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REGULAR ARTICLE

Invariance of multipole polarisabilities of nuclear magnetic shielding within the approach of continuous transformation of the origin of the current density

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Abstract Electric multipole polarisabilities of nuclear magnetic shielding of a molecule in the presence of external fields—a uniform magnetic and a non-uniform electric field—calculated via the approach of continuous transformation of the origin of the current density, are shown to be invariant in a translation of the gauge of the vector potential. However, multipole polarisabilities depend upon the origin of the coordinate system for multipole higher than dipole, because of the intrinsic origin dependence of the related operators.

Keywords Electric quadrupole polarisability of nuclear magnetic shielding · Origin dependence of magnetic shielding multipole polarisabilities · Invariance of magnetic shielding multipole polarisabilities in a gauge translation

1 Introduction

An electric field leads to changes of chemical shift in nuclear magnetic resonance (NMR) spectroscopy. The phenomenology is rationalized via a molecular response property referred to as electric dipole polarisability of nuclear magnetic shielding, introduced by Buckingham [1] and much studied by other authors [2–20]. Review articles by Raynes [21,22], Augspurger et al. [23], and Jameson and de Dios [24–26] give a wide theoretical account.

At present there is interest on the possible applications of NMR spectroscopy for chiral discrimination via dipole polarisabilities of nuclear magnetic shielding, as they are odd with respect to parity, i.e., they have the same value but opposite sign for the D and L enantiomers of a chiral species [27,28]. In disordered phase, the key property is the isotropic part of this tensor [27–29].

Higher-order polarisabilities can be defined via the Buckingham approach [1]. The quadrupole polarisability of nuclear magnetic shielding is parity even, and therefore it is not suitable for chiral discrimination—the next parity odd property is the octupole polarisability. Although multipole polarisabilities are small in magnitude, and probably difficult to measure, they are theoretically appealing for the reasons discussed in this note.

Although the dipole polarisability is origin independent, the quadrupole polarisability of nuclear magnetic shielding, like other properties needed to interpret response to an electric field gradient [30–32], is not uniquely defined, because its value depends on the origin of the coordinate system [33]. Moreover, its basic origin dependence, arising from that of the electric quadrupole operator that appears in the quantum mechanical definition, is complicated by the general question of the vector potential, which varies in a gauge translation [33]. Thus the quadrupole polarisability of nuclear magnetic shielding provides the easiest, non trivial, case to analyze for understanding how the two aspects, apparently related to one another, can be formally separated.

We show in this note that multipole polarisabilities of any order, calculated via the approach of continuous transformation of the origin of the current density—diamagnetic zero (CTOCD-DZ) [34], are invariant to a gauge translation, irrespective of the quality of the basis set employed. Their

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intrinsic origin dependence is only related to that of the electric multipole operator.

2 Nuclear magnetic shielding polarisabilities by the CTOCD–DZ method

Let us consider a diamagnetic molecule—a closed-shell system even under time reversal—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 $-e, m_e, \mathbf{r}_i, \hat{\mathbf{p}}_i, \hat{\mathbf{l}}_i = \mathbf{r}_i \times \hat{\mathbf{p}}_i, i = 1, 2 \cdots n$. Capital letters denote total operators, e.g., $\hat{\mathbf{P}} = \sum_{i=1}^n \hat{\mathbf{p}}_i, \hat{\mathbf{L}} = \sum_{i=1}^n \hat{\mathbf{l}}_i$. Corresponding quantities for nucleus I are indicated by $Z_I e$, M_I, $\mathbf{R}_I$, etc. Throughout this note we use SI units and the Einstein convention of summing over two repeated Greek subscripts. The molecule is in the electronic reference state $\left|\Psi_a^{(0)}\right\rangle \equiv |a\rangle$, denoted by $\left|\Psi_j^{(0)}\right\rangle$ the eigenstates to the unperturbed Hamiltonian, $H^{[0]}\left|\Psi_j^{(0)}\right\rangle = E_j^{[0]}\left|\Psi_j^{(0)}\right\rangle$, and $\hbar\omega_{ja}$ is the excitation energy of the transition $|j\rangle \leftarrow |a\rangle$.

