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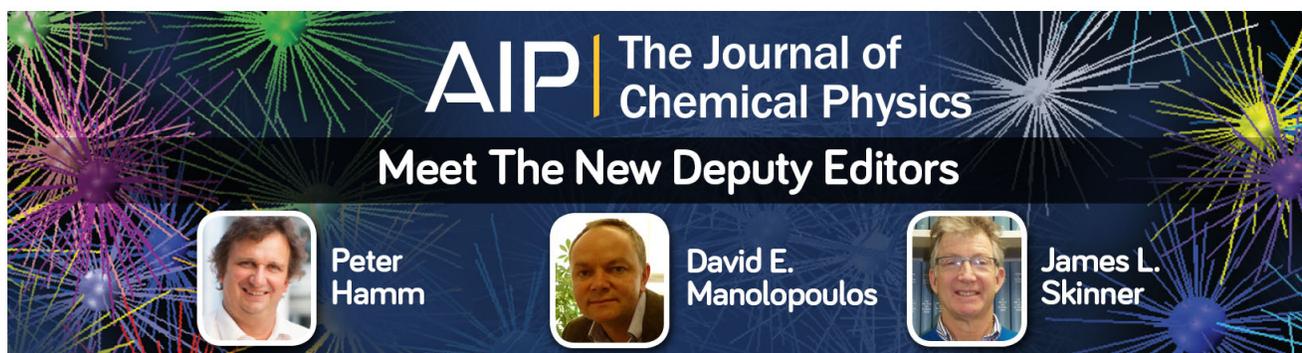
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On the resolution of the optical rotatory power of chiral molecules into atomic terms. A study of hydrogen peroxide

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An additive scheme for resolving average optical rotatory power of a molecule into atomic contributions, based on the acceleration gauge for the electric dipole, and/or the torque formalism, has been applied to hydrogen peroxide. Extended calculations have been carried out to test the reliability of the partition method. Gross atomic isotropic contributions to the average molecular property from oxygen and hydrogen atoms have been evaluated. The force and torque gauges provide different numerical values for atomic contributions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1461816]

I. INTRODUCTION

Several interesting questions related to the idea of molecular structure arise, concerning the reliability of theoretical schemes for partitioning global molecular properties into atomic contributions, which constitutes an object of widespread interest from the early days of chemistry. The concept of atoms-in-molecules (AIM) as spatial domains bounded in space is deeply rooted within the preliminary assumption that a molecular structure can be theoretically defined and experimentally observed.^{1–20} In a fully *a priori* context, an axiomatic foundation for the idea of AIM has been attempted by Ayers, on the demand of maximum transferability of properties of atoms from molecule to molecule,²¹ and found consistent with the partitioning scheme of Hirshfeld.⁵

Experimental evidence on the fact that atoms and functional groups conserve some peculiar properties in a wide range of different molecular environments has long been known, see, for instance, the work of Pascal on magnetic susceptibilities,^{22–25} and that of Denbigh²⁶ and Vogel²⁷ for electric dipole polarizabilities of molecules in static fields.

Within this general framework, a number of questions naturally emerge. It can be asked whether *dynamic* molecular properties, e.g., frequency dependent electric polarizabilities, or optical rotatory power, can be reliably partitioned into atomic contributions, consistent with the equilibrium structure retained for a molecule responding to an external electromagnetic field. Answering these questions is by no means trivial. Particularly problematic, for the reasons expounded hereafter, seems the problem of optical rotatory power in a series of homologous chiral species.

The quantum mechanics of a molecule, that is a many-body system with structure, properties, and phenomenology much richer and complicate than an atom, is by no means a

simple branch of physics. A number of very general chemical,²⁸ physical,^{29–32} and epistemological questions, see, for instance, a recent paper,³³ and references therein, are still wide open as regards the general understanding and implications of words like “shape,” “bond,” “isomerism,” “symmetry,” and phrases like “bond lengths,” “bond angles,” “internal rotation barriers,” “nuclear vibrations,” “molecular chirality,” “lone-pair electrons,” to quote but a few.

Moreover, there is no widespread consensus between chemist's and physicist's points of view as to what special, unique properties fully characterize a “molecule.” For example, whereas the former relies on “an almost concrete, if not dogmatic, position,” and puts the emphasis on concepts like molecular structure, i.e., something intrinsically rigid and static, the latter is mainly concerned in dynamical aspects which rarely make explicit reference to this idea: “a physicist's grip on a molecule is rather slippery,” in the felicitous words of Monkhorst.³⁴

Nowadays the search for the “optimized geometry” of a given molecule, with its paraphernalia of optimum bond distances and angles, constitutes a preliminary step of many quantum chemical studies aimed at determining its “structure.” Such an attitude of theoretical chemists arises from accepting the Born–Oppenheimer (BO) approximation,³⁵ a cornerstone that in a way constitutes their imprinting.

However, the clamped-nuclei representation brings in a number of conceptual difficulties.^{30–32} For instance, the existence of two enantiomeric structures of a chiral molecule is hard to explain, if the idea of massive nuclei, frozen in one spatial configuration, has been postulated within the framework of the BO assumptions. In fact, it can be easily seen that the time-independent electronic wave function of a given enantiomer is not an eigenstate to the parity-conserving electronic Hamiltonian of the molecule, Refs. 30 and 36, which has been a matter of considerable concern for

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the founding fathers of quantum mechanics, as most enantiomeric species are very stable in time.

