Theor Chem Acc (2006) 116: 420–426
DOI 10.1007/s00214-006-0093-5

REGULAR ARTICLE

Paolo Lazzeretti

Forces on the nuclei of a molecule in optical fields

Received: 9 November 2004 / Accepted: 7 March 2005 / Published online: 21 February 2006

Abstract The electric Lorentz forces acting upon the nuclei of a vibrating molecule cause variations of dynamical regime and determine the intensity of the absorbed radiation. These forces, depending on the local electric field, can be evaluated by frequency-dependent electric and electromagnetic shielding and hypershielding tensors at the nuclei. A general expression from time-dependent perturbation theory is all that one needs to rationalize the molecular response by predicting the effective electric field at the nuclei of a molecule perturbed by an external monochromatic wave. The electric and electromagnetic hypershieldings are connected with the geometrical derivatives of the frequency-dependent dipole polarisability and of the optical rotatory power, respectively. Intensities in Raman spectroscopy and in vibrational Raman optical activity, usually interpreted in terms of these derivatives, can also be discussed via nuclear electromagnetic hypershieldings. Conditions for translational and rotational invariance can be expressed via sum rules for the dynamic hypershieldings.

1 Introduction

Two descriptions of infra-red (IR) intensities are available within the harmonic approximation. The first one is given in terms of the square of derivatives, with respect to normal coordinates, of the intrinsic electric dipole moment $\mathcal{M}_\alpha^{(0)}$ of a molecule in the electronic reference state $\Psi_a^{(0)}$. The second one emphasizes the role of the effective electric Lorentz forces acting upon the charged nuclei and driving a change of dynamical regime. These descriptions are equivalent, as can be shown by applying the Hellmann-Feynman theorem [1–4]. The Lorentz force at a given nucleus is obtained via the local electric field. This is the vector sum of the field of the perturbing radiation and the field generated by the electrons of the molecule in the presence of the perturbation.

The contributions from the electrons are evaluated via the approach of nuclear electric shielding tensors first introduced by Sambe [5] for diatomics, extended to polyatomics [1,2, 6–8], and to the dynamic case [9–11]. The static nuclear electric shielding is related to the geometrical derivatives of the molecular electric dipole moment $\mathcal{M}_\alpha^{(0)}$, i.e., the atomic polar tensor (APT) [12–16] as shown in Refs. [1,11,17,18]. Therefore, both approaches are viable to interpret IR intensities either in terms of the square of the transition dipole moment, or the square of the electric dipole shielding at the nuclei.

An analogous treatment is available for the differential absorption of left- and right-circularly polarised light in vibrational circular dichroism (VCD). In this spectroscopy, the electric Lorentz forces at the nuclei are induced by the time-derivative of the magnetic field, i.e., by an out-of-phase magnetic field, of the external radiation [19,20]. The molecular response property used to rationalize absorption intensities is, in this case, the nuclear electromagnetic shielding tensor [11,19–21], recently rediscovered [22], connected with the Stephens integral [23] and with the atomic axial tensor (AAT) [24].

Rotational Raman intensities are proportional to the square of the anisotropy of molecular polarisability, and vibrational Raman intensities to the square of the transition polarisability, i.e., the square of the geometrical derivatives of polarisability [25,26]. The concept of static nuclear electric hypershielding has been first proposed by Fowler and Buckingham to account for quadratic response in the external electric field. They showed its connection with Raman intensities [2,27]. Estimates of nuclear electric hypershieldings have been reported for diatomics [28,29] and for polyatomics [30] at the Hartree-Fock level of accuracy.

Intensities in vibrational Raman optical activity (VROA) also depend on the geometrical derivatives of the optical rotatory power tensor [31–34].

The present paper is aimed at: (i) generalizing the definition of nuclear electromagnetic hypershieldings to the

Article submitted for the issue in honour of J. P. Malrieu

P. Lazzeretti
Dipartimento di Chimica,
Università degli Studi di Modena e Reggio Emilia,
via G. Campi 183, 41100 Modena, Italy
E-mail: lazzeret@unimore.it

time-dependent case, (ii) connecting these quantities with geometrical derivatives of dynamical polarisability and optical rotatory power, and (iii) obtaining conditions for translational and rotational invariance in the form of quantum-mechanical sum rules.

Forces acting on the nuclei of a molecule as a result of nuclear displacements are discussed in Sect. 2. The static nuclear electric hypershielding tensor is examined in Sect. 3. The more general case of a dynamic perturbation is analyzed in Sect. 4, introducing the Hellmann-Feynman geometrical derivatives of the frequency-dependent electric dipole polarisability and of the optical rotatory power. Connections with third-rank tensors, which can respectively be referred to as dynamic electric and electromagnetic hypershielding at the nucleus, are established. Conditions for translational and rotational invariance are discussed in Sect. 5.

2 Forces at the nuclei of a molecule

The notation adopted in Refs. [11,35] is used. For a molecule with n electrons and N nuclei, charge, mass, position, canonical, and angular momentum of the i-th 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, $\mathbf{R}_I$, $\mathbf{P}_I$, *etc.* Capital letters are used for collective electronic operators, e.g., $\hat{\mathbf{R}} = \sum_{i=1}^{n} \mathbf{r}_i$, $\hat{\mathbf{P}} = \sum_{i=1}^{n} \mathbf{p}_i$, *etc.* Standard tensor notation is employed, e.g., $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor and the Einstein convention of implicit summation over two repeated Greek subscripts is in force. The real and imaginary parts of a quantity are denoted by $\Re$ and $\Im$, respectively.

