

Atomic partition of the optical rotatory power of methylhydroperoxide

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We applied a methodology capable of resolving the optical rotatory power into atomic contributions. The individual atomic contributions to the optical rotatory power and molecular chirality of the methylhydroperoxide are obtained via a canonical transformation of the Hamiltonian by which the electric dipolar moment operator is transformed to the acceleration gauge formalism and the magnetic dipolar moment operator to the torque formalism. The gross atomic isotropic contributions have been evaluated for the carbon, the nonequivalent oxygen, and the nonequivalent hydrogen atoms of methylhydroperoxide, employing a very large Gaussian basis set which is close to the *Hartree-Fock limit*. © 2008 American Institute of Physics. [DOI: [10.1063/1.2826351](https://doi.org/10.1063/1.2826351)]

I. INTRODUCTION

The ability of a crystal or a solution to rotate the plan of polarized light is known as optical rotation or optical activity. Since its discovery in the beginning of the 19th century it has been used as an experimental tool to measure the enantiopurity of chemical compounds.¹

Among the different properties that influence the optical rotatory power (ORP), several articles have been devoted recently to the effect of the molecular aggregation of the molecule of interest with itself²⁻⁴ or with the solvent.⁵⁻⁷

The idea that molecular properties can be rationalized in terms of atomic contributions, transferable from molecule to molecule, constitutes an object of interest from the early days of chemistry. Pascal introduced the specific transferable magnetic atomic susceptibilities near a century ago.⁸⁻¹⁰ Attempts have also been made to define a resolution of electric dipole polarizability into atomic terms, see, for instance, the sets of transferable contributions determined by Denbigh¹¹ and Vogel.¹²

Bader *et al.*¹³ introduced the concept of atoms in molecules (AIMs),¹⁴ as spatial domains bounded in space, to demonstrate the additivity of group polarizabilities and susceptibilities.

Two alternative methodologies have been described in the literature for partitioning the calculated values of ORP into atomic contributions. The first one, developed by Kondru *et al.*,¹⁵ describes the first order changes in the ground state in terms of electric and magnetic field perturbations

using coupled-perturbed Hartree-Fock methods, and the results are analyzed employing an approach analogous to the Mulliken population analysis. It has been applied to a series of oxirane derivatives and 2,7,8-trioxabicyclo[3.2.1]octanes¹⁵ and to the conformational dependence of the optical rotation angle in the (*R*)-indoline molecule.¹⁶ The second one, described by some of us,¹⁷ uses a canonical transformation of the Hamiltonian to resolve the average ORP of a molecule into atomic contributions, applying a partitioning scheme based on rigorous definitions of quantum mechanical operators suitable to investigate the optical rotatory power. This approach has been used for the study of the conformational profile of the ORP of hydrogen peroxide¹⁷ and hydrazine.¹⁸ Related theoretical procedures and algorithms have been implemented within the SYSMO suite of computer programs.¹⁹

The derivatives of the hydrogen peroxide are among the simple systems that present chirality at theoretical level: note that the low racemization barrier does not allow to isolate the separate enantiomers. Two possible transition state structures have been considered in the literature for the racemization, both planar, with the substituents in *cis* or *trans* dispositions around the central O–O bond. In most of the cases, the lower barrier corresponds to the *trans* structure but depending on the substituent it can be the *cis* one.³

In the present article, we are investigating the partitioning of the optical rotatory power of the methylhydroperoxide (MHP) (also called hydroperoxymethane) molecule into atomic contributions employing the method applied in Refs. 17 and 18. Furthermore the behavior of the total ORP and its atomic contributions is investigated under a change of the

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molecular structure, i.e., a rotation about the bond between the two oxygen atoms, because one of them is a chiral atom. The atomic contribution has been evaluated for each geometrical configuration and rationalized. The rotatory power is a frequency dependent property. We have therefore also studied the behavior of the atomic contributions for various frequencies of the incident light at the equilibrium geometry. MHP is one of the main organic peroxides in the atmosphere²⁰⁻²⁴ (it is even present in the galactic center),²⁵ and for this reason, it has been the subject of many theoretical studies.^{3,26-29} In the present work its optical activity is studied in detail.

A brief outline of the theoretical method employed in the calculation is given in Secs. II and the results of our calculations are discussed in Sec. III.

II. METHODOLOGY

A. Tensors related to optical rotatory power

In a molecule with n electrons with charge $-e$, mass m_e , and coordinates \mathbf{r}_i , respect to an arbitrary origin, the canonical and angular momenta of the i th electron are indicated by \mathbf{p}_i , \mathbf{l}_i , ($\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$, $i = 1 \dots n$).

