

RESEARCH ARTICLE

On the transferability of atomic contributions to the optical rotatory power of hydrogen peroxide, methyl hydroperoxide and dimethyl peroxide

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The chirality of molecules expresses itself, for example, in the fact that a solution of a chiral molecule rotates the plane of linear polarised light. The underlying molecular property is the optical rotatory power (ORP) tensor, which according to time-dependent perturbation theory can be calculated as mixed linear response functions of the electric and magnetic dipole moment operators. Applying a canonical transformation of the Hamiltonian, which reformulates the magnetic dipole moment operator in terms of the operator for the torque acting on the electrons, the ORP of a molecule can be partitioned into atomic and group contributions. In the present work, we investigate the transferability of such individual contributions in a series of small, chiral molecules: hydrogen peroxide, methyl hydroperoxide and dimethyl peroxide. The isotropic atomic or group contributions have been evaluated for the hydrogen, oxygen and carbon atoms as well as for the methyl group at the level of time-dependent density functional theory with the B3LYP exchange–correlation functional employing a large Gaussian basis set. We find that the atomic or group contributions are not transferable among these three molecules.

Keywords: optical rotatory power; chirality; atomic contributions; hydrogen peroxide; methyl hydroperoxide; dimethyl peroxide; density functional theory

1. Introduction

The ability of a crystal or a solution to rotate the plane of linear polarised light is known as optical rotation or optical activity. Since its discovery in the beginning of the nineteenth century, it has been used as an experimental tool for measuring the enantiopurity of chemical compounds [1]. Among the different properties that influence the optical rotatory power (ORP), the effect of the molecular aggregation of the molecule of interest with itself [2–4], with the solvent [5–7] or with electrolytes [8] has recently been the topic of several studies.

Different theoretical schemes have been used to evaluate ORP. Polavarapu *et al.* [9] found that it depends strongly on the level of *ab initio* theory used, and that for hydrogen peroxide, the calculations at the Hartree–Fock level are not able to reproduce the correct dihedral angle dependence, as found in multiconfigurational Hartree–Fock calculations or in time-dependent density functional theory (TD-DFT) calculations with the B3LYP exchange–correlation functional as shown by Grimme [10]. Crawford and Stephens [11] compared the abilities of TD-DFT and coupled cluster (CC) methods to reproduce the experimental rotation in a set of chiral molecules. The deficiencies were attributed to vibrational, temperature and mainly to solvent effects. The importance of solvent effects was shown also in

another comparison of optical rotations with experimental data [12], confirming that in many cases it is necessary to include solvent molecules in quantum mechanical calculations [13,14]. Lattanzi *et al.* [15] determined the absolute configuration of norcamphor-derived furyl hydroperoxide by the calculation of optical rotation and vibrational circular dichroism for the most populated conformers at DFT level, which allowed the identification of the synthesised compound. Srebro *et al.* [16] analysed the performance of different functionals in TD-DFT to reproduce ORP ranging from 2 to 2×10^4 deg cm² dmol^{−1} for a set of 42 organic molecules and 3 metal complexes. They showed that structural parameters are determinant in the calculations, but for metal complexes the results are far off, indicating that chiroptical response properties also are a challenge for metal compounds. Also, the second-order polarisation propagator approximations (SOPPA) [17] and SOPPA with CC singles and doubles amplitudes (SOPPA(CCSD)) [18] have been employed in a previous calculation of the ORP in methyl hydroperoxide (MHP) [19]. A different contribution to the understanding of structure–chiroptical property relationships has been reviewed for both the measurement and computation of chiroptical properties of oriented systems [20]. This minireview is dedicated to natural chiroptical properties of achiral crystals revealed by polarimetry, and

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of achiral molecules predicted by computation, with particular interest on the structure–chiroptics relationships of simple achiral compounds.

The idea that molecular properties can be rationalised in terms of atomic contributions, which are transferable from molecule to molecule, constitutes an object of interest from the early days of chemistry. Pascal introduced the specific transferable magnetic atomic susceptibilities nearly a century ago [21]. Attempts have also been made to define a resolution of the electric dipole polarisability into atomic terms, see for instance, the sets of transferable contributions determined by Vogel [22]. Bader *et al.* [23] introduced the concept of atoms in molecules [24], defined as spatial domains bounded in space, to demonstrate the additivity of group polarisabilities and susceptibilities.

McAlexander *et al.* [25] applied the locally optimised orbital coupled cluster (LOO-CC) method to the calculation of optical rotations of a number of chiral molecules. This is a localised orbital version of the optimised orbital coupled cluster linear response method (OO-CC), where the domains were augmented by coupled perturbed Hartree–Fock calculations [26,27]. In particular, they applied the LOO-CC to optical rotation in a set of medium-size systems. They found that the method produces values comparable to canonical CC and maintains the scaling benefits of local CC [28]. The goal of the method is the possibility of studying large molecules employing a local correlation scheme. The additivity of atomic contributions to ORP is not discussed in other authors' articles, but a very interesting interpretation in terms of familiar concepts of chemical bonding, aided by first-principles calculations, has been presented recently by Moore *et al.* [29]. They developed a method to analyse the ORP of norbornenone in terms of individual bonds and lone pairs using DFT.