The expression of the electronic energy of the molecule in the presence of two external perturbations, i.e., a uniform magnetic field, and a non-uniform electric field with uniform gradient, and of a permanent magnetic dipole at a nucleus, contains cross terms which account for linear and non-linear response. Including terms up to third-order in perturbation theory,

$$
\begin{aligned}
W_a = {} & W_a^{(0)} + \sigma^I_{\alpha\beta} m_{I\alpha} B_\beta \\
& + \varsigma^I_{\alpha\beta,\gamma} m_{I\alpha} B_\beta E_\gamma + \varsigma^I_{\alpha\beta,\gamma\delta} m_{I\alpha} B_\beta E_{\delta\gamma},
\end{aligned}
\tag{1}
$$

where $W_a^{(0)}$ is the energy of the isolated molecule, E_α, B_α, and $E_{\beta\alpha} \equiv \nabla_\beta E_\alpha$ indicate electric field, magnetic field, and electric field gradient at the origin of the coordinate system, and $m_{I\alpha}$ is an intrinsic magnetic dipole at nucleus I. $\sigma^I_{\alpha\beta}$ is the nuclear magnetic shielding in the absence of additional external electric perturbations [35,36], $\varsigma^I_{\alpha\beta,\gamma}$ and $\varsigma^I_{\alpha\beta,\gamma\delta}$ rationalize the non-linear response of the electron cloud to first order in the external electric perturbations.

The magnetic shielding at nucleus I, when a non-uniform electric field with a uniform gradient is switched on, becomes [1,33]

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

The tensors $\varsigma^I_{\alpha\beta,\gamma}$ and $\varsigma^I_{\alpha\beta,\gamma\delta}$ are colloquially referred to as dipole and quadrupole shielding polarisabilities, or nuclear magnetic hypershieldings.

Molecular properties can be described via the following response functions

$$
\left\{\hat{A}, \hat{B}\right\}_{-1} \equiv \frac{2}{\hbar} \sum_{i \neq a} \omega_{ia}^{-1} \Re \left\{ \left\langle a \left| \hat{A} \right| i \right\rangle \left\langle i \left| \hat{B} \right| a \right\rangle \right\}, \tag{3}
$$

$$
\begin{aligned}
\left\{\hat{A}, \hat{B}, \hat{C}\right\}_{-2} \equiv {} & \mathbf{S}\left(\hat{A}, \hat{B}, \hat{C}\right) \\
& \times \left(\frac{1}{\hbar^2} \sum_{j \neq a} \sum_{k \neq a} \omega_{ja}^{-1} \omega_{ka}^{-1} \left\langle a \left| \hat{A} \right| j \right\rangle \left\langle j \left| \overline{\hat{B}} \right| k \right\rangle \left\langle k \left| \hat{C} \right| a \right\rangle \right),
\end{aligned}
\tag{4}
$$

where overlined fluctuation operators are defined

$$
\overline{\hat{A}} \equiv \hat{A} - \left\langle a \left| \hat{A} \right| a \right\rangle, \tag{5}
$$

and the symbol $\mathbf{S}(\ldots)$ indicates the sum of all the terms obtained by permuting the operators within brackets.

The electronic operators for electric dipole, magnetic dipole, and electric quadrupole are [33,37]

$$
\hat{\mu}_\alpha = -e \sum_{i=1}^n r_{i\alpha} = -e \hat{R}_\alpha, \tag{6}
$$

$$
\hat{m}_\alpha = -\frac{e}{2m_e} \sum_{i=1}^n \hat{l}_{i\alpha} = -\frac{e}{2m_e} \hat{L}_\alpha, \tag{7}
$$

$$
\hat{\mu}_{\alpha\beta} = -\frac{e}{2} \sum_{i=1}^n r_{i\alpha} r_{i\beta} \equiv -\frac{e}{2} \sum_{i=1}^n \left(r_\alpha r_\beta\right)_i . \tag{8}
$$

The ith electron of the molecule exerts an instantaneous electric field on nucleus I,

$$
\mathbf{E}_I^i = \frac{1}{4\pi\epsilon_0} e \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}, \tag{9}
$$

then the total field of n electrons on the Ith nucleus is represented by the operator

$$
\hat{\mathbf{E}}_I^n = \sum_{i=1}^n \hat{\mathbf{E}}_I^i. \tag{10}
$$

The operator for the magnetic field induced by the n electron cloud at nucleus I in the absence of external perturbation is [33]

$$
\hat{\mathbf{B}}_I^n = -\frac{e}{m_e} \hat{\mathbf{M}}_I^n, \quad \hat{\mathbf{M}}_I^n = \frac{\mu_0}{4\pi} \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \times \hat{\mathbf{p}}_i. \tag{11}
$$