The corresponding quantities for the N nuclei are $\mathbf{Z}_I e$, \mathbf{M}_I , \mathbf{R}_I , etc. The electronic global operators are \mathbf{R} for position, \mathbf{P} for total canonical momentum, and \mathbf{L} for angular momentum. The electric, $\boldsymbol{\mu} = -e\mathbf{R}$, and magnetic, $\mathbf{m} = -(e/2m_e c)\mathbf{L}$, dipole moments are also defined. \mathbf{R} and \mathbf{L} operators are defined respect to an explicit origin \mathbf{r}_0 of the coordinate system,

$$\mathbf{R}_\alpha(\mathbf{r}_0) = \sum_{i=1}^n (\mathbf{r}_{i\alpha} - \mathbf{r}_{0\alpha}), \quad (1)$$

$$\mathbf{L}_\alpha(\mathbf{r}_0) = \sum_{i=1}^n \mathbf{l}_{i\alpha}(\mathbf{r}_0) = \varepsilon_{\alpha\beta\gamma} \sum_{i=1}^n (\mathbf{r}_{i\beta} - \mathbf{r}_{0\beta}) p_{i\gamma}. \quad (2)$$

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

The optical rotatory power of a chiral molecule can be rationalized via the tensor³⁰

$$\kappa_{\alpha\beta}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \text{Im}(\langle a | \boldsymbol{\mu}_\alpha | j \rangle \langle j | \mathbf{m}_\beta | a \rangle), \quad (3)$$

where Im takes the imaginary part of the term within brackets, ω_{ja} 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 electromagnetic wave incident on the molecule.

The trace of the tensor defined in Eq. (3) is a pseudoscalar, changing sign under inversion of the coordinate system because $\boldsymbol{\mu}$ and \mathbf{m} are, respectively, a polar and an axial vector. The optical rotatory parameter α is measured experimentally³¹ and related to the tensor κ by

$$[\alpha]_D = 1.343 \times 10^{-4} \kappa \nu^2 (n^2 + 2) / 3 \text{MW}, \quad (4)$$

where MW is the molar mass, n is the refractive index of the medium, and ν is the frequency of the sodium D line.

Equation (3) defines a second-order property in the length-angular momentum \mathbf{R} - \mathbf{L} picture, i.e.,

$$(R, L): \kappa^{(R, L)}(\omega) = \kappa(\omega).$$

Using the expressions for the total force of the nuclei on the electrons,

$$\frac{i}{\hbar} [H^{(0)}, \mathbf{P}] = \mathbf{F}_n^N = -e^2 \sum_{l=1}^N \mathbf{Z}_l \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_l}{|\mathbf{r}_i - \mathbf{R}_l|^3}, \quad (5)$$

the torque about the origin acting on the electrons,

$$\frac{i}{\hbar} [H^{(0)}, \mathbf{L}(\mathbf{r}_0)] = \mathbf{K}_n^N(\mathbf{r}_0) = e^2 \sum_{l=1}^N \mathbf{Z}_l \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_l}{|\mathbf{r}_i - \mathbf{R}_l|^3} \times (\mathbf{R}_l - \mathbf{r}_0), \quad (6)$$

and the hypervirial relationships, within the notation of Ref. 30,

$$\langle a | \mathbf{R}_\alpha | j \rangle = \frac{i}{m_e} \omega_{ja}^{-1} \langle a | \mathbf{P}_\alpha | j \rangle = \frac{1}{m_e} \omega_{ja}^{-2} \langle a | \mathbf{F}_{n\alpha}^N | j \rangle \quad (7)$$

$$= \frac{e}{m} \omega_{ja}^{-2} \sum_{l=1}^N \mathbf{Z}_l \langle a | \mathbf{E}_{l\alpha}^N | j \rangle, \quad (8)$$

with $\mathbf{E}_{l\alpha}^N$ the electric field on nucleus l , arising from the electron cloud, five alternative expressions are found for the rotatory power tensor, see Refs. 30, 32, and 33,

$$\kappa_{\alpha\beta}^{(R, K)}(\omega) = \frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \text{Re}(\langle a | \mathbf{R}_\alpha | j \rangle \langle j | \mathbf{K}_{n\beta}^N | a \rangle), \quad (9)$$

$$\kappa_{\alpha\beta}^{(P, L)}(\omega) = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \text{Re}(\langle a | \mathbf{P}_\alpha | j \rangle \langle j | \mathbf{L}_\beta | a \rangle), \quad (10)$$

$$\kappa_{\alpha\beta}^{(P, K)}(\omega) = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \times \text{Im}(\langle a | \mathbf{P}_\alpha | j \rangle \langle j | \mathbf{K}_{n\beta}^N | a \rangle), \quad (11)$$

$$\kappa_{\alpha\beta}^{(F, L)}(\omega) = \frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \times \text{Im}(\langle a | \mathbf{F}_{n\alpha}^N | j \rangle \langle j | \mathbf{L}_\beta | a \rangle), \quad (12)$$

$$\kappa_{\alpha\beta}^{(F, K)}(\omega) = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3(\omega_{ja}^2 - \omega^2)} \times \text{Re}(\langle a | \mathbf{F}_{n\alpha}^N | j \rangle \langle j | \mathbf{K}_{n\beta}^N | a \rangle). \quad (13)$$

As $\mathbf{F}_{n\alpha}^N$ and $\mathbf{K}_{n\alpha}^N$ are, respectively, polar and axial vectors, the $\kappa_{\alpha\beta}(\omega)$ is a pseudotensor, this character is unaffected by the change of picture.