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.* [30], describes the first-order changes in the ground state in terms of perturbations of the molecule's occupied molecular orbitals by the electric and magnetic fields using coupled–perturbed Hartree–Fock methods, and analyses the results using 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]octanes [30], and to the conformational dependence of the optical rotation angle in the (*R*)-indoline molecule [31]. The second approach, described by some of us [32], uses a canonical transformation of the Hamiltonian to resolve the average ORP of a molecule into atomic contributions, based on the torque formalism for the magnetic dipole moment operator and/or the acceleration gauge for the electric dipole moment operator. This approach has been used for the study of the conformational profile of the ORP of hydrogen peroxide [32], hydrazine [33] and MHP [19]. Corresponding

algorithms have been implemented within the SYStems MOdena suite of computer programs [34].

Hydrogen peroxide and its derivatives are among the simplest chiral systems, which can be studied theoretically. However, their low racemisation barrier prevents the isolation of separate enantiomers experimentally. Two possible transition-state structures have been considered in the literature for the racemisation, both planar, with the substituents in either *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 also be the *cis* one [3]. The structures of several of the derivatives have been studied experimentally in the gas phase, including hydrogen peroxide [35], dimethyl peroxide (DMP) [36,37], bis(trifluoromethyl) peroxide [37] and difluoroperoxide [38]. The simplest dialkyl peroxide, DMP, is a gas that boils at $-13\text{ }^{\circ}\text{C}$. It is a commercially available compound, used as an oxidising reagent in organic and organometallic chemistry [39]. It has been proposed that DMP can be generated in star-forming regions [40], and its thermal decomposition has been used as a model for the O–O bond strength in dialkyl peroxide [41]. A number of theoretical studies have been devoted to this molecule [42], especially due to the difficulties to reproduce the experimental dihedral angle [43]. In addition, the chiral discrimination of its complexes with a lithium cation has been studied theoretically [44]. DMP also forms hydrogen-bonded complexes with nitric acid [45].

In the present article, we investigate the partitioning of the ORP of the DMP molecule into atomic contributions and compare them to corresponding atomic contributions in hydrogen peroxide and MHP. Furthermore, the behaviour of the total ORP and its atomic contributions as a function of the dihedral angle across the bond between the two oxygen atoms are investigated for the three molecules. The question we want to study is whether atomic contributions could be transferable between the members of this homologous series of molecules. The advantage of getting transferable quantities would be the ability to study much larger molecules, that is, biological systems, than are nowadays accessible.

A brief outline of the theoretical method employed in the calculation is given in Section 2 and the results of our investigations are discussed in Section 3.

2. Methodology

2.1. Tensors related to optical rotatory power

The optical rotatory parameter α_D of a substance with molar mass M in a medium with refractive index n is measured experimentally [46] at the angular frequency ω_D of the sodium D line. The underlying molecular property of the substance is the isotropic component of the frequency-dependent ORP tensor $\hat{k}(\omega) = \frac{1}{3} \sum_{\alpha=x,y,z} \hat{k}_{\alpha\alpha}(\omega)$, which is

related to the macroscopic parameter α_D by

$$[\alpha]_D = 1.343 \times 10^{-4} \frac{\omega_D^3}{(2\pi)^2} \hat{\kappa}(\omega_D) \frac{n^2 + 2}{3M}. \quad (1)$$

Expressions for the components of the ORP tensor of a chiral molecule for the angular frequency ω of a monochromatic electromagnetic wave can be obtained by time-dependent perturbation theory [47]:

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

where Im takes the imaginary part of the term within brackets, $\omega_{ja} = (E_j^{(0)} - E_a^{(0)})/\hbar$ are the angular frequencies of the electronic transitions of the unperturbed molecule from the reference state $|\psi_a^{(0)}\rangle \equiv |a\rangle$, with energy eigenvalue $E_a^{(0)}$, to the excited states $|\psi_j^{(0)}\rangle \equiv |j\rangle$ with energies $E_j^{(0)}$; μ_α and m_β are components of the electronic electric and magnetic dipole operators, $\boldsymbol{\mu} = -e\mathbf{R}$ and $\mathbf{m} = -(e/2m_e)\mathbf{L}$, respectively. The total electronic position and angular momentum operators \mathbf{R} and \mathbf{L} of a molecule with n electrons are defined with respect to an explicit origin \mathbf{r}_0 of the coordinate system, that is,

$$\mathbf{R}_\alpha(\mathbf{r}_0) = \sum_{i=1}^n (r_{i\alpha} - r_{0\alpha}), \quad (3)$$

$$\mathbf{L}_\alpha(\mathbf{r}_0) = \varepsilon_{\alpha\beta\gamma} \sum_{i=1}^n (r_{i\beta} - r_{0\beta}) p_{i\gamma}, \quad (4)$$

where here and in the following a summation over repeated Greek subscripts is implicitly implied and $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita unit tensor. The position and canonical momentum operators of electron i are denoted as \mathbf{r}_i and \mathbf{p}_i , respectively, and for the total electronic canonical momentum operator the symbol \mathbf{P} is used in the following, where the position vectors of the N nuclei with charge $Z_I e$ and mass M_I are denoted as \mathbf{R}_I .