A possible way-out of this dilemma, in terms of chiral shapes that can tunnel between two limit mirror structures, has been proposed by Hund³⁷ by using time-dependent perturbation theory. The time required for an oscillation might be comparable with the age of the universe, which would explain the experimentally observed stability of enantiomeric molecules occurring in terrestrial biochemistry. However, in the spirit of Hund's solution to homochirality,³⁷ the hypothesis of molecular structure gets loose, and the BO approximation becomes a burden.

At a single frequency, the rotation angle of plane-polarized light by a solution of chiral molecules is related to the differential absorption of left and right circularly polarized light.^{38–40} In optical rotatory dispersion spectroscopy, optical rotation is measured as a function of the frequency of a monochromatic wave passing through chiral species in solution. The mechanisms which determine the rotation angle and the spectroscopical parameters in connection with molecular structure are quite complicated and yet insufficiently understood.

Firstly, can we reasonably suppose that, for instance, within the series of amino acids in aqueous solution, $R-NH_4^+-CO_2^-R'$, the contributions from the $NH_4^+-CO_2^-$ -moiety is transferable? Secondly, there is an atomic environment, or group, e.g., an asymmetric carbon within a chiral molecule, which is mainly responsible for the global rotatory power, and provides the largest contribution? Thirdly, can we make any progress in the assignment of absolute stereochemical configuration through the knowledge of bulk and sign of atomic and group contributions in a given pattern of chemical bonds? A tabulation of these contributions would be quite helpful and provide quantitative probes of molecular chirality.⁴¹

As a preliminary attempt, this paper sets out to devise a suitable theoretical procedure for resolving the optical activity of a very simple systems, H_2O_2 , in frozen chiral arrangements of the nuclei, into atomic contributions. It is also investigated how these contributions vary in a change of molecular structure, i.e., a rotation about the bond between the heavier atoms. Besides the considerable theoretical interest of these topics, discovering the relations between molecular structure, and atomic contributions to rotation angle is a matter of practical importance, e.g., in view of medical applications.⁴¹

II. TENSORS RELATED TO OPTICAL ROTATORY POWER

Allowing for current notation,⁴² let us consider 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 , \mathbf{p}_i , $\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$, $i = 1, 2, \dots, n$. Corresponding quantities for nucleus I are $Z_I e$, M_I , \mathbf{R}_I , etc. Let us also introduce a series of global electronic operators for position \mathbf{R} , total canonical momentum \mathbf{P} , angular momentum \mathbf{L} , electric, $\boldsymbol{\mu} = -e\mathbf{R}$, and magnetic, $\mathbf{m} = -(e/2m_e c)\mathbf{L}$, dipole moments. To discuss the behavior of molecular properties in a coordinate

transformation, it is expedient to give definitions for \mathbf{R} , \mathbf{L} , etc., which explicitly specify the origin \mathbf{r}_0 of the coordinate system, e.g.,

$$R_\alpha(\mathbf{r}_0) = \sum_{i=1}^n (r_{i\alpha} - r_{0\alpha}),$$

$$L_\alpha(\mathbf{r}_0) = \sum_{i=1}^n l_{i\alpha}(\mathbf{r}_0) = \epsilon_{\alpha\beta\gamma} \sum_{i=1}^n (r_{i\beta} - r_{0\beta}) p_{i\gamma}. \quad (1)$$

Sum over repeated Greek suffixes is implied, and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita unit tensor.

The optical rotatory power of a chiral molecule can be rationalized via the tensor⁴²

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

where \Im takes the imaginary part of the term within brackets,

$$\omega_{ja} = \frac{1}{\hbar} (E_j^{(0)} - E_a^{(0)}), \quad (3)$$

are the natural transition frequencies of the molecule in the reference state $|\Psi_a^{(0)}\rangle \equiv |a\rangle$, with energy eigenvalue $E_a^{(0)}$, excited state energies $E_j^{(0)}$, determined by solving the Schrödinger equation for the unperturbed Hamiltonian $H^{(0)}$, and ω is the angular frequency of a monochromatic wave impinging on the molecule.

As $\boldsymbol{\mu}$ and \mathbf{m} are, respectively, a polar and an axial vector, the trace of the tensor defined by Eq. (2), which is related to quantities experimentally accessible,³⁸ is a pseudoscalar, changing sign under inversion of the coordinate system. Equation (2) defines a second-order property in the length-angular momentum RL picture, i.e., $\hat{\kappa}_{\alpha\beta}^{(RL)}(\omega) \equiv \hat{\kappa}_{\alpha\beta}(\omega)$. At any rate, owing to the peculiar features of quantum mechanics, one is free to choose different representations, or gauges, via canonical transformations of the Hamiltonian. Alternative definitions for the tensor introduced via expression (2) can be immediately arrived at by Ehrenfest, off-diagonal hypervirial relations⁴³ allowing for the force and the torque gauges.⁴²

Total force and torque about the origin acting on the electrons are only due to the nuclei in an unperturbed molecule, as total electron-electron forces cancel out by action equals reaction. Therefore,

$$\frac{i}{\hbar} [H^{(0)}, \mathbf{P}] = \mathbf{F}_n^N = -e^2 \sum_{I=1}^N Z_I \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}, \quad (4)$$

$$\frac{i}{\hbar} [H^{(0)}, \mathbf{L}(\mathbf{r}_0)] = \mathbf{K}_n^N(\mathbf{r}_0) = e^2 \sum_{I=1}^N Z_I \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \times (\mathbf{R}_I - \mathbf{r}_0). \quad (5)$$

The operators for total force and torque can also be conveniently rewritten in terms of the electric field

$$\mathbf{E}_I^i = e \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3}, \quad (6)$$

on nucleus I , arising from electron i .

