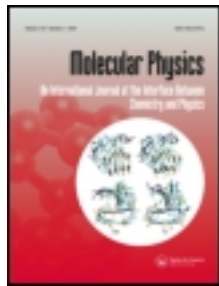


This article was downloaded by: [Maria Cristina Caputo]

On: 21 June 2013, At: 08:34

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tmph20>

On the origin independence of the Verdet tensor[†]

M. C. Caputo^a, S. Coriani^b, S. Pelloni^c & P. Lazzeretti^c

^a Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. I, Buenos Aires, 1428, Argentina

^b Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, Trieste, 34127, Italy

^c Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Via G. Campi 183, Modena, 41124, Italy

Accepted author version posted online: 09 Apr 2013. Published online: 13 May 2013.

To cite this article: M. C. Caputo, S. Coriani, S. Pelloni & P. Lazzeretti (2013): On the origin independence of the Verdet tensor[†], *Molecular Physics: An International Journal at the Interface Between Chemistry and Physics*, DOI:10.1080/00268976.2013.793845

To link to this article: <http://dx.doi.org/10.1080/00268976.2013.793845>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

RESEARCH ARTICLE

On the origin independence of the Verdet tensor[†]

M. C. Caputo^a, S. Coriani^b, S. Pelloni^c and P. Lazzeretti^{c,*}

^aDepartamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. I, (1428) Buenos Aires, Argentina; ^bDipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy; ^cDipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Via G. Campi 183, 41124 Modena, Italy

(Received 13 February 2013; final version received 2 April 2013)

The condition for invariance under a translation of the coordinate system of the Verdet tensor and the Verdet constant, calculated via quantum chemical methods using gaugeless basis sets, is expressed by a vanishing sum rule involving a third-rank polar tensor. The sum rule is, in principle, satisfied only in the ideal case of optimal variational electronic wavefunctions. In general, it is not fulfilled in non-variational calculations and variational calculations allowing for the algebraic approximation, but it can be satisfied for reasons of molecular symmetry. Group-theoretical procedures have been used to determine (i) the total number of non-vanishing components and (ii) the unique components of both the polar tensor appearing in the sum rule and the axial Verdet tensor, for a series of symmetry groups. Test calculations at the random-phase approximation level of accuracy for water, hydrogen peroxide and ammonia molecules, using basis sets of increasing quality, show a smooth convergence to zero of the sum rule. Verdet tensor components calculated for the same molecules converge to limit values, estimated via large basis sets of gaugeless Gaussian functions and London orbitals.

Keywords: Faraday effect; Verdet tensor; Verdet constant; sum rule for origin independence; symmetry unique components

1. Introduction

The Faraday effect accounts for a magneto-optical phenomenon, i.e. the interaction of light and magnetic field [1–7]. It manifests itself in certain substances as the rotation of the plane of polarisation of a light beam when a magnetic field is applied parallel to it. The rotation angle, ϕ , is proportional to the modulus of the magnetic flux density B , the length l of the material in the field and its Verdet constant, v , named after the French physicist Marcel Verdet (1824–66) [8–11], who used the name ‘pouvoir rotatoire magnetique’ for the first time in 1858 [10,12]. The sense of rotation with respect to the magnetic field’s direction does not depend on the direction of light propagation, due to conservation of parity [13,14]. Time reversal, implying inversion of all the motions, leads exactly to the same phenomenology observed from the opposite direction, therefore the Faraday experiment is also characterised by reversality [13,14].

Assuming that B is spatially uniform throughout a transparent sample, the rotation of the polarisation angle is expressed by

$$\phi = vBl. \quad (1)$$

The Verdet constant, measured in $\text{rad T}^{-1}\text{m}^{-1}$ within the Système International (SI) of units, is a scalar [2–4,15–33], obtained by spatial averaging from a third-rank axial tensor $\mathcal{V}_{\alpha\beta\gamma}$, hereafter referred to as Verdet tensor, also taken into account to rationalise the inverse Faraday effect, in which optical magnetisation is induced by applying circularly polarised light [34,35]. A tensor with analogous properties has been considered to predict nuclear magnetic resonance (NMR) chemical shift induced by a circularly polarised laser beam [35–37].

Experimental values of v , as well as optically induced NMR shifts [35–37] are independent of the laboratory reference system, but theoretical definitions of the former are not explicitly invariant to a coordinate translation, unless one uses exact eigenfunctions to a model Hamiltonian.

In quantum chemical calculations, London atomic orbitals (LAO) [38], also referred to as gauge including atomic orbitals (GIAO) [39], are currently used to ensure origin independence of theoretical estimates of v [27,30,32,33]. A few studies on the invariance of the molecular tensor used to rationalise the Faraday effect, in a shift of origin $\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}$ of the coordinate system, have been reported [5,40–42]. A hint was offered for the gauge-origin

*Corresponding author. Email: lazzeret@unimore.it

[†]This paper is dedicated to Prof. Trygve Helgaker on the occasion of his 60th birthday.

Table 1. Non-vanishing components of the polar tensor $\Im\langle\langle\hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\mu\rangle\rangle_{\omega,0}$ from finite basis set calculations, for various molecular symmetries.^a

Point group	Number of non-vanishing components		Non-vanishing components
	Total	Unique	
$C_i, C_{nh}, n \geq 2,$ $D_{nh}, n \geq 2, D_{\infty h},$ $S_6, S_8, D_{3d}, D_{4d}, D_{5d}, D_{6d},$ T_h, T_d, O_h, I_h, R_3	0	0	
C_1	18	9	$xyx = -yxx, yxy = -xyy,$ $xzx = -zxx, yzy = -zyy,$ $zxx = -xzz, zyz = -yzz,$ $xyz = -yxz, xzy = -zxy,$ $yzx = -zyx$
C_2	10	5	$xzx = -zxx, yzy = -zyy,$ $xyz = -yxz, xzy = -zxy,$ $yzx = -zyx$
C_s	8	4	$xyx = -yxx, yxy = -xyy,$ $zxx = -xzz, zyz = -yzz$
D_2	6	3	$xyz = -yxz, xzy = -zxy,$ $yzx = -zyx$
C_{2v}	4	2	$xzx = -zxx, yzy = -zyy$
C_3, C_4, C_6	10	3	$xzx = -zxx = yzy = -zyy,$ $xyz = -yxz,$ $xzy = -zxy = -yzx = zyx$
S_4	8	2	$xzx = -yzy = -zxx = zyy$ $zxy = zyx = -yzx = -xzy$
C_{3v}, C_{4v}, C_{6v}	4	1	$xzx = -zxx = yzy = -zyy$
D_{2d}	4	1	$zyx = -yzx = zxy = -xzy$
D_3, D_4, D_6	6	2	$xyz = -yxz,$ $xzy = -yzx = -zxy = zyx$
T, O	6	1	$xyz = zxy = yzx$ $= -xzy = -yxz = -zyx$

^aThe coordinate system is defined according to the Mulliken conventions [65,66]

invariance of the Verdet constant by considering third-order expressions for, e.g. hyperpolarisabilities in systems possessing an inversion centre, by Parkinson and Oddershede [25]. The present paper stems to provide a simple and general proof of the origin independence of the Verdet tensor $\mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0)$. It is organised as follows.

