_\beta + \bar{\chi}^{d}_{\alpha\beta;\gamma} B(\mathbf{0}, t)_{\gamma\beta}$$
$$+ \bar{\chi}^{d}_{\alpha\beta;\gamma\delta} B(\mathbf{0}, t)_{\delta\gamma\beta} + \bar{\chi}^{d}_{\alpha\beta;\gamma\delta\varepsilon} B(\mathbf{0}, t)_{\varepsilon\delta\gamma\beta} + \cdots, \tag{14}$$

$$m'_{\alpha\beta} = m_{\alpha\beta} + \bar{\chi}^{d}_{\alpha\gamma;\beta} B(\mathbf{0}, t)_\gamma + \tfrac{16}{9}\bar{\chi}^{d}_{\alpha\gamma;\beta\delta} B(\mathbf{0}, t)_{\delta\gamma}$$
$$+ \tfrac{5}{2}\bar{\chi}^{d}_{\alpha\gamma;\beta\delta\varepsilon} B(\mathbf{0}, t)_{\varepsilon\delta\gamma} + \cdots, \tag{15}$$

$$m'_{\alpha\beta\gamma} = m_{\alpha\beta\gamma} + \bar{\chi}^{d}_{\alpha\delta;\beta\gamma} B(\mathbf{0}, t)_\delta + \tfrac{5}{2}\bar{\chi}^{d}_{\alpha\delta;\beta\gamma\varepsilon} B(\mathbf{0}, t)_{\varepsilon\delta} + \cdots, \tag{16}$$

etc., where:

$$\bar{\chi}^{d}_{\alpha\beta} = -\frac{e^2}{4m_e c^2}\sum_{i=1}^{n} (r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta)_i, \tag{17}$$

$$\bar{\chi}^{d}_{\alpha\beta;\gamma} = -\frac{e^2}{6m_e c^2}\sum_{i=1}^{n} [(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta) r_\gamma]_i, \tag{18}$$

$$\bar{\chi}^{d}_{\alpha\beta;\gamma\delta} = -\frac{e^2}{16m_e c^2}\sum_{i=1}^{n} [(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta) r_\gamma r_\delta]_i, \tag{19}$$

$$\bar{\chi}^{d}_{\alpha\beta;\gamma\delta\varepsilon} = -\frac{e^2}{60m_e c^2}\sum_{i=1}^{n} [(r_\nu^2\delta_{\alpha\beta} - r_\alpha r_\beta) r_\gamma r_\delta r_\varepsilon]_i, \tag{20}$$

etc. In these formulae a semicolon separates symmetric indices which can be freely permuted.

3 Magnetic susceptibilities

The diamagnetic contributions to the magnetic susceptibilities in the reference state $|a\rangle$ are defined:

$$\chi^{d}_{\alpha\beta} = \langle a|\bar{\chi}^{d}_{\alpha\beta}|a\rangle, \tag{21}$$

$$\chi^{d}_{\alpha\beta;\gamma} = \langle a|\bar{\chi}^{d}_{\alpha\beta;\gamma}|a\rangle, \tag{22}$$

etc. The paramagnetic contributions are obtained via time-dependent perturbation theory [7]. Let us consider an operator which is characterized by a perturbation expansion:

$$T = T_0 + T_1 + \cdots, \tag{23}$$

where T_0 does not depend explicitly on time and T_1, etc., involving the perturbation, may be explicitly time-dependent. The expectation value of operator (23) in the perturbed electronic state is:

$$\langle T\rangle_a = \langle a|T_0|a\rangle + \langle a|T_1|a\rangle + 2\mathscr{R}\left[\sum_{j\neq a}\langle a|T_0|j\rangle \exp(-i\omega_{ja}t)c_{ja}(t)\right], \tag{24}$$

where

$$c_{ja}(t) = -\frac{1}{\hbar(\omega_{ja}^2-\omega^2)}\left[\langle j|H^{(1)}|a\rangle\omega_{ja} + i\left\langle j\left|\frac{\partial H^{(1)}}{\partial t}\right|a\right\rangle\right]\exp(i\omega_{ja}t). \tag{25}$$

Substituting for the operators (10) the paramagnetic contributions to the susceptibilities are obtained. They are:

$$\begin{aligned}\chi^{p}_{\alpha,\beta}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathscr{R}(\langle a|m_\alpha|j\rangle\langle j|m_\beta|a\rangle)\\ &= \chi^{p}_{\beta,\alpha}(\omega) \equiv \chi^{p}_{\alpha\beta}(\omega),\end{aligned} \tag{26}$$

$$\begin{aligned}\chi^{p}_{\alpha,\beta\gamma}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathscr{R}(\langle a|m_\alpha|j\rangle\langle j|m_{\beta\gamma}|a\rangle)\\ &= \chi^{p}_{\beta\gamma,\alpha}(\omega),\end{aligned} \tag{27}$$

$$\begin{aligned}\chi^{p}_{\alpha,\beta\gamma\delta}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathscr{R}(\langle a|m_\alpha|j\rangle\langle j|m_{\beta\gamma\delta}|a\rangle)\\ &= \chi^{p}_{\beta\gamma\delta,\alpha}(\omega),\end{aligned} \tag{28}$$

$$\begin{aligned}\chi^{p}_{\alpha\beta,\gamma\delta}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathscr{R}(\langle a|m_{\alpha\beta}|j\rangle\langle j|m_{\gamma\delta}|a\rangle)\\ &= \chi^{p}_{\gamma\delta,\alpha\beta}(\omega),\end{aligned} \tag{29}$$

$$\begin{aligned}\chi^{p}_{\alpha\beta,\gamma\delta\varepsilon}(\omega) &= \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathscr{R}(\langle a|m_{\alpha\beta}|j\rangle\langle j|m_{\gamma\delta\varepsilon}|a\rangle)\\ &= \chi^{p}_{\gamma\delta\varepsilon,\alpha\beta}(\omega),\end{aligned} \tag{30}$$

where, owing to Eq. (11):

$$\chi^{p}_{\alpha,\beta\beta}(\omega) = 0 = \chi^{p}_{\alpha\beta,\gamma\gamma}(\omega), \tag{31}$$

etc. In these formulae a comma separates groups of indices which can be permuted in the definition of the various susceptibilities, as each group refers to a given magnetic multipole (10).