Allowing for the hypervirial relationships,^{42,43}

$$\begin{aligned} \langle a|R_\alpha|j\rangle &= \frac{i}{m_e} \omega_{ja}^{-1} \langle a|P_\alpha|j\rangle \\ &= -\frac{1}{m_e} \omega_{ja}^{-2} \langle a|F_{n\alpha}^N|j\rangle \\ &= \frac{e}{m_e} \omega_{ja}^{-2} \sum_{I=1}^N Z_I \langle a|E_{I\alpha}^n|j\rangle, \end{aligned} \quad (7)$$

$$\langle a|L_\alpha|j\rangle = i \omega_{ja}^{-1} \langle a|K_{n\alpha}^N|j\rangle, \quad (8)$$

five alternative expressions are found for the rotatory power tensor, see Refs. 42 and 44

$$\begin{aligned} \hat{\kappa}_{\alpha\beta}^{(RK)}(\omega) &= \frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \\ &\quad \times \Re(\langle a|R_\alpha|j\rangle \langle j|K_{n\beta}^N|a\rangle), \end{aligned} \quad (9)$$

$$\begin{aligned} \hat{\kappa}_{\alpha\beta}^{(PL)}(\omega) &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \\ &\quad \times \Re(\langle a|P_\alpha|j\rangle \langle j|L_\beta|a\rangle), \end{aligned} \quad (10)$$

$$\begin{aligned} \hat{\kappa}_{\alpha\beta}^{(PK)}(\omega) &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \\ &\quad \times \Im(\langle a|P_\alpha|j\rangle \langle j|K_{n\beta}^N|a\rangle), \end{aligned} \quad (11)$$

$$\begin{aligned} \hat{\kappa}_{\alpha\beta}^{(FL)}(\omega) &= \frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \\ &\quad \times \Im(\langle a|F_{n\alpha}^N|j\rangle \langle j|L_\beta|a\rangle), \end{aligned} \quad (12)$$

$$\begin{aligned} \hat{\kappa}_{\alpha\beta}^{(FK)}(\omega) &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3(\omega_{ja}^2 - \omega^2)} \\ &\quad \times \Re(\langle a|F_{n\alpha}^N|j\rangle \langle j|K_{n\beta}^N|a\rangle). \end{aligned} \quad (13)$$

Obviously enough, the pseudo tensor character of $\hat{\kappa}_{\alpha\beta}(\omega)$ is unaffected by the change of picture, as $F_{n\alpha}^N$ and $K_{n\alpha}^N$ are, respectively, polar and axial vectors. All these definitions are equivalent in quantum mechanics, as a consequence of the invariance of the theory in a canonical transformation. However, the estimates for the property are numerically the same only if the eigenfunctions $|a\rangle$ and $|j\rangle$ are the exact eigenstates to a model Hamiltonian,⁴³ a condition that is hardly met in practice. In a calculation based on the algebraic approximation, values arrived at by relationships (2) and (9)–(13) can be appreciably different: Their numerical agreement gives a benchmark of basis set completeness and an *a priori* quality criterion.

In a translation of origin of the coordinate frame, $\mathbf{r}'' = \mathbf{r}' + \mathbf{d}$, the rotatory power tensor changes according to the relationship⁴²

$$\begin{aligned} \hat{\kappa}_{\alpha\beta}(\mathbf{r}'') &= \hat{\kappa}_{\alpha\beta}(\mathbf{r}') - \frac{1}{2c} \epsilon_{\beta\gamma\delta} d_\delta \alpha_{\alpha\gamma}, \\ \text{Tr}\{\hat{\kappa}(\mathbf{r}'')\} &= \text{Tr}\{\hat{\kappa}(\mathbf{r}')\}, \end{aligned} \quad (14)$$

Eq. (14) is valid, and the trace of the tensor stays the same, if the hypervirial relations, Eqs. (7), are exactly satisfied. For instance, to fulfill this requirement within the algebraic ap-

proximation, a complete basis set should be used.⁴³ In any practical calculation adopting a truncated basis, the equations describing the origin dependence of molecular tensors must be properly interpreted. Thus, for instance, if the optical activity tensor is defined via Eq. (2), then in Eq. (14) the electric polarizability in mixed length-velocity gauge⁴² must be used. In any event, the trace of the tensor in the (P, L) gauge, Eq. (10), will be invariant in any approximate calculation, which makes this formalism useful if only gaugeless basis sets are available. Another way-out of the origin-dependence problem is provided by basis sets of London orbitals,⁴⁵ i.e., gauge-including atomic orbitals (GIAO), as they have been renamed for the first time by Hansen and Bouman,⁴⁶ implemented in DALTON.⁴⁷