In a static external uniform magnetic field, the total magnetic field operator becomes

$$
\hat{B}_{I\alpha}^{n\prime} = \hat{B}_{I\alpha}^n - \hat{\sigma}_{\alpha\beta}^{\mathrm{d}I} B_\beta, \tag{12}
$$

where

$$
\hat{\sigma}_{\alpha\beta}^{\mathrm{d}I} = \frac{e}{2m_e c^2} \sum_{i=1}^n \left(r_{i\lambda} \hat{E}_{I\lambda}^i \delta_{\alpha\beta} - r_{i\alpha} \hat{E}_{I\beta}^i \right) \tag{13}
$$

defines the operator for the diamagnetic contribution to magnetic shielding at nucleus I. The auxiliary Hermitian operator

$$\hat{T}^{n}_{I\alpha\beta}(\mathbf{r}') = \frac{1}{2}\sum_{i=1}^{n}\left[\left(r_{i\alpha} - r'_{\alpha}\right)\hat{M}^{i}_{I\beta} + \hat{M}^{i}_{I\beta}\left(r_{i\alpha} - r'_{\alpha}\right)\right] \quad (14)$$

will be used in the CTOCD–DZ approach.

Within the common origin (CO) formulation by Ramsey [35,36], the diamagnetic contribution to nuclear shielding is evaluated in a reference frame with origin $\mathbf{r}'$ as the expectation value

$$\sigma^{\mathrm{d}I}_{\alpha\beta} = \frac{e}{2m_e c^2}\left\langle a\left|\sum_{i=1}^{n}\left[\left(r_{i\lambda}-r'_{\lambda}\right)\hat{E}^{i}_{I\lambda}\delta_{\alpha\beta}-\left(r_{i\alpha}-r'_{\alpha}\right)\hat{E}^{i}_{I\beta}\right]\right|a\right\rangle, \quad (15)$$

and, choosing the same origin for the angular momentum in eq. (7), the total nuclear magnetic shielding is

$$\sigma^{I}_{\alpha\beta} = \sigma^{\mathrm{p}I}_{\alpha\beta} + \left\langle a|\hat{\sigma}^{\mathrm{d}I}_{\alpha\beta}|a\right\rangle, \quad \sigma^{\mathrm{p}I}_{\alpha\beta} = -\left\{\hat{B}^{n}_{I\alpha}, \hat{m}_{\beta}\right\}_{-1}. \quad (16)$$

The higher-rank tensors $\varsigma^{I}_{\alpha\beta,\gamma}$ and $\varsigma^{I}_{\alpha\beta,\gamma\delta}$ in relationships (1) and (2) are the sum of diamagnetic and paramagnetic contributions obtained via Rayleigh–Schrödinger perturbation theory (RSPT) [33],

$$\varsigma^{I}_{\alpha\beta,\gamma} = \varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma} + \varsigma^{\mathrm{d}I}_{\alpha\beta,\gamma}, \quad (17)$$

$$\varsigma^{\mathrm{d}I}_{\alpha\beta,\gamma} = \left\{\hat{\sigma}^{\mathrm{d}I}_{\alpha\beta}, \hat{\mu}_{\gamma}\right\}_{-1}, \quad (18)$$

$$\varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma} = -\left\{\hat{B}^{n}_{I\alpha}, \hat{m}_{\beta}, \hat{\mu}_{\gamma}\right\}_{-2}, \quad (19)$$

$$\varsigma^{I}_{\alpha\beta,\gamma\delta} = \varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma\delta} + \varsigma^{\mathrm{d}I}_{\alpha\beta,\gamma\delta}, \quad (20)$$

$$\varsigma^{\mathrm{d}I}_{\alpha\beta,\gamma\delta} = \left\{\hat{\sigma}^{\mathrm{d}I}_{\alpha\beta}, \hat{\mu}_{\gamma\delta}\right\}_{-1}, \quad (21)$$

$$\varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma\delta} = -\left\{\hat{B}^{n}_{I\alpha}, \hat{m}_{\beta}, \hat{\mu}_{\gamma\delta}\right\}_{-2}. \quad (22)$$