Equation (2) defines the second-order property, ORP, in the length–angular momentum (\mathbf{R}, \mathbf{L}) picture, that is, $\hat{\kappa}^{(\mathbf{R}, \mathbf{L})}(\omega) = \hat{\kappa}(\omega)$. Using hypervirial relationships,

$$\langle a | R_\alpha | j \rangle = \frac{i}{m_e} \omega_{ja}^{-1} \langle a | P_\alpha | j \rangle, \quad (5)$$

$$\langle a | L_\alpha | j \rangle = i \omega_{ja}^{-1} \langle a | K_{n\alpha}^N | j \rangle, \quad (6)$$

three alternative expressions can be derived for the elements of the rotatory power tensor (see e.g. [47–49]), among

which the length–torque (\mathbf{R}, \mathbf{K}) formulation is given as

$$\hat{\kappa}_{\alpha\beta}^{(\mathbf{R}, \mathbf{K})}(\omega) = \frac{e^2}{2m_e \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \text{Re}(\langle a | R_\alpha | j \rangle \langle j | K_{n\beta}^N | a \rangle) \quad (7)$$

where \mathbf{K}_n^N is the operator for the torque acting on the electrons,

$$\begin{aligned} \mathbf{K}_n^N(\mathbf{r}_0) &= e^2 \sum_{l=1}^N Z_l \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_l}{|\mathbf{r}_i - \mathbf{R}_l|^3} \times (\mathbf{R}_l - \mathbf{r}_0) \\ &= \frac{i}{\hbar} [H^{(0)}, \mathbf{L}(\mathbf{r}_0)]. \end{aligned} \quad (8)$$

Both definitions (Equations (2) and (7)) are equivalent in exact quantum mechanics. In actual calculations, however, the results for the rotatory power tensor will only be equal in both formalisms, for the case of optimal variational wave functions like in the random phase approximation, its multiconfigurational extensions or in full configuration interaction calculations and in the limit of a complete one-electron basis set [48]. Values obtained from Equations (2) and (7) can therefore 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 (SCF) calculations, we commonly say that the *Hartree–Fock* limit has been achieved for this property.

The rotatory power tensor depends on the origin employed in the definition of the electric and magnetic dipole moment operators (Equations (3) and (4)). For a change of this origin, $\mathbf{r}'' \rightarrow \mathbf{r}' + \mathbf{d}$, the rotatory power tensor changes according to the relationship [47]:

$$\hat{\kappa}_{\alpha\beta}(\mathbf{r}'') = \hat{\kappa}_{\alpha\beta}(\mathbf{r}') - \frac{1}{2c} \varepsilon_{\alpha\beta\gamma} d_\delta \alpha_{\alpha\gamma}, \quad (9)$$

$$\text{Tr}\{\hat{\kappa}(\mathbf{r}'')\} = \text{Tr}\{\hat{\kappa}(\mathbf{r}')\}, \quad (10)$$

if the hypervirial relations (Equations (5) and (6)) are exactly satisfied, which requires again optimal variational wave functions and a complete one-electron basis set. Another way of solving the problem of the gauge invariance is provided by basis sets of London or gauge-including atomic orbitals (GIAO) [50] as, for example, implemented in Dalton programme [51–53].

2.2. Atomic contributions to optical rotatory power

Chiroptical phenomena in molecules have been known since the early days of Quantum Mechanics. Rosenfeld presented a quantum mechanical description of the rotation

angle [54], while Kirkwood [55] and Moffit [56] proposed models based on polarisable interacting atoms or chemical groups. However, these models do not provide a general strategy for assigning the contributions of individual atoms, contrary to the method of Lazzeretti and co-workers [47,57] for calculating numerical estimates of atomic contributions. The latter method is simple: the operator for the torque of the nuclei on the electrons, in Equations (7) and (8),

$$\mathbf{K}_n^N(\mathbf{r}_0) = \sum_{l=1}^N \sum_{i=1}^n \mathbf{K}_i^l(\mathbf{r}_0) = \sum_{l=1}^N \mathbf{K}_n^l(\mathbf{r}_0) \quad (11)$$

contains a sum over all nuclei and can therefore be partitioned into contributions from atomic operators:

$$\mathbf{K}_n^l(\mathbf{r}_0) = \sum_{i=1}^n e^2 Z_l \frac{\mathbf{r}_i - \mathbf{R}_l}{|\mathbf{r}_i - \mathbf{R}_l|^3} \times (\mathbf{R}_l - \mathbf{r}_0). \quad (12)$$