III. ATOMIC CONTRIBUTIONS TO OPTICAL ROTATORY POWER

Although some qualitative discussions in terms of atomic and group contributions to the rotation angle of polarized light in chiral species have been put forward along the years,^{48–50} attempts to numerical estimates became available only recently.⁴¹ Within this context, the nice features of quantum-mechanical definitions like those given by Eqs. (9) and (12) are readily seen. Total force and torque of the nuclei on the electrons can be partitioned as sums of corresponding atomic operators

$$\mathbf{F}_n^N = \sum_{I=1}^N \mathbf{F}_n^I = \sum_{i=1}^n \mathbf{F}_i^N, \quad (15)$$

$$\mathbf{F}_i^I = -e^2 Z_I \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3},$$

$$\mathbf{K}_n^N = \sum_{I=1}^N \mathbf{K}_n^I = \sum_{i=1}^n \mathbf{K}_i^N, \quad (16)$$

$$\mathbf{K}_i^I = e^2 Z_I \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \times \mathbf{R}_I.$$

Accordingly, the trace of the tensor for optical activity can be partitioned into atomic terms. For instance, in the low-frequency limit, i.e., $\hat{\kappa}_{\alpha\alpha}(0) \equiv \hat{\kappa}_{\alpha\alpha}$, we can introduce an $[RK(I)]$ scheme

$$\hat{\kappa}_{\alpha\alpha} = \sum_{I=1}^N \hat{\kappa}_{\alpha\alpha}^{[RK(I)]}, \quad (17)$$

$$\hat{\kappa}_{\alpha\alpha}^{[RK(I)]} = \frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \Re(\langle a|R_\alpha|j\rangle \langle j|K_{n\alpha}^I|a\rangle),$$

a $[PK(I)]$ scheme

$$\hat{\kappa}_{\alpha\alpha} = \sum_{I=1}^N \hat{\kappa}_{\alpha\alpha}^{[PK(I)]}, \quad (18)$$

$$\begin{aligned} \hat{\kappa}_{\alpha\alpha}^{[PK(I)]} &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^4} \\ &\quad \times \Im(\langle a|P_\alpha|j\rangle \langle j|K_{n\alpha}^I|a\rangle), \end{aligned}$$

an $[F(I)L]$ scheme

$$\hat{\kappa}_{\alpha\alpha} = \sum_{I=1}^N \hat{\kappa}_{\alpha\alpha}^{[F(I)L]},$$

$$\hat{\kappa}_{\alpha\alpha}^{[F(I)L]} = \frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^4} \Im(\langle a | F_{n\alpha}^I | j \rangle \langle j | L_{\alpha} | a \rangle),$$

an $[F(I)K]$ scheme

$$\hat{\kappa}_{\alpha\alpha} = \sum_{I=1}^N \hat{\kappa}_{\alpha\alpha}^{[F(I)K]},$$

$$\hat{\kappa}_{\alpha\alpha}^{[F(I)K]} = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \times \Re(\langle a | F_{n\alpha}^I | j \rangle \langle j | K_{n\alpha}^I | a \rangle)$$

and an $[FK(I)]$ scheme

$$\hat{\kappa}_{\alpha\alpha} = \sum_{I=1}^N \hat{\kappa}_{\alpha\alpha}^{[FK(I)]},$$

$$\hat{\kappa}_{\alpha\alpha}^{[FK(I)]} = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \times \Re(\langle a | F_{n\alpha}^I | j \rangle \langle j | K_{n\alpha}^I | a \rangle).$$

This method of using the transition matrix elements of nuclear centered operators avoids the need to ever *a priori* partitioning of the molecule into overlapping atoms: The resolution is instead accomplished by averaging the operator over the total system, the form and the properties of the operator determining the “atomic” contribution.^{51–55} Possibly such an “operator averaging method” (OAM), as it has been called by a referee,⁵⁶ cannot yield atomic and group contributions that are transferable as those obtained using Bader’s atoms-in-molecules, because the operator averaging will extend into what are in reality basins of neighboring atoms. At any rate, it relies on completely general and very simple quantum mechanical recipes, easy to understand and to apply in numerical applications.

An “atom-in-molecule” within Bader’s approach^{4,9,12,15–17,19,20} is topologically defined by asymptotic lines of the gradient field. Its “geometry” can be visualized in a streamline map of that field. Alternatively, in the present case of optical rotatory power, we could suppose

that an “atom” within a given molecule is a region of space defined by the actual domain of “atomic” operators like $F_{n\alpha}^I$ and $K_{n\alpha}^I$.⁵⁵

Such a domain is not necessarily closed and is not uniquely determined, depending on the form of the operator itself: Thus, $F_{n\alpha}^I$ and $K_{n\alpha}^I$ may actually sample different regions of space, leading to different definitions of “effective” atomic basin.

It should also be recalled that the numerical values for the atomic contributions to the optical rotatory power obtained via Eqs. (17)–(21) depend on the gauge of the vector potential, or, more simply, on the coordinate system adopted in the calculation. At any rate, the reliability of partitioning methods based on these relationships can only be established via empirical criteria and numerical tests, of the type attempted in the present study.