Within the CTOCD–DZ method [34], the diamagnetic term, eq. (15), is replaced by a Δ contribution,

$$\sigma^{\Delta I}_{\alpha\beta} = -\frac{e^2}{2m_e^2}\epsilon_{\beta\lambda\mu}\left\{\hat{P}_{\lambda}, \hat{T}^{n}_{I\mu\alpha}\right\}_{-1}, \quad (23)$$

allowing for relationship (14). Thus the total CTOCD–DZ magnetic shielding becomes

$$\sigma^{I}_{\alpha\beta} = \sigma^{\mathrm{p}I}_{\alpha\beta} + \sigma^{\Delta I}_{\alpha\beta}. \quad (24)$$

3 Invariance of the CTOCD–DZ approach to a gauge translation

Electric multipole polarisabilities of nuclear magnetic shielding defined within the CTOCD–DZ scheme are invariant to a gauge translation, see eq. (28). To prove this, consider the one-electron Hamiltonian

$$\hat{h} = \frac{1}{2m_e}(\hat{\mathbf{p}} + e\mathbf{A})^2 + V. \quad (25)$$

The vector potential $\mathbf{A}$ contains two terms,

$$\mathbf{A}^{\mathbf{B}} = \frac{1}{2}\mathbf{B}\times\mathbf{r},$$
$$\mathbf{A}^{\mathbf{m}_I} = \frac{\mu_0}{4\pi}\mathbf{m}_I \times \frac{(\mathbf{r}-\mathbf{R}_I)}{|\mathbf{r}-\mathbf{R}_I|^{-3}} \equiv \frac{1}{ec^2}\mathbf{m}_I\times\mathbf{E}_I, \quad (26)$$

related to the magnetic field $\mathbf{B}$ and to the nuclear magnetic dipole $\mathbf{m}_I$. The electric field $\mathbf{E}_I$ at nucleus I is defined in eq. (9). A change of coordinate system is specified by an arbitrary shift vector $\mathbf{d}$. For two different origins, a translation

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d} \quad (27)$$

is equivalent to a transformation of the vector potential within the Coulomb gauge

$$A^{\mathbf{B}'}_{\alpha} \rightarrow A^{\mathbf{B}''}_{\alpha} = A^{\mathbf{B}'}_{\alpha} + \nabla_{\alpha} f, \quad (28)$$

in which

$$A^{\mathbf{B}''}_{\alpha} = \frac{1}{2}\epsilon_{\alpha\beta\gamma}B_{\beta}(r_{\gamma} - r''_{\gamma}), \quad f = (\mathbf{r}'' - \mathbf{r}')\cdot\mathbf{A}^{\mathbf{B}'}. \quad (29)$$

In the gauge translation (28)–(29), the one-electron Hamiltonian

$$\hat{h}^{\mathbf{B}} = \frac{e}{m_e}A^{\mathbf{B}}_{\alpha}\hat{p}_{\alpha} \equiv \frac{e}{2m_e}B_{\alpha}\hat{l}_{\alpha},$$

obtained from the kinetic term in eq. (25), changes as

$$\hat{h}^{\mathbf{B}''} = \hat{h}^{\mathbf{B}'} - \frac{e}{2m_e}\epsilon_{\alpha\beta\gamma}B_{\alpha}d_{\beta}\hat{p}_{\gamma}. \quad (30)$$

The cross product between the vector potentials in eq. (25) also changes,

$$A^{\mathbf{m}_I}_{\alpha}A^{\mathbf{B}''}_{\alpha} = A^{\mathbf{m}_I}_{\alpha}A^{\mathbf{B}'}_{\alpha} + A^{\mathbf{m}_I}_{\alpha}\nabla_{\alpha} f, \quad (31)$$

and the transformation law of the diamagnetic contribution to the one-electron second-order Hamiltonian in eq. (25) is

$$\hat{h}^{\mathbf{m}_I\mathbf{B}''} = \frac{e^2}{m_e}\mathbf{A}^{\mathbf{m}_I}\cdot\mathbf{A}^{\mathbf{B}''} = \hat{h}^{\mathbf{m}_I\mathbf{B}'} + \frac{e^2}{m_e}\mathbf{A}^{\mathbf{m}_I}\cdot\nabla f. \quad (32)$$