Some definitions are recalled in Section 2, where it is shown that the condition for origin independence of the Verdet tensor $\mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ can be expressed via the vanishing sum rule [43] for a third-rank polar tensor,

$$\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0) = -\Im\langle\langle\hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\gamma\rangle\rangle_{\omega,0} = 0, \quad (2)$$

involving the matrix elements of electric dipole and canonical momentum. Throughout this paper, the symbols \Im and \Re imply taking the imaginary and real part of the propagator, respectively.

The sum rule, Equation (2), is exactly satisfied using optimal variational wavefunctions [44], e.g. within the

Hartree–Fock method in the limit of a complete basis set of expansion.

The natural optical activity is related to the trace of a second-rank axial tensor. Within the velocity gauge for the electric dipole, this trace, calculated via either variational or non-variational electronic wavefunctions using gaugeless basis sets, is invariant in a translation of the gauge origin [45–47], but an origin-independent expression of the Verdet constant cannot be obtained by an analogous choice of the gauge, as shown in Section 2.1. On the other hand, the sum rule (2) for invariance can be fulfilled owing to a combination of spatial symmetry and permutational symmetry,

$$\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0) = -\mathcal{Z}_{\beta\alpha\gamma}(-\omega; \omega, 0), \quad (3)$$

typical of antisymmetric polarisabilities, see, for instance, Equation (12) of Ref. [36]. Thus $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ vanishes identically for molecules belonging to symmetry groups specified in Table 1. The Verdet tensor for molecules of these symmetries is origin independent, irrespective

Table 2. Non-vanishing components of the axial tensor $\mathfrak{S}(\langle\langle\hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{m}_\gamma(\mathbf{R}_{CM})\rangle\rangle_{\omega,0})$ for some molecular symmetries.^a

Point group	Number of non-vanishing components		Non-vanishing components
	Total	Unique	
C_1, C_i	18	9	$xyx = -yxx, yxy = -xyy, xzx = -zxx,$ $yyz = -zyy, zxz = -xzz, zyz = -yzz,$ $xyz = -yxz, xzy = -zxy, yzx = -zyx$
C_2, C_s, C_{2h}	10	5	$xzx = -zxx, yzy = -zyy, xyz = -yxz,$ $xzy = -zxy, yzx = -zyx$
D_2, C_{2v}, D_{2h}	6	3	$xyz = -yxz, xzy = -zxy, yzx = -zyx$
$C_4, S_4, C_{4h},$ $C_3, S_6, C_{3h},$ C_6, C_{6h}	10	3	$xzx = -zxx = yzy = -zyy,$ $xyz = -yxz,$ $xzy = -zxy = -yzx = zyx$
$D_3, C_{3v}, D_{3d},$ $D_4, C_{4v}, D_{2d},$ $D_6, C_{6v}, D_{nh}, n \geq 3,$ $D_{\infty h}$	6	2	$xyz = -yxz,$ $xzy = -zxy = zyx = -yzx$
$T, T_h, O, T_d, O_h, I_h, R_3$	6	1	$xyz = xzy = yzx$ $= -yxz = -xzy = -zyx$

^aThe coordinate system is defined according to the Mulliken conventions [65,66].

of basis set quality and approximate method employed in the calculations. Moreover, group theoretical procedures [48,49] recalled in Section 2.2 provide *a priori* simple criteria to evaluate only the symmetry-unique, non-vanishing tensor components of the Verdet tensor (see Table 2).

In the attempt at investigating the effect of increasing quality of gaugeless basis sets on convergence of $\mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ and $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ to the limit values for a complete basis, calculations have been carried out for water, hydrogen peroxide, and ammonia molecules using Dunning's basis sets [50]. The results are reported in Section 3 and concluding remarks in Section 4.

2. The Verdet tensor

We use the notation adopted in previous papers [45,46]. For a molecule with n electrons and N nuclei, charge, mass, position with respect to an arbitrary origin, canonical, and angular momentum of the i th electron are indicated by $-e$, m_e , \mathbf{r}_i , $\hat{\mathbf{p}}_i$, $\hat{\mathbf{l}}_i = \mathbf{r}_i \times \hat{\mathbf{p}}_i$, $i = 1, 2, \dots, n$ in the configuration space. Corresponding quantities for nucleus I are indicated by, e.g. $Z_I e$, M_I , \mathbf{R}_I . Capital letters denote total electronic operators, e.g. $\hat{\mathbf{R}} = \sum_{i=1}^n \mathbf{r}_i$, $\hat{\mathbf{P}} = \sum_{i=1}^n \hat{\mathbf{p}}_i$, $\hat{\mathbf{L}} = \sum_{i=1}^n \hat{\mathbf{l}}_i$, etc. Throughout this article we use SI units and tensor notation, e.g. the Einstein convention of summing over two repeated Greek subscripts, and $\epsilon_{\alpha\beta\gamma}$ denotes the Levi-Civita third-rank skew tensor.

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

$$\langle\langle\hat{A}; \hat{B}, \hat{C}\rangle\rangle_{\omega_1, \omega_2} = \frac{1}{\hbar^2} \sum_P \sum_{j, k \neq a} \frac{\langle a | \hat{A} | j \rangle \langle j | \overline{\hat{C}} | k \rangle \langle k | \hat{B} | a \rangle}{(\omega_{ja} - \omega_\sigma)(\omega_{ka} - \omega_1)}, \quad (4)$$

using the notation of Bishop *et al.* [21,51,52] for the propagator [43,53]. In this relationship $\omega_\sigma = \omega_1 + \omega_2$, and \sum_P means the sum over all permutations of the pairs $(\hat{A} / -\omega_\sigma)$, (\hat{B} / ω_1) , (\hat{C} / ω_2) . Overlined operators are defined, e.g.

$$\overline{\hat{A}} = \hat{A} - \langle a | \hat{A} | a \rangle.$$

In the following we will assume that a field of frequency ω_1 and one of frequency ω_2 are applied to the molecular system.