Total dynamic susceptibilities could be defined so that:

$$\chi_{\alpha\beta}(\omega) = \chi^{p}_{\alpha\beta}(\omega) + \chi^{d}_{\alpha\beta}, \tag{32}$$

$$\chi_{\alpha,\beta\gamma}(\omega) = \chi^{p}_{\alpha,\beta\gamma}(\omega) + \chi^{d}_{\alpha\beta;\gamma} \tag{33}$$

$$\chi_{\alpha,\beta\gamma\delta}(\omega) = \chi^{p}_{\alpha,\beta\gamma\delta}(\omega) + \chi^{d}_{\alpha\beta;\gamma\delta} \neq \chi_{\beta\gamma\delta,\alpha}(\omega) \tag{34}$$

$$\chi_{\alpha\beta,\gamma}(\omega) = \chi^{p}_{\alpha\beta,\gamma}(\omega) + \chi^{d}_{\alpha\gamma;\beta} \neq \chi_{\gamma,\alpha\beta}(\omega), \tag{35}$$

$$\chi_{\alpha\beta,\gamma\delta}(\omega) = \chi^{p}_{\alpha\beta,\gamma\delta}(\omega) + \tfrac{16}{9}\chi^{d}_{\alpha\gamma;\beta\delta} = \chi_{\gamma\delta,\alpha\beta}(\omega), \tag{36}$$

$$\chi_{\alpha\beta,\gamma\delta\varepsilon}(\omega) = \chi^{p}_{\alpha\beta,\gamma\delta\varepsilon}(\omega) + \tfrac{5}{2}\chi^{d}_{\alpha\gamma;\beta\delta\varepsilon} \neq \chi_{\gamma\delta\varepsilon,\alpha\beta}(\omega). \tag{37}$$

Therefore the contributions to the induced magnetic moments arising from the non uniform magnetic field can be written:

$$\Delta\langle m'_{\lambda}\rangle = \chi_{\lambda\alpha}B(\mathbf{0},t)_{\alpha} + \chi_{\lambda,\alpha\beta}B(\mathbf{0},t)_{\beta\alpha} + \chi_{\lambda,\alpha\beta\gamma}B(\mathbf{0},t)_{\gamma\beta\alpha} + \cdots, \tag{38}$$

$$\Delta\langle m'_{\lambda\mu}\rangle = \chi_{\lambda\mu,\alpha}B(\mathbf{0},t)_{\alpha} + \chi_{\lambda\mu,\alpha\beta}B(\mathbf{0},t)_{\beta\alpha} + \chi_{\lambda\mu,\alpha\beta\gamma}B(\mathbf{0},t)_{\gamma\beta\alpha} + \cdots, \tag{39}$$

etc.

4 Nuclear magnetic shielding

In the presence of an intrinsic magnetic dipole $\boldsymbol{\mu}_I$ on nucleus I, the operator $-\mu_{I\alpha}B^{n}_{I\alpha}$ and a cross term:

$$H^{(11)} = \frac{e^2}{m_e c^2}\sum_{i=1}^{n}(A_\alpha A^{\mu_I}_{\alpha})_i, \qquad A^{\mu_I}_{i\alpha} = \varepsilon_{\alpha\beta\gamma}\mu_{I\beta}\frac{r_{i\gamma} - R_{I\gamma}}{|\mathbf{r}_i - \mathbf{R}_I|^3}, \tag{40}$$

add to the Hamiltonian (1). The operator for the magnetic field of the electrons on nucleus I in the absence of external perturbation is [7]:

$$\mathbf{B}^{n}_{I} = -\frac{e}{cm_e}\mathbf{M}^{n}_{I} = \mathbf{B}^{n}_{I0}, \qquad \mathbf{M}^{n}_{I} = \sum_{i=1}^{n}\frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}\times\mathbf{p}_i. \tag{41}$$

In non uniform magnetic fields the perturbed operator is obtained from Eqs. (4) and (40):

$$B^{n'}_{I\alpha} = B^{n}_{I\alpha} - \bar{\sigma}^{dI}_{\alpha\beta}B(\mathbf{0},t)_{\beta} - \bar{\sigma}^{dI}_{\alpha,\beta\gamma}B(\mathbf{0},t)_{\gamma\beta} - \bar{\sigma}^{dI}_{\alpha,\beta\gamma\delta}B(\mathbf{0},t)_{\delta\gamma\beta} + \cdots, \tag{42}$$

where, introducing the operator for the electric field of electron i on nucleus I:

$$\mathbf{E}^{i}_{I} = e\frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}, \tag{43}$$

the operators for the diamagnetic contributions to nuclear shielding are defined:

$$\bar{\sigma}^{\mathrm{d}I}_{\alpha\beta} = \frac{e}{2m_e c^2} \sum_{i=1}^{n} (r_{i\lambda} E^i_{I\lambda} \delta_{\alpha\beta} - r_{i\alpha} E^i_{I\beta}), \tag{44}$$

$$\bar{\sigma}^{\mathrm{d}I}_{\alpha,\beta\gamma} = \frac{e}{3m_e c^2} \sum_{i=1}^{n} (r_{i\lambda} E^i_{I\lambda} \delta_{\alpha\beta} - r_{i\alpha} E^i_{I\beta}) r_{i\gamma}, \tag{45}$$

$$\bar{\sigma}^{\mathrm{d}I}_{\alpha,\beta\gamma\delta} = \frac{e}{8m_e c^2} \sum_{i=1}^{n} (r_{i\lambda} E^i_{I\lambda} \delta_{\alpha\beta} - r_{i\alpha} E^i_{I\beta}) r_{i\gamma} r_{i\delta}. \tag{46}$$

