

Positive chirality measures from chiroptical pseudoscalars: applications to carbon-containing molecular systems

A.V.Luzanov

STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Received May 20, 2015

A new chirality quantification scheme is proposed based on a special procedure transforming molecular pseudoscalar into positive index. The optical rotatory strengths (estimated semiempirically) are used for the corresponding characterization of chiral molecules. We show several specific examples of using the present method. The focus is made on dissymmetric π -conjugated systems constituting some special molecular materials (helixes etc.). A simplified technique of partitioning the chirality index into atomic contributions is reported. For most presented examples, the atomic distribution of chirality are found to be highly delocalized over the whole carbon backbone.

Keywords: dissymmetry, rotatory polarizability, chirality index, chiral materials, twisted conjugated hydrocarbons

Предложена новая количественная мера молекулярной хиральности. Она основана на специальной процедуре, преобразующей молекулярный псевдоскаляр в положительный индекс. Для соответствующей характеристики хиральности используются рассчитанные полуэмпирически силы оптического вращения. Приведено несколько характерных примеров использования предложенного метода. Основной акцент сделан на диссимметрических π -сопряженных системах, входящих в состав ряда специальных молекулярных материалов (в частности, класса гелиценов). Описана упрощенная методика разбиения индекса хиральности на атомные вклады. В большинстве представленных в статье примеров атомное распределение хиральности обнаруживает высокую степень делокализации по соответствующему углеродному остову.

Позитивна міра хиральності з хіроптичних псевдоскалярів. Застосування до вуглецьмістких молекулярних систем. А.В.Лузанов

Запропоновано нову кількісну міру молекулярної хиральності. Вона базується на спеціальній процедурі, що перетворює молекулярний псевдоскаляр у позитивний індекс. Для відповідної характеристики хиральності використовуються сили оптичного обертання у напівемпіричному наближенні. Наведено декілька характерних прикладів використання запропонованого підходу. Головний акцент зроблено на диссиметричні π -спряжені системи, що входять до складу низки спеціальних молекулярних матеріалів (зокрема, геліценового класу). Окреслено спрощену методику поділу індексу хиральності на атомні складові. У більшості прикладів, що їх представлено у статті, атомний розподіл визначається значною делокалізацією хиральності з відповідного вуглецевого остова.

1. Introduction

An important feature common to many modern sciences is the universal notion of

chirality (see, e.g., [1–10]). More than 150 years after Pasteur's brilliant breakthrough, molecular chirality is still a topi-

cal issue of broad scientific and engineering interest. However, the molecular chirality measurement remains an elusive problem. Usually, Kitaigorodski [11] is cited as the first who outlined a rather general theoretical scheme for quantifying molecular chirality by the nonnegative measure. This measure was identified with a maximal overlap volume of left- and right-handed enantiomers (see [12, 13] for detail and further development). There exist now a great number of approaches which can more or less satisfactorily describe the molecular chirality (or simply, chirality). Reviews [14–19] and recent papers [20–24] are a good source of references to published descriptions of the previously given procedures, and we will not attempt to duplicate these references.

We only stress that it is important to distinguish between scalar and pseudoscalar chirality measures. The usual nonnegative (simply, positive) measures, which are based on a formal mathematical reasoning, are, of course, the scalar quantities. The essential advantage of them is that by construction the positive scalar measures are nonzero if and only if the system in study is chiral. Another kind of the indices are the pseudoscalar measures. A fundamental property of the pseudoscalars is to have opposite signs for left- and right-handed enantiomers (optical antipodes). The physical and physicochemical chirality manifestations are just described by pseudoscalars (chiroptic effects, twisting power of a chiral dopant in nematics, violating parity conservation etc.). We must also recognize an important merit of the physical pseudoscalars, namely their additivity (additive separability, in quantum-chemical terms). It provides a correct behavior of pseudoscalar quantities in various physicochemical processes (e.g., the pseudoscalar measures vanish for the racemats). It is also possible to construct the special pseudoscalars which offer suitable independent quantification schemes [25–29]. However, as clearly shown in [27, 30], in this way one may face with unexpected difficulties.

In the last two cited works, a behavior of arbitrary pseudoscalar chirality measure on reaction paths is considered. It is proved the occurrence the so-called chiral zeros for any chiral structure [30]. This means that there always exists such a reaction point where the given pseudoscalar quantity vanishes even for the surely chiral configuration. From this result the authors of [30]

inferred that positive chirality measures are the only permissible quantities for chirality quantification.