From definition (4) it follows

$$\langle\langle\hat{A}; \hat{B}, \hat{C}\rangle\rangle_{\omega_1, \omega_2} = \langle\langle\hat{C}; \hat{B}, \hat{A}\rangle\rangle_{\omega_1, -\omega_\sigma}. \quad (5)$$

From the equations of motion satisfied by the propagator, Equation (4), for exact and optimal variational wavefunctions [44], one has [43,53]

$$(\omega_1 + \omega_2) \langle\langle\hat{A}; \hat{B}, \hat{C}\rangle\rangle_{\omega_1, \omega_2} = \langle\langle[\hat{A}, \hat{H}^{(0)}]; \hat{B}, \hat{C}\rangle\rangle_{\omega_1, \omega_2} + \langle\langle[\hat{A}, \hat{B}]; \hat{C}\rangle\rangle_{\omega_2} + \langle\langle[\hat{A}, \hat{C}]; \hat{B}\rangle\rangle_{\omega_1}. \quad (6)$$

Allowing for Equation (4), the Verdet tensor is defined [21]

$$\begin{aligned} \mathcal{V}_{\alpha\beta\gamma}(-\omega_\sigma; \omega_1, \omega_2) &= -\Im \langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{m}_\gamma \rangle \rangle_{\omega_1, \omega_2} \\ &= -\frac{1}{\hbar^2} \sum_P \sum_{j,k \neq a} \frac{\Im \left(\langle a | \hat{\mu}_\alpha | j \rangle \langle j | \hat{\mu}_\beta | k \rangle \langle k | \hat{m}_\gamma | a \rangle \right)}{(\omega_{ja} - \omega_\sigma)(\omega_{ka} - \omega_2)}. \end{aligned} \quad (7)$$

The operators for the electric and magnetic dipole moment of electrons are

$$\hat{\mu}_\alpha = -e\hat{R}_\alpha \quad (8)$$

and

$$\hat{m}_\alpha = -\frac{e}{2m_e} \hat{L}_\alpha. \quad (9)$$

Within the SI system, the Verdet tensor is measured in $\text{Kg}^{-2} \text{s}^3 \text{C}^3$. In non-ordered phase it is expedient to make molecular averages, defining the scalar quantity [3,21,26]

$$\mathcal{V}(\omega) = \frac{1}{6} \epsilon_{\alpha\beta\gamma} \mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0). \quad (10)$$

Introducing the multiplicative factor

$$C = \frac{1}{2c} \frac{\mathcal{N}}{\epsilon_0} \quad (11)$$

with \mathcal{N} the number density, the Verdet constant which appears in the definition of the rotation angle, Equation (1), can eventually be expressed in the form [21,26]

$$v(\omega) = \omega C \mathcal{V}(\omega) \quad (12)$$

for a given ω value. Within the SI, \mathcal{N} is expressed in m^{-3} , C in $\text{m}^{-3} \text{s F}^{-1}$ and v in $\text{rad m}^{-1} \text{T}^{-1}$.

2.1. Origin dependence of the Verdet tensor

In a change

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d} \quad (13)$$

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

$$\begin{aligned} A^B(\mathbf{r} - \mathbf{r}') &\rightarrow A^B(\mathbf{r} - \mathbf{r}'') = A^B(\mathbf{r} - \mathbf{r}') \\ &+ \nabla[A^B(\mathbf{r} - \mathbf{r}') \cdot \mathbf{d}], \end{aligned} \quad (14)$$

of the vector potential $A^B = (1/2)\mathbf{B} \times \mathbf{r}$, the magnetic dipole operator changes according to

$$\hat{m}_\gamma(\mathbf{r}'') = \hat{m}_\gamma(\mathbf{r}') + \frac{e}{2m_e} \epsilon_{\gamma\lambda\mu} d_\lambda \hat{P}_\mu. \quad (15)$$

The diagonal matrix elements of pure imaginary Hermitian operators vanish for non-degenerate electronic states, then $\overline{\hat{m}}_\alpha = \hat{m}_\alpha$ and $\overline{\hat{P}}_\alpha = \hat{P}_\alpha$. For the electric dipole operator,

$$\overline{\hat{\mu}}_\alpha(\mathbf{r}'') = \overline{\hat{\mu}}_\alpha(\mathbf{r}') = \hat{\mu}_\alpha(\mathbf{r}') - \langle a | \hat{\mu}_\alpha(\mathbf{r}') | a \rangle. \quad (16)$$

The isotropic natural optical activity and the Verdet constant, calculated via approximate methods of quantum chemistry using gaugeless basis sets, depend on the origin of the coordinate system. However, origin-independent values of the former are obtained within the dipole velocity gauge[45–47,54–56]. To the best of our knowledge, analogous procedures have not been developed for the latter. The state of affairs is briefly recalled hereafter.

The optical rotatory power tensor within the dipole length gauge can be expressed in the form [45,47,57]

$$\begin{aligned} \kappa'_{\alpha\beta}(-\omega_\sigma; \omega_1) &= \Im \langle \langle \hat{\mu}_\alpha; \hat{m}_\beta \rangle \rangle_\omega \\ &\equiv -\frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega}{\omega_{ja}^2 - \omega^2} \Im \left(\langle a | \hat{\mu}_\alpha | j \rangle \langle j | \hat{m}_\beta | a \rangle \right). \end{aligned} \quad (17)$$

Allowing for Equations (15) and (16), its transformation in the origin translation, Equation (13), is described by the relationships [45]

$$\begin{aligned} \kappa'_{\alpha\beta}(\mathbf{r}'') &= \kappa'_{\alpha\beta}(\mathbf{r}') - \frac{\omega}{2} \epsilon_{\beta\gamma\delta} d_\delta \alpha_{\alpha\gamma}, \\ \text{Tr}\{\kappa'(\mathbf{r}'')\} &= \text{Tr}\{\kappa'(\mathbf{r}')\}. \end{aligned} \quad (18)$$