Within the common origin approach [35,36]

$$\frac{e^2}{m_e}A^{\mathbf{m}_I}_{\alpha}\nabla_{\alpha} f = \frac{e}{2m_e c^2}(E_{I\gamma}d_{\beta} - E_{I\delta}d_{\delta}\delta_{\beta\gamma})m_{I\beta}B_{\gamma}. \quad (33)$$

The CTOCD–DZ scheme for magnetic shielding is obtained replacing the scalar product in eqs. (31)–(32) by the commutator [34,38]

$$A^{\mathbf{m}_I}_\alpha A^{\mathbf{B}''}_\alpha = \frac{i}{2\hbar} B_\gamma m_{I\delta}\epsilon_{\alpha\beta\gamma}\left[r_\alpha, (r_\beta - r''_\beta)\hat{M}_{I\delta}\right]. \tag{34}$$

Analogously, the gauge term in relationship (33) is replaced by the commutator

$$\frac{e^2}{m_e} A^{\mathbf{m}_I}_\alpha \nabla_\alpha f = -\frac{ie^2}{2\hbar m_e} B_\gamma m_{I\delta}\epsilon_{\alpha\beta\gamma}\left[r_\alpha, \hat{M}_{I\delta}\right] d_\beta. \tag{35}$$

Within the CTOCD–DZ scheme, this procedure is equivalent to the change of coordinate system (27). The CTOCD–DZ equations for a molecule with n electrons are obtained [34, 38] by inserting the resolution of the identity $\sum_i^\infty |j\rangle\langle j|$ within the commutators (34) and (35) and allowing for the hypervirial relation

$$\left\langle a\left|\hat{P}_\alpha\right|i\right\rangle = -i m_e\omega_{ia}\left\langle a\left|\hat{R}_\alpha\right|i\right\rangle. \tag{36}$$

In the change of gauge origin, eq. (27), the transformation law of operator (14) is

$$\hat{T}^n_{I\alpha\beta}(\mathbf{r}'') = \hat{T}^n_{I\alpha\beta}(\mathbf{r}') - d_\alpha \hat{M}^n_{I\beta}, \tag{37}$$

therefore gauge terms with equal value and opposite sign cancel by summing the terms on the r.h.s. of relationships that define paramagnetic and diamagnetic contributions, e.g.,

$$\sigma^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\mathrm{p}I}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{2m_e^2} d_\delta\epsilon_{\beta\gamma\delta}\left\{\hat{M}^n_{I\alpha}, \hat{P}_\gamma\right\}_{-1}, \tag{38}$$

$$\sigma^{\Delta I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\Delta I}_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{2m_e^2} d_\delta\epsilon_{\beta\gamma\delta}\left\{\hat{M}^n_{I\alpha}, \hat{P}_\gamma\right\}_{-1}. \tag{39}$$

The second equation (39) replaces that for the CO diamagnetic contribution, obtained via eq. (33)

$$\sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}') - \frac{e}{2m_e c^2}\left(d_\gamma\left\langle a\left|\hat{E}^n_{I\gamma}\right|a\right\rangle\delta_{\alpha\beta} - d_\alpha\left\langle a\left|\hat{E}^n_{I\beta}\right|a\right\rangle\right). \tag{40}$$

The sum rule for invariance

$$\left\{\hat{P}_\alpha, \hat{M}^n_{I\beta}\right\}_{-1} = \frac{m_e}{ec^2}\epsilon_{\alpha\beta\gamma}\left\langle a\left|\hat{E}^n_{I\gamma}\right|a\right\rangle \tag{41}$$

is satisfied by symmetry in some special situations, e.g., for the carbon shielding in methane. Generally, within current procedures for molecular orbitals via linear combination of atomic orbitals (MO-LCAO), it is satisfied in the limit of a complete basis set. The CO scheme would give the same shielding for any origin only in this ideal case. On the other hand, the total $\sigma^I_{\alpha\beta} = \sigma^{\mathrm{p}I}_{\alpha\beta} + \sigma^{\Delta I}_{\alpha\beta}$ is gauge invariant for an arbitrary basis set. Exactly the same procedure (28)–(36) is applied, for any electric multipole, to evaluate CTOCD–DZ multipole polarisabilities which are also invariant in a gauge translation.