The electronic Hamiltonian $\hat{H}^{(0)}$ of the isolated molecule contains a kinetic term $\hat{T}_n$, a nuclear–electron attraction term

$$\hat{V}_{nN} = -\sum_{I=1}^{N}\sum_{i=1}^{n} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_i|}, \tag{1}$$

an electron repulsion term $\hat{V}_{nn}$, and a nuclear repulsion

$$V_{NN} = \frac{1}{2}\sum_{I=1}^{N}\sum_{J\neq I}^{N} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \tag{2}$$

The Born-Oppenheimer (BO) approximation is retained. It is assumed that the molecule has a reference geometrical configuration, which may or may not coincide with the equilibrium configuration. If the nuclei are displaced by small shifts $\delta\mathbf{R}_I$,

$$\mathbf{R}_I \to \mathbf{R}_I + \delta\mathbf{R}_I, \quad I = 1, 2 \ldots N, \tag{3}$$

any function $f(\mathbf{R}_I)$ will undergo an active transformation described by the corresponding translation operator

$$\hat{\mathcal{T}}_I(-\delta\mathbf{R}_I) = \exp\left(\frac{i}{\hbar}\delta\mathbf{R}_I \cdot \hat{\mathbf{P}}_I\right) = \exp\left(\delta\mathbf{R}_I \cdot \nabla_I\right). \tag{4}$$

The translations Eq. (3) change terms of $\hat{H}^{(0)}$ depending on the electron–nucleus distances, e.g., in Eq. (1)

$$\begin{aligned}\hat{\mathcal{T}}_I(-\delta\mathbf{R}_I)\frac{1}{|\mathbf{r}_i - \mathbf{R}_I|} &= \frac{1}{|\mathbf{r}_i - \mathbf{R}_I - \delta\mathbf{R}_I|}\\ &= (1 + \delta\mathbf{R}_I \cdot \nabla_I + \cdots)\frac{1}{|\mathbf{r}_i - \mathbf{R}_I|}\\ &= \frac{1}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{(\mathbf{r}_i - \mathbf{R}_I)\cdot\delta\mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} + \cdots\end{aligned} \tag{5}$$

Analogous variations are caused by a shift of nuclear positions in Eq. (2) which describes nuclear repulsions. Defining the global translation operator

$$\hat{\mathcal{T}}_N(-\delta\mathbf{R}_I) = \Pi_{I=1}^{N}\hat{\mathcal{T}}_I(-\delta\mathbf{R}_I) = \exp\left(\sum_{I=1}^{N}\delta\mathbf{R}_I \cdot \nabla_I\right), \tag{6}$$

we obtain a Taylor series for the unperturbed potential

$$\begin{aligned}&\exp\left(\sum_{I=1}^{N}\delta\mathbf{R}_I \cdot \nabla_I\right)\left(\hat{V}_{nN} + V_{NN}\right)\\ &\to \left(\hat{V}_{nN} + V_{NN}\right) - \left(\sum_{I=1}^{N}\hat{\mathbf{F}}_I^{n} + \sum_{I=1}^{N}\mathbf{F}_I^{N-I}\right)\cdot\delta\mathbf{R}_I + \cdots,\end{aligned} \tag{7}$$

where the operator for the force of n electrons on nucleus I

$$\hat{\mathbf{F}}_I^{n} = Z_I e\,\hat{\mathbf{E}}_I^{n}, \tag{8}$$

is related to the electric field of the electrons on that nucleus

$$\hat{\mathbf{E}}_I^{n} = e\sum_{i=1}^{n}\frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}. \tag{9}$$

The force of the other nuclei on nucleus I is

$$\mathbf{F}_I^{N-I} = Z_I e\sum_{K\neq I}^{N} Z_K e\frac{\mathbf{R}_I - \mathbf{R}_K}{|\mathbf{R}_I - \mathbf{R}_K|^3}. \tag{10}$$

In the presence of an external electric field $\mathbf{E}$ the Lorentz force on nucleus I is

$$\mathbf{F}_I^{\mathbf{E}} = Z_I e\mathbf{E}. \tag{11}$$

3 Hellmann-Feynman forces and static nuclear shieldings

The energy of a molecule in a static electric field is written as a Taylor series [36]

$$\begin{aligned}W = W^{(0)} &- \mathcal{M}_\alpha^{(0)}E_\alpha - \frac{1}{2}\alpha_{\alpha\beta}E_\alpha E_\beta\\ &-\frac{1}{6}\beta_{\alpha\beta\gamma}E_\alpha E_\beta E_\gamma + \cdots,\end{aligned} \tag{12}$$

where tensors of increasing rank denote intrinsic response properties, namely the permanent electric dipole $\mathcal{M}_\alpha^{(0)}$, the electric polarisability $\alpha_{\alpha\beta}$, and hyperpolarisability $\beta_{\alpha\beta\gamma}$.

On account of Eqs. (7) – (11), the molecular Hamiltonian is given as a perturbation expansion in the vicinity of the reference geometry

$$\hat{H}(\{\mathbf{R}_I\}, \mathbf{E}) = \hat{T}_n + \hat{V}_{nN} + \hat{V}_{nn} + V_{NN} - \sum_{I=1}^{N} \hat{\mathbf{F}}_I^n \cdot \delta\mathbf{R}_I - \sum_{I=1}^{N} \mathbf{F}_I^{N-I} \cdot \delta\mathbf{R}_I - \sum_{I=1}^{N} Z_I e\mathbf{E} \cdot \mathbf{R}_I - \hat{\boldsymbol{\mu}} \cdot \mathbf{E} \tag{13}$$

with

$$\hat{\mu}_\alpha = -e\hat{R}_\alpha, \tag{14}$$

the electronic operator for the electric dipole. The first-order electronic interaction is written as

$$\hat{H}^{\mathbf{E}} = -\hat{\mu}_\alpha E_\alpha. \tag{15}$$

If the Hellmann-Feynman theorem is satisfied, the average total force on nucleus I in the absence of external fields becomes the sum of an attractive electronic term and a simple classical repulsion term due to the remaining $N-I$ nuclei, e.g., for the reference electronic state $|a\rangle$ (usually the ground state)

$$-\nabla_I W_a^{(0)} = \left\langle a \left| \hat{\mathbf{F}}_I^n \right| a \right\rangle + \mathbf{F}_I^{N-I}. \tag{16}$$

This quantity vanishes identically for an equilibrium state. However, the derivative $\nabla_I W_j^{(0)}$ will be different from zero, in general, for the $|j\rangle$ excited eigenstate. For the sake of generality, we will assume that $|a\rangle$ is no equilibrium state.