The diamagnetic contributions to the shielding tensors are:

$$\sigma^{\mathrm{d}I}_{\alpha\beta} = \langle a | \bar{\sigma}^{\mathrm{d}I}_{\alpha\beta} | a \rangle$$

$$\sigma^{\mathrm{d}I}_{\alpha,\beta\gamma} = \langle a | \bar{\sigma}^{\mathrm{d}I}_{\alpha,\beta\gamma} | a \rangle, \tag{47}$$

etc. The paramagnetic contributions are obtained via Eqs. (24), (25) and (41):

$$\sigma^{\mathrm{p}I}_{\alpha,\beta}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a | B^n_{I\alpha} | j \rangle \langle j | m_\beta | a \rangle) \equiv \sigma^{\mathrm{p}I}_{\alpha\beta}(\omega), \tag{48}$$

$$\sigma^{\mathrm{p}I}_{\alpha,\beta\gamma}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a | B^n_{I\alpha} | j \rangle \langle j | m_{\beta\gamma} | a \rangle), \tag{49}$$

$$\sigma^{\mathrm{p}I}_{\alpha,\beta\gamma\delta}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a | B^n_{I\alpha} | j \rangle \langle j | m_{\beta\gamma\delta} | a \rangle). \tag{50}$$

Therefore the magnetic field induced on nucleus I by the electron cloud perturbed by a non-uniform magnetic field is:

$$\Delta \langle B^{n'}_{I\alpha} \rangle = -\sigma^I_{\alpha\beta} B(\mathbf{0}, t)_\beta - \sigma^I_{\alpha,\beta\gamma} B(\mathbf{0}, t)_{\gamma\beta} - \sigma^I_{\alpha,\beta\gamma\delta} B(\mathbf{0}, t)_{\delta\gamma\beta} + \cdots, \tag{51}$$

where the total dynamic magnetic shieldings are:

$$\sigma^I_{\alpha\beta}(\omega) = \sigma^{\mathrm{p}I}_{\alpha\beta}(\omega) + \sigma^{\mathrm{d}I}_{\alpha\beta}, \tag{52}$$

$$\sigma^I_{\alpha,\beta\gamma}(\omega) = \sigma^{\mathrm{p}I}_{\alpha,\beta\gamma}(\omega) + \sigma^{\mathrm{d}I}_{\alpha\beta,\gamma}, \tag{53}$$

$$\sigma^I_{\alpha,\beta\gamma\delta}(\omega) = \sigma^{\mathrm{p}I}_{\alpha,\beta\gamma\delta}(\omega) + \sigma^{\mathrm{d}I}_{\alpha,\beta\gamma\delta}. \tag{54}$$

5 Nuclear electromagnetic shielding and optical rotatory power

The electric dipole moment induced in the electron cloud by the electromagnetic field is [7]:

$$\begin{aligned} \Delta \langle \mu_\alpha \rangle = {} & \alpha_{\alpha\beta} E(\mathbf{0}, t)_\beta + \alpha_{\alpha,\beta\gamma} E(\mathbf{0}, t)_{\gamma\beta} \\ & + \alpha_{\alpha,\beta\gamma\delta} E(\mathbf{0}, t)_{\delta\gamma\beta} + \cdots \qquad (55) \\ & + \hat{\kappa}_{\alpha\beta} \dot{B}(\mathbf{0}, t)_\beta + \hat{\kappa}_{\alpha,\beta\gamma} \dot{B}(\mathbf{0}, t)_{\gamma\beta} \\ & + \hat{\kappa}_{\alpha,\beta\gamma\delta} \dot{B}(\mathbf{0}, t)_{\delta\gamma\beta} + \cdots, \qquad (56) \end{aligned}$$

where the electric dipole and mixed dipole-quadrupole polarizabilities are:

$$\alpha_{\alpha,\beta}(\omega) = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a|\mu_\alpha|j\rangle\langle j|\mu_\beta|a\rangle) \equiv \alpha_{\alpha\beta}(\omega), \tag{57}$$

$$\alpha_{\alpha,\beta\gamma}(\omega) = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a|\mu_\alpha|j\rangle\langle j|\mu_{\beta\gamma}|a\rangle), \tag{58}$$

$$\alpha_{\alpha,\beta\gamma\delta}(\omega) = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a|\mu_\alpha|j\rangle\langle j|\mu_{\beta\gamma\delta}|a\rangle), \tag{59}$$

using the non-traceless form of Eq. (9) for electric multipoles. The optical rotatory power is described via the tensors:

$$\hat{\kappa}_{\alpha,\beta}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a|\mu_\alpha|j\rangle\langle j|m_\beta|a\rangle) \equiv \hat{\kappa}_{\alpha\beta}(\omega) \tag{60}$$

$$\hat{\kappa}_{\alpha,\beta\gamma}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a|\mu_\alpha|j\rangle\langle j|m_{\beta\gamma}|a\rangle), \tag{61}$$

$$\hat{\kappa}_{\alpha,\beta\gamma\delta}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a|\mu_\alpha|j\rangle\langle j|m_{\beta\gamma\delta}|a\rangle). \tag{62}$$