All these definitions [Eqs. (9)–(13)] are equivalent in quantum mechanics, as a consequence of the invariance of the theory in a canonical transformation. However, in actual calculations of the rotatory power tensor the results will only be independent of the chosen formalism in the case of optimal variational wave functions and in the limit of a complete one-electron basis set. Values arrived at by relationships (3) and (9)–(13) can be appreciably different: their numerical agreement gives a benchmark of basis set completeness and an *a priori* quality criterion. When that agreement is met in self-consistent field calculations, we commonly say that the *Hartree-Fock* limit has been achieved.

The rotatory power tensor depends on the origin assumed for the multipole expansion. For instance, in a change of origin, $r'' \rightarrow r' + d$, the rotatory power tensor changes according to the relationship³⁰

$$\kappa_{\alpha\beta}(r'') = \kappa_{\alpha\beta}(r') - \frac{1}{2c} \varepsilon_{\alpha\beta\gamma} d_{\delta} \alpha_{\alpha\gamma} \quad (14)$$

$$\text{Tr}\{\kappa(r'')\} = \text{Tr}\{\kappa(r')\}.$$

Equation (14) is valid, and the trace of the tensor stays the same, if the hypervirial relations, Eqs. (7) and (8), are exactly satisfied. For instance, to fulfill this requirement within the algebraic approximation, i.e., employing the coupled Hartree-Fock method or random-phase approximation a complete basis set should be used.³⁴ If only gaugeless basis sets are available, the trace of the tensor in the (**P**, **L**) gauge, Eq. (11), will be invariant, but its quality depends always on the quality of the basis set. Another way of solving the problem of the gauge invariance is provided by basis sets of London orbitals,³⁵ i.e., gauge-including atomic orbitals (GIAOs), as they have been renamed for the first time by Hansen and Bouman.³⁶ GIAO calculations of optical rotatory power are implemented in DALTON program.^{37,38}

B. Atomic contributions to optical rotatory power

The chiroptical phenomena in molecules have been known since the early days of quantum mechanics. Rosenfeld derived the quantum mechanical description of the rotation angle.³⁹ Kirkwood⁴⁰ and Moffit^{40,41} proposed models based on polarizable interacting atoms or chemical groups. These models do not provide a general strategy for assigning the contributions of individual atoms. However, recently a method for the calculating numerical estimates of atomic contributions has become available.^{17,30} The method is simple: total force and torque of the nuclei on the electrons, appearing in Eqs. (12)–(14) can be partitioned as sums of corresponding atomic operators.

$$F_n^N = \sum_{l=1}^N F_n^l = \sum_{i=1}^n F_i^N, \quad (15)$$

$$F_i^l = -e^2 Z_l \frac{r_i - R_l}{|r_i - R_l|^3},$$

$$K_n^N = \sum_{l=1}^N K_n^l = \sum_{i=1}^n K_i^N, \quad (16)$$

$$K_i^l = e^2 Z_l \frac{r_i - R_l}{|r_i - R_l|^3} \times R_l.$$

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

$$\kappa_{\alpha\alpha} = \sum_{l=1}^N \kappa_{\alpha\alpha}^{[RK(l)]}, \quad (17)$$

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

a [**PK**(**I**)] scheme,

$$\kappa_{\alpha\alpha} = \sum_{l=1}^N \kappa_{\alpha\alpha}^{[PK(l)]}, \quad (18)$$

$$\kappa_{\alpha\alpha}^{[PK(l)]} = -\frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^4} \text{Im}(\langle a | P_{\alpha} | j \rangle \langle j | K_{n\alpha}^l | a \rangle),$$

and [**F**(**I**)**L**] scheme,

$$\kappa_{\alpha\alpha} = \sum_{l=1}^N \kappa_{\alpha\alpha}^{[F(l)L]}, \quad (19)$$

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

an [**F**(**I**)**K**] scheme,

$$\kappa_{\alpha\alpha} = \sum_{l=1}^N \kappa_{\alpha\alpha}^{[F(l)K]}, \quad (20)$$

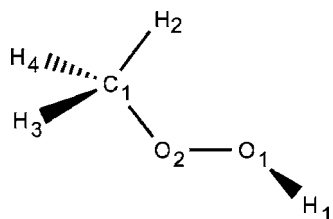
$$\kappa_{\alpha\alpha}^{[F(l)K]} = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \text{Re}(\langle a | F_{n\alpha}^l | j \rangle \langle j | K_{n\alpha}^N | a \rangle),$$

and an [**FK**(**I**)] scheme,

$$\kappa_{\alpha\alpha} = \sum_{l=1}^N \kappa_{\alpha\alpha}^{[FK(l)]}, \quad (21)$$

$$\kappa_{\alpha\alpha}^{[FK(l)]} = -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \text{Re}(\langle a | F_{n\alpha}^N | j \rangle \langle j | K_{n\alpha}^l | a \rangle).$$

The atomic contributions are transferable between members of a homologous series, and the method relies on completely general and simple quantum mechanical recipes. The *atom domain* is defined by the *actual domain* of atomic operators such as $F_{n\alpha}^l$ and $K_{n\alpha}^N$. Such domain is not uniquely defined, it depends on the form of the operator itself. That means that each operator, $F_{n\alpha}^l$ and $K_{n\alpha}^l$, weights differently the molecular domain leading to different definitions of *ef*-

FIG. 1. Scheme of O_2HCH_3 .

fective atomic basins. A detailed discussion between the operator averaging method: OAM (Ref. 42) and Bader's AIM (Ref. 14) is included in Ref. 17.