Equation (18) is valid, and the trace of the tensor stays the same, if the off-diagonal hypervirial Ehrenfest theorem [44]

$$\frac{e}{m_e} \langle a | \hat{P}_\alpha | j \rangle = i\omega_{ja} \langle a | \hat{\mu}_\alpha | j \rangle \quad (19)$$

is fulfilled [45–47]. To satisfy this requirement within the algebraic approximation, a complete basis set of gaugeless functions should be used [44]. However, in any calculation adopting a truncated basis, the equations describing the origin dependence of molecular tensors must be properly interpreted [45–47]. Thus, for instance, if the optical activity tensor is defined within the electric dipole velocity (P, L) formalism,

$$\begin{aligned} \kappa'_{\alpha\beta}(P,L) &= -\frac{e^2}{2m_e^2 \hbar} \sum_{j \neq a} \frac{2\omega}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \\ &\quad \times \Re \langle a | \hat{P}_\alpha | j \rangle \langle j | \hat{L}_\beta | a \rangle, \end{aligned} \quad (20)$$

then the electric polarisability in the (P, P) dipole velocity gauge,

$$\alpha_{\alpha\beta}^{(P,P)} = \frac{e^2}{m_e^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \Re \langle a | \hat{P}_\alpha | j \rangle \langle j | \hat{P}_\beta | a \rangle, \quad (21)$$

must be used [45,46] in Equation (18). By all means, the trace of the $\kappa'_{\alpha\beta}$ tensor in the velocity gauge is invariant in any approximate calculation, which makes the (P, L) formalism useful if only gaugeless basis sets are available [46,47]. Such a procedure provides an interesting alternative to using LAO basis sets [58].

This remarkable result is a mere consequence of the symmetry of the polarisability tensor $\alpha_{\alpha\beta}^{(P,P)} = \alpha_{\beta\alpha}^{(P,P)}$ within the velocity gauge and the antisymmetry of the Levi-Civita tensor used in Equation (18) [46,47]. An analogous result is not possible for the Verdet constant, as shown in the following.

The origin independence of the Verdet propagator necessarily implies that, in the coordinate translation, Equations (13)–(16), and in the resulting transformation

$$\begin{aligned} \langle \langle \hat{\mu}_\alpha(\mathbf{r}'''); \hat{\mu}_\beta(\mathbf{r}''), \hat{m}_\gamma(\mathbf{r}'') \rangle \rangle_{\omega,0} &= \langle \langle \hat{\mu}_\alpha(\mathbf{r}'); \hat{\mu}_\beta(\mathbf{r}'), \hat{m}_\gamma(\mathbf{r}') \rangle \rangle_{\omega,0} \\ &+ \frac{e}{2m_e} \epsilon_{\gamma\lambda\mu} d_\lambda \langle \langle \hat{\mu}_\alpha(\mathbf{r}'); \hat{\mu}_\beta(\mathbf{r}'), \hat{P}_\mu \rangle \rangle_{\omega,0}, \end{aligned} \quad (22)$$

the sum rule [43], Equation (2), must be satisfied for any origin \mathbf{r}' , since the polar tensor on the right-hand side, $\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\mu \rangle \rangle_{\omega,0}$, is origin independent. Relationship (2) is easily proven via the off-diagonal hypervirial relationship (19) allowing for Equation (5), so that

$$\begin{aligned} \langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\mu \rangle \rangle_{\omega,0} &= \langle \langle \hat{P}_\mu; \hat{\mu}_\beta, \hat{\mu}_\alpha \rangle \rangle_{\omega,-\omega} \\ &= \frac{im_e}{e\hbar} \langle \langle [\hat{\mu}_\mu, H^{(0)}]; \hat{\mu}_\beta, \hat{\mu}_\alpha \rangle \rangle_{\omega,-\omega}, \end{aligned} \quad (23)$$

which vanishes identically according to the equation of motion (6).

It should be emphasised that the sum rule, Equations (2) and (23), is satisfied only in the case of exact and optimal variational wavefunction, for which the hypervirial theorem (19) is fulfilled. In actual calculations, the constraint for translational invariance is, in general, met only in the limit of a complete basis set. The degree to which Equation (2) is satisfied actually provides a measure of quality of the basis set. For that reason, gauge including atomic orbitals are usually adopted in the calculation of magneto-optical activity [59] and Verdet constant [27,30,32–33].

2.2. Restrictions imposed by molecular symmetry

The sum rule (2) may simply be satisfied on account of molecular point group symmetry and antisymmetry

Table 3. Non-vanishing components of the polar tensor $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ of H₂O from four basis sets.^a

Component	DZ(47)	TZ(119)	QZ(249)	5Z(461)
$xzx = -zxx$	0.16002	0.06514	0.01926	0.00895
$yz y = -zyy$	0.01588	0.00729	-0.00187	-0.00147

^aIn au. The basis sets are specified in the text. Here and in the following tables, the entries between parentheses specify the number of basis functions. $\omega = 0.0345439$ au.

under permutation of the first two indices of the tensor $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$, Equation (3). The situation is similar to that of nuclear magnetic shieldings calculated within the common origin approach via gaugeless basis sets [60]. Computed shielding tensors depend on the gauge origin only for nuclear site symmetries C_1, C_s, C_n, C_{nv} , $n = 2, 3, \dots$. They are origin independent if the nuclear site symmetry is higher [60].

Allowing for tables 4 a and 4e in the Birss book [49], it is immediately found that the polar tensor

Table 4. Non-vanishing components of the axial tensor $\mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ of H₂O from four basis sets.^a

Component	DZ(47)	TZ(119)	QZ(249)	5Z(461)
$xyz = -yxz$	0.6454	0.7224	0.7481	0.7542
	0.7354	0.7716	0.7674	0.7596
$xzy = -zxy$	-0.7542	-0.8171	-0.8424	-0.8495
	-0.8186	-0.8583	-0.8618	-0.8564
$yzx = -zyx$	0.5852	0.6587	0.6789	0.6846
	0.7117	0.7156	0.7013	0.6944
$\epsilon_{\alpha\beta\gamma} \mathcal{V}_{\alpha\beta\gamma}$	3.9693	4.3964	4.5389	4.5764
	4.5315	4.6910	4.6609	4.6209
$v \times 10^9$	4.1717	4.6206	4.7703	4.8097
	4.7626	4.9301	4.8985	4.8565

^aIn au. Here and in Tables 6 and 8, the conversion factor from au to SI units is $1 v = ea_0/\hbar = 8.03961763 \times 10^4 \text{ rad m}^{-1} \text{ T}^{-1}$ from the CODATA compilation [67]. In au, the constant in Equation (11) is $C = 2\pi\mathcal{N}/c = 4.585061844 \times 10^{-2}\mathcal{N}$. For an ideal gas at 273.15 K, $\mathcal{N} = 3.98139 \times 10^{-6} a_0^3$, from Ref. [32]. For each set of components, results from gaugeless basis sets are given in the first line and corresponding LAO results in the second line. The scalar $\mathcal{V} = (1/6)\epsilon_{\alpha\beta\gamma}\mathcal{V}_{\alpha\beta\gamma}$ and the Verdet constant v are defined in Equations (10) and (12) respectively. The origin of the coordinate system coincides with the centre of mass. Nuclear coordinates: O (0.0, 0.0, 0.124144), H₁ (0.0, 1.431530, -0.985266), in bohr. $\omega = 0.0345439$ au.