The electric field, induced on nucleus I by the external field via the perturbed electron cloud, is:

$$\begin{aligned} \Delta\langle E_{I\alpha}^n\rangle = & -\gamma_{\alpha\beta}^I E(\mathbf{0},t)_\beta + \gamma_{\alpha,\beta\gamma}^I E(\mathbf{0},t)_{\gamma\beta} + \gamma_{\alpha,\beta\gamma\delta}^I E(\mathbf{0},t)_{\delta\gamma\beta} + \cdots \\ & + \hat{\xi}_{\alpha\beta}^I \dot{B}(\mathbf{0},t)_\beta + \hat{\xi}_{\alpha,\beta\gamma}^I \dot{B}(\mathbf{0},t)_{\gamma\beta} + \hat{\xi}_{\alpha,\beta\gamma\delta}^I \dot{B}(\mathbf{0},t)_{\delta\gamma\beta} + \cdots, \end{aligned} \tag{63}$$

where the nuclear electric shielding tensors [7] are:

$$\gamma_{\alpha,\beta}^I(\omega) = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a|E_{I\alpha}^n|j\rangle\langle j|\mu_\beta|a\rangle) \equiv \gamma_{\alpha\beta}^I(\omega), \tag{64}$$

$$\gamma_{\alpha,\beta\gamma}(\omega) = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a|E_{I\alpha}^n|j\rangle\langle j|\mu_{\beta\gamma}|a\rangle) \tag{65}$$

$$\gamma_{\alpha,\beta\gamma\delta}(\omega) = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathscr{R}(\langle a|E_{I\alpha}^n|j\rangle\langle j|\mu_{\beta\gamma\delta}|a\rangle), \tag{66}$$

and the electromagnetic shielding tensors, related to vibrational circular dichroism [7], are:

$$\hat{\xi}_{\alpha,\beta}^I(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a|E_{I\alpha}^n|j\rangle\langle j|m_\beta|a\rangle) \equiv \hat{\xi}_{\alpha\beta}^I(\omega), \tag{67}$$

$$\hat{\xi}_{\alpha,\beta\gamma}^I(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a|E_{I\alpha}^n|j\rangle\langle j|m_{\beta\gamma}|a\rangle), \tag{68}$$

$$\hat{\xi}_{\alpha,\beta\gamma\delta}^I(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a|E_{I\alpha}^n|j\rangle\langle j|m_{\beta\gamma\delta}|a\rangle). \tag{69}$$

The various quantities are connected and satisfy a series of sum rules which can be easily proven via off-diagonal hypervirial relations [7]:

$$\hat{\kappa}_{\alpha,\beta\gamma}(\omega) = -\frac{e^2}{m_e}\omega^{-2}\sum_{I=1}^{N} Z_I\,[\hat{\xi}_{\alpha,\beta\gamma}(\omega) - \hat{\xi}_{\alpha,\beta\gamma}(0)], \tag{70}$$

$$\sum_{I=1}^{N} Z_I e\hat{\xi}^I(0)_{\alpha,\beta\gamma} = -\frac{2}{3c}\varepsilon_{\alpha\beta\lambda}\langle a|\mu_{\gamma\lambda}|a\rangle, \tag{71}$$

$$\sum_{I=1}^{N} Z_I\varepsilon_{\alpha\beta\gamma}R_{I\beta}\hat{\xi}^I(\omega)_{\gamma,\delta\varepsilon} = \frac{2m_e c}{e^2}\chi^{\mathrm{P}}(\omega)_{\alpha,\delta\varepsilon}. \tag{72}$$

6 Origin dependence of magnetic properties

The definition of some molecular tensors introduced in the previous sections depends on the origin of the coordinate system. Thus in a change of origin:

$$\mathbf{r}'' = \mathbf{r}' + \mathbf{d}, \tag{73}$$

the diamagnetic contributions to the dipole-quadrupole magnetic susceptibilities transform:

$$\begin{aligned}\chi^{\mathrm{d}}_{\gamma\alpha;\beta}(\mathbf{r}'') = {} & \chi^{\mathrm{d}}_{\gamma\alpha;\beta}(\mathbf{r}') - \tfrac{2}{3}\chi^{\mathrm{d}}_{\gamma\alpha}(\mathbf{r}')d_\beta + \frac{e}{6m_e c^2} \\ & \times [2(\langle a|\mu_{\alpha\beta}(\mathbf{r}')|a\rangle d_\gamma + \langle a|\mu_{\beta\gamma}(\mathbf{r}')|a\rangle d_\alpha \\ & - 2\langle a|\mu_{\beta\nu}(\mathbf{r}')|a\rangle d_\nu\delta_{\alpha\gamma}) \\ & - (\langle a|\mu_\alpha(\mathbf{r}')|a\rangle d_\gamma + \langle a|\mu_\gamma(\mathbf{r}')a\rangle d_\alpha \\ & - 2\langle a|\mu_\nu(\mathbf{r}')|a\rangle\delta_\nu d_{\alpha\gamma})d_\beta \\ & + (\langle a|\mu_\beta(\mathbf{r}')|a\rangle + ned_\beta)(d_\nu^2\delta_{\alpha\gamma} - d_\alpha d_\gamma)].\end{aligned} \tag{74}$$

The corresponding transformation of static paramagnetic contributions is obtained from the origin dependence of the magnetic moments:

$$m_\gamma(\mathbf{r}'') = m_\gamma(\mathbf{r}') + \frac{e}{2m_e c}\varepsilon_{\gamma\lambda\mu}d_\lambda P_\mu, \tag{75}$$

$$\begin{aligned}m_{\alpha\beta}(\mathbf{r}'') = {} & m_{\alpha\beta}(\mathbf{r}') + \frac{e}{6m_e c}\sum_{i=1}^{n}[p_\delta(r_\beta - r'_\beta) + (r_\beta - r'_\beta)p_\delta]_i\,\varepsilon_{\alpha\gamma\delta}d_\gamma \\ & + \frac{e}{3m_e c}\sum_{i=1}^{n}[(r_\gamma - r'_\gamma)p_\delta]_i\,\varepsilon_{\alpha\gamma\delta}d_\beta - \frac{e}{3m_e c}\varepsilon_{\alpha\gamma\delta}d_\beta d_\gamma P_\delta.\end{aligned} \tag{76}$$