The tensor of the rotatory power in the (\mathbf{R}, \mathbf{K}) formulation can therefore be partitioned into atomic terms introducing the $[\mathbf{R}\mathbf{K}(I)]$ scheme:

$$\hat{\kappa}_{\alpha\beta}^{(\mathbf{R}, \mathbf{K})} = \sum_{l=1}^N \hat{\kappa}_{\alpha\beta}^{[\mathbf{R}\mathbf{K}(I)]}, \quad (13)$$

with

$$\hat{\kappa}_{\alpha\beta}^{[\mathbf{R}\mathbf{K}(I)]} = \frac{e^2}{2m_e \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \text{Re}(\langle a | R_\alpha | j \rangle \langle j | K_{n\beta}^l(\mathbf{r}_0) | a \rangle). \quad (14)$$

It must be recalled that also the atomic contributions to the ORP depend on the origin employed in the definition of the electric and magnetic dipole moment operators (Equations (3) and (4)). However, the molecular rotatory power is origin independent if the hypervirial relations (Equations (5) and (6)) are exactly satisfied. It is therefore important to choose comparable origins in calculations of the atomic contributions in different molecules. Finally, one should note that there exists also an analogous formulation based on the total force of the nuclei on the electrons

[19,32,33,57], in which, however, the corresponding hypervirial relations cannot be fulfilled with the basis sets employed in the present study. We will therefore not discuss it here.

3. Computational details

The geometrical parameters of the COOC skeleton of the H_3COOCH_3 molecule have been obtained experimentally by gas electron diffraction [36] (1.457 and 1.420 Å for the O–O and O–C distances, 105.2° for the OOC angle and 119° for the COOC dihedral angle). Since the positions of the hydrogen atoms have not been determined experimentally, they have been optimised at the MP2/6-311++G(d,p) level of theory, while maintaining the rest of the variables fixed at the experimental values indicated above. The equilibrium geometry of H_3COOH had previously been optimised at the same level of theory [19], whereas the equilibrium geometry of hydrogen peroxide had previously been optimised at the SCF level with the 6-31G* basis set [32]. See Figure 1 for the labelling of the atoms in the three molecules.

To study the dependence of the ORP properties on the R–O₁–O₂–R dihedral angle ϕ of H_3COOCH_3 , we have generated additional geometries by varying the dihedral angle from 0° to 180°, in steps of 10° while keeping the rest of the variables fixed at the values previously described. The structures at $\phi = 0^\circ$ and 180° correspond to non-chiral transition states of the racemisation process of this molecule. The equilibrium configurations correspond to $\phi = 119^\circ$ (C_2 point group) for H_3COOCH_3 , $\phi = 134.918^\circ$ (C_1 point group) for H_3COOH and $\phi = 115.977^\circ$ for HOOH (C_2 point group).

All the calculations of the atomic contributions to the average ORP $\hat{\kappa}^{(\mathbf{R}, \mathbf{K})}(\omega = 0)$ in the low-frequency limit $\omega = 0$ in H_3COOCH_3 , H_3COOH and HOOH were carried out at the TD-DFT level with the B3LYP exchange-correlation functional [58] and gauge-independent basis functions. The same Cartesian and completely uncontracted basis set [59] was employed as in our previous study on MHP [19], meaning an (13s10p5d2f/8s4p1d) basis set for (O&C/H) with in total 528, 383 and 238 Cartesian Gaussian basis functions for H_3COOCH_3 , H_3COOH and HOOH . In all these calculations, the origin of the coordinate system

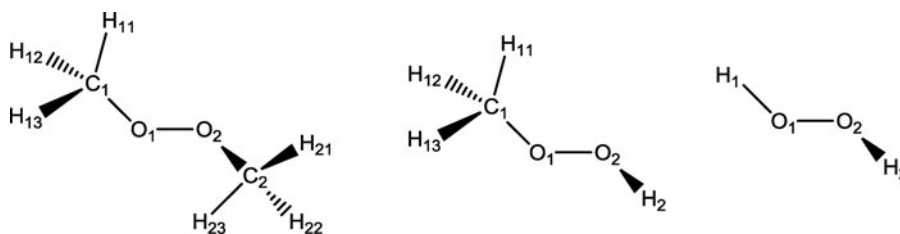


Figure 1. Scheme and numbering of the H_3COOCH_3 , H_3COOH and HOOH molecules.

Table 1. Comparison of various correlated calculations of the isotropic component of the rotatory power tensor, $\hat{\kappa}(\omega)$, in the **(R,L)** formulation (in ppt a.u.) of HOOH, H₃COOH and H₃COOCH₃ at their equilibrium geometry in the low-frequency limit, $\omega = 0$. The calculations were carried out with GIAOs or with gauge-less basis functions. In the latter case, the gauge origin was at the centre of mass (CM), which was also the origin of the coordinate system.