Table 5. Non-vanishing components of the polar tensor $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ of H₂O₂ from four basis sets.^a

Component	DZ(72)	TZ(188)	QZ(388)	5Z(712)
$xzx = -zxx$	-0.06249	-0.02143	-0.00561	-0.00271
$xyz = -yxz$	-0.01258	-0.01183	-0.00444	-0.00299
$yz y = -zyy$	-0.07718	-0.02370	-0.00534	-0.00261
$xzy = -zxy$	0.00664	0.00078	-0.00122	-0.00023
$yzx = -zyx$	0.03145	0.01714	0.00434	0.00333

^aIn au, $\omega = 0.0345439$ au.

Table 6. Non-vanishing components of the axial tensor $\mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ of H_2O_2 from four basis sets.^a

Component	DZ(72)	TZ(188)	QZ(388)	5Z(712)
$xzx = -zxx$	0.1194	0.0556	0.0267	0.0177
$zyz = -zyy$	0.0598	0.0447	0.0370	0.0346
$xyz = -yxz$	0.5814	0.6991	0.7475	0.7585
	0.7149	0.7604	0.7688	0.7676
$xzy = -zxy$	-0.7854	-0.8453	-0.8617	-0.8642
	-0.8345	-0.8708	-0.8692	-0.8668
$yzx = -zyx$	0.5243	0.6515	0.7185	0.7373
	0.7087	0.7320	0.7467	0.7496
$\epsilon_{\alpha\beta\gamma} \mathcal{V}_{\alpha\beta\gamma}$	3.7822	4.3918	4.6555	4.7202
	4.5161	4.7265	4.7694	4.7679
$v \times 10^9$	3.9751	4.6157	4.8928	4.9609
	4.7464	4.9675	5.0126	5.0109

^aIn au. See footnote to Table 3 for the conventions used. The origin of the coordinate system coincides with the centre of mass. Nuclear coordinates:

O₁ (0.0, 1.3824839, -0.06604896),
H₁ (1.4219547, 1.6931360, 1.0482451), in bohr.
 $\omega = 0.0345439$ au.

Table 7. Non-vanishing components of the polar tensor $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ of NH_3 from four basis sets.^a

Component	DZ(56)	TZ(144)	QZ(304)	5Z(566)
$xzx = -zxx = yzy$ $= -zyy$	0.01493	-0.00536	-0.00561	-0.00285

^aIn au, $\omega = 0.0345439$ au.

$\mathfrak{S}\langle\langle\hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\mu\rangle\rangle_{\omega,0}$ vanishes for, e.g. C_i , C_{2h} , D_{2h} , C_{4h} , D_{4h} , S_6 , D_{3d} , C_{6h} , D_{6h} , T_h and O_h groups. The symmetry-unique components of the axial Verdet tensor can also be obtained from the Birss compilation [49,61,62].

At any rate, the Birss tables provide the tensor components which are unique due to spatial symmetry alone.

According to Equation (3),

$$\mathfrak{S}\langle\langle\hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\mu\rangle\rangle_{\omega,0} = -\mathfrak{S}\langle\langle\hat{\mu}_\beta; \hat{\mu}_\alpha, \hat{P}_\mu\rangle\rangle_{\omega,0}, \quad (24)$$

so that, e.g. $\alpha = x = \beta$,

$$\mathfrak{S}\langle\langle\hat{\mu}_x; \hat{\mu}_x, \hat{P}_\mu\rangle\rangle_{\omega,0} = 0.$$

Owing to Equation (24), it is easily verified that the Verdet tensor is origin independent also for molecules with T_d symmetry. From the Birss tables [49], one finds that the six non-vanishing components of $\mathcal{Z}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ obtained from permuting x, y, z are all equal. Therefore they vanish because of permutational symmetry, i.e. by Equation (24). Analogously, allowing for D_{3h} point group symmetry and using the notation of Birss [49], the unique tensor components are xxx and $yyx(3) = -xxx$, which vanish on account of Equation (24). The same conclusion is, e.g. arrived at for the C_{3h} point group. Then, in these cases, the sum rule (2) is exactly satisfied for both spatial and permutational symmetry.

The change of the Verdet scalar, Equation (10), in the coordinate transformation, Equation (13), is given by

$$\mathcal{V}(\mathbf{r}'') = \mathcal{V}(\mathbf{r}') + \frac{e}{6m_e} d_\alpha \mathcal{Z}_{\alpha\beta\beta}(-\omega; \omega, 0), \quad (25)$$

allowing for the permutational symmetry, see Equation (24). According to this relationship, an extension of the dipole velocity formalism, used to define an invariant isotropic optical activity via Equations (20) and (21), to the Verdet tensor, Equation (7), does not seem practical, since the $\mathcal{Z}_{\alpha\beta\beta}(-\omega; \omega, 0)$ vector does not vanish in general. On the other hand, the symmetry considerations expounded above can be used to predict the origin independence of the Verdet constant, Equation (12).

Table 8. Non-vanishing components of the axial tensor $\mathcal{V}_{\alpha\beta\gamma}(-\omega; \omega, 0)$ of NH_3 from four basis sets.^a

Component	DZ(56)	TZ(144)	QZ(304)	5Z(566)
$xyz = -yxz$	0.9085	1.0439	1.0685	1.0751
	1.0319	1.0753	1.0749	1.0795
$xzy = -zxy = zyx = -yzx$	-1.2219	-1.4191	-1.4784	-1.5011
	-1.4235	-1.4834	-1.4991	-1.5103
$\epsilon_{\alpha\beta\gamma} \mathcal{V}_{\alpha\beta\gamma}$	6.7044	7.7642	8.0505	8.1545
	7.7579	8.0844	8.1464	8.2000
$v \times 10^9$	7.0462	8.1600	8.4610	8.5703
	8.1534	8.4966	8.5617	8.6183

^aIn au. See footnote to Table 3 for the conventions used. The origin of the coordinate system coincides with the centre of mass. Nuclear coordinates: N (0.0, 0.0, 0.11898517),
H₁ (1.7624493, 0.0, -0.55107391), in bohr. $\omega = 0.0345439$ au.