Accordingly:

$$\chi^{\mathrm{p}}_{\gamma,\alpha\beta}(\mathbf{r}'') = \chi^{\mathrm{p}}_{\gamma,\alpha\beta}(\mathbf{r}') + \mathscr{A}_1 + \mathscr{A}_2 + \mathscr{A}_3 + \mathscr{A}_4 + \mathscr{A}_5 + \mathscr{A}_6 + \mathscr{A}_7, \tag{77}$$

where the various terms are

$$\mathscr{A}_1 = \frac{e}{2m_e c\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}(\langle a|m_{\alpha\beta}(\mathbf{r}')|j\rangle\langle j|P_\mu|a\rangle)\varepsilon_{\gamma\lambda\mu} d_\lambda$$

$$= \frac{e}{3m_e c^2}(\langle a|\mu_{\beta\nu}(\mathbf{r}')|a\rangle d_\nu \delta_{\alpha\gamma} - \langle a|\mu_{\beta\gamma}(\mathbf{r}')|a\rangle d_\alpha) \tag{78}$$

$$\mathscr{A}_2 = \frac{e}{6m_e c\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \times \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^{n} [p_\delta(r_\beta - r'_\beta) + (r_\beta - r'_\beta)p_\delta]_i\right|j\right\rangle\langle j|m_\gamma(\mathbf{r}')|a\rangle\right)\varepsilon_{\alpha\sigma\delta} d_\sigma$$

$$= \tfrac{1}{3}(\chi_{\nu\gamma} d_\nu \delta_{\alpha\beta} - \chi_{\alpha\gamma}) d_\beta + \frac{e}{3m_e c^2}(\langle a|\mu_{\beta\nu}(\mathbf{r}')|a\rangle d_\nu \delta_{\alpha\gamma} - \langle a|\mu_{\alpha\beta}(\mathbf{r}')|a\rangle d_\gamma) \tag{79}$$

$$\mathscr{A}_3 = \frac{e^2}{12m_e^2 c^2\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^{n} [p_\delta(r_\beta - r'_\beta) + (r_\beta - r'_\beta)p_\delta]_i\right|j\right\rangle \times \langle j|P_\mu|a\rangle\right)\varepsilon_{\alpha\sigma\delta}\varepsilon_{\gamma\lambda\mu} d_\sigma d_\lambda$$

$$= -\frac{e}{6m_e c^2}\langle a|\mu_\beta(\mathbf{r}')|a\rangle(d_\nu^2 \delta_{\alpha\gamma} - d_\alpha d_\gamma) \tag{80}$$

$$\mathscr{A}_4 = \frac{e}{3m_e c\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \times \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^{n} [(r_\sigma - r'_\sigma)p_\delta]_i\right|j\right\rangle\langle j|m_\gamma\mathbf{r}')|a\rangle\right)\varepsilon_{\alpha\sigma\delta} d_\beta$$

$$= -\tfrac{2}{3}\chi^{\mathrm{p}}_{\alpha\gamma}(\mathbf{r}') d_\beta \tag{81}$$

$$\mathscr{A}_5 = \frac{e^2}{6m_e^2 c^2\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \times \mathscr{R}\left(\left\langle a\left|\sum_{i=1}^{n} [(r_\sigma - r'_\sigma)p_\delta]_i\right|j\right\rangle\langle j|P_\mu|a\rangle\right)\varepsilon_{\alpha\sigma\delta}\varepsilon_{\gamma\lambda\mu} d_\beta d_\lambda$$

$$= \frac{e}{6m_e c^2}(\langle a|\mu_\gamma(\mathbf{r}')|a\rangle d_\alpha - \langle a|\mu_\nu(\mathbf{r}')|a\rangle d_\nu \delta_{\alpha\gamma}) d_\beta, \tag{82}$$

$$\mathscr{A}_6 = -\frac{e}{3m_e c\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}(\langle a|P_\delta|j\rangle\langle j|m_\gamma(\mathbf{r}')|a\rangle)\varepsilon_{\alpha\sigma\delta} d_\beta d_\sigma$$

$$= \frac{e}{6m_e c^2}(\langle a|\mu_\alpha(\mathbf{r}')|a\rangle d_\gamma - \langle a|\mu_\nu(\mathbf{r}')|a\rangle d_\nu \delta_{\alpha\gamma}) d_\beta \tag{83}$$

$$\mathscr{A}_7 = -\frac{e^2}{6m_e^2 c^2\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathscr{R}(\langle a|P_\delta|j\rangle\langle j|P_\mu|a\rangle)\varepsilon_{\alpha\sigma\delta}\varepsilon_{\gamma\lambda\mu} d_\beta d_\lambda d_\sigma$$

$$= -\frac{e^2}{6m_e c^2} n d_\beta(d_\nu^2 \delta_{\alpha\gamma} - d_\alpha d_\gamma). \tag{84}$$

In these identities the expressions on the r.h.s. are obtained via off-diagonal hypervirial relations [7] involving μ_α, P_α, L_α, etc., and:

$$2r_{k\beta}p_{k\delta} = r_{k\beta}p_{k\delta} + p_{k\delta}r_{k\beta} + i\hbar\delta_{\beta\delta} = \varepsilon_{\tau\beta\delta}l_{k\tau} + \frac{im_e}{\hbar}[H_0, r_{k\beta}r_{k\delta}]. \tag{85}$$

They hold only if $|a\rangle$ and $|j\rangle$ are the exact eigenstates to a model Hamiltonian [7]. For instance, they are identically satisfied for *true* Hartree–Fock wavefunctions. Actual calculations relying on the algebraic approximation fulfill the hypervirial constraints to a satisfactory degree if good quality basis sets are adopted [18]. From Eqs. (74–84) one eventually finds the formula for the origin dependence of total mixed dipole-quadrupole magnetic susceptibility in the static case:

$$\chi_{\gamma,\alpha\beta}(\mathbf{r}'') = \chi_{\gamma,\alpha\beta}(\mathbf{r}') - \chi_{\gamma\alpha}\delta_\beta + \tfrac{1}{3}\chi_{\gamma\delta}d_\delta d_{\alpha\beta}. \tag{86}$$