Finally, it must be recalled that the atomic contributions to the optical rotatory power depend on the gauge of the vector potential. The molecular rotatory power is gauge invariant if the hypervirial relations, Eqs. (7) and (8), are exactly satisfied.

III. RESULTS AND DISCUSSION

The geometry of methylhydroperoxide has been fully optimized with the MP2 computational method⁴³ and the 6-311++G(d,p) basis set⁴⁴ within the GAUSSIAN-03 program.⁴⁵ In order to study the evolution of the ORP properties as a function of the $\text{H}_1\text{-O}_1\text{-O}_2\text{-C}_3$ dihedral angle (Φ), we performed the internal rotation about the $\text{O}_1\text{-O}_2$ bond, from -180° to 0° , by 10° steps, and the corresponding structures have been reoptimized while restraining the mentioned dihedral angle to the desired value. Thus, the obtained structures at -180° and 0° correspond to nonchiral transition states of the racemization process of this molecule.³ The equilibrium configuration corresponds to $\Phi=134.918^\circ$ (C_1 point group), in agreement with the results of previous reports.^{3,28} In all the calculations of the κ optical rotatory power tensor, the origin of the coordinate system was fixed on the O_1 atom. (see Fig. 1).

The results of our calculations are reported in Tables I–III and Figs. 2–8. All the calculations in the figures and in Tables I and II were carried out at the level of the random-phase approximation (RPA), employing the different formal-

TABLE I. Average rotatory power tensor of HOCH_3 at equilibrium geometry (dihedral angle: 134.9°). The number of contracted Gaussian-type functions is given in parentheses for Gaussian basis-sets 1–3 (in parts per thousand units). The self-consistent field (SCF) energy is given in atomic units.

Formalism ^a	Basis set			
	1 (65) 6-31G(d)	2 (307) aug-cc-pCVTZ	3 ^b (383)	3 ^c (383)
(R,L)	-1.44	-1.19	-1.19	-1.19
(P,L)	-1.14	-1.19	-1.18	-1.19
(F,L)	-138.5	-15.9	-1.80	-1.77
(R,K)	4.19	-0.53	-1.16	-1.17
(P,K)	5.30	-0.52	-1.15	-1.16
(F,K)	-927.30	-24.10	-1.79	-1.81
E_{SCF}	-189.802078	-189.878380	-189.891328	-189.891328

^aSee Eqs. (4), (9), and (3).

^bThe origin of coordinates is taken in the O_1 position.

^cThe origin of coordinates is taken in the O_2 position.

isms implemented in the SYSMO code.¹⁹ In addition we report some correlated calculations in Table III in order to estimate the importance of electron correlation on the ORP phenomena in methylhydroperoxide. The average trace of the rotatory power tensor $\kappa(\omega)=1/3 \kappa_{\alpha\alpha}(\omega)$ in the low-frequency limit $\omega=0$ is reported in Table I for the molecular equilibrium geometry for three basis sets: 6-31G(d) (basis set 1); aug-cc-pCVTZ (basis set 2),⁴⁶ and a completely free (13s10p5d2f/8s4p1d) set of atomic Gaussian functions,⁴⁷ which is expected to be close to the *Hartree-Fock limit* for this property. The results corresponding to the (**P,L**), (**R,K**), and (**P,K**) formalisms are close to (**R,L**) results for basis sets 2 and 3. From the comparison of the results for the three basis sets, we conclude that the quality of basis set 3 is good enough to assure that the Hartree-Fock limit has been reached because the calculations of κ carried out with two origins of the coordinate system, O_1 and O_2 atoms, differ in less than 1% of the property, satisfying condition (14), and the κ values are very similar for all the formalisms.

The total and the nonequivalent hydrogen, oxygen, and carbon, contributions to the average $\kappa(\omega)$ tensor are displayed in Table II for frequencies up to 0.3 a.u. The results displayed in Table II show that (i) the basis set 3 is still too small to represent the average rotatory power tensor in the force gauge, (ii) the schemes based on torque, Eqs. (17), (18), and (21), provide atomic contributions to the average tensor that are similar among them, but different from those provided by the scheme based on the force formalism, Eqs. (19) and (20). We bring these two observations together to emphasize that the quality of the basis set is not the reason for the disagreement between the schemes as it will be explained in the following discussion.