Molecule	Gauge origin	B3LYP	SOPPA	SOPPA(CCSD)	CC2	CCSD
HOOH	GIAO	-0.002	-	-	-	-
HOOH	CM	-0.003	0.101	0.111	0.060	-0.009
H ₃ COOH	GIAO	-1.154	-	-	-	-
H ₃ COOH	CM	-1.169	-1.127	-1.097	-0.925	-0.987
H ₃ COOCH ₃	GIAO	-6.062	-	-	-	-
H ₃ COOCH ₃	CM	-6.075	-6.038	-6.064	-5.740	-5.110

and the gauge origin were fixed at the middle point of the O–O bond for each compound. The ORP in the **(R,L)** formulation at the equilibrium geometries of the three molecules was also calculated using gauge less as well as GIAO basis functions at the TD-DFT/B3LYP level.

To study the effect of electron correlation on $\hat{\kappa}^{(\mathbf{R},\mathbf{L})}(\omega = 0)$ for these molecules, we have carried out additional correlated calculations at the level of the SOPPA [17], the SOPPA(CCSD) [18] and the unrelaxed CC linear response theory for CC2 and CCSD wave functions [60]. All calculations were carried out with the Dalton programme [53].

4. Results and discussion

4.1. Basis set and electron correlation

In Table 1, the results of the electron correlation study are presented for the average rotatory power $\kappa(\omega = 0)$ in the low-frequency limit $\omega = 0$ and gauge origin dependent **(R,L)** formalism for all three molecules in their equilibrium geometries. Comparing first of all the GIAO and gauge-less basis set calculations at the TD-DFT/B3LYP level, we can see that the differences are at most 1%. This implies that one would not gain an advantage in employing GIAO basis sets.

Another check for the quality of the employed basis sets is the agreement between the results for the total average rotatory power $\hat{\kappa}(\omega = 0)$ obtained with the **(R,L)** and

(R,K) formulations (Equations (2) and (7)). In Table 2, we have therefore collected TD-DFT/B3LYP values for the total average rotatory power $\kappa(\omega = 0)$ of all three molecules at the equilibrium geometry, and in Figure 2 for all dihedral angles. They were calculated with the gauge and coordinate system origins at the middle point of the O–O bond. For MHP and DMP, the results obtained with the **(R,K)** formalisms differ by less than 1% from the **(R,L)** results, while for HOOH the difference in percentage is larger due to the small value but in absolute values the difference is not larger. This and the good agreement between the GIAO and gauge-less results in Table 1 indicate that the quality of basis set is good enough to assure that the *Hartree–Fock limit* has been nearly reached for these formulations.

Turning now to the effect of electron correlation on the average rotatory power in the **(R,L)** formulation, we observe a rather divergent picture for the three molecules. For MHP and DMP all results are negative and the B3LYP values are the most negative results and relatively close to the SOPPA and SOPPA(CCSD) values, while the CC2 or CCSD values are the least negative results and differ by

Table 2. Isotropic component of the rotatory power tensor, $\hat{\kappa}(\omega)$, at the TD-DFT/B3LYP level in the **(R,L)** and **(R,K)** formulations (in ppt a.u.) of HOOH, H₃COOH and H₃COOCH₃ at their equilibrium geometry in the low-frequency limit $\omega = 0$. The gauge origin and the origin of coordinates are fixed at the same position, the *middle point* of the O–O bond.

Molecule	(R,L)	(R,K)
HOOH	-0.003	-0.001
H ₃ COOH	-1.169	-1.168
H ₃ COOCH ₃	-6.075	-6.040

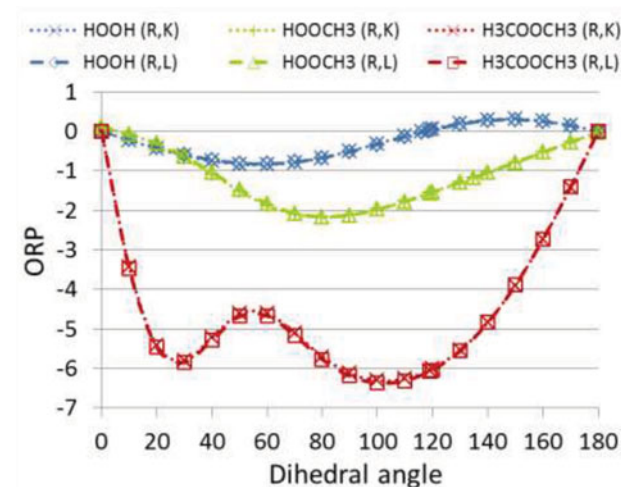


Figure 2. The total average rotatory power in the limit $\omega = 0$, in the **(R,L)** and **(R,K)** formalisms, as a function of the XOOX dihedral angle, calculated at the TD-DFT/B3LYP level.

up to 26% or 18% from the B3LYP results. The corresponding deviation of the SOPPA(CCSD) results from the CCSD values is 11% and 18%, and thus larger than normally observed for linear response properties depending on the electric [61] or magnetic dipole operator [62]. For hydrogen peroxide, on the other side, the B3LYP and CCSD results are almost equal, very small and negative, while the SOPPA, SOPPA(CCSD) and CC2 results are positive.