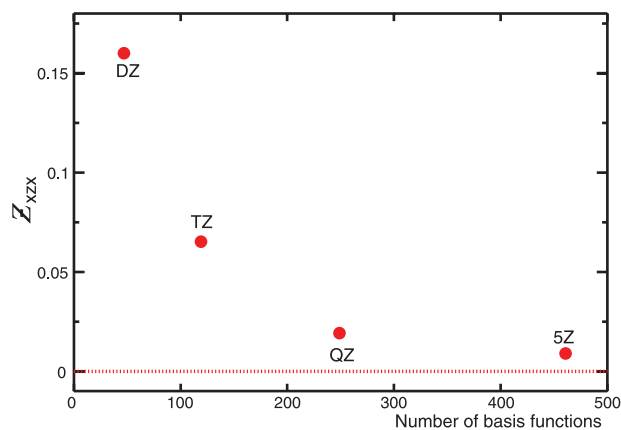


Figure 1. Water molecule. Convergence $Z_{xzx}(-\omega; \omega, 0) \rightarrow 0$ for basis sets of increasing quality.

3. Calculations

The calculations were carried out for the equilibrium geometry of water, $R_{OH} = 0.9584 \text{ \AA}$ and $\widehat{HOH} = 104.45^\circ$. The molecular geometries of hydrogen peroxide and ammonia have been optimised using the GAUSSIAN code [63] at the Hartree–Fock level of accuracy. The geometrical parameters are, respectively, $R_{OH} = 0.9700 \text{ \AA}$, $R_{OO} = 1.4632 \text{ \AA}$ and $\widehat{OOH} = 99.76^\circ$, for hydrogen peroxide, and $R_{NH} = 0.9978 \text{ \AA}$ and $\widehat{HNH} = 108.09^\circ$ for ammonia.

Woon–Dunning aug-cc-pCVXZ basis sets, X=D, T, Q, 5 of increasing size and flexibility [64], have been used to calculate the $\langle\langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{P}_\mu \rangle\rangle_{\omega,0}$ and $\langle\langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{m}_\gamma \rangle\rangle_{\omega,0}$ propagators. The results are reported in Tables 3–8.

Smooth convergence to a null value of the sum rule for origin independence, Equation (2), is observed for some components of the $Z_{\alpha\beta\gamma}(-\omega; \omega, 0)$ tensor, on increasing size and quality of the basis sets, in Tables 3–8 and Figures 1–4. The Verdet tensor was also calculated via LAO basis sets constructed by the same gaugeless basis sets from

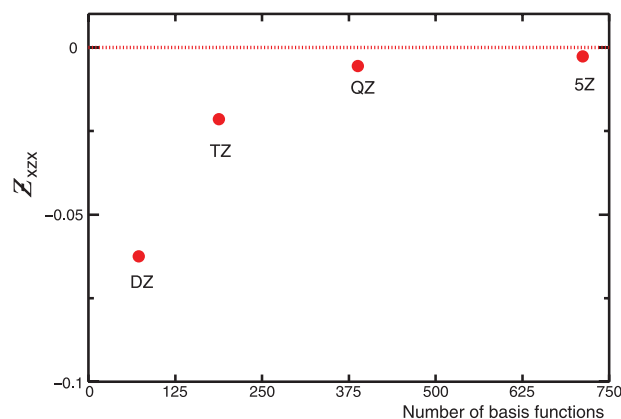


Figure 2. Hydrogen peroxide molecule. Convergence $Z_{xzx}(-\omega; \omega, 0) \rightarrow 0$ for basis sets of increasing quality.

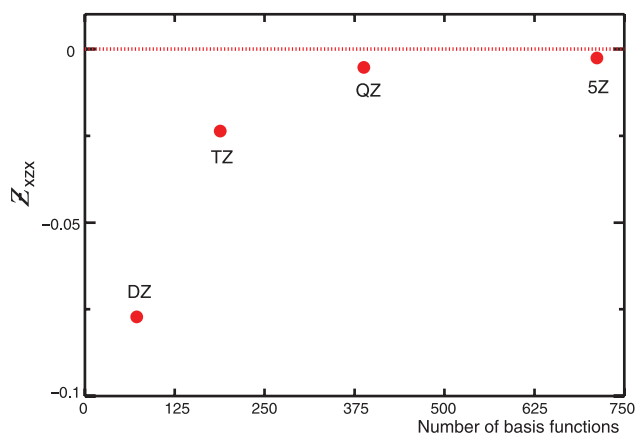


Figure 3. Hydrogen peroxide molecule. Convergence $Z_{yzy}(-\omega; \omega, 0) \rightarrow 0$ for basis sets of increasing quality.

Refs [50,64]. Tests of convergence for values from gaugeless basis sets were made for two different origins. As can be observed in Figure 5 for the water molecule, the results for the $\mathcal{V}_{zxy}(-\omega; \omega, 0)$ component, computed by taking the gauge-origin on the centre of mass and a hydrogen nucleus, approach the same limit, estimated via the coinciding values from the gaugeless aug-cc-pCV5Z and LAO basis calculations. The predictions obtained for hydrogen peroxide, Figure 6, and ammonia, Figure 7, are virtually the same for two different origins. From the results displayed in the tables, and from the figures, we can observe that LAO results from smaller basis sets are, as a rule, much closer to the limit than those from the corresponding gaugeless basis sets. At any rate, fully converged results can be arrived at only by adopting large basis sets, at least of aug-cc-pVQZ quality. If basis sets of this size are used, including gauge phase-factors seems unnecessary.

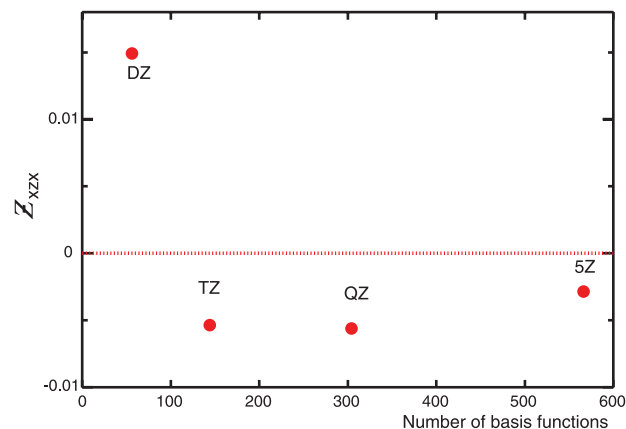


Figure 4. Ammonia molecule. Convergence $Z_{xzx}(-\omega; \omega, 0) \rightarrow 0$ for basis sets of increasing quality.