In Table III we have gathered some correlated results for the gauge origin dependent (**R,L**) formalism in the limit of zero frequency in order to get an idea of the size of the correlation effects on the total average ORP. Calculations at the SOPPA,^{48–51} SOPPA(CCSD),⁵² CC2 linear response,^{53–55} CCSD linear response,⁵⁶ TDDFT/B3LYP,^{57–61} and multiconfigurational RPA (MCRPA) (Ref. 37) computational level were carried out with the DALTON program.³⁸ In order to keep the number of basis functions below 255, we have used a locally dense basis set,⁶² where the aug-cc-pCVTZ basis set,⁴⁶ basis set 2, was used for the HO_1O_2 moiety, but the second polarization functions were removed for the atoms in the methyl group. The MCRPA calculation was of the complete active space (CAS) type⁶³ with 14 electrons in 14 active orbitals (14,14) and the 1s and 2s orbitals of carbon and oxygen inactive, i.e., with one correlating orbital per occupied orbital in the active space. In the TDDFT/B3LYP and MCRPA calculations we have used also GIAO basis functions in addition to the normal gaugeless basis functions leading to gauge origin independent (**R,L**) results. The differences between the GIAO and common origin results are very small at the RPA and MCRPA level and the GIAO RPA (**R,L**) result agrees perfectly with the (**P,L**) results for basis sets 2 and 3 from Table I. This proves again that basis sets of the size of basis set 2 and 3 are close to the Hartree-Fock limit at least for the (**R,L**) and (**P,L**) formalisms. The difference between the GIAO and common origin results is

TABLE II. Partition of the average rotatory power of the *P* enantiomer of HOOCH₃ at equilibrium geometry, $\kappa(\omega)=1/3\kappa_{\text{tot}}(\omega)$ (in ppt. a.u.), into atomic contributions versus the angular frequency ω of the perturbing monochromatic wave. Results are from basis set III, with origin in the O₁ oxygen atom (O₁). Values of ω (in a.u.) are given in parentheses.

Atom	Formalism	$K(0.0)$	$K(0.20)$	$K(0.25)$	$K(0.28)$	$K(0.29)$	$K(0.30)$
	(R, L)	-1.194	0.024	-6.139	-11.686	-22.940	22.768
	(P, L)	-1.186	0.081	-6.159	-11.713	-23.016	22.990
O ₁	[R, K(O ₁)]	0.000	0.000	0.000	0.000	0.000	0.000
O ₂	[R, K(O ₂)]	-0.374	3.236	-3.025	-2.006	-1.735	3.187
H ₁	[R, K(H ₁)]	0.194	-1.098	1.008	-0.121	-3.346	16.619
C ₁	[R, K(C ₁)]	-0.148	-0.861	-1.037	-3.664	-9.057	14.198
H ₂ +H ₃ +H ₄	[R, K(H _{2,3,4})]	-0.839	-0.949	-3.249	-6.049	-9.012	-11.322
Total	(R, K)	-1.167	0.328	-6.303	-11.841	-23.149	22.681
O ₁	[P, K(O ₁)]	0.000	0.000	0.000	0.000	0.000	0.000
O ₂	[P, K(O ₂)]	-0.368	3.317	-3.067	-2.048	-1.822	3.427
H ₁	[P, K(H ₁)]	0.192	-1.123	1.024	-0.104	-3.320	16.621
C ₁	[P, K(C ₁)]	-0.150	-0.882	-1.025	-3.655	-9.049	14.228
H ₂ +H ₃ +H ₄	[P, K(H _{2,3,4})]	-0.833	-0.925	-3.255	-6.063	-9.036	-11.371
Total	(P, K)	-1.158	0.387	-6.323	-11.869	-23.228	22.904
O ₁	[F(O ₁), L]	-2.974	-12.302	2.222	7.327	28.322	-90.547
O ₂	[F(O ₂), L]	2.026	8.449	-0.437	-3.342	-18.791	77.504
H ₁	[F(H ₁), L]	-0.691	-2.833	-2.009	-6.084	-12.895	11.900
C ₁	[F(C ₁), L]	0.040	-1.732	0.831	-0.321	-2.731	11.091
H ₂ +H ₃ +H ₄	[F(H _{2,3,4}), L]	-0.223	1.434	-2.693	-3.944	-5.356	-8.437
Total	(F, L)	-1.822	-6.984	-2.086	-6.363	-11.451	1.511
O ₁	[F(O ₁), K]	-3.530	-18.042	5.311	11.056	36.002	-103.783
O ₂	[F(O ₂), K]	2.589	14.351	-3.633	-7.153	-26.510	90.325
H ₁	[F(H ₁), K]	-0.803	-4.016	-1.413	-5.491	-11.822	10.304
C ₁	[F(C ₁), K]	0.088	-1.206	0.517	-0.765	-3.736	13.087
H ₂ +H ₃ +H ₄	[F(H _{2,3,4}), K]	-0.152	2.094	-2.957	-4.083	-5.440	-8.702
Total	(F, K)	-1.808	-6.819	-2.175	-6.435	-11.506	1.230
O ₁	[F, K(O ₁)]	0.000	0.000	0.000	0.000	0.000	0.000
O ₂	[F, K(O ₂)]	-1.517	-8.331	3.013	5.054	12.760	-22.483
H ₁	[F, K(H ₁)]	0.609	2.685	-0.674	-1.603	-5.834	19.707
C ₁	[F, K(C ₁)]	0.238	2.423	-2.356	-4.577	-10.217	14.579
H ₂ +H ₃ +H ₄	[F, K(H _{2,3,4})]	-1.137	-3.596	-2.157	-5.309	-8.214	-10.574
Total	(F, K)	-1.808	-6.819	-2.175	-6.435	-11.506	1.230

slightly larger in the B3LYP calculation than at the RPA level as was observed previously also for shielding calculations.⁶⁴