4.2. Atomic contributions

In Table 3, we compare finally the atomic and chemical group contributions to the isotropic component of the rotatory power tensor $\hat{k}(\omega = 0)$ in the low-frequency limit $\omega = 0$ for HOOH, H₃COOH and H₃COOCH₃. They were calculated at the B3LYP level in the [R,K(I)] torque formalism (Equation (14)). The gauge origin and the origin of coordinates are fixed at the same position, the *middle point* of the O–O bond. In addition, the dihedral angle X–O–O–X was fixed at 119° for all three compounds, which is the equilibrium geometry dihedral angle of H₃COOCH₃, in order to employ the same conformation in the comparison of the atomic contributions to ORP. The interatomic bonds and bond angles were kept, however, at the values reported in Refs. [32] and [19].

Comparing the atomic contributions in the three different molecules, we see first of all that not only the total average rotatory power but also almost all individual atomic contributions increase in absolute values on going from hydrogen peroxide via MHP to DMP. Furthermore, we can observe that the contributions of the oxygen atoms are almost always the largest individual contributions and that

Table 3. Comparison of the atomic isotropic contributions to the rotatory power of HOOH, H₃COOH and H₃COOCH₃ calculated with the [R,K(I)] torque formalisms at the TD-DFT/B3LYP level for a fixed dihedral angle XOOX of 119°, the equilibrium dihedral angle for CH₃OOCH₃. The origin of the coordinate system and the gauge origin are taken at the middle point of O–O bond for each compound.

Atom I	HOOH	H ₃ COOH	CH ₃ OOCH ₃
O ₁	0.194	0.036	−1.627
O ₂	0.194	−0.625	−1.627
H ₁	−0.169	–	–
H ₂	−0.169	0.215	–
C ₁	–	−0.278	0.863
C ₂	–	–	0.863
(H ₁₁ ,H ₁₂ ,H ₁₃)/3	–	–	−0.752
(H ₂₁ ,H ₂₂ ,H ₂₃)/3	–	−0.302	−0.752
O ₁ H ₁	0.025	–	–
O ₂ H ₂	0.025	−0.409	–
O ₁ CH ₃	–	−1.146	−3.020
O ₂ CH ₃	–	–	−3.020
Total	0.050	−1.556	−6.040

the contributions of the carbon or hydrogen atoms directly bound to the oxygen atoms have the opposite sign.

However, the fact that the atomic contributions increase with increasing number of atoms (and electrons) in the molecules, see, for example, the oxygen atoms, implies that the atomic contributions are not transferable from one molecule to another. Therefore, we also included chemical group contributions in Table 3, which are calculated as the sum of the atomic contributions. But even for those group contributions we cannot detect any transferability between these three closely related molecules. Supported by the checks on the basis set in the previous section, we do not assign this to a deficiency in the basis set or the lack of electron correlation but to the inherent differences in the electronic structure of the seemingly related molecules and to a correlation of the ORP with the size of a molecule. However, it is important to recall that even for exact wave functions, the individual ‘atomic contributions’, in Equation (14), are by no means invariant under a change of coordinate system but only their sum in Equation (13).

4.3. Variation with the dihedral angle

Finally, we have investigated whether the lack of transferability of the atomic contributions between the three compounds might be due to our choice of dihedral angle in the calculations, which we had fixed for all three molecules at the equilibrium geometry value of DMP. It has been demonstrated that the optical rotation as a function of dihedral angle in small molecules such as H₂O₂ and H₂S₂ depends strongly on the proper treatment of electron correlation [9]. The reason for this can be traced to the accidental degeneracy of excited states of opposite polarisations that almost cancel at dihedral angles of about 90° [63]. This cancellation is not well represented at the Hartree–Fock level [9]. We have, therefore, calculated the total average rotatory power as well as some of the atomic contributions to it for all three molecules as a function of the XOOX dihedral angle within the range from 0° to +180° at the TD-DFT/B3LYP level in the (R,L) or (R,K) formalisms. The results are illustrated in Figures 2–7. For all dihedral angles, the values of the ORP are always negative for the P enantiomer of DMP, and positive for the M enantiomer, with a maximum (minimum) close to a dihedral angle of −119° (+119°) for the M(P) enantiomer of DMP. Similar trends were described for MHP [19] (positive values for the M enantiomer and negative for the P one), while positive and negative values of the ORP were found for the hydrogen peroxide depending on the dihedral angle considered [32]. From Figure 2, we can also see that the maximum value of the ORP is for hydrogen peroxide ~0.8 ppt a.u., for the monomethyl derivative ~2.1 ppt a.u. and ~6.4 ppt a.u. in the DMP. These values are for all molecules larger than the values at the dihedral angle of the DMP equilibrium geometry. Furthermore, the dihedral angle variation in DMP