IV. RESULTS AND DISCUSSION

The molecular equilibrium geometry of H_2O_2 adopted in the calculations has been optimized at the 6-31G* SCF (self-consistent field) level of accuracy via the GAMESS code.⁵⁷ The geometrical parameters for a series of rotamers, corresponding to different HOO–OOH dihedral angles, have been obtained keeping fixed equilibrium bond distances. In all the calculations of the $\kappa_{\alpha\beta}(\omega)$ tensor the origin of the coordinate system is in the center of mass.

Six basis sets from Ref. 58, of increasing extension and quality, have been used in the calculation of the rotatory power tensor and its average atomic contributions. Basis set *I* is $(14s14p5d/5s5p) \rightarrow [6s6p2d/2s2p]$, basis set *II* is $(18s18p7d/7s7p) \rightarrow [6s6p7d/2s2p]$, with uncontracted d functions on the oxygen atom, basis set *III* is the same as basis set *I*, where all the GTOs are allowed to vary freely, i.e., the uncontracted $(14s14p5d/5s5p)$. Basis set *IV* is $(18s18p7d/7s7p) \rightarrow [6s18p7d/2s2p]$ with uncontracted p functions and d polarization functions on oxygen atom. The use of steep p functions, obtained by allowing the $18p$ subset to vary freely, is recommended to improve the representation of force operators.^{59,60} Basis set *V* is $(18s18p7d/7s7p) \rightarrow [6s18p7d/7s7p]$ with uncontracted p and d functions on the oxygen atom, and p polarization functions on hydrogen

TABLE I. Average rotatory power tensor of H_2O_2 at equilibrium geometry^a (in p.p.t. a.u.).

Formalism ^b	<i>I</i> (88)	<i>II</i> (148)	<i>III</i> (212)	<i>IV</i> (220)	<i>V</i> (260)	<i>VI</i> (284)
(<i>R,L</i>)	−0.281	−0.186	−0.174	−0.171	−0.157	−0.160
(<i>R,L</i>) ^c	−0.331	−0.169	−0.201	−0.167	−0.159	−0.160
(<i>P,L</i>)	−0.263	−0.142	−0.155	−0.118	−0.137	−0.137
(<i>F,L</i>)	−0.414	−0.285	−0.284	−0.244	−0.220	−0.219
(<i>R,K</i>)	−0.313	−0.199	−0.203	−0.184	−0.161	−0.168
(<i>P,K</i>)	−0.298	−0.155	−0.186	−0.131	−0.142	−0.146
(<i>F,K</i>)	−0.444	−0.296	−0.307	−0.257	−0.216	−0.218
$E_{\text{SCF}}^{\text{d}}$	−150.791 708	−150.840 667	−150.845 520	−150.841 458	−150.849 289	−150.850 927

^aNumber of CGTOs is given in parentheses for Gaussian basis sets *I*–*VI*.

^bSee Eqs. (2), (9)–(13) in the text.

^cCalculations made by the Dalton program (Ref. 47), using basis sets of gauge-including atomic orbitals (GIAO) corresponding to the same basis sets *I*–*VI*.

^dSCF energy in bohr.

TABLE II. Partition of the average rotatory power of hydrogen peroxide at equilibrium geometry, $\bar{\kappa}(\omega) = (1/3)\kappa_{\alpha\alpha}(\omega)$, (in p.p.t. a.u.) into atomic contributions vs the angular frequency ω of the perturbing monochromatic wave. Results are from basis set VI, with the origin in the center of mass (c.m.). Values of ω (in a.u.) are given in parentheses.

Atom	Formalism	$\bar{\kappa}(0.0)$	$\bar{\kappa}(0.10)$	$\bar{\kappa}(0.15)$	$\bar{\kappa}(0.20)$	$\bar{\kappa}(0.26)$	$\bar{\kappa}(0.27)$	$\bar{\kappa}(0.28)$	$\bar{\kappa}(0.30)$
	(R,L)	-0.160	-0.124	-0.034	0.304	6.579	47.535	-12.488	-1.851
	(R,L) ^a	-0.165	-0.130	-0.041	0.294	6.591	48.222	-12.574	-2.000
	(P,L)	-0.137	-0.097	0.000	0.361	6.998	50.402	-13.253	-2.176
O	(R,K ^O)	-0.065	-0.026	0.062	0.372	6.430	48.353	-13.940	-6.386
H	(R,K ^H)	-0.019	-0.041	-0.087	-0.238	-3.331	-25.977	8.094	5.664
Total	(R,K)	-0.168	-0.135	-0.051	0.268	6.198	44.752	-11.692	-1.443
O	(P,K ^O)	-0.037	0.006	0.103	0.438	6.876	51.322	-14.710	-6.704
H	(P,K ^H)	-0.036	-0.061	-0.113	-0.278	-3.580	-27.783	8.504	5.830
Total	(P,K)	-0.146	-0.110	-0.019	0.321	6.592	47.449	-12.412	-1.750
O	(E ^O ,L)	0.608	0.726	0.926	1.374	2.386	-5.663	9.634	17.559
H	(E ^H ,L)	-0.718	-0.825	-0.998	-1.336	-0.449	19.085	-12.745	-16.630
Total	(F,L)	-0.219	-0.199	-0.144	0.077	3.874	26.843	-6.222	1.859
O	(F ^O ,K)	0.628	0.748	0.952	1.409	2.515	-4.989	9.514	17.569
H	(F ^H ,K)	-0.737	-0.848	-1.026	-1.376	-0.676	17.645	-12.393	-16.507
Total	(F,K)	-0.218	-0.200	-0.147	0.066	3.677	25.313	-5.758	2.124
O	(F,K ^O)	-0.171	-0.158	-0.120	0.037	3.405	26.744	-7.873	-3.358
H	(F,K ^H)	0.062	0.058	0.047	0.004	-1.567	-14.088	4.994	4.420
Total	(F,K)	-0.218	-0.200	-0.147	0.066	3.677	25.313	-5.758	2.124