All the correlated methods agree that the total averaged ORP is slightly overestimated at the RPA level, however, there are some difference between the methods to which extend this is the case. The second-order Møller-Plesset perturbation or coupled cluster theory based linear response methods SOPPA, SOPPA(CCSD), CC2 and CCSD predicts a reduction in the range of 16%–19%, whereas B3LYP predicts only 4% and the (14,14) CAS as much as 26%. The latter might not be surprising because the active space is too

small for recovering enough of the dynamic correlation, but that B3LYP predicts a smaller correlation correction than CCSD, contrary to what was observed recently for the optical rotatory parameter α in H₂O₂, H₂S₂, allene, and biphenyl.⁶¹ The fact that CC2 tends to overestimates the results of CCSD calculations is also not unknown,⁶⁵ but that SOPPA(CCSD) also overestimates the CCSD results is normally not seen, at least for electric polarizabilities.^{66–68}

The evolution of the total average ORP as function of the HOOC angle is depicted in Fig. 2 for the range of -180° – 180° for basis set 3. In all the range considered, the

TABLE III. Comparison of various correlated calculations with and without GIAOs of the average **(R, L)** rotatory power tensor (in ppt. a.u.) of HOOCH₃ at equilibrium geometry (dihedral angle: 134.9°) in the low-frequency limit. The basis set is a locally dense version of the aug-cc-pCVTZ basis set, basis set 2, where the second polarization functions were removed on the atoms in the methyl group. The origin of the coordinate system is at the O₁ oxygen atom (O₁) and the CO gauge origin is at the center of mass.

Gauge origin	RPA	B3LYP	CAS (14,14) MCRPA	SOPPA	SOPPA (CCSD)	CC2	CCSD
GIAO	-1.185	-1.131	-0.879				
CO	-1.191	-1.144	-0.880	-1.006	-0.969	-0.963	-0.992

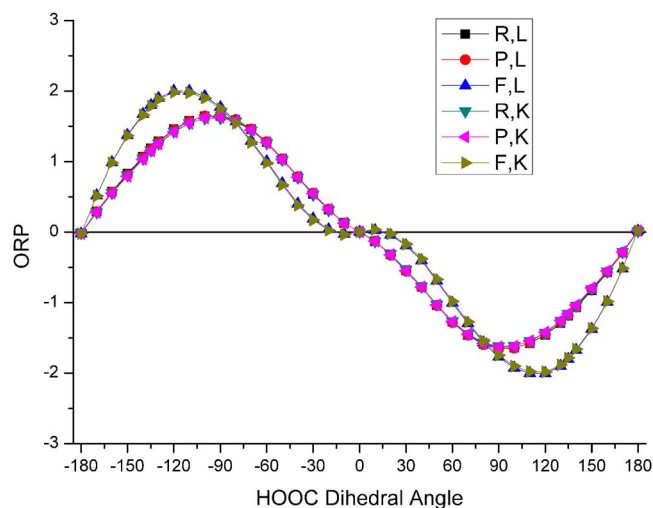


FIG. 2. (Color online) The average rotatory power of O_2HCH_3 , $1/3 \text{Tr} K(w)$, in the limit $w=0$, in various formalisms, as function of the $\text{HO}_1\text{O}_2\text{C}$ dihedral angle.

values of the ORP are always negative for the *P* enantiomer, and positive for the *M* enantiomer, except for the (*F*,*L*) and (*F*,*K*) formalisms and angles close to 0° , where small values of ORP are found with the opposite sign to the other values obtained for the same enantiomer. In contrast, the values of the ORP in the hydrogen peroxide molecule can be positive or negative for a given enantiomer depending on the dihedral angle considered.^{17,61} In more detail, the (*F*,*L*) and (*F*,*K*) formalisms are different to the rest, with a maximum value at -120° , while in the rest it is around -90° . The different profiles of these two methods have been already described for the HOOH and H_2NNH_2 molecules.^{17,18}

Figures 3–5 show the dependence of the atomic contributions to the rotatory average tensor $\kappa(0)$ $\text{HO}_1\text{O}_2\text{C}$ for carbon, and the nonequivalent oxygen and hydrogen atoms, C_1 , O_1 , O_2 , H_1 , and ($\text{H}_2, \text{H}_3, \text{H}_4$) belonging to the methyl group. The [**R**,**K(I)**] and [**P**,**K(I)**] values are close to each other and define a homogeneous set of numerical values, which are