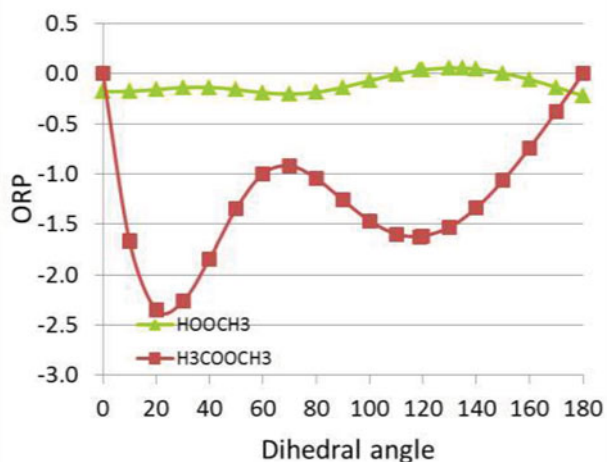


Figure 3. Contribution of the O_1 oxygen atom to the average rotatory power of H_3COOH and H_3COOCH_3 , in the limit $\omega = 0$, in the (\mathbf{R}, \mathbf{K}) formalisms, as a function of the XOOX dihedral angle, calculated at the TD-DFT/B3LYP level.

exhibits two extrema, one around 30° and one around 100° , whereas it is only one shallow minimum for the other two molecules.

The dihedral angle variation of the atomic contributions within the (\mathbf{R}, \mathbf{K}) formalisms is shown in Figures 3–7. The dihedral angle variation for the methoxy-group oxygen (O_1) contribution to the ORP is shown in Figure 3 for H_3COOH and DMP. The absolute minima for DMP and maxima for MHP, and vice versa, are located at similar dihedral angles. The variation, however, is quite different with ≈ -2.3 ppt a.u. for DMP versus -0.4 for MHP. Besides, the O_1 contribution in DMP also exhibits two minima like the total ORP. The dihedral angle variation of the carbon contribution to

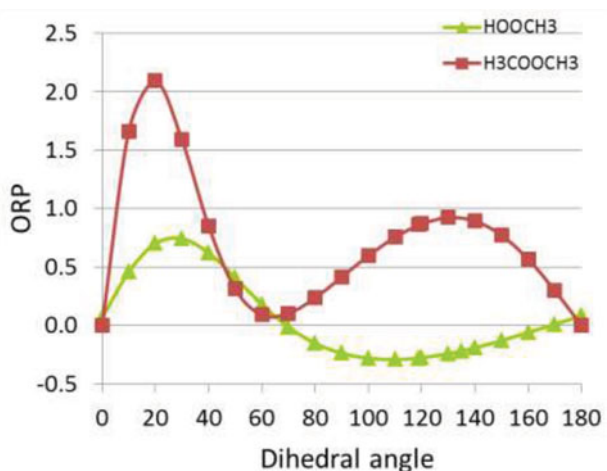


Figure 4. Contribution of the C_1 carbon atom to the average rotatory power of H_3COOH and H_3COOCH_3 , in the limit $\omega = 0$, in the (\mathbf{R}, \mathbf{K}) formalisms, as a function of the XOOX dihedral angle, calculated at the TD-DFT/B3LYP level.

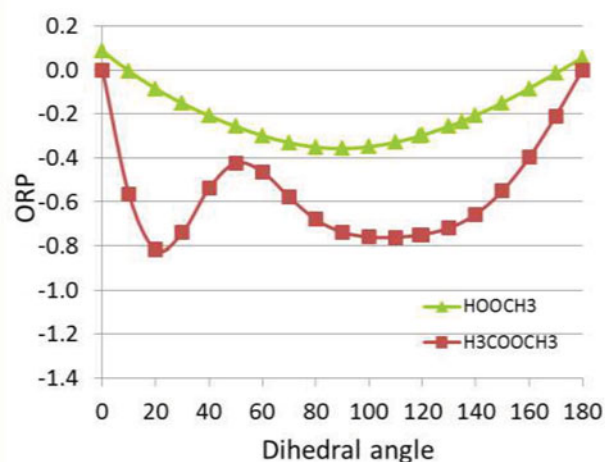


Figure 5. Average contribution of the three hydrogen atoms in the methyl group to the average rotatory power of H_3COOH and H_3COOCH_3 , in the limit $\omega = 0$, in the (\mathbf{R}, \mathbf{K}) formalisms, as a function of the XOOX dihedral angle, calculated at the TD-DFT/B3LYP level.