^aCalculations made by the DALTON program (Ref. 47), using basis set of gauge-including atomic orbitals (GIAO) corresponding to the same basis set.

atom. Basis set VI is the fully uncontracted (18s18p7d/7s7p) basis set II.

The average trace of the rotatory power tensor, $\bar{\kappa}(\omega) = (1/3)\kappa_{\alpha\alpha}(\omega)$ in the low-frequency limit $\omega=0$, calculated

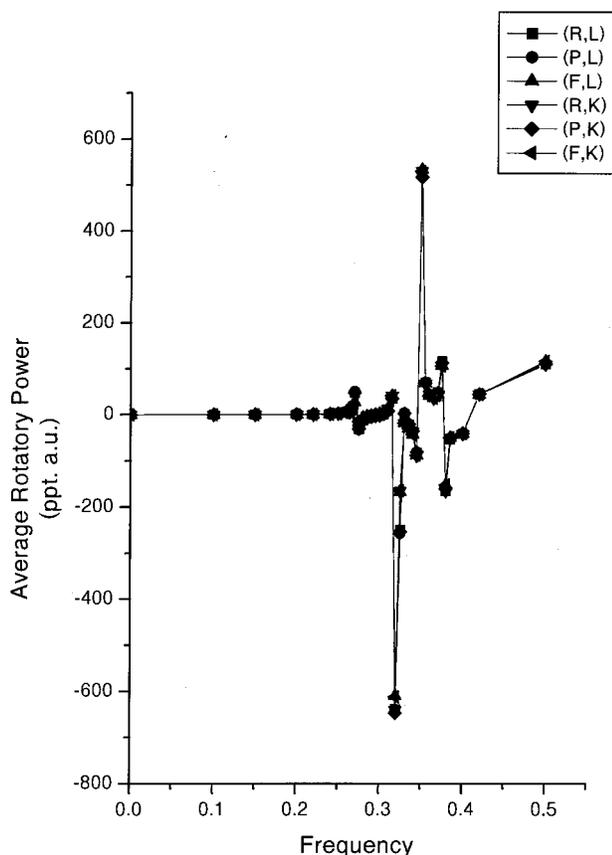


FIG. 1. The average rotatory power of hydrogen peroxide, expressed as $(1/3)\text{Tr } \kappa(\omega)$, in various formalisms, as a function of the frequency ω (in part per thousand atomic units).

for the molecular equilibrium geometry of hydrogen peroxide at the random-phase approximation (RPA) level of accuracy via various formalisms, implemented in the SYSMO code⁶¹ according to Eqs. (2), and (9)–(13), is reported in Table I. Comparison with values obtained via the DALTON code⁴⁷ within the (R,L) representation, using GIAO basis sets constructed by including field dependent phase factors in the functions of basis sets I–VI, shows that fairly stable results are only obtained via basis sets of higher flexibility, i.e., IV–VI. Convergence of predictions from GIAOs does not seem to be much better than for gaugeless basis sets. In any event, excellent agreement is observed for theoretical (R,L) estimates arrived at by larger basis sets IV, V, and VI, which are expected to be close to the Hartree–Fock limit for the property. The results obtained within (P,L), (R,K),

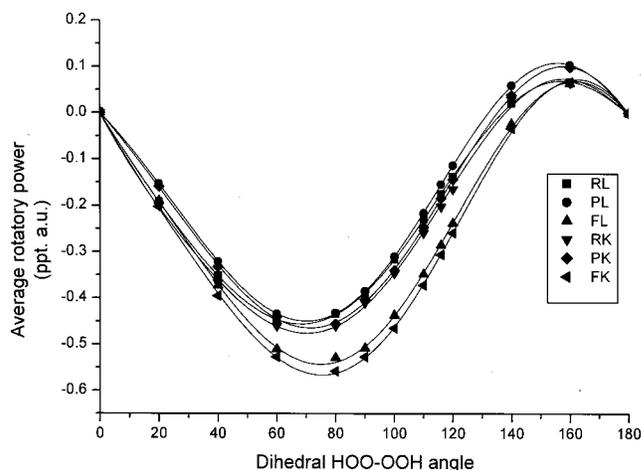


FIG. 2. The average rotatory power of hydrogen peroxide, $(1/3)\text{Tr } \kappa(\omega)$, in the limit $\omega=0$, in various formalisms, as a function of the dihedral angle HOO–OOH (in part per thousand atomic units).