The importance of this result cannot be overemphasized. It implies that, in actual CTOCD–DZ calculations of multipole polarisabilities of nuclear magnetic shieldings, the origin of the magnetic operators (7) and (14) can be chosen *ad libitum*. However, in some codes, e.g., SYSMO [39], the matrix elements of (14) are conveniently evaluated by fixing the origin on the nucleus in question. Other choices are possible, e.g., within the DALTON code [40].

4 Origin dependence of quadrupole polarisabilities of nuclear magnetic shielding

In a change (27) of coordinate system, the quadrupole operator varies as

$$\hat{\mu}_{\alpha\beta}(\mathbf{r}'') = \hat{\mu}_{\alpha\beta}(\mathbf{r}') - \frac{1}{2}\hat{\mu}_\alpha(\mathbf{r}')d_\beta - \frac{1}{2}\hat{\mu}_\beta(\mathbf{r}')d_\alpha - \frac{1}{2}ne\, d_\alpha d_\beta, \tag{42}$$

and the transformation laws for the fourth-rank quadrupole shielding polarizability within the CTOCD–DZ scheme are [33]

$$\begin{aligned}\varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma\delta}(\mathbf{r}'') &= \varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma\delta}(\mathbf{r}') - \frac{1}{2}d_\delta\, \varsigma^{\mathrm{p}I}_{\alpha\beta,\gamma}(\mathbf{r}') - \frac{1}{2}d_\gamma\, \varsigma^{\mathrm{p}I}_{\alpha\beta,\delta}(\mathbf{r}')\\ &\quad - \frac{e}{2m_e}d_\lambda\epsilon_{\beta\lambda\mu}\left\{\hat{B}^n_{I\alpha}, \hat{P}_\mu, \hat{\mu}_{\gamma\delta}(\mathbf{r}')\right\}_{-2}\\ &\quad + \frac{e}{4m_e}d_\lambda\epsilon_{\beta\lambda\mu}\left(d_\delta\left\{\hat{B}^n_{I\alpha}, \hat{P}_\mu, \hat{\mu}_\gamma(\mathbf{r}')\right\}_{-2}\right.\\ &\quad \left. + d_\gamma\left\{\hat{B}^n_{I\alpha}, \hat{P}_\mu, \hat{\mu}_\delta(\mathbf{r}')\right\}_{-2}\right),\end{aligned} \tag{43}$$

$$\begin{aligned}\varsigma^{\Delta I}_{\alpha\beta,\gamma\delta}(\mathbf{r}'') &= \varsigma^{\Delta I}_{\alpha\beta,\gamma\delta}(\mathbf{r}') - \frac{1}{2}d_\delta\, \varsigma^{\Delta I}_{\alpha\beta,\gamma}(\mathbf{r}') - \frac{1}{2}d_\gamma\, \varsigma^{\Delta I}_{\alpha\beta,\delta}(\mathbf{r}')\\ &\quad + \frac{e}{2m_e}d_\lambda\epsilon_{\beta\lambda\mu}\left\{\hat{B}^n_{I\alpha}, \hat{P}_\mu, \hat{\mu}_{\gamma\delta}(\mathbf{r}')\right\}_{-2}\\ &\quad - \frac{e}{4m_e}d_\lambda\epsilon_{\beta\lambda\mu}\left(d_\delta\left\{\hat{B}^n_{I\alpha}, \hat{P}_\mu, \hat{\mu}_\gamma(\mathbf{r}')\right\}_{-2}\right.\\ &\quad \left. + d_\gamma\left\{\hat{B}^n_{I\alpha}, \hat{P}_\mu, \hat{\mu}_\delta(\mathbf{r}')\right\}_{-2}\right).\end{aligned} \tag{44}$$

The terms of same magnitude but opposite sign on the r.h.s. of eqs. (43) and (44), arising from the change of gauge (28) and (35) cancel out. Therefore the gauge-invariant CTOCD–DZ quadrupole polarisability varies as [33]

$$\varsigma^{I}_{\alpha\beta,\gamma\delta}(\mathbf{r}'') = \varsigma^{I}_{\alpha\beta,\gamma\delta}(\mathbf{r}') - \frac{1}{2}d_\delta\, \varsigma^{I}_{\alpha\beta,\gamma}(\mathbf{r}') - \frac{1}{2}d_\gamma\, \varsigma^{I}_{\alpha\beta,\delta}(\mathbf{r}'). \tag{45}$$

Its origin dependence arises only from relationship (42).