the ORP, shown in Figure 4, differs significantly between H_3COOH and DMP. In DMP, all values are positive with two very pronounced maxima, the larger one around 20° and the somewhat smaller one close to 130° , while in MHP, the dihedral angle dependence is much less pronounced but includes both positive and negative values. The values reported in Figure 5 correspond to the average values of the atomic contributions: $H_{11} + H_{12} + H_{13}$ of the methyl protons for both compounds, H_3COOH and DMP. Negative values are obtained for both molecules, but in DMP again two minima are found versus one shallow for MHP. Finally,

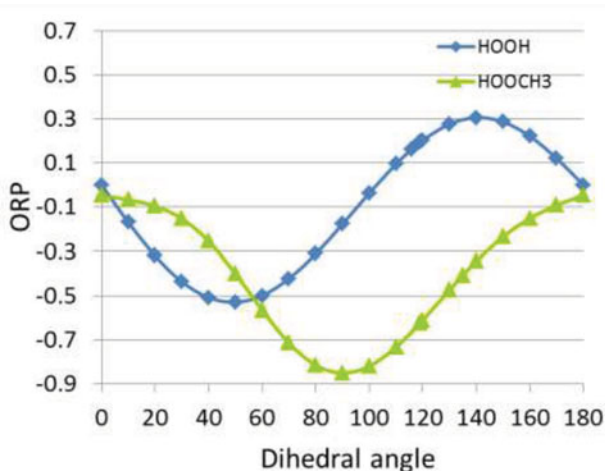


Figure 6. Contribution of the O_2 oxygen atom to the average rotatory power of $HOOH$ and H_3COOH , in the limit $\omega = 0$, in the (\mathbf{R}, \mathbf{K}) formalisms, as a function of the XOOX dihedral angle, calculated at the TD-DFT/B3LYP level.

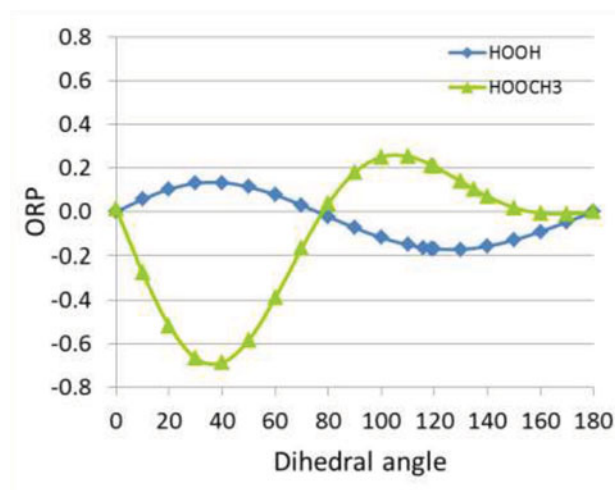


Figure 7. Contribution of the H_2 hydrogen atom to the average rotatory power of HOOH and H_3COOH , in the limit $\omega = 0$, in the (R,K) formalisms, as a function of the XOOX dihedral angle, calculated at the TD-DFT/B3LYP level.

in Figures 6 and 7, the atomic contributions from the OH groups in hydrogen peroxide and MHP as a function of the dihedral angle are shown. In particular for the hydrogen atom, the variation is quite different in the two molecules with MHP having the larger variation. This means that clear differences between atomic or group contributions of identical groups, as observed in Table 3, are not due to our choice of a fixed dihedral angle, but are found for all angles.

5. Conclusions

The ORP and its atomic contributions as a function of the XOOX dihedral angle have been evaluated at the TD-DFT/B3LYP level using a large uncontracted Gaussian basis set. We observed good agreement between the results in the length–angular momentum and length–torque formalisms and using GIAO. This indicates that the basis set is sufficiently large to nearly fulfil the hypervirial relations involving the position, linear and angular momentum and torque operators.

Comparing the three molecules, we find that the maximum value of the ORP as well as the ORP at a fixed value of the dihedral angles increase with increasing number of methyl groups. This also applies to the individual atomic contributions. Furthermore, we observe some pattern with respect to the importance and sign of the contributions of the individual atoms in all three molecules: oxygen making almost always the largest contribution and the contribution of the atom directly connected to the oxygen having the opposite sign. However, we do not observe any transferability of the atomic or chemical group contributions to the total rotatory power in this series of molecules. And although the variation of the total ORP and its atomic contributions with the dihedral angle ex-

hibit some similarities among the three molecules, there is still no sign of transferability. We interpret this as inherent difference in the properties of the electronic structure of otherwise seemingly similar molecules. However, it is possible that due to their relatively small values, the atomic or chemical group contributions to the ORP in these molecules are more sensitive to the changes in the electronic structure. We cannot exclude, therefore, that transferability could be observed in larger molecules as Bader [64] has shown that in long hydrocarbons, the methylene groups are transferrable.

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