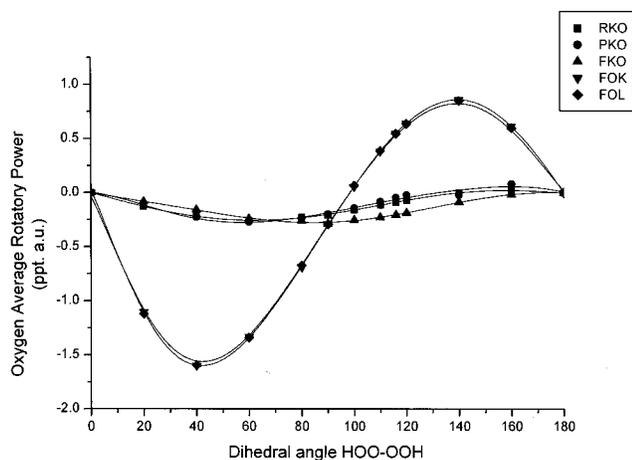


FIG. 3. Contribution of one oxygen atom to the average rotatory power of hydrogen peroxide in the limit $\omega=0$, in various formalisms, as a function of the dihedral angle HOO-OOH (in part per thousand atomic units).

and (P,K) gauges are in satisfactory agreement with (R,L) only for basis sets V and VI .

Higher deviations are found for (F,L) and (F,K) formalisms. A systematic increase of accuracy is observed in Table I in theoretical determinations of these quantities via basis sets $I-VI$. However, even for basis set VI , the calculated values are still $\sim 50\%$ larger in modulus than (R,L) , indicating that, despite their extension and quality, the Gaussian basis sets employed in the present calculation are not sufficiently suitable for accurate representation of the force operators.

Eventually, we recall that, whereas the (R,L) estimates from DALTON calculation are independent of the origin, only (P,L) values are independent of it for the gaugeless basis sets used here.

The frequency dependence of oxygen and hydrogen atomic contributions to the average tensor, $\bar{\kappa}(\omega)$, for a number of ω values up to 0.30 a.u., is shown in Table II. A dramatic change of magnitude and oscillation of sign can be observed on increasing ω , see also Fig. 1. In fact, when the value of the frequency ω of the perturbing monochromatic wave approaches the natural frequencies ω_{ja} , the optical rotatory power formally goes to $\pm\infty$, see Eqs. (2) and (9)–(13), i.e., resonance occurs with light absorption. The phenomenon is rationalized via Kramers–Krönig relationships.⁶²

The results displayed in this table clearly show that the schemes based on torque, Eqs. (17), (18), (21), and on force formalisms, Eqs. (19) and (20), respectively, for partitioning the optical rotatory power of hydrogen peroxide into hydrogen and oxygen contributions, provide radically different results. As it can also be seen in Figs. 2–4, despite the problem of incomplete convergence, the $[RK(I)]$, $[PK(I)]$, and $[FK(I)]$ estimates are close to one another, and define a homogeneous set of numerical values. They would become the same if the hypervirial relationships, Eq. (7), were fulfilled.

The force scheme, Eqs. (19), and (20), yields another set of internally consistent predictions for $[F(I)L]$ and $[F(I)K]$, which would become the same in the limit of com-

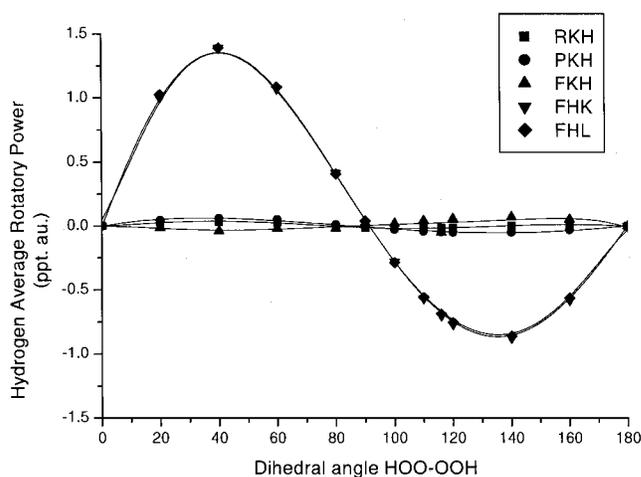


FIG. 4. Contribution of one hydrogen atom to the average rotatory power of hydrogen peroxide in the limit $\omega=0$, in various formalisms, as a function of the dihedral angle HOO-OOH (in part per thousand atomic units).

plete set of expansion, when Eq. (8) holds. It is observed that the atomic contributions defined the force picture, Eqs. (19), and (20), are systematically larger, in absolute value, than those given by the torque scheme, Eqs. (17), (18), and (21).

In a previous paper⁵⁵ we proposed a definition of the I th atom in a molecule as that region which essentially coincides with the domains weighed by atomic operators like those appearing in Eqs. (15) and (16). The present findings imply that, as expected,⁵⁵ the basins of the operators \mathbf{F}_n^I and \mathbf{K}_n^I do not coincide. In other words they define different “atoms in a molecule” within the OAM approach, see the Appendix hereafter and Refs. 51–55.

A plot of total average tensor $\bar{\kappa}(\omega)$ versus the frequency of the monochromatic plane wave is shown in Fig. 1. In the scale used, the calculated values from different formalisms appear close to one another. The oscillations of the plot occur in the vicinity of natural frequencies, at ≈ 0.27 , ≈ 0.32 , ≈ 0.36 au within the present RPA calculations.