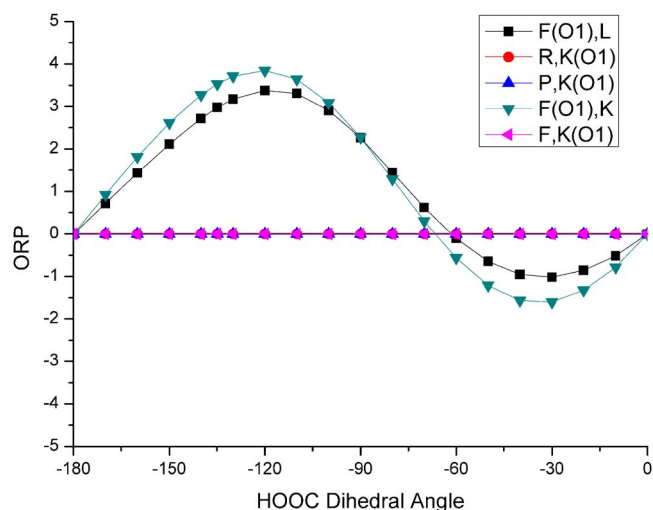


FIG. 3. (Color online) Contribution of O_1 oxygen atom to the average rotatory power of O_2HCH_3 , in the limit $w=0$, in various formalisms, as function of the $\text{HO}_1\text{O}_2\text{C}$ dihedral angle.

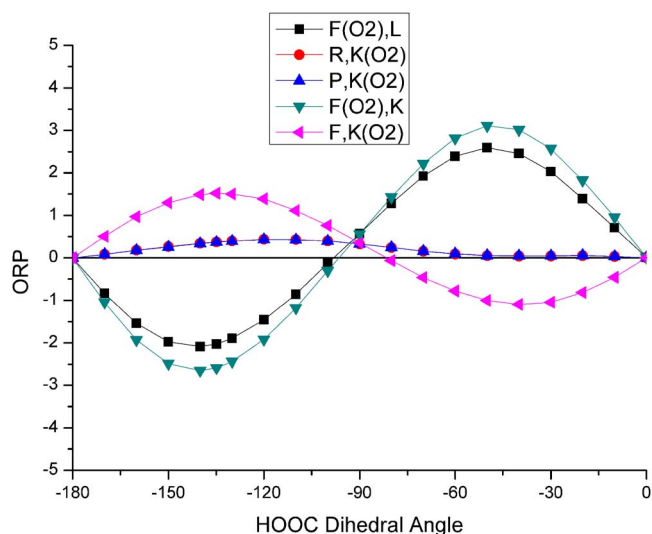


FIG. 4. (Color online) Contribution of O_2 oxygen atom to the average rotatory power of O_2HCH_3 , in the limit $w=0$, in various formalisms, as function of the $\text{HO}_1\text{O}_2\text{C}$ dihedral angle.

slightly different from the set defined by [**F**,**K(I)**], for the torque partitioning scheme. The force scheme, partitioning [**F(I)**,**L**] and [**F(I)**,**K**], which would become the same in the Hartree-Fock limit, defines another set of numerical values. The atomic contributions provided by the *force scheme* are systematically larger, in absolute value than those given by the *torque scheme*. In Ref. 42 we proposed a definition of the *l*th atom in the molecule as that region of space which essentially coincides with the domain weighted by operators like those appearing in Eqs. (15) and (16). Both scale as the same inverse power of electron-nucleus distance, i.e., $|r_i - R_l|^{-2}$, but K_n^l also depends on \mathbf{R}_l . The present findings confirm those of the previous paper on H_2O_2 :¹⁷ the basins of the operators $F_{n\alpha}^l$ and $K_{n\alpha}^l$ do not coincide. They define different atoms in molecule within the operator averaging method (OAM) approach. See the appendix of the same reference.

Figure 3 shows that the [**R**,**K(O₁)**], [**P**,**K(O₁)**] constri-

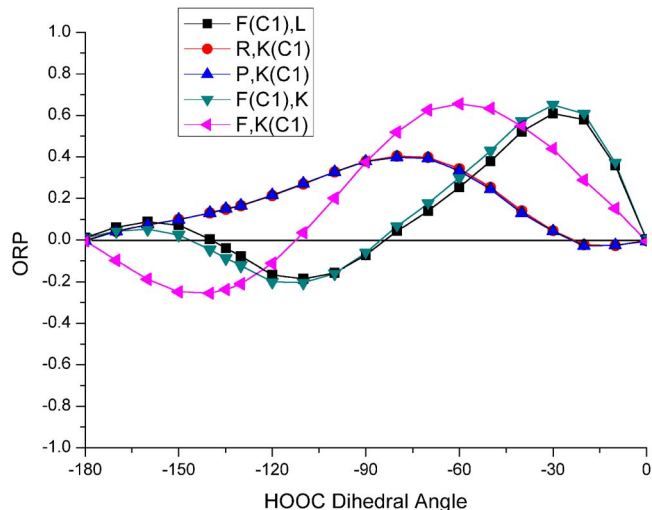


FIG. 5. (Color online) Contribution of C_1 carbon atom to the average rotatory power of O_2HCH_3 , in the limit $w=0$, in various formalisms, as function of the $\text{HO}_1\text{O}_2\text{C}$ dihedral angle.