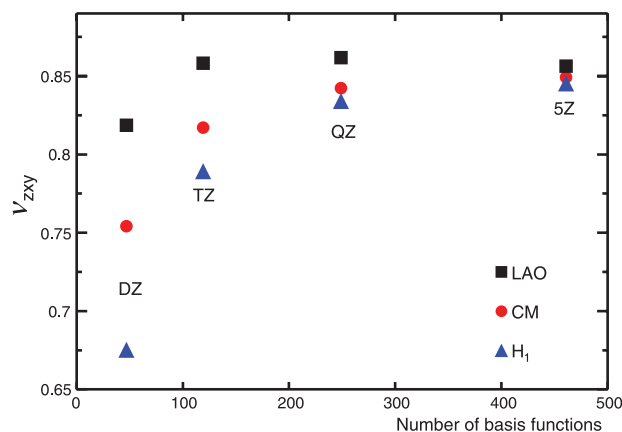


Figure 5. Water molecule. Convergence of the $V_{zxy}(-\omega; \omega, 0)$ component for two different origins, R_{CM} and R_{H_1} , and corresponding LAO results.

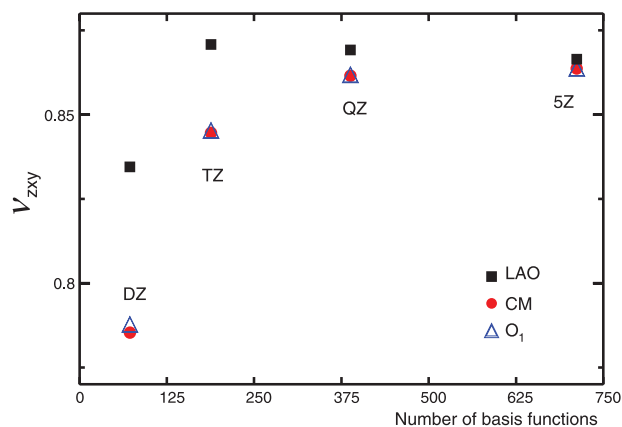


Figure 6. Hydrogen peroxide molecule. Convergence of the $V_{zxy}(-\omega; \omega, 0)$ component for two different origins, R_{CM} and R_{O_1} , and corresponding LAO results.

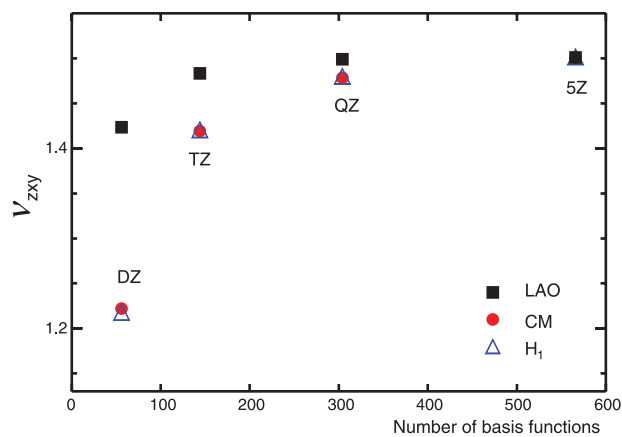


Figure 7. Ammonia molecule. Convergence of the $V_{zxy}(-\omega; \omega, 0)$ component for two different origins, R_{CM} and R_{H_1} , and corresponding LAO results.

4. Concluding remarks

The constraint for independence of calculated Verdet tensor and Verdet constant in a translation of coordinate system is given by a sum rule exactly fulfilled by optimal variational electronic wavefunctions satisfying a momentum theorem, i.e. the Ehrenfest off-diagonal hypervirial relationship for the electric dipole operator. This condition is ideally met, for instance, in the limit of a complete basis set for the self-consistent field approximation to the Hartree–Fock approach. Within the algebraic approximation, the nearness to zero of the sum rule yields a measure of origin independence of computed Verdet tensor and basis set quality. Calculations for some reference compounds, water, hydrogen peroxide and ammonia, using basis sets of increasing size and flexibility, show a smooth convergence to null values. However, it is found that often the sum rule will be fulfilled simply for reasons of spatial symmetry, and/or permutational symmetry of tensor components: the Verdet tensor calculated by gaugeless sets of atomic functions is origin independent for the symmetry groups C_i , C_{nh} , $n \geq 2$, D_{nh} , $n \geq 2$, $D_{\infty h}$, S_6 , S_8 , D_{3d} , D_{4d} , D_{5d} , D_{6d} , T_h , T_d , O_h , I_h , R_3 . There is no need to use gauge-including atomic orbitals for systems having these symmetries.

Acknowledgements

Financial support to the present research from the Italian MIUR (Ministero dell’Istruzione, Universit  e Ricerca), via PRIN 2009 funds, from CONICET(PIP0369) and UBACYT(W197) is gratefully acknowledged.

References

- [1] R. Serber, Phys. Rev. **41**, 489 (1932).
- [2] M. Groenewege, Mol. Phys. **5**, 541 (1962).
- [3] A.D. Buckingham and P. Stephens, Ann. Rev. Phys. Chem. **17**, 399 (1966).
- [4] P.J. Stephens, J. Chem. Phys. **52**, 3489 (1970).
- [5] D.J. Caldwell and H. Eyring, *The Theory of Optical Activity* (Wiley-Interscience, New York, 1971).
- [6] D.J. Caldwell and H. Eyring, Adv. Quantum Chem. **6**, 143 (1972).
- [7] P.J. Stephens, Ann. Rev. Phys. Chem. **25**, 201 (1974).
- [8] M. Verdet, Ann. Chim. Phys. [iii] **41**, 370 (1854).
- [9] M. Verdet, Ann. Chim. Phys. [iii] **43**, 37 (1855).
- [10] M. Verdet, Ann. Chim. Phys. [iii] **52**, 129 (1858).
- [11] M. Verdet, Ann. Chim. Phys. [iii] **69**, 415 (1863).
- [12] ‘... Il convient donc de lui donner un nom, et celui de *pouvoir rotatoire magnetique* me par it pouvoir  tre adopt .’.
- [13] P.M. Rinard and J.W. Calvert, Am. J. Phys. **39**, 753 (1971).
- [14] L.D. Barron, Nature **238**, 17 (1972).
- [15] Y.J. I’Haya and F. Matsukawa, Int. J. Quantum Chem. **7**, 181 (1973).
- [16] P. J rgensen, J. Oddershede, and N.H.F. Beebe, J. Chem. Phys. **68**, 2527 (1978).
- [17] P. J rgensen, J. Oddershede, P. Albertsen, and N.H.F. Beebe, J. Chem. Phys. **68**, 2533 (1978).
- [18] C. Leycuras, H.L. Gall, M. Guillot, and A. Marchand, J. Appl. Phys. **55**, 2161 (1984).