The origin dependence of the diamagnetic contribution to nuclear magnetic shielding provided by electron magnetic quadrupole terms is given by:

$$\begin{aligned}\sigma^{dI}_{\gamma,\alpha\beta}(\mathbf{r}'') = {}& \sigma^{dI}_{\gamma,\alpha\beta}(\mathbf{r}') - \tfrac{2}{3}\sigma^{dI}_{\gamma\alpha}(\mathbf{r}')d_\beta \\ & + \frac{e}{3m_ec^2}\Bigg[(\langle a|E^n_{I\nu}|a\rangle d_\nu\delta_{\gamma\alpha} - \langle a|E^n_{I\alpha}|a\rangle d_\gamma)d_\beta \\ & - \left\langle a\left|\sum_{i=1}^n (r_{i\beta}-r'_\beta)E^i_{I\nu}\right|a\right\rangle d_\nu\delta_{\gamma\alpha} \\ & + \left\langle a\left|\sum_{i=1}^n (r_{i\beta}-r'_\beta)E^i_{I\alpha}\right|a\right\rangle d_\gamma\Bigg],\end{aligned} \tag{87}$$

and for the static paramagnetic contributions,

$$\sigma^{pI}_{\gamma,\alpha\beta}(\mathbf{r}'') = \sigma^{pI}_{\gamma,\alpha\beta}(\mathbf{r}') + \mathscr{B}_1 + \mathscr{B}_2 + \mathscr{B}_3, \tag{88}$$

where

$$\begin{aligned}\mathscr{B}_1 = {}& -\frac{e}{6m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\mathscr{R}\Bigg(\langle a|B^n_{I\gamma}|j\rangle \\ & \times\left\langle j\left|\sum_{i=1}^n [p_\delta(r_\beta - r'_\beta) + (r_\beta - r'_\beta)p_\delta]_i\right|a\right\rangle\Bigg)\varepsilon_{\alpha\sigma\delta}d_\sigma \\ = {}& -\tfrac{1}{3}(\sigma^I_{\gamma\alpha}d_\beta - \sigma^I_{\gamma\nu}d_\nu\delta_{\alpha\beta}) + \frac{e}{3m_ec^2}\Bigg[\left\langle a\left|\sum_{i=1}^n (r_{i\beta}-r'_\beta)E^i_{I\nu}\right|a\right\rangle d_\nu\delta_{\alpha\gamma} \\ & - \left\langle a\left|\sum_{i=1}^n (r_{i\beta}-r'_\beta)E^i_{I\alpha}\right|a\right\rangle d_\gamma\Bigg],\end{aligned} \tag{89}$$

$$\begin{aligned}\mathscr{B}_2 = {}& -\frac{e}{3m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\mathscr{R}\left(\langle a|B^n_{I\gamma}|j\rangle\left\langle j\left|\sum_{i=1}^n [(r_\nu - r'_\nu)p_\delta]_i\right|a\right\rangle\right)\varepsilon_{\alpha\nu\delta}d_\beta \\ = {}& -\tfrac{2}{3}\sigma^{pI}_{\gamma\alpha}(\mathbf{r}')d_\beta,\end{aligned} \tag{90}$$

$$\begin{aligned}\mathscr{B}_3 = {}& \frac{e}{3m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\mathscr{R}(\langle a|B^n_{I\gamma}|j\rangle\langle j|P_\delta|a\rangle)\varepsilon_{\alpha\sigma\delta}d_\beta d_\sigma \\ = {}& -\frac{e}{3m_ec^2}(\langle a|E^n_{I\nu}|a\rangle d_\nu\delta_{\gamma\alpha} - \langle a|E^n_{I\alpha}|a\rangle d_\gamma)d_\beta.\end{aligned} \tag{91}$$

The identities on the r.h.s. are, also in this case, satisfied for exact eigenstates to any model Hamiltonian.

Therefore the total magnetic quadrupole contribution to static magnetic shielding depends on the origin according to:

$$\sigma^I_{\gamma,\alpha\beta}(\mathbf{r}'') = \sigma^I_{\gamma,\alpha\beta}(\mathbf{r}') - \sigma^I_{\gamma\alpha}\, d_\beta + \tfrac{1}{3}\sigma^I_{\gamma\delta}\, d_\delta\, \delta_{\alpha\beta}. \tag{92}$$

Similar equations are found for electron magnetic quadrupole contribution to the optical rotatory power. For any frequency ω:

$$\hat{\kappa}_{\gamma,\alpha\beta}(\mathbf{r}'') = \hat{\kappa}_{\gamma,\alpha\beta}(\mathbf{r}') + \mathscr{C}_1 + \mathscr{C}_2 + \mathscr{C}_3, \tag{93}$$

where

$$\begin{aligned}\mathscr{C}_1 = &-\frac{e}{6m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^2-\omega^2}\mathscr{I}\Bigg(\langle a|\mu_\gamma|j\rangle \\ &\times\left\langle j\left|\sum_{i=1}^{n}[p_\delta(r_\beta-r'_\beta)+(r_\beta-r'_\beta)p_\delta]_i\right|a\right\rangle\Bigg)\varepsilon_{\alpha\sigma\delta}\, d_\sigma \\ &= \tfrac{1}{3}[\hat{\kappa}_{\gamma\sigma}(\mathbf{r}')\, d_\sigma\delta_{\alpha\beta} - \hat{\kappa}_{\gamma\alpha}(\mathbf{r}')\, d_\beta] + \frac{1}{3c}\alpha_{\gamma,\beta\delta}(\mathbf{r}')\,\varepsilon_{\alpha\sigma\delta}\, d_\sigma,\end{aligned} \tag{94}$$

