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Citation: The Journal of Chemical Physics 128, 064318 (2008); doi: 10.1063/1.2826351
View online: http://dx.doi.org/10.1063/1.2826351
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/128/6?ver=pdfcov
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Atomic partition of the optical rotatory power of methylhydroperoxide

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(Received 17 October 2007; accepted 27 November 2007; published online 13 February 2008)

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]

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 enantio purity of chemical compounds.1,11

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 Kondrus 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 SYMOSO 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
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 atmosphere and coordinates

\[ \pi, \cal = \text{and angular momenta of the Schrödinger equation for the unperturbed Hamiltonian} \]

\[ A. \text{ Tensors related to optical rotatory power} \]

In a molecule with \( n \) electrons with charge \( -e \), mass \( m_e \), and coordinates \( r_i \), respect to an arbitrary origin, the canonical and angular momenta of the \( i \)th electron are indicated by \( p_i, l_i, (l_i = r_i \times p_i, i = 1 \ldots n) \).

The corresponding quantities for the \( N \) nuclei are \( Z_i e_i, M_i, R_i, \) etc. The electronic global operators are \( R \) for position, \( P \) for total canonical momentum, and \( L \) for angular momentum. The electric, \( \mu = -e \mathbf{R} \), and magnetic, \( m = -e/(2m_e c) \mathbf{L} \), dipole moments are also defined. \( R \) and \( L \) operators are defined respect to an explicit origin \( r_0 \) of the coordinate system.

\[ R_a(r_0) = \sum_{i=1}^{n} (r_{ia} - r_{0a}), \]

\[ L_\alpha(r_0) = \sum_{l=1}^{n} l_{i\alpha}(r_0) = \sum_{l=1}^{n} (r_{i\beta} - r_{0\beta}) p_{l\gamma}, \]

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

The rotatory power of a chiral molecule can be rationalized via the tensor \( \kappa_{a\beta}^{(R,K)}(\omega) \)

\[ \kappa_{a\beta}(\omega) = \frac{e^2}{2m_e c h} \sum_{j+a} \frac{2}{\omega_{ja}} |\langle a| p_{a\beta}\rangle| |\langle j|m_{\beta\alpha}\rangle|, \]

where \( \Im \) takes the imaginary part of the term within brackets, \( \omega_{ja} \) are the natural transition frequencies of the molecule in the reference state \( |\eta_{a}^{(0)}\rangle \equiv |a\rangle \), 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 \( \omega \) 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 \( \mu \) and \( m \) are, respectively, a polar and an axial vector. The optical rotatory parameter \( \alpha \) is measured experimentally and related to the tensor \( \kappa \) by

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

where \( MW \) is the molar mass, \( n \) is the refractive index of the medium, and \( \nu \) is the frequency of the sodium D line.

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

\[ (R,L): \kappa_{a\beta}(\omega) = \kappa(\omega). \]

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

\[ \frac{i}{\hbar} [H^{(0)}, P] = F_a^{(N)} = -e^2 \sum_{i=1}^{N} Z_i \sum_{l=1}^{n} \frac{r_i - R_l}{|r_i - R_l|^3}, \]

the torque about the origin acting on the electrons,

\[ \frac{i}{\hbar} [H^{(0)}, L(r_0)] = K_a^{(N)}(r_0) = e^2 \sum_{i=1}^{N} Z_i \sum_{l=1}^{n} \frac{r_i - R_l}{|r_i - R_l|^3} \times (R_l - r_0), \]