The operator for the total force on nucleus I in the presence of the external field $\mathbf{E}$ is obtained from the Hamiltonian

$$-\frac{\partial \hat{H}(\{\mathbf{R}_I\}, \mathbf{E})}{\partial R_{I\gamma}} = \hat{F}_{I\gamma}^n + F_{I\gamma}^{N-I} + Z_I e E_\gamma. \tag{17}$$

The expectation value for the total average force is

$$-\left\langle \frac{\partial \hat{H}(\{\mathbf{R}_I\}, \mathbf{E})}{\partial R_{I\gamma}} \right\rangle = \left\langle \Psi_a^{(0)} + \Psi_a^{E_\delta} E_\delta + \Psi_a^{E_\delta E_\epsilon} E_\delta E_\epsilon \times \left| \hat{F}_{I\gamma}^n + F_{I\gamma}^{N-I} + Z_I e E_\gamma \right| \times \Psi_a^{(0)} + \Psi_a^{E_\eta} E_\eta + \Psi_a^{E_\eta E_\theta} E_\eta E_\theta \right\rangle, \tag{18}$$

where the first- and second-order functions, respectively

$$\left| \Psi_a^{E_\alpha} \right\rangle = \frac{1}{\hbar} \sum_{j \neq a} \omega_{ja}^{-1} |j\rangle \langle j|\hat{\mu}_\alpha|a\rangle, \tag{19}$$

and

$$\left| \psi_a^{E_\alpha E_\beta} \right\rangle = \frac{1}{\hbar^2} \left(\sum_{j\neq a} \sum_{k \neq a} \omega_{ja}^{-1} \omega_{ka}^{-1} |j\rangle \langle j|\hat{\mu}_\alpha|k\rangle \langle k|\hat{\mu}_\beta|a\rangle - \langle a|\hat{\mu}_\alpha|a\rangle \sum_{j\neq a} \omega_{ja}^{-2} |j\rangle \langle j|\hat{\mu}_\beta|a\rangle - \frac{1}{2} |a\rangle \sum_{j \neq a} \omega_{ja}^{-2} \langle a|\hat{\mu}_\alpha|j\rangle \langle j|\hat{\mu}_\beta|a\rangle \right), \tag{20}$$

are determined by the Rayleigh-Schrödinger perturbation theory [35]. The natural transition frequencies are defined by $\omega_{ja} = (W_j^{(0)} - W_a^{(0)})/\hbar$.

The static electric shielding and hypershielding tensors are obtained from the Hellmann-Feynman theorem [1,2,5–7,17,35], e.g., using Eqs. (12) and (18)

$$-\left.\frac{\partial^3 W}{\partial R_{I\gamma} \partial E_\alpha \partial E_\beta}\right|_{\mathbf{E}\to\mathbf{0}} = \frac{\partial}{\partial R_{I\gamma}} \alpha_{\alpha\beta} = \frac{\partial^2}{\partial E_\alpha \partial E_\beta} \left\langle -\frac{\partial \hat{H}(\{\mathbf{R}_I\}, \mathbf{E})}{\partial R_{I\gamma}} \right\rangle = Z_I e \phi_{\gamma,\alpha\beta}^I \tag{21}$$

where

$$\phi_{\alpha,\beta\gamma}^I = \mathbf{S}(\hat{E}_{I\alpha}^n, \hat{\mu}_\beta, \hat{\mu}_\gamma) \frac{1}{\hbar^2} \sum_{j\neq a} \sum_{k\neq a} \omega_{ja}^{-1} \omega_{ka}^{-1} \times \left\langle a \left| \hat{E}_{I\alpha}^n \right| j \right\rangle \left\langle j \left| \overline{\hat{\mu}}_\beta \right| k \right\rangle \langle k|\hat{\mu}_\gamma|a\rangle \tag{22}$$

is the static electric hypershielding [2,17,35] at nucleus I. The symbol $\mathbf{S}(\ldots)$ implies a summation of all the terms in which the operators within the brackets are permuted. Barred fluctuation operators are defined via

$$\overline{\hat{A}} \equiv \hat{A} - \left\langle a \left| \hat{A} \right| a \right\rangle. \tag{23}$$

Equation (21) explicitly connects nuclear electric hypershieldings to geometrical derivatives of electric polarisability. The electronic eigenstates

$$\left| \Psi_j^{(0)} \right\rangle \equiv |j\rangle$$

and the energy eigenvalues, $W_j^{(0)}$, are obtained by solving the eigenvalue problem for $\hat{H}^{(0)}$ within the BO approximation.

4 The dynamic electric field induced at a nucleus

The electric dipole induced in the electron cloud by an impinging electromagnetic field with pulsation ω is [11,36]

$$\Delta \langle \hat{\mu}_\alpha(t) \rangle = \alpha_{\alpha\beta} E_\beta(\mathbf{0}, t) + \frac{1}{2} \beta_{\alpha\beta\gamma} E_\beta(\mathbf{0}, t) E_\gamma(\mathbf{0}, t) + \frac{1}{6} \gamma_{\alpha\beta\gamma\delta} E_\beta(\mathbf{0}, t) E_\gamma(\mathbf{0}, t) E_\delta(\mathbf{0}, t) + \cdots + \kappa'_{\alpha\beta} \dot{B}_\beta(\mathbf{0}, t) \omega^{-1} + \cdots, \tag{24}$$

where $E_\alpha(\mathbf{0},t)$ and $B_\alpha(\mathbf{0},t)$ are the electric and magnetic fields at the origin of the coordinate system and a dot denotes partial derivative with respect to time.

Adopting the notation proposed by Orr and Ward [37] and Bishop [38] (OWB), the dynamic polarisability in the a reference state is written as

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1) = \frac{1}{\hbar}\sum_P \sum_{j\neq a} \frac{\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|a\rangle}{\omega_{ja}-\omega_\sigma}, \tag{25}$$

where $\sum_P$ means the sum over permutations of the pairs $(\hat{\mu}_\alpha/-\omega_\sigma)$ and $(\hat{\mu}_\beta/\omega_1)$, and $\omega_\sigma = \omega_1 \equiv \omega$.