$$\begin{aligned}\mathscr{C}_2 = &-\frac{e}{3m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^2-\omega^2}\mathscr{I}\left(\langle a|\mu_\gamma|j\rangle\left\langle j\left|\sum_{i=1}^{n}[(r_\nu-r'_\nu)p_\delta]_i\right|a\right\rangle\right)\varepsilon_{\alpha\nu\delta}\, d_\beta \\ = &-\tfrac{2}{3}\hat{\kappa}_{\gamma\alpha}(\mathbf{r}')\, d_\beta,\end{aligned} \tag{95}$$

$$\begin{aligned}\mathscr{C}_3 = &\frac{e}{3m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^2-\omega^2}\mathscr{I}(\langle a|\mu_\gamma|j\rangle\langle j|P_\delta|a\rangle)\,\varepsilon_{\alpha\nu\delta}\, d_\beta\, d_\nu \\ = &-\frac{1}{3c}\alpha_{\gamma\delta}\varepsilon_{\alpha\nu\delta}\, d_\beta\, d_\nu.\end{aligned} \tag{96}$$

Thus the origin dependence of the magnetic quadrupole contribution to the optical rotatory power is obtained from:

$$\begin{aligned}\hat{\kappa}_{\gamma,\alpha\beta}(\mathbf{r}'') = &\hat{\kappa}_{\gamma,\alpha\beta}(\mathbf{r}') - \hat{\kappa}_{\gamma\alpha}(\mathbf{r}'')\, d_\beta + \tfrac{1}{3}\hat{\kappa}_{\gamma\delta}(\mathbf{r}')\, d_\delta\,\delta_{\alpha\beta} \\ &-\frac{1}{3c}\alpha_{\gamma\delta}\,\varepsilon_{\alpha\nu\delta}\, d_\nu\, d_\beta + \frac{1}{3c}\alpha_{\gamma,\beta\delta}(\mathbf{r}')\,\varepsilon_{\alpha\nu\delta}\, d_\nu.\end{aligned} \tag{97}$$

For the electromagnetic shielding:

$$\hat{\xi}^I_{\gamma,\alpha\beta}(\mathbf{r}'') = \hat{\xi}^I_{\gamma,\alpha\beta}(\mathbf{r}') + \mathscr{D}_1 + \mathscr{D}_2 + \mathscr{D}_3, \tag{98}$$

$$\begin{aligned}\mathscr{D}_1 = &-\frac{e}{6m_ec\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^2-\omega^2}\mathscr{I}\Bigg\{\langle a|E^n_{I\gamma}|j\rangle \\ &\times\left\langle j\left|\sum_{i=1}^{n}[p_\delta(r_\beta-r'_\beta)+(r_\beta-r'_\beta)p_\delta]_i\right|a\right\rangle\Bigg\}\varepsilon_{\alpha\sigma\delta}\, d_\sigma \\ &= \tfrac{1}{3}[\hat{\xi}^I_{\gamma\nu}(\mathbf{r}')\, d_\nu\,\delta_{\alpha\beta} - \hat{\xi}^I_{\gamma\alpha}(\mathbf{r}')\, d_\beta] + \frac{1}{3c}\gamma^I_{\gamma,\beta\delta}(\mathbf{r}')\,\varepsilon_{\alpha\nu\delta}\, d_\nu\end{aligned} \tag{99}$$

$$\mathscr{D}_2 = -\frac{e}{3m_e c\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}\left(\langle a | E_{I\gamma}^n | j \rangle \left\langle j \middle| \sum_{i=1}^{n} [(r_\nu - r'_\nu) p_\delta]_i \middle| a \right\rangle \right) \varepsilon_{\alpha\nu\delta} d_\beta$$
$$= -\tfrac{2}{3} \xi_{\gamma\alpha}^I(\mathbf{r}') d_\beta, \tag{100}$$

$$\mathscr{D}_3 = \frac{e}{3m_e c\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \mathscr{I}(\langle a | E_{I\gamma}^n | j \rangle \langle j | P_\delta | a \rangle) \varepsilon_{\alpha\nu\delta} d_\beta d_\nu$$
$$= \frac{1}{3c} \gamma_{\gamma\delta}^I \varepsilon_{\alpha\nu\delta} d_\beta d_\nu. \tag{101}$$

Therefore the origin dependence for the magnetic quadrupole contribution to electromagnetic shielding is given by:

$$\xi_{\gamma,\alpha\beta}^I(\mathbf{r}'') = \xi_{\gamma,\alpha\beta}^I(\mathbf{r}') - \xi_{\gamma\alpha}^I(\mathbf{r}') d_\beta + \tfrac{1}{3} \xi_{\gamma\delta}^I(\mathbf{r}') d_\delta \delta_{\alpha\beta}$$
$$+ \frac{1}{3c} \gamma_{\gamma\delta}^I \varepsilon_{\alpha\nu\delta} d_\beta d_\nu + \tfrac{1}{3} \gamma_{\gamma,\beta\delta}^I(\mathbf{r}') \varepsilon_{\alpha\nu\delta} d_\nu. \tag{102}$$

7 Conclusions

A series of tensors describing the linear response of a molecule in non-uniform magnetic field has been defined, consistent with the Bloch [9] interaction Hamiltonian. Contributions arising from magnetic multipole moments of the electron distribution to magnetic susceptibility, nuclear magnetic shielding, optical rotatory power and nuclear electromagnetic shielding can be rationalized accordingly. On a macroscopic level, the effects associated with higher multipoles are small, for instance, the magnetic quadrupole contribution to NMR chemical shifts, compare for Eqs. (45) and (49), is $\approx 1 \times 10^{-14}$ cm in the Gaussian system of units. Therefore detecting and measuring these tiny contributions would seem out of reach with present experimental set-ups, due to the difficulties of constructing magnets with very high gradient. An ideal experiment can be conceived, in which the magnetic equivalence of nuclei (say, protons in a single, fixed benzene molecule) in ordinary NMR experiments, using spatially uniform magnetic fields, would be removed in the presence of field gradient. In practice, the NMR spectrum of an assembly of fixed molecules in non uniform fields would contain extremely complicate patterns. On a microscopic scale, however, the role of magnetic multipoles beyond the magnetic dipole cannot be dismissed, as they lead to observable pseudo-contact shifts [17]. The effect of distant charge distributions on the magnetic shielding of a nucleus can therefore be analyzed in terms of the molecular tensors introduced in this paper.