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

\[ \langle a| R_{a\beta}^j |j \rangle = i \frac{m_e}{\omega_{ja}} \langle a| P_{a\beta} |j \rangle = \frac{1}{m_e} \omega_{ja}^{-2} \langle a| F_{a\beta}^{(N)} |j \rangle \]

\[ = \frac{e}{m} \omega_{ja}^{-2} \sum_{i=1}^{N} Z_i \langle a| E_{ia\alpha}^{(N)} |j \rangle, \]

with \( E_{ia}^{(N)} \) the electric field on nucleus I, arising from the electron cloud, five alternative expressions are found for the rotatory power tensor, see Refs. 30, 32, and 33,

\[ K_{a\beta}^{(R,K)}(\omega) = \frac{e^2}{2m_e c h} \sum_{j+a} \frac{2}{\omega_{ja}} \omega_{ja} |\langle a| p_{a\beta}\rangle| |\langle j|m_{\beta\alpha}\rangle|, \]

\[ K_{a\beta}^{(P,K)}(\omega) = -\frac{e^2}{2m_e c h} \sum_{j+a} \frac{2}{\omega_{ja}} \omega_{ja} |\langle a| p_{a\beta}\rangle| |\langle j|m_{\beta\alpha}\rangle|, \]

\[ K_{a\beta}^{(F,L)}(\omega) = \frac{e^2}{2m_e c h} \sum_{j+a} \frac{2}{\omega_{ja}} \omega_{ja} |\langle a| F_{a\beta}^{(N)} |j \rangle| |\langle j|m_{\beta\alpha}\rangle|, \]

As \( F_{a\beta}^{(N)} \) and \( K_{a\beta}^{(N)} \) are, respectively, polar and axial vectors, the \( \kappa_{a\beta}(\omega) \) 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. In instance, in a change of origin, \( r' \rightarrow r' + \alpha \), the rotatory power tensor changes according to the relationship\(^{36}\)

\[
\kappa_{ab}(r') = \kappa_{ab}(r) - \frac{1}{2c} \varepsilon_{a\beta\gamma} \partial_{\alpha \beta \gamma}
\]

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

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 \( \text{Hartree-Fock} \) 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 quantity of the basis set. Another way of solving the problem of the gauge invariance is provided by basis sets of London orbitals,\(^{15} \) 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.\(^{39} \) Kirkwood\(^{40,41} \) and Moffit\(^{40} \) 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.\(^{17,39} \) 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.

\[
K^N = \sum_{i=1}^{N} K^N_i = \sum_{i=1}^{n} K^N_i,
\]

\[
K^i = e^2 Z_i \frac{r_i - R_i}{|r_i - R_i|^3} \times R_i.
\]

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

\[
\kappa_{aa}^\text{[RK]} = \sum_{i=1}^{N} \kappa_{aa}^{\text{[RK]}(I)},
\]

\[
\kappa_{aa}^{\text{[RK]}(I)} = \frac{e^2}{2m_i c \omega_{ja}^3} \sum_{j=1}^{N} \text{Re}((a| R_{aa}| j)(a) | K_{aa}^{N}(a))
\]

a \([\text{PK}(I)]\) scheme,

\[
\kappa_{aa}^\text{[PK]} = \sum_{i=1}^{N} \kappa_{aa}^{\text{[PK]}(I)},
\]

\[
\kappa_{aa}^{\text{[PK]}(I)} = -\frac{e^2}{2m_i c \omega_{ja}^3} \sum_{j=1}^{N} \text{Im}((a| P_{aa}| j)(a) | K_{aa}^{N}(a))
\]

and \([\text{FL}(I)]\) scheme,

\[
\kappa_{aa}^\text{[FL]} = \sum_{i=1}^{N} \kappa_{aa}^{\text{[FL]}(I)},
\]

\[
\kappa_{aa}^{\text{[FL]}(I)} = -\frac{e^2}{2m_i c \omega_{ja}^3} \sum_{j=1}^{N} \text{Im}((a| F_{aa}^{N}| j)(a) | L_{aa}^{N}(a))
\]

an \([\text{FK}(I)]\) scheme,

\[
\kappa_{aa}^\text{[FK]} = \sum_{i=1}^{N} \kappa_{aa}^{\text{[FK]}(I)},
\]

\[
\kappa_{aa}^{\text{[FK]}(I)} = -\frac{e^2}{2m_i c \omega_{ja}^3} \sum_{j=1}^{N} \text{Re}((a| F_{aa}^{N}| j)(a) | K_{aa}^{N}(a))
\]