Denoting by $\hat{m}_\alpha = -(e/2m_e c)\hat{L}_\alpha$ the magnetic dipole operator, the analogous relationship for the optical rotatory power is [35,36]

$$\kappa'_{\alpha\beta}(-\omega_\sigma;\omega_1) = \frac{i}{\hbar}\sum_P \sum_{j\neq a} \frac{\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\hat{m}_\beta|a\rangle}{\omega_{ja}-\omega_\sigma}, \quad (\hat{\mu}_\alpha/-\omega_\sigma) \leftrightarrow (\hat{m}_\beta/\omega_1) \tag{26}$$

and $\omega_\sigma = \omega_1 \equiv \omega$. Tensor (26) is related by

$$\kappa'_{\alpha\beta} = \omega\,\hat{\kappa}_{\alpha\beta} \tag{27}$$

to that defined in Refs. [11,34,35].

The third- and fourth-rank electric hyperpolarisabilities in the OWB notation [37,38] are

$$\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = \frac{1}{\hbar^2}\sum_P \sum_{j,k\neq a} \frac{\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\overline{\hat{\mu}_\gamma}|k\rangle\langle k|\hat{\mu}_\beta|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)}, \tag{28}$$

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{\hbar^3}\sum_P \left[\sum_{j,k,l\neq a} \frac{\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\overline{\hat{\mu}_\delta}|k\rangle\langle k|\overline{\hat{\mu}_\gamma}|l\rangle\langle l|\hat{\mu}_\beta|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1-\omega_2)(\omega_{la}-\omega_1)} - \sum_{j,k\neq a} \frac{\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\delta|a\rangle\langle a|\hat{\mu}_\gamma|k\rangle\langle k|\hat{\mu}_\beta|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)(\omega_{ka}+\omega_2)}\right], \tag{29}$$

where $\omega_\sigma = \omega_1+\omega_2+\omega_3$ and $\sum_P$ means the sum over all permutations of the pairs $(\hat{\mu}_\alpha/-\omega_\sigma)$, $(\hat{\mu}_\beta/\omega_1)$, $(\hat{\mu}_\gamma/\omega_2)$, $(\hat{\mu}_\delta/\omega_3)$.

The expression for the expectation value of the oscillating electric field induced at the position of nucleus I by the n electrons in the presence of the external electromagnetic field is obtained by time-dependent perturbation theory [34,37,39–41]

$$\begin{aligned}\Delta\left\langle \hat{E}^n_{I\alpha}(t)\right\rangle = & -\gamma^I_{\alpha\beta}E_\beta(\mathbf{0},t) \\ & +\frac{1}{2}\phi^I_{\alpha,\beta\gamma}E_\beta(\mathbf{0},t)E_\gamma(\mathbf{0},t)+\cdots \\ & +\xi'^I_{\alpha\beta}\dot{B}_\beta(\mathbf{0},t)\omega^{-1} \\ & +\psi'^I_{\alpha,\beta\gamma}E_\beta(\mathbf{0},t)\dot{B}_\gamma(\mathbf{0},t)\omega^{-1}+\cdots \\ & +\frac{1}{2}\rho^I_{\alpha,\beta\gamma}B_\beta(\mathbf{0},t)B_\gamma(\mathbf{0},t)+\cdots,\end{aligned} \tag{30}$$

with $\gamma^I_{\alpha\beta}$ and $\xi'^I_{\alpha\beta}$ the electric and electromagnetic shieldings defined in previous papers [34,35].

The third-rank hypershieldings at nucleus I are expressed, within the quadratic response scheme [41], by

$$\phi^I_{\alpha,\beta\gamma} = \left\langle\left\langle \hat{E}^n_{I\alpha};\hat{\mu}_\beta,\hat{\mu}_\gamma\right\rangle\right\rangle_{\omega_1,\omega_2}, \tag{31}$$

$$\psi'^I_{\alpha,\beta\gamma} = -\Im\left\langle\left\langle \hat{E}^n_{I\alpha};\hat{\mu}_\beta,\hat{m}_\gamma\right\rangle\right\rangle_{\omega_1,\omega_2}, \tag{32}$$

assuming that a homogeneous electromagnetic field of frequency ω_1 and one of frequency ω_2 are applied to the molecular system. The electric hypershielding accounting for quadratic response to the external magnetic field is the sum of paramagnetic and diamagnetic contributions

$$\rho^I_{\alpha,\beta\gamma} = \rho^{I\mathrm{p}}_{\alpha,\beta\gamma} + \rho^{I\mathrm{d}}_{\alpha,\beta\gamma}, \tag{33}$$

$$\rho^{I\mathrm{p}}_{\alpha,\beta\gamma} = \left\langle\left\langle \hat{E}^n_{I\alpha};\hat{m}_\beta,\hat{m}_\gamma\right\rangle\right\rangle_{\omega_1,\omega_2}, \tag{34}$$

$$\rho^{I\mathrm{d}}_{\alpha,\beta\gamma} = -\left\langle\left\langle \hat{E}^n_{I\alpha};\hat{\chi}^{\mathrm{d}}_{\beta\gamma}\right\rangle\right\rangle_{\omega}, \tag{35}$$

where the operator for the diamagnetic contribution is

$$\hat{\chi}^{\mathrm{d}}_{\alpha\beta} = -\frac{e^2}{4m_e c^2}\sum_{i=1}^{n}\left(r_\nu^2\delta_{\alpha\beta}-r_\alpha r_\beta\right)_i. \tag{36}$$

The third-rank nuclear electric hypershielding in the OWB notation [37,38] becomes

$$\phi^I_{\alpha,\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = \frac{1}{\hbar^2}\sum_P\sum_{j,k\neq a}\frac{\left\langle a\left|\hat{E}^n_{I\alpha}\right|j\right\rangle\left\langle j\left|\overline{\hat{\mu}_\gamma}\right|k\right\rangle\langle k|\hat{\mu}_\beta|a\rangle}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)}, \tag{37}$$

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

The third-rank nuclear electromagnetic hypershielding is written as

$$\psi'^I_{\alpha,\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = -\frac{1}{\hbar^2}\sum_P\sum_{j,k\neq a}\frac{\Im\left(\left\langle a\left|\hat{E}^n_{I\alpha}\right|j\right\rangle\left\langle j\left|\overline{\hat{m}_\gamma}\right|k\right\rangle\langle k|\hat{\mu}_\beta|a\rangle\right)}{(\omega_{ja}-\omega_\sigma)(\omega_{ka}-\omega_1)}, \tag{38}$$

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

The $'$ index is used in definitions (30), (32), and (38) for consistency with the Buckingham notation [36] for $\kappa'_{\alpha\beta}$ in (26) and (27).