Eventually, an efficient computational strategy for the *ab initio* determination of the various tensors defined in the present study has been devised according to the coupled Hartree–Fock and random-phase approximation techniques previously developed and implemented within the SYSMO suite of computer programs [18, 19]. Numerical studies on water molecule have been undertaken [20].

Appendix: the Bloch potentials

The MacLaurin series for the magnetic field:

$$B(\mathbf{r}, t)_\alpha = \sum_{k=0}^{\infty} \frac{1}{k!} r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} B(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha}, \tag{103}$$

and for the electric field:

$$E(\mathbf{r}, t)_\alpha = \sum_{k=0}^{\infty} \frac{1}{k!} r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} E(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha}, \tag{104}$$

where partial derivatives with respect to coordinates, taken at the origin, are denoted by:

$$B(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha} \equiv \left[\frac{\partial^k B(\mathbf{r}, t)_\alpha}{\partial r_{\alpha_k} \partial r_{\alpha_{k-1}} \ldots \partial r_{\alpha_1}} \right]_{\mathbf{r}=\mathbf{0}}, \tag{105}$$

etc., are not compatible with the analogous power expansions for the vector and scalar potentials:

$$A(\mathbf{r}, t)_\alpha = \sum_{k=0}^{\infty} \frac{1}{k!} r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} A(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha}, \tag{106}$$

$$\phi(\mathbf{r}, t)_\alpha = \phi(\mathbf{0}, t) + \sum_{k=1}^{\infty} \frac{1}{k!} r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} \phi(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1}, \tag{107}$$

using the same notation as in Eq. (105) for derivatives with respect to coordinates of the scalar potential, i.e.:

$$\phi(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1} \equiv \left[\frac{\partial^k \phi(\mathbf{r}, t)}{\partial r_{\alpha_k} \partial r_{\alpha_{k-1}} \ldots \partial r_{\alpha_1}} \right]_{\mathbf{r}=\mathbf{0}}. \tag{108}$$

In fact, Eqs. (106) and (107) do not satisfy the equations for the fields:

$$B(\mathbf{r}, t)_\alpha = \varepsilon_{\alpha\beta\gamma} A(\mathbf{r}, t)_{\beta\gamma}, \tag{109}$$

$$E(\mathbf{r}, t)_\alpha = -\phi(\mathbf{r}, t)_\alpha - \frac{1}{c} \dot{A}(\mathbf{r}, t)_\alpha, \tag{110}$$

therefore, following Bloch [9], we carry out a gauge transformation:

$$A_\alpha \to A_\alpha^{\mathscr{B}} = A_\alpha + f_\alpha^{\mathscr{B}}, \qquad f_\alpha^{\mathscr{B}} \equiv \nabla_\alpha f^{\mathscr{B}}, \tag{111}$$

$$\phi \to \phi^{\mathscr{B}} = \phi - \frac{1}{c} \dot{f}^{\mathscr{B}}, \tag{112}$$

where the gauge function is:

$$f^{\mathscr{B}}(\mathbf{r}, t) = -\sum_{k=1}^{\infty} \frac{1}{k!} r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} A(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1}, \tag{113}$$

so that, using Eqs. (109) and (110), the Bloch potentials are:

$$A^{\mathscr{B}}(\mathbf{r}, t)_\alpha = \sum_{k=0}^{\infty} \frac{k+1}{(k+2)!} \varepsilon_{\alpha\beta\gamma} r_\gamma r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} B(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \beta}, \tag{114}$$

$$\phi^{\mathscr{B}}(\mathbf{r}, t) = -\sum_{k=0}^{\infty} \frac{1}{(k+1)!} r_\alpha r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} E(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \alpha}. \tag{115}$$

Within the Bloch gauge:

$$A^{\mathscr{B}}(\mathbf{r}, t)_{\alpha\alpha} = \sum_{k=0}^{\infty} \frac{(k+1)(k+2)}{(k+3)!} \varepsilon_{\alpha\beta\gamma} r_\alpha r_{\alpha_1} r_{\alpha_2} \ldots r_{\alpha_k} B(\mathbf{0}, t)_{\alpha_k \alpha_{k-1} \ldots \alpha_1 \beta_\gamma}. \tag{116}$$

The new potentials (114) and (115) satisfy Eqs. (109) and (110). The Lorentz condition is not satisfied by the Bloch potentials, i.e.:

$$\frac{1}{c}\dot{\phi}^{\mathscr{B}} + A^{\mathscr{B}}_{\alpha\alpha} \neq 0, \tag{117}$$

as can be checked by using the Maxwell equation (in the absence of external currents):

$$\varepsilon_{\alpha\beta\gamma} B_{\beta\gamma} = \frac{1}{c}\dot{E}_{\alpha}, \tag{118}$$

in Eqs. (115) and (116). However, owing to Eq. (118), for a static electric field one has:

$$A^{\mathscr{B}}_{\alpha\alpha} = 0, \tag{119}$$

analogous to the condition for the Coulomb gauge $A_{\alpha\alpha} = 0$ in time independent uniform magnetic fields.

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