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 \( F_{aa}^{\text{FL}} \) and \( K_{aa}^{\text{FL}} \). Such domain is not uniquely defined, it depends on the form of the operator itself. That means that each operator, \( F_{aa}^{\text{FL}} \) and \( K_{aa}^{\text{FL}} \), weights differently the molecular domain leading to different definitions of ef-
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 method and the 6-311+ +G(d,p) basis set within the GAUSSIAN-03 program. In order to study the evolution of the ORP properties as a function of the H₁−O₁−O₂−C₂ dihedral angle (Φ), we performed the internal rotation about the O₁−O₂ bond, from −180° to 0°, by 10° steps, and the corresponding structures have been reoptimized while restraining the mentioned dihedral angle to the desire value. Thus, the obtained structures at −180° and 0° correspond to nonchiral transition states of the racemization process of this molecule. The equilibrium configuration corresponds to Φ=134.918° (C₁ point group), in agreement with the results of previous reports. In all the calculations of the optical rotatory power tensor, the origin of the coordinate system was fixed on the O₂ 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 formalisms implemented in the SYMMS code. 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 κ(0)=1/3 κ₃₃(0), in the low-frequency limit ω=0 is reported in Table I for the molecular equilibrium geometry for three basis sets: 6-31G(d) (basis set 1); aug-cc-pVTZ (basis set 2), and a completely free (13s10p5d2f/8s4p1d) set of atomic Gaussian functions, 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, O₁ and O₂ 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 κ(ω) 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, SOPPA(CCSD), CC2 linear response, CCSD linear response, TDDFT/B3LYP, and multiconfigurational RPA (MCRPA) (Ref. 37) computational level were carried out with the DALTON program. In order to keep the number of basis functions below 255, we have used a locally dense basis set, where the aug-cc-pCVTZ basis set, basis set 2, was used for the HO₃O molecule, but the second polarization functions were removed for the atoms in the methyl group. The MCRPA calculation was of the complete active space (CAS) type 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

![FIG. 1. Scheme of O₂HCH₃.](image-url)
There are some differences between the methods to which ORP is slightly overestimated at the RPA level, however, as was observed previously also for shielding calculations. All the correlated methods agree that the total averaged ORP is slightly overestimated at the RPA level, however, there are some differences between the methods to which extend this is the case. The second-order Möller-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. The fact that CC2 tends to overestimates the results of CCSD calculations is also not unknown, but that SOPPA(CCSD) also overestimates the CCSD results is normally not seen, at least for electric polarizabilities.