The hypershieldings (34) and (35) in the OWB notation [37,38] become

$$\rho^{I\mathrm{p}}_{\alpha,\beta\gamma}\left(-\omega_\sigma;\omega_1,\omega_2\right) = \frac{1}{\hbar^2}\sum_P \sum_{j,k\neq a} \frac{\left\langle a\left|\hat{E}^n_{I\alpha}\right|j\right\rangle\left\langle j\left|\overline{\hat{m}_\gamma}\right|k\right\rangle\left\langle k\left|\hat{m}_\beta\right|a\right\rangle}{\left(\omega_{ja}-\omega_\sigma\right)\left(\omega_{ka}-\omega_1\right)}, \tag{39}$$

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

$$\rho^{I\mathrm{d}}_{\alpha\beta}\left(-\omega_\sigma;\omega_1\right) = \frac{1}{\hbar}\sum_P \sum_{j\neq a} \frac{\left\langle a\left|\hat{E}^n_{I\alpha}\right|j\right\rangle\left\langle j\left|\hat{\chi}^{\mathrm{d}}_{\beta\gamma}\right|a\right\rangle}{\omega_{ja}-\omega_\sigma}, \tag{40}$$

with $\left(\hat{E}^n_{I\alpha}/-\omega_\sigma\right) \leftrightarrow \left(\hat{\chi}^{\mathrm{d}}_{\beta\gamma}/\omega_1\right)$ and $\omega_\sigma = \omega_1 \equiv \omega$.

5 Rototranslational sum rules for the geometrical derivatives of static and frequency-dependent properties

An arbitrary second-order electronic property is expressed as an algebraic sum of terms having the general form

$$F = f\left(\omega_{ja}\right)\left\langle a\left|\hat{A}\right|j\right\rangle\left\langle j\left|\hat{B}\right|a\right\rangle, \tag{41}$$

where, by hypothesis, the operators $\hat{A}$ and $\hat{B}$ do not depend on nuclear coordinates. Thus the Hellmann-Feynman derivative of any (static or dynamic) second-order property will contain terms of the form [42]

$$\begin{aligned}\nabla_{I\alpha}F = &\left\langle a|\hat{A}|j\right\rangle\left\langle j|\hat{B}|a\right\rangle\nabla_{I\alpha}f\left(\omega_{ja}\right)\\ &+f\left(\omega_{ja}\right)\left(\left\langle\nabla_{I\alpha}a|\hat{A}|j\right\rangle\left\langle j|\hat{B}|a\right\rangle\right.\\ &+\left\langle a|\hat{A}|j\right\rangle\left\langle j|\hat{B}|\nabla_{I\alpha}a\right\rangle\\ &+\left\langle a|\hat{A}|\nabla_{I\alpha}j\right\rangle\left\langle j|\hat{B}|a\right\rangle\\ &\left.+\left\langle a|\hat{A}|j\right\rangle\left\langle\nabla_{I\alpha}j|\hat{B}|a\right\rangle\right).\end{aligned} \tag{42}$$

This result has been used to obtain the derivatives of the dynamic polarisability and of the optical rotatory power, showing that they are related respectively to the electric and electromagnetic hypershieldings [34] by expressions that generalize Eq. (21)

$$\nabla_{I\gamma}\alpha_{\alpha\beta}\left(-\omega;\omega\right) = Z_I e\phi^I_{\gamma,\alpha\beta}(0;-\omega,\omega), \tag{43}$$

$$\nabla_{I\gamma}\kappa'_{\alpha\beta}\left(-\omega;\omega\right) = Z_I e\,\psi'^I_{\gamma,\alpha\beta}(0;-\omega,\omega). \tag{44}$$

These relationships are established via the Hellmann-Feynman theorem from Eqs. (24) and (30).

The geometrical derivative of $f\left(\omega_{ja}\right)$ is

$$\nabla_{I\alpha}f\left(\omega_{ja}\right) = \frac{\partial f}{\partial\omega_{ja}}\nabla_{I\alpha}\omega_{ja}, \tag{45}$$

with

$$\begin{aligned}\nabla_{I\alpha}\omega_{ja} &= \frac{1}{\hbar}\nabla_{I\alpha}\left(\left\langle j\left|\hat{H}^{(0)}\right|j\right\rangle-\left\langle a\left|\hat{H}^{(0)}\right|a\right\rangle\right)\\ &= \frac{2}{\hbar}\Re\left(\left\langle\nabla_{I\alpha}j\left|\hat{H}^{(0)}\right|j\right\rangle-\left\langle\nabla_{I\alpha}a\left|\hat{H}^{(0)}\right|a\right\rangle\right)\\ &\quad+\frac{1}{\hbar}\left(\left\langle a\left|\hat{\mathbf{F}}^n_I\right|a\right\rangle-\left\langle j\left|\hat{\mathbf{F}}^n_I\right|j\right\rangle\right).\end{aligned} \tag{46}$$

The gradient of the electronic wavefunctions with respect to nuclear displacements is obtained by the Rayleigh-Schrödinger perturbation theory, using Eqs. (7) and (13) for the first-order perturbed Hamiltonian [43]

$$\left|\nabla_I a\right\rangle = \frac{1}{\hbar}\sum_{j\neq a}|j\rangle\left\langle j\left|\hat{\mathbf{F}}^n_I\right|a\right\rangle\omega^{-1}_{ja}, \tag{47}$$

$$\left|\nabla_I j\right\rangle = \frac{1}{\hbar}\sum_{k\neq j}|k\rangle\left\langle k\left|\hat{\mathbf{F}}^n_I\right|j\right\rangle\omega^{-1}_{kj}. \tag{48}$$