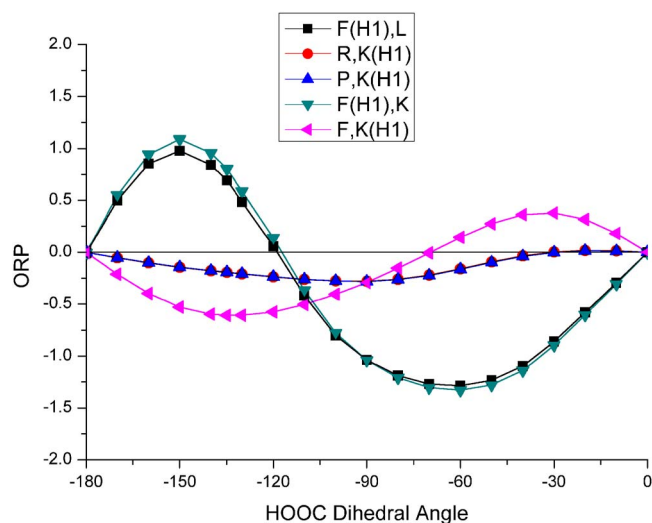


FIG. 6. (Color online) Contribution of H₁ hydrogen atom to the average rotatory power of O₂HCH₃, in the limit $w=0$, in various formalisms, as function of the HO₁O₂C dihedral angle.

Contributions are virtually the same, and [F,K(O₁)] ones are slightly different on the scale of the plot, defining atomic contributions in the torque scheme. [F(O₁),L] and [F(O₁),K] curves are close to one another, but they are characterized by a different pattern with a minimum at conformations in the proximity of $\Phi=-30^\circ$. Figure 4 shows that also the [R,K(O₂)], [P,K(O₂)], and [F,K(O₂)] show a similar behavior to those commented for O₁, defining atomic contributions in the torque scheme. [F(O₂),L] and [F(O₂),K] curves are close to one another, but they are characterized by a different pattern with a minimum and a maximum, respectively, at conformations in the proximity of $\Phi=-45^\circ$. Such trends are not because of insufficient convergence of atomic contributions in the force gauge.

Similar conclusions are arrived at from inspection of Fig. 5, for the carbon atom contributions to the rotatory average tensor, and Figs. 6 and 7, showing that the curves corresponding to [RK(H)], [PK(H)] are very close, and near [FK(H)], for each hydrogen, and different from that defined by the [F(H)L] and [F(H)K] curves. The values reported in Fig. 7 correspond to the sum of the atomic contributions: H₂+H₃+H₄ of the methyl protons.

Another difference between Figs. 6 and 7 is that the

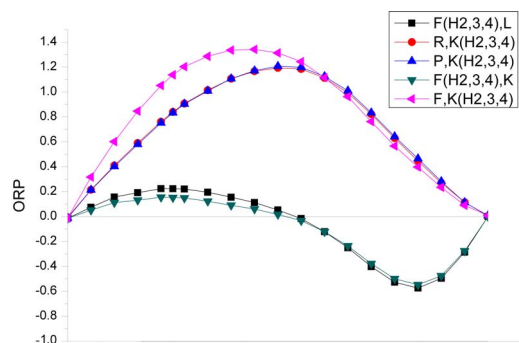


FIG. 7. (Color online) Contribution of H₂+H₃+H₄ hydrogen atoms to the average rotatory power of O₂HCH₃, in the limit $w=0$, in various formalisms, as function of the HO₁O₂C dihedral angle.

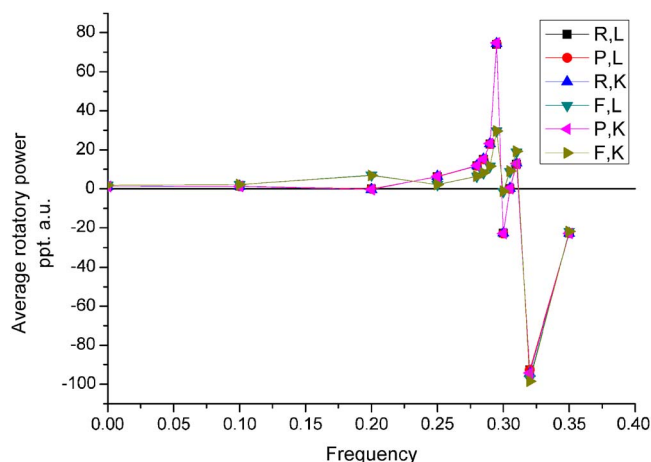


FIG. 8. (Color online) Average rotatory power, expressed as $(1/3)\text{Tr } k(\omega)$, in various formalisms, as a function of the frequency ω (in part per thousand atomic units).

hydrogens of the nonequivalent H₁ and (H₂,H₃,H₄) contributions do not exhibit the same behavior. The formalism based in the torque scheme shows only that a maximum for the (H₂+H₃+H₄) contributions but the force formalisms exhibit a minimum and a maximum in the same range. For contributions to H₁ average rotatory power there are minimum and maximum for all the formalisms.

The atoms in molecule defined by the force F_n^I and torque K_n^I operators, do not coincide, in general, for molecular properties. This can be explained by the different dependences of these operators on the inverse power of the electron nucleus distance, see Eqs. (15) and (16).

The dependence of the average κ tensor with the frequency of the monochromatic wave is plotted in Fig. 8. The resonance between the frequency of the incident light and the natural frequencies ω_{ja} is clearly observed.

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