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>
<thead>
<tr>
<th>Atom</th>
<th>Formalism</th>
<th>K(0.0)</th>
<th>K(0.20)</th>
<th>K(0.25)</th>
<th>K(0.28)</th>
<th>K(0.29)</th>
<th>K(0.30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R, L)</td>
<td>−1.194</td>
<td>0.024</td>
<td>−6.139</td>
<td>−11.686</td>
<td>−22.940</td>
<td>22.768</td>
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<tr>
<td>(P, L)</td>
<td>−1.186</td>
<td>0.081</td>
<td>−6.159</td>
<td>−11.713</td>
<td>−23.016</td>
<td>22.990</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>[R, K(O1)]</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>O2</td>
<td>[R, K(O2)]</td>
<td>−0.374</td>
<td>3.236</td>
<td>−3.025</td>
<td>−2.006</td>
<td>−1.735</td>
<td>3.187</td>
</tr>
<tr>
<td>H1</td>
<td>[R, K(H1)]</td>
<td>0.194</td>
<td>−1.098</td>
<td>1.008</td>
<td>−0.121</td>
<td>−3.346</td>
<td>16.619</td>
</tr>
<tr>
<td>C1</td>
<td>[R, K(C1)]</td>
<td>−0.148</td>
<td>−0.861</td>
<td>−1.037</td>
<td>−3.664</td>
<td>−9.057</td>
<td>14.198</td>
</tr>
<tr>
<td>H2+H1+H4</td>
<td>[R, K(H2,3,4)]</td>
<td>−0.839</td>
<td>−0.949</td>
<td>−3.249</td>
<td>−6.049</td>
<td>−9.012</td>
<td>−11.322</td>
</tr>
<tr>
<td>Total</td>
<td>(P, K)</td>
<td>−1.167</td>
<td>0.328</td>
<td>−6.303</td>
<td>−11.841</td>
<td>−23.149</td>
<td>22.681</td>
</tr>
<tr>
<td>O1</td>
<td>[P, K(O1)]</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>O2</td>
<td>[P, K(O2)]</td>
<td>−0.368</td>
<td>3.317</td>
<td>−3.067</td>
<td>−2.048</td>
<td>−1.822</td>
<td>3.427</td>
</tr>
<tr>
<td>H1</td>
<td>[P, K(H1)]</td>
<td>0.192</td>
<td>−1.123</td>
<td>1.024</td>
<td>−0.104</td>
<td>−3.320</td>
<td>16.621</td>
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<tr>
<td>C1</td>
<td>[P, K(C1)]</td>
<td>−0.150</td>
<td>−0.882</td>
<td>−1.025</td>
<td>−3.655</td>
<td>−9.049</td>
<td>14.228</td>
</tr>
<tr>
<td>H2+H1+H4</td>
<td>[P, K(H2,3,4)]</td>
<td>−0.833</td>
<td>−0.925</td>
<td>−3.255</td>
<td>−6.063</td>
<td>−9.036</td>
<td>−11.371</td>
</tr>
<tr>
<td>Total</td>
<td>(F, L)</td>
<td>−1.822</td>
<td>−6.984</td>
<td>−2.086</td>
<td>−6.363</td>
<td>−11.451</td>
<td>1.511</td>
</tr>
<tr>
<td>O1</td>
<td>[F(O1), L]</td>
<td>−3.530</td>
<td>−18.042</td>
<td>5.311</td>
<td>11.056</td>
<td>36.002</td>
<td>−103.783</td>
</tr>
<tr>
<td>H1</td>
<td>[F(H1), K]</td>
<td>−0.803</td>
<td>−4.016</td>
<td>−1.413</td>
<td>−5.491</td>
<td>−11.822</td>
<td>10.304</td>
</tr>
<tr>
<td>C1</td>
<td>[F(C1), K]</td>
<td>0.088</td>
<td>−1.206</td>
<td>0.517</td>
<td>−0.765</td>
<td>−3.736</td>
<td>13.087</td>
</tr>
<tr>
<td>H2+H1+H4</td>
<td>[F(H2,3,4), K]</td>
<td>−0.152</td>
<td>2.094</td>
<td>−2.957</td>
<td>−4.083</td>
<td>−5.440</td>
<td>−8.702</td>
</tr>
<tr>
<td>Total</td>
<td>(F, K)</td>
<td>−1.808</td>
<td>−6.819</td>
<td>−2.175</td>
<td>−6.435</td>
<td>−11.506</td>
<td>1.230</td>
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<tr>
<td>O1</td>
<td>[F, K(O1)]</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>O2</td>
<td>[F, K(O2)]</td>
<td>−1.517</td>
<td>−8.331</td>
<td>3.013</td>
<td>5.054</td>
<td>12.760</td>
<td>−22.483</td>
</tr>
<tr>
<td>H1</td>
<td>[F, K(H1)]</td>
<td>0.609</td>
<td>2.685</td>
<td>−0.674</td>
<td>−1.603</td>
<td>−5.834</td>
<td>19.707</td>
</tr>
<tr>
<td>C1</td>
<td>[F, K(C1)]</td>
<td>0.238</td>
<td>2.423</td>
<td>−2.356</td>
<td>−4.577</td>
<td>−10.217</td>
<td>14.579</td>
</tr>
<tr>
<td>H2+H1+H4</td>
<td>[F, K(H2,3,4)]</td>
<td>−1.137</td>
<td>−3.596</td>
<td>−2.157</td>
<td>−5.309</td>
<td>−8.214</td>
<td>−10.574</td>
</tr>
<tr>
<td>Total</td>
<td>(F, K)</td>
<td>−1.808</td>
<td>−6.819</td>
<td>−2.175</td>
<td>−6.435</td>
<td>−11.506</td>
<td>1.230</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gauge origin</th>
<th>RPA</th>
<th>B3LYP</th>
<th>CAS (14,14)</th>
<th>MCRPA</th>
<th>SOPPA (CCSD)</th>
<th>CC2</th>
<th>CCSD</th>
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</thead>
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<tr>
<td>GIAO</td>
<td>−1.185</td>
<td>−1.131</td>
<td>−0.879</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CO</td>
<td>−1.191</td>
<td>−1.144</td>
<td>−0.880</td>
<td>−1.006</td>
<td>−0.969</td>
<td>−0.963</td>
<td>−0.992</td>
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</table>
values of the ORP are always negative for the $P$ enantiomer, and positive for the $M$ enantiomer, except for the $\text{H}_2\text{O}_2\text{H}$, $\text{F}$, $\text{L}$ and $\text{K}$ formalisms and angles close to $0^\circ$, 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.\textsuperscript{17,61} In more detail, the $\text{F}, \text{L}$ and $\text{F}, \text{K}$ formalisms are different to the rest, with a maximum value at $-120^\circ$, while in the rest it is around $-90^\circ$. The different profiles of these two methods have been already described for the $\text{HOOH}$ and $\text{H}_2\text{NNH}_2$ molecules.\textsuperscript{17,18}