On account of Eqs. (47) and (48), the first line in the second equality in Eq. (46) vanishes. The second line also vanishes if $|a\rangle$ and $|j\rangle$ are both equilibrium states with the same nuclear geometry, see Eq. (16). However,

$$\sum_{I=1}^N \nabla_{I\alpha}\omega_{ja} = 0 \tag{49}$$

for any state, equilibrium or not, if the hypervirial theorem for the momentum operator, i.e. the force theorem [44]

$$\left\langle a\left|\hat{F}^N_{n\alpha}\right|a\right\rangle = 0 = \left\langle j\left|\hat{F}^N_{n\alpha}\right|j\right\rangle, \tag{50}$$

is fulfilled. The operator for the total force exerted by the nuclei on the electrons is obtained via Eq. (8):

$$\hat{\mathbf{F}}^N_n = -\hat{\mathbf{F}}^n_N = -\sum_{I=1}^N\hat{\mathbf{F}}^n_I. \tag{51}$$

Then the first line in Eq. (42) will not contribute to the rototranslational sum rules for the geometrical derivatives of second- and higher-order response properties. Using the hypervirial relation [35,44]

$$i\left\langle a\left|\hat{P}_\alpha\right|j\right\rangle = -\omega^{-1}_{ja}\left\langle a\left|\hat{F}^N_{n\alpha}\right|j\right\rangle \tag{52}$$

and the fact that the diagonal elements of pure imaginary Hermitian operators vanish, we find

$$\left|\sum_{I=1}^N\nabla_{I\alpha}a\right\rangle = -\frac{i}{\hbar}\left|\hat{P}_\alpha a\right\rangle. \tag{53}$$

Then, summing over I, one obtains

$$\begin{aligned}\sum_{I=1}^N\nabla_{I\alpha}F = \frac{i}{\hbar}f\left(\omega_{ja}\right)&\left\{\left\langle a\left|\left[\hat{P}_\alpha,\hat{A}\right]\right|j\right\rangle\left\langle j\left|\hat{B}\right|a\right\rangle\right.\\ &\left.+\left\langle a\left|\hat{A}\right|j\right\rangle\left\langle j\left|\left[\hat{P}_\alpha,\hat{B}\right]\right|a\right\rangle\right\}\end{aligned} \tag{54}$$

from the second and third lines of Eq. (42). Accordingly, the condition for translational invariance of an arbitrary second-order property is obtained by specifying $\hat{A}$ and $\hat{B}$.

For instance, let us evaluate the translational sum rules for the geometrical derivatives of the dynamic polarizability (25) and of the optical rotatory power tensor (26). A straightforward application of Eq. (54) gives:

$$\sum_{I=1}^{N} \nabla_{I\alpha} \alpha_{\beta\gamma} = 0, \tag{55}$$

$$\sum_{I=1}^{N} \nabla_{I\alpha} \kappa'_{\beta\gamma} = \frac{1}{2c}\, \omega\, \epsilon_{\alpha\gamma\delta}\, \alpha_{\beta\delta}. \tag{56}$$

If tensor (26) in the dipole length–angular momentum gauge is used on the l.h.s., the dynamic polarisability in the mixed length–velocity gauge appears on the r.h.s. of Eq. (56). Its definition is given in propagator [41] and OWB [37,38] notations

$$\alpha_{\alpha\beta}^{(RP)} = -\frac{ie}{m_e} \omega^{-1} \left\langle\left\langle \hat{\mu}_\alpha; \hat{P}_\beta \right\rangle\right\rangle_\omega, \tag{57}$$

$$\alpha_{\alpha\beta}^{(RP)}(-\omega_\sigma;\omega_1) = \frac{ie}{m_e \hbar} \sum_P \sum_{j\neq a} \frac{\langle a \left| \hat{\mu}_\alpha \right| j\rangle \left\langle j \left| \hat{P}_\beta \right| a \right\rangle}{\left(\omega_{ja} - \omega_\sigma\right)\omega_\sigma}, \tag{58}$$

where $\sum_P$ indicates the sum over permutations of the pairs $\left(\hat{\mu}_\alpha / -\omega_\sigma\right) \leftrightarrow \left(-\hat{P}_\beta/\omega_1\right)$ and $\omega_\sigma = \omega_1 \equiv \omega$. If the off-diagonal momentum theorem is satisfied [35,44], this quantity is the same as the dipole-length polarisability defined in Eq. (25) as

$$\alpha_{\alpha\beta} \equiv \alpha_{\alpha\beta}^{(RP)} = \alpha_{\alpha\beta}^{(RR)} = -\langle\langle \hat{\mu}_\alpha; \hat{\mu}_\beta \rangle\rangle_\omega. \tag{59}$$

According to Eq. (56), the trace $\kappa'_{\alpha\alpha}$, related to experimental quantities, is translationally invariant.

Let us now obtain an expression for the rotational sum rule. From Eq. (47) one finds

$$\left|\epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} a\right\rangle = -\frac{1}{\hbar} \sum_{j\neq a} |j\rangle \left\langle j \left| \hat{K}_{n\alpha}^{I} \right| a\right\rangle \omega_{ja}^{-1}, \tag{60}$$

where

$$\hat{K}_{n\alpha}^{I} = \epsilon_{\alpha\beta\gamma} R_{I\beta} \hat{F}_{n\gamma}^{I} \tag{61}$$

is the torque exerted by nucleus I on the n electrons. Denoting by

$$\hat{K}_{n\alpha}^{N} = \sum_{I=1}^{N} \hat{K}_{n\alpha}^{I} \tag{62}$$

the torque of the N nuclei on the electrons and using the hypervirial sum rule

$$\left\langle j \left| \hat{K}_{n\alpha}^{N} \right| a \right\rangle = i\omega_{ja} \left\langle j \left| \hat{L}_\alpha \right| a \right\rangle, \tag{63}$$

one finds

$$\left| \sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} a \right\rangle = -\frac{i}{\hbar} \left| \hat{L}_\alpha a \right\rangle. \tag{64}$$

Then Eq. (42) gives

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} F = \frac{i}{\hbar} f\left(\omega_{ja}\right) \left\{ \left\langle a \left| \left[\hat{L}_\alpha, \hat{A}\right] \right| j \right\rangle \left\langle j \left| \hat{B} \right| a \right\rangle + \left\langle a \left| \hat{A} \right| j \right\rangle \left\langle j \left| \left[\hat{L}_\alpha, \hat{B}\right] \right| a \right\rangle \right\}. \tag{65}$$

This relationship can be used to determine the rotational sum rules for geometrical derivatives of static and dynamic second-order properties by specifying the function $f\left(\omega_{ja}\right)$, e.g., for dipole electric polarisabilities and for optical rotatory power