5 A numerical study of the water molecule

The magnitude of quadrupole polarisabilities of hydrogen and oxygen nuclei in the water molecule was estimated at the coupled Hartree–Fock (CHF) level of accuracy via an aug-cc-pCVDZ basis set [41,42]. The results are given in atomic units (au) in Tables 1 and 2. The conversion factor to SI units is $(ea_0^2/E_h) \times 10^{-6} = 1.029\ 085\ 93 \times 10^{-28}$ V^{-1} m^2 via the CODATA tabulation [43].

One can ask whether the obtained numbers are in a range detectable by experiment. The biggest value calculated for the $zzzy$ component of ^{1}H is ≈46.6 au, corresponding to $\approx 5 \times 10^{-27}$ V^{-1} m^2. To observe approximately 0.5 ppm, in an experiment in ordered phase, an electric field gradient of the order of 1/100 of au, i.e., as big as $\approx 1 \times 10^{20}$ V m^{-2} should be applied, which would seem out of reach on a macroscopic scale. The calculated $zzxx$ component of ^{17}O is one order of magnitude bigger, ≈692 au in absolute value. However, ^{17}O is most probably all but an ideal probe, due to low receptivity and high nuclear spin (I=5/2), which may cause signal broadening. On the other hand, strong internal gradients can arise within a molecular domain. Therefore, quadrupole shielding polarisabilities may be useful to rationalize the chemical shift in terms of contributions arising from chemical functions in the vicinity of the probe.

Table 1 CTOCD–DZ quadrupole polarisability of ^{1}H nuclear magnetic shielding in H_2O (in ppm au) by aug-cc-pCVDZ basis set

$\alpha\beta\gamma\delta$[a]	$\varsigma^{\Delta H}_{\alpha\beta\gamma\delta}(H)$	$\varsigma^{pH}_{\alpha\beta\gamma\delta}(H)$	$\varsigma^{\Delta H}_{\alpha\beta\gamma\delta}(O)$	$\varsigma^{pH}_{\alpha\beta\gamma\delta}(O)$	$\varsigma^{(\Delta+p)H}_{\alpha\beta\gamma\delta}$
xxxx	28.86	−13.83	9.08	5.95	15.03
xxyy	3.55	−50.16	−36.06	−10.55	−46.61
xxyz	4.38	52.40	31.99	24.79	56.78
xxzz	1.43	−9.08	−16.52	8.87	−7.65
xyxy	7.98	2.25	4.38	5.85	10.23
xyxz	2.05	−14.50	−3.23	−9.22	−12.45
xzxy	1.12	−10.85	−3.53	−6.20	−9.73
xzxz	10.44	−7.46	3.63	−0.65	2.98
yxxy	4.97	3.61	9.52	−0.94	8.58
yxxz	0.72	−17.15	−4.25	−12.18	−16.43
yyxx	10.24	6.07	8.30	8.01	16.31
yyyy	4.06	−12.12	−6.99	−1.09	−8.08
yyyz	11.09	27.12	20.71	17.50	38.21
yyzz	6.92	−22.88	−8.18	−7.78	−15.96
yzxx	3.12	24.97	0.61	27.48	8.09
yzyy	5.00	−31.70	−9.24	−17.46	−26.70
yzyz	1.60	21.80	14.00	9.40	23.40
yzzz	9.06	−26.39	−10.45	−6.90	−17.35
zxxy	1.40	−18.17	−8.93	−7.84	−16.77
zxxz	9.57	−9.42	8.15	−8.00	0.15
zyxx	2.56	25.99	4.35	24.20	28.55
zyyy	11.19	−47.78	−14.25	−22.34	−36.59
zyyz	3.83	17.97	12.85	8.95	21.80
zyzz	8.48	−26.58	0.45	−18.55	−18.10
zzxx	2.56	19.34	4.87	17.03	21.90
zzyy	−0.51	−43.64	−33.35	−10.80	−44.15
zzzy	38.30	7.98	19.93	26.65	46.58
zzzz	11.97	−7.95	1.62	2.40	4.02