- [19] D.M. Bishop, J. Pipin, and M. Rérat, *J. Chem. Phys.* **92**, 1902 (1990).
- [20] D.M. Bishop and S.M. Cybulski, *Mol. Phys.* **71**, 667 (1990).
- [21] D.M. Bishop and S.M. Cybulski, *J. Chem. Phys.* **93**, 590 (1990).
- [22] D.M. Bishop, S.M. Cybulski, and J. Pipin, *J. Chem. Phys.* **94**, 6686 (1991).
- [23] W.A. Parkinson, S.P.A. Sauer, J. Oddershede, and D.M. Bishop, *J. Chem. Phys.* **98**, 487 (1993).
- [24] M. Jaszunski, P. Jørgensen, A. Rizzo, K. Ruud, and T. Helgaker, *Chem. Phys. Lett.* **222**, 263 (1994).
- [25] W.A. Parkinson and J. Oddershede, *Int. J. Quantum Chem.* **64**, 599 (1997).
- [26] S. Coriani, C. Hättig, P. Jørgensen, A. Halkier, and A. Rizzo, *Chem. Phys. Lett.* **281**, 445 (1997).
- [27] S. Coriani, C. Hättig, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **113**, 3561 (2000).
- [28] S. Coriani, P. Jørgensen, O. Christiansen, and J. Gauss, *Chem. Phys. Lett.* **330**, 463 (2000).
- [29] E. Botek, B. Champagne, T. Verbiest, P. Gangopadhyay, and A. Persoons, *Chem. Phys. Chem.* **7**, 1654 (2006).
- [30] T. Kjaergaard, P. Jørgensen, A.J. Thorvaldsen, P. Salek, and S. Coriani, *J. Chem. Theor. Comp.* **5**, 1997 (2009).
- [31] S. Ikäläinen, M.V. Romalis, P. Lantto, and J. Vaara, *Phys. Rev. Lett.* **105**, 153001 (2010).
- [32] M. Krykunov, A. Banerjee, T. Ziegler, and J. Autschbach, *J. Chem. Phys.* **122**, 074105 (2005).
- [33] A. Banerjee, J. Autschbach, and T. Ziegler, *Int. J. Quantum Chem.* **101**, 572 (2005).
- [34] J.P. van der Ziel, P.S. Pershan, and L.D. Malmstrom, *Phys. Rev. Lett.* **15**, 190 (1965).
- [35] A.D. Buckingham and L.C. Parlett, *Science, N. Y.* **264**, 1748 (1994).
- [36] A.D. Buckingham and L.C. Parlett, *Mol. Phys.* **91**, 805 (1997).
- [37] M. Jaszunski and A. Rizzo, *Mol. Phys.* **96**, 855 (1999).
- [38] F. London, *J. Phys. Radium* **8**, 397 (1937), 7ème Série.
- [39] A.E. Hansen and T.D. Bouman, *J. Chem. Phys.* **82**, 5035 (1985); this is the first reference in which the reinterpretation of the GIAO acronym for gauge-including-atomic-orbitals has been proposed, see footnote 6, p. 5047.
- [40] C. Duprez-Quesnoit and J. Tillieu, *Int. J. Quantum Chem.* **17**, 155 (1980).
- [41] C. Duprez-Quesnoit, *Int. J. Quantum Chem.* **17**, 169 (1980).
- [42] C. Duprez-Quesnoit, *Int. J. Quantum Chem.* **19**, 191 (1981).
- [43] S. Coriani, M. Pecul, A. Rizzo, P. Jørgensen, and M. Jaszunski, *J. Chem. Phys.* **117**, 6417 (2002).
- [44] S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic Press, New York, 1974).
- [45] P. Lazzeretti, *Adv. Chem. Phys.* **75**, 507 (1987).
- [46] P. Lazzeretti, in *Handbook of Molecular Physics and Quantum Chemistry* (John Wiley & Sons, Ltd., Chichester, 2003), Vol. 3, Part 1, Chap. 3, pp. 53–145; See eqs. (857), (866), (943), and the discussion after Equation (946).
- [47] A. Ligabue, P. Lazzeretti, M.P.B. Varela, and M.B. Ferraro, *J. Chem. Phys.* **116**, 6427 (2002).
- [48] E.P. Wigner, *Group Theory* (Academic Press, New York, 1959).
- [49] R.R. Birss, *Symmetry and Magnetism* (North-Holland Publishing Co., Amsterdam, 1966).
- [50] T.H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- [51] B.J. Orr and J.F. Ward, *Mol. Phys.* **20**, 513 (1971).
- [52] D.M. Bishop, *Rev. Mod. Phys.* **62**, 343 (1990).
- [53] J. Olsen and P. Jørgensen, *J. Chem. Phys.* **82**, 3235 (1985).
- [54] W. Moffitt, *J. Chem. Phys.* **25**, 467 (1956).
- [55] A. Moscowitz, in *Modern Quantum Chemistry*, edited by O. Sinanoglu (Academic Press, New York, 1965), Vol. 3, pp. 45–66.
- [56] A.E. Hansen and T.D. Bouman, *Adv. Chem. Phys.* **44**, 545 (1980).
- [57] P. Lazzeretti, in *Fundamental World of Quantum Chemistry*, edited by E.J. Brändas and E.S. Kryacko (Kluwer Academic, Netherlands, 2004), Vol. III, pp. 199–213.
- [58] T.B. Pedersen, H. Koch, L. Boman, and A.M.S. de Merás, *Chem. Phys. Lett.* **393**, 319 (2004).
- [59] L. Seamans and J. Linderberg, *Mol. Phys.* **24**, 1393 (1972).
- [60] S. Pelloni and P. Lazzeretti, *J. Chem. Phys.* **136**, 164110 (2012).
- [61] R.R. Birss, *Rep. Prog. Phys.* **26**, 307 (1963).
- [62] In Table 4e of Ref. [49] and in Table 2e of Ref. [61] the lines for H_3 and P_3 and the lines for I_3 and Q_3 are identical.
- [63] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D. K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, *et al.*, *Gaussian 2003, Revision B.05* (Gaussian, Inc., Pittsburgh PA, 2003).
- [64] D.E. Woon and T.H. Dunning, *J. Chem. Phys.* **103**, 4572 (1995).
- [65] *J. Chem. Phys.* **23**, 1997 (1955).
- [66] R.S. Mulliken, *J. Chem. Phys.* **24**, 1118 (1956).
- [67] P.J. Mohr and B.N. Taylor, *Rev. Mod. Phys.* **77**, 1 (2005).