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} \alpha_{\delta\epsilon} = \epsilon_{\alpha\beta\delta} \alpha_{\beta\epsilon} + \epsilon_{\alpha\beta\epsilon} \alpha_{\delta\beta}, \tag{66}$$

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} \kappa'_{\delta\epsilon} = \epsilon_{\alpha\beta\delta} \kappa'_{\beta\epsilon} + \epsilon_{\alpha\beta\epsilon} \kappa'_{\delta\beta}. \tag{67}$$

The rototranslational sum rules for the second-rank magnetisability

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^{\mathrm{p}} + \chi_{\alpha\beta}^{\mathrm{d}} \tag{68}$$

require a wider discussion. The paramagnetic contributions to the dynamic property is

$$\chi_{\alpha\beta}^{\mathrm{p}}(-\omega_\sigma;\omega_1) = \frac{1}{\hbar} \sum_P \sum_{j\neq a} \frac{\langle a \left| \hat{m}_\alpha \right| j\rangle \langle j \left| \hat{m}_\beta \right| a\rangle}{\omega_{ja} - \omega_\sigma}, \tag{69}$$

where $\sum_P$ indicates the sum over permutations of the pairs $\left(\hat{m}_\alpha / -\omega_\sigma\right)$ and $\left(\hat{m}_\beta/\omega_1\right)$ and $\omega_\sigma = \omega_1 \equiv \omega$. Allowing for the identity

$$\frac{\omega_{ja}}{\omega_{ja}^2 - \omega^2} = \frac{1}{\omega_{ja}} + \frac{\omega^2}{\omega_{ja}\left(\omega_{ja}^2 - \omega^2\right)}, \tag{70}$$

Eq. (69) is recast in the equivalent form

$$\chi_{\alpha\beta}^{\mathrm{p}}(-\omega;\omega) = \chi_{\alpha\beta}^{\mathrm{p}}(0;0) + \frac{1}{\hbar} \sum_{j\neq a} \frac{2\omega^2}{\omega_{\mathrm{ja}}(\omega_{\mathrm{ja}}^2 - \omega^2)} \times \Re\left(\langle a \left| m_\alpha \right| j\rangle \left\langle j \left| m_\beta \right| a\right\rangle\right). \tag{71}$$

The diamagnetic contribution to the magnetisability is

$$\chi_{\alpha\beta}^{\mathrm{d}} = \left\langle a \left| \hat{\chi}_{\alpha\beta}^{\mathrm{d}} \right| a \right\rangle, \tag{72}$$

using the definition of Eq. (36).

From the expression for the Hellmann-Feynman geometrical derivatives of the expectation value (72), see Eq. (783) of Ref. [35] and from Eqs. (35) and (40)

$$\nabla_{I\alpha} \chi_{\beta\gamma}^{\mathrm{d}} = Z_I \frac{e}{\hbar} \sum_{j\neq a} \frac{2}{\omega_{ja}} \Re\left(\left\langle a \left| \hat{E}_{I\alpha}^{n} \right| j \right\rangle \left\langle j \left| \hat{\chi}_{\beta\gamma}^{\mathrm{d}} \right| a \right\rangle\right) = -Z_I e \left\langle\left\langle \hat{E}_{I\alpha}^{n}; \hat{\chi}_{\beta\gamma}^{\mathrm{d}} \right\rangle\right\rangle_0 \equiv Z_I\, e\, \rho_{\alpha,\beta\gamma}^{I\mathrm{d}}(0;0). \tag{73}$$

Using Eq. (54) for the first addendum on the r.h.s. of Eq. (71), one finds a condition of translational invariance for the static magnetisability (see the discussion of Eq. (792) in Ref. [35]), i.e.,

$$\sum_{I=1}^{N} \nabla_{I\gamma} \left[\chi^{\mathrm{p}}_{\alpha\beta}(0;0) + \chi^{\mathrm{d}}_{\alpha\beta} \right] = \sum_{I=1}^{N} Z_I\, e\, \rho^{I\mathrm{p}}_{\alpha,\beta\gamma}(0;0,0) + \sum_{I=1}^{N} Z_I\, e\, \rho^{I\mathrm{d}}_{\alpha,\beta\gamma}(0;0) = 0. \tag{74}$$

The contribution from the second addendum on the r.h.s. of Eq. (71) can be expressed via the optical rotatory tensor in the dipole velocity-angular momentum gauge [35]

$$\kappa'^{(PL)}_{\alpha\beta}(-\omega_\sigma;\omega_1) = \frac{e}{m_e\hbar} \sum_P \sum_{j\neq a} \frac{\left\langle a \left| \hat{P}_\alpha \right| j \right\rangle \langle j \left| \hat{m}_\beta \right| a \rangle}{\omega_{ja}\left(\omega_{ja} - \omega_\sigma\right)}, \tag{75}$$

where $\sum_P$ means the sum over permutations of the pairs $\left(\hat{P}_\alpha / -\omega_\sigma\right)$ and $\left(-\hat{m}_\beta/\omega_1\right)$ and $\omega_\sigma = \omega_1 \equiv \omega$. The tensor (75) in the (PL) formalism is identical to that in the dipole lenght gauge defined in Eq. (26) if off-diagonal hypervirial relationships are fulfilled [11,35]. By using Eqs. (54), (71), and (74), one obtains the translational sum rule for the geometrical derivatives of the total dynamic magnetisability (68)

$$\sum_{I=1}^{N} \nabla_{I\gamma} \left[\chi^{\mathrm{p}}_{\alpha\beta} + \chi^{\mathrm{d}}_{\alpha\beta} \right] = \frac{1}{2c}\,\omega \left(\kappa'_{\delta\beta}\epsilon_{\alpha\delta\gamma} + \kappa'_{\delta\alpha}\epsilon_{\beta\delta\gamma} \right). \tag{76}$$

The relationship for rotational invariance of the paramagnetic contribution to the dynamic magnetisability (69) is arrived at via Eq. (65)

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} \chi^{\mathrm{p}}_{\delta\epsilon} = \epsilon_{\alpha\beta\delta} \chi^{\mathrm{p}}_{\beta\epsilon} + \epsilon_{\alpha\beta\epsilon} \chi^{\mathrm{p}}_{\delta\beta}. \tag{77}$$