Figures 2–4 show the variation of total $\bar{\kappa}(0)$ and its atomic contributions for a series of different HOO-OOH dihedral angles, ϕ . Figure 2 gives an overall measure of the systematic deviation of the curves for (F,L) and (F,K) estimates from corresponding ones for (R,L) , (P,L) , (R,K) , and (P,K) . In fact, two separate sets of curves are found, consistent with numerical values in Table 1 for the equilibrium geometry.

Figures 3 and 4, showing the atomic contributions of oxygen and hydrogen atoms, respectively, as a function of ϕ , provide analogous information. (R,K^O) and (P,K^O) are virtually the same on the scale of the plot, but slightly different from (F,K^O) , which is consistent, *vide supra*, with lesser accuracy of the force formalism calculations. In the case of a complete basis set, the numerical values (R,K^O) , (P,K^O) , and (F,K^O) would converge, defining atomic contributions in the torque representation.

On the other hand, the (F^O,L) and (F^O,K) curves are close to one another. They are characterized by a very different pattern, with a minimum and a maximum, respectively, in the proximity of 40 and 140 degree. Such a trend cannot be

imputed to insufficient convergence of atomic contributions in the force gauge. It is due to the peculiar structure of the \mathbf{F}_n^I operator, *vide supra*.

Similar conclusions are arrived at from inspection of Fig. 4, showing that (R, K^H) and (P, K^H) are close to one another and slightly different from (F, K^H) . The corresponding values lie in a set of three curves, whereas the two curves relative to (F^H, L) and (F^H, K) belong to a different set. These findings confirm that the atoms-in-molecule weighed by the force, \mathbf{F}_n^I , and torque, \mathbf{K}_n^I , operators do not coincide in general for a large set of molecular geometries. This can be understood by comparing the definitions, Eqs. (15) and (16). Both scale as the same inverse power of electron-nucleus distance, i.e., $\propto |\mathbf{r}_i - \mathbf{R}_I|^{-2}$, but the second one also depends on \mathbf{R}_I .

Another striking difference between Figs. 3 and 4 is that the maximum atomic contribution of the former almost coincide with the minimum of the latter, i.e., oxygen and hydrogen atoms provide contribution of different sign to total average optical rotatory power.

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APPENDIX: CONNECTIONS BETWEEN AIM AND OAM METHODS

Commenting on the connection between the Bader’s AIM method and the partitioning criteria for electric dipole polarizability, a referee of Ref. 55 made a series of fundamental remarks that are reported hereafter.⁵⁶ They are instrumental to understand the connection between the partitioning criteria for electronic charge,^{51,52} electric dipole polarizability,^{53,55} and optical rotatory power based on Eqs. (4) and (5), and the Bader’s AIM method.^{4,9,12,15–17,19,20} The case of electric dipole polarizability is examined hereafter, but essentially the same considerations would apply to partitioning of any global second-rank molecular property.

Typical expressions like

$$\alpha_{\alpha\beta}^I = -\frac{e^2}{m_e \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \Re(\langle a | R_{\alpha} | j \rangle \langle j | F_{n\beta}^I | a \rangle), \quad (\text{A1})$$

for the atomic contribution to the polarizability, such that total average molecular polarizability can be resolved according to an operator averaging method (OAM),⁵⁶ as^{53,55}

$$\alpha_{Av} = \sum_{I=1}^N \alpha_{Av}^I, \quad (\text{A2})$$

are a sum over states of terms proportional to a product of matrix elements, one being the component of the dipole operator, the other the component of the force operator referenced to a particular nucleus. The expression for the atomic contribution to the polarizability using AIM consists of two terms: one a contribution from the induced atomic polarization, the other from the induced flux in the electric field through the atomic surface.²⁰ The contribution of the induced atomic dipole to the polarizability of atom Ω , the term $\alpha_p(\Omega)$, is similar in important respects to OAM expression. The AIM term can be expressed as a sum over states of products of dipole moment matrix elements

$$\alpha_p(\Omega) = \sum_{k \neq n} \mathbf{M}_{kn} \mathbf{M}_{nk}(\Omega) (E_n^{(0)} - E_k^{(0)})^{-1}, \quad (\text{A3})$$

where \mathbf{M}_{kn} is obtained by averaging the dipole moment operator weighted by the transition density $\rho_{nk}(\mathbf{r})$ over the total system, while $\mathbf{M}_{nk}(\Omega)$ is the corresponding moment obtained by integration of the dipole moment operator (referenced to nucleus Ω) weighted by the transition density $\rho_{nk}(\mathbf{r})$ over the basin of atom Ω . This expression makes clear that the polarization density, like other property densities, is a ‘‘dressed density.’’ The term \mathbf{M}_{kn} determines how the transition density at \mathbf{r} or the induced atomic dipole $\mathbf{M}_{nk}(\Omega)$ depends upon the effect of the applied field over the entire molecule. Thus the AIM expression and those proposed in this paper, e.g., Eq. (A1), both consist of a product of terms. In both cases one term corresponds to an average of the dipole operator over the entire system, the other to a term specific to a particular atom. In AIM this latter term is an average over the atomic basin of the dipole operator referenced to the nucleus of Ω . In OAM the corresponding term is an average over the total system of a force operator also referenced to the nucleus in question. Because of the inverse distance dependence of the force operator, its average is heavily weighted within the basin of the atom.

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