Figures 3–5 show the dependence of the atomic contributions to the rotatory average tensor $K(0)$ for carbon, and the nonequivalent oxygen and hydrogen atoms, $\text{C}_1$, $\text{O}_1$, $\text{O}_2$, $\text{H}_1$, and ($\text{H}_2$, $\text{H}_3$, $\text{H}_4$) belonging to the methyl group. The $[\text{R}, \text{K}(\text{I})]$ and $[\text{P}, \text{K}(\text{I})]$ values are close to each other and define a homogeneous set of numerical values, which are slightly different from the set defined by $[\text{F}, \text{K}(\text{I})]$, for the torque partitioning scheme. The force scheme, partitioning $[\text{F}(\text{I}), \text{L}]$ and $[\text{F}(\text{I}), \text{K}]$, 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.\textsuperscript{42} we proposed a definition of the $\text{I}$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., $|r_j - R_j|^{-2}$, but $K_{\text{ac}}^\text{R}$ also depends on $\text{R}_I$. The present findings confirm those of the previous paper on $\text{H}_2\text{O}_2$\textsuperscript{17} the basins of the operators $F_{\text{ac}}^\text{R}$ and $K_{\text{ac}}^\text{R}$ 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 $[\text{R}, \text{K}(\text{O}_1)]$, $[\text{P}, \text{K}(\text{O}_1)]$ contribu-
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 Φ = −30°. Such trends are not because of insufficient convergence of 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 Φ = −45°. 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(H1)], [PK(H1)], and [FK(H1)] are very close, and near [FK(H1)], for each hydrogen, and different from that defined by the [F(H1)L] and [F(H1)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 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 and torque K_n, 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_n is clearly observed.

ACKNOWLEDGMENTS

This work was carried out with financial support from the Ministerio de Ciencia y Tecnología de Spain (Project No. CTQ2006-14487-C02-01/BQU) and Comunidad Autónoma de Madrid (Project MADRISOLAR, Ref. S-0505/PPQ/0225). Thanks are given to the CTI (CSIC) and DCSC for allocation of computer time. M.S. thanks the IQM for the financial support while visiting this institution. Financial support from Universidad de Buenos Aires, CONICET, and from the Danish Research Council (FNU) is gratefully acknowledged.