Therefore, adding the diamagnetic contribution provided by the terms (73), and using Eqs. (8) and (61)–(63), Eq. (77) is rewritten for the total property (68)

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} \nabla_{I\gamma} \chi_{\delta\epsilon} = \epsilon_{\alpha\beta\delta} \chi_{\beta\epsilon} + \epsilon_{\alpha\beta\epsilon} \chi_{\delta\beta}. \tag{78}$$

Eventually, one can observe that in the relationships for the origin dependence of the optical rotatory power tensor and dynamic magnetisability, Eqs. (258) and (260), respectively, of Ref. [11], terms to first order in the origin shift d_α have the opposite sign with respect to the translational sum rules (56) and (76). In fact, Eqs. (258) and (260) of Ref. [11] describe a passive transformation, whereas (56) and (76) are obtained to first order in d_α by active transformation via the translation operator (6).

The procedure based on Eqs. (41) – (45) is easily extended to geometrical derivatives of response properties of any order. Therefore, the results obtained for the static hyperpolarisabilities, see Eqs. (752), (753), (757), and (758) of Ref. [35], also hold for dynamic hyperpolarisabilities (28) and (29).

Owing to the relationships connecting geometrical derivatives of polarisabilities to hypershieldings, Eqs. (43) and (44), sum rules (55), (56), (66), and (67) are also valid for $\phi^{I}_{\alpha,\beta\gamma}$ and $\psi'^{I}_{\alpha,\beta\gamma}$. Analogously, Eq. (78) can be rewritten in terms of the hypershieldings (33).

Acknowledgements Financial support to the present research from the Italian MIUR (Ministero dell'Università e della Ricerca Scientifica e Tecnologica), via FIRB and 60% funds, is gratefully acknowledged.

References

1. Lazzeretti P, Zanasi R (1984) Chem Phys Lett 112:103
2. Fowler PW, Buckingham AD (1985) Chem Phys 98:167
3. Stone A (1997) In: Clary DC (ed), Optical, electric, and magnetic properties of molecules. A review of the work of A. D. Buckingham, Elsevier, Amsterdam, pp 133–136
4. Buckingham AD (1998) Annu Rev Phys Chem 49, xiii
5. Sambe H (1973) J Chem Phys 58:4779
6. Lazzeretti P, Zanasi R (1980) Chem Phys Lett 71:529
7. Lazzeretti P, Zanasi R (1981) Phys Rev A 24:1696
8. Lazzeretti P, Zanasi R (1982) Phys Rev A 25:1790, erratum
9. Lazzeretti P, Rossi E, Zanasi R (1983) Phys Rev A 27:1301, and references therein
10. Lazzeretti P, Rossi E, Zanasi R (1983) J Chem Phys 83:889
11. Lazzeretti P (1987) Adv Chem Phys 75:507
12. Biarge JF, Herranz J, Morcillo J (1961) An R Soc Esp Fis Quim A 57:81
13. Morcillo J, Zamorano LJ, Heredia JMV (1966) Spectrochim Acta 22:1969
14. Person WB, Newton JH (1974) J Chem Phys 61:1040
15. Newton JH, Person WB (1976) J Chem Phys 64:3036
16. Zilles BA, Person WB (1983) J Chem Phys 79:65
17. Lazzeretti P, Defranceschi M, Berthier G (1995) Adv Quantum Chem 26:1
18. Liu P-H, Hunt KLC (1995) J Chem Phys 103:10597
19. Fowler PW, Buckingham A, Galwas PA (1987) Chem Phys 112:1
20. Lazzeretti P , Zanasi R, Stephens PJ (1986) J Phys Chem 90:6761
21. Lazzeretti P, Zanasi R (1986) Phys Rev A 33:3727
22. Bouř P, McCann J, Wieser H (1998) J Chem Phys 108:8782
23. Stephens PJ (1985) J Phys Chem 89:748
24. Stephens PJ, Jalkanen KJ, Amos RD, Lazzeretti P, Zanasi R (1990) J Phys Chem 94:1811
25. van Caillie C, Amos RD (2000) Phys Chem Chem Phys 2:2123
26. Quinet O, Champagne B (2001) J Chem Phys 115:6293
27. Buckingham AD (1989) In: Banerjee SB, Jha SS (ed) Recent trends in raman spectroscopy, World Scientific, Singapore p 1
28. McDowell AC, Buckingham AD (1992) J Chem Soc Faraday Trans 88:3281
29. Caputo MC, Lazzeretti P (2002) Chem Phys 284:601
30. Soncini A, Lazzeretti P, Bakken V, Helgaker T (2003) J Chem Phys 120:3142
31. Ruud K, Helgaker T, Bour P (2002) J Phys Chem A 106:7448
32. Pecul M, Rizzo A, Leszczynski J (2002) J Phys Chem A 106:11008
33. Pecul M, Rizzo A (2003) Mol Phys 101:2073
34. Lazzeretti P (2004) Brandas EJ, Kryachko ES (eds), In: Fundamental world of quantum chemistry: a tribute volume to the memory of Per-Olov Löwdin, vol.III, Kluwer, The Netherlands, pp 199–213
35. Lazzeretti P (2003) Wilson S(ed), In: Handbook of molecular physics and quantum chemistry, vol.3, Part 1, Chap. 3, Wiley, Chichester, pp 53–145
36. Buckingham AD (1967) Adv Chem Phys 12:107
37. Orr BJ, Ward JF (1971) Mol Phys 20:513
38. Bishop DM (1990) Rev Mod Phys 62:343
39. Langhoff PW, Epstein ST, Karplus M (1972) Rev Mod Phys 44:602
40. BJ Orr, MP Bogaard (1975) Buckingham AD In International review of science. Molecular structure and properties. Physical chemistry series two, Vol. 2, Butterworths, London pp 149–194
41. Olsen J, Jørgensen P (1985) J Chem Phys 82:3235
42. Lazzeretti P, Zanasi R (1987) Chem Phys Lett 135:571
43. Lazzeretti P, Zanasi R (1985) Chem Phys Lett 118:217
44. Epstein ST (1974) The variation method in quantum chemistry, Academic Press, New York