H ≡(0, 1.43153, −0.98526); O ≡(0, 0, 0.12414) in bohr

[a] Nonvanishing components. The entry within the brackets specifies the gauge origin

Table 2 CTOCD–DZ quadrupole polarisability of ^{17}O nuclear magnetic shielding in H_2O (in ppm au) by aug-cc-pCVDZ basis set

$\alpha\beta\gamma\delta$[a]	$\varsigma^{\Delta O}_{\alpha\beta\gamma\delta}(O)$	$\varsigma^{pO}_{\alpha\beta\gamma\delta}(O)$	$\varsigma^{\Delta O}_{\alpha\beta\gamma\delta}(H)$	$\varsigma^{pO}_{\alpha\beta\gamma\delta}(H)$	$\varsigma^{(\Delta+p)O}_{\alpha\beta\gamma\delta}$
xxxx	22.94	−73.41	46.69	−97.16	−50.47
xxyy	12.41	419.75	8.67	423.49	432.16
xxzz	10.83	−121.84	−7.02	−103.99	−111.01
xyxy	3.07	−100.33	14.96	−112.22	−97.26
xzxz	4.23	61.48	4.23	61.48	65.71
yxxy	2.00	253.30	−91.82	347.12	255.30
yyxx	20.14	−470.14	153.22	−603.22	−450.00
yyyy	22.48	383.12	−90.52	496.12	405.60
yyzz	19.02	425.44	316.06	128.40	444.46
yzyz	3.94	−384.11	3.94	−384.11	−380.15
zxxz	3.90	365.56	54.86	314.60	369.46
zyyz	2.84	−501.69	66.61	−565.46	−498.85
zzxx	17.04	−708.73	17.03	−708.72	−691.69
zzyy	14.13	495.51	14.13	495.51	509.64
zzzz	21.24	250.18	21.22	250.20	271.42

H ≡(0, 1.43153, −0.98526); O ≡(0, 0, 0.12414) in bohr

[a] Nonvanishing components. The entry within the brackets specifies the gauge origin

Diamagnetic and paramagnetic contributions for two gauge origins (hydrogen and oxygen nuclei) are different, but their sum is the same, as shown in the tables. The Δ -diamagnetic and paramagnetic contributions to the components $xzxz$, $yzyz$, $zzxx$, $zzyy$, and $zzzz$ of the oxygen polarisability are invariant (see Table 2). In all cases the numerical tests allowing for a small basis set MOLCAO scheme verify the invariance of the CTOCD–DZ quadrupole polarisabilities in a gauge translation discussed in Sect. 3.

To evaluate the quadrupole polarisabilities for any other origin of the quadrupole operator, the dipole electric polarisabilities reported in Table 3 are needed. The conversion factor to SI units [43] is $(ea_0/E_h) \times 10^{-6} = 1.944\ 690\ 57 \times 10^{-18}$ V^{-1} m. The values reported in Tables 1 and 2 should be regarded as preliminary estimates. Further investigations necessary to evaluate basis set effects and convergence to the CHF limit are planned for future works.

Table 3 CTOCD–DZ dipole polarisability of ^{1}H and ^{17}O nuclear magnetic shielding in H_2O (in ppm au) by aug-cc-pCVDZ basis set

$\alpha\beta\gamma^a$	$\sigma^{(\Delta+p)H}_{\alpha\beta,\gamma}$	$\alpha\beta\gamma^\ddagger$	$\sigma^{(\Delta+p)H}_{\alpha\beta,\gamma}$	$\alpha\beta\gamma^\ddagger$	$\sigma^{(\Delta+p)O}_{\alpha\beta,\gamma}$
xxy	−85.30	yzy	−30.61	xxz	−286.18
xxz	53.12	yzz	24.02	xzx	97.13
xyx	33.99	zxx	−5.78	yyz	−588.22
xzx	−21.81	zyy	−21.26	yzy	442.92
yxx	9.85	zyz	54.82	zxx	−83.96
yyy	−48.80	zzy	−88.38	zyy	536.23
yyz	42.69	zzz	24.73	zzz	−351.01

H ≡(0, 1.43153, −0.98526); O ≡(0, 0, 0.12414) in bohr

[a] Nonvanishing components

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