Nevertheless, the positive measures have their own drawback. Namely, unlike pseudoscalars, the such measures never fulfill the important requirement of additivity (this fact was found in our study [31]). It poses an unresolvable dilemma which cannot be avoided in any chirality theory, although most researchers in the field seemingly do not suspect about this fact. In this situation, we should choose the less imperfect between the above alternatives. Positive scalar measures seem to be more preferable because they are nulled only on achiral structures. At the same time, pseudoscalar quantities are more rooted in the physical nature of molecular chirality. A possible way to somehow reconcile the two approaches is to produce positive chirality measures from physical pseudoscalars. This is the underlying philosophy which is adopted in the present paper.

More specifically, the goal of the study below is to elaborate a new chirality quantification scheme based on the optical rotation theory. In so doing we invoke, for corresponding electron problems, an elementary semiempirical technique in the form of the extended Huckel theory (EHT) [32, 33]. It enables us to make computations easily even for large chiral molecules.

2. Optical rotatory polarizability

At first, we recall basic relations of the quantum theory of optical activity. For simplicity, all the expressions will be given here for the ground electronic state. In the required context, the key quantity is the so-called rotatory (or electric-dipole magnetic-dipole) polarizability [34]. We define it, up to a non significant constant, by the expression

$$\tilde{\beta}(\omega) = \sum_j \frac{R_j}{(\lambda_j)^2 - \omega^2}. \quad (1)$$

Here ω is a formal variable (the incident light frequency, in practice), R_j is a rotatory strength (see below) for electronic transition $0 \rightarrow j$ with excitation energy λ_j . The fundamental quantities in Eq.(1) are the rotatory strengths R_j . They are computed from matrix elements of the full electronic momentum, P , and angular momentum, L , as follows:

$$R_j = \text{Im}[\langle \Psi_0 | P | \Psi_j \rangle \cdot \langle \Psi_0 | L | \Psi_j \rangle] / \lambda_j \quad (2)$$

with $|\Psi_0\rangle$ and $|\Psi_j\rangle$ being the ground and excited state wave functions, respectively. The rotatory strengths obey the Rosenfald sum rule [35]:

$$\sum R_j = 0. \quad (3)$$

Eq. (1) loses validity near the resonance values $\omega = \lambda_j$ where a resonance-line shape with finite width is required. The conventional resonance shape is the Lorentian one. Then the respective expression for rotatory polarizability is

$$\beta(\omega) = \sum_j \frac{(\lambda_j^2 - \omega^2)R_j}{[(\lambda_j^2 - \omega^2)^2 + (\Gamma_j\omega)^2]}, \quad (4)$$

where Γ_j is a width parameter for transition $0 \rightarrow j$ [36]. These standard relations will be basic for all that follows. Plot of rotatory polarizability (4) against frequency ω gives in fact optical rotatory dispersion (ORD) curve.

3. Chirality from positive and negative parts of optical rotations

In searching ways to the new positive chirality index, let us look with more scrutiny at Eq. (4). From Eq. (3) it follows that there exist positive values of rotatory strengths together with negative ones. We denote the positive R_j by R_j^+ and negative R_j by R_j^- . Then the corresponding sums

$$R^+ = \sum R_j^+, \quad R^- = \sum R_j^-$$

satisfy the rule $R^+ + R^- = 0$ as a consequence of sum rule (3). It may be tempting to introduce the positive chirality measure as

$$R_{\pm} = |R^+ - R^-|. \quad (5)$$

However, such a quantity (justifiable in principle) can be inappropriate in practice, as is clear from a detailed analysis in Appendix A.

One of the source of this unsuitability is due to the fact that for possible degenerate states the respective energy sublevels can produce incorrect (i.e., nonzero) rotatory strengths in achiral molecules. Only appropriate combinations of contributions from degenerate states give the correct (zero) results for the such specific symmetry systems. Unfortunately, this peculiarity is in fact impossible to take into account in pro-

gramming numerical algorithms. At the same time, rotatory polarizabilities always behave correctly because degenerate states of any symmetry contribute properly to $\beta(\omega)$, if employing Eq. (4).

We see that $\beta(\omega)$ rather than a set $\{R_j\}$ should be used in this setting. We suggest that instead of R^+ and R^- , the positive and negative parts of $\beta(\omega)$ must come into play. We define them as follows:

$$\beta^+(\omega) = \beta(\omega), \text{ if } \beta(\omega) > 0, \quad (6)$$

$$\text{otherwise } \beta^+(\omega) = 0,$$

$$\beta^-(\omega) = \beta(\omega), \text{ if } \beta(\omega) \leq 0, \quad (7)$$

$$\text{otherwise } \beta^-(\omega) = 0.$$

These functions should be integrated over the characteristic frequency range $[0, \omega_{max}]$, and it produces "chirally significant" areas restricted by curves $\beta^+(\omega)$ and $\beta^-(\omega)$, respectively:

$$I^+ = \int_0^{\omega_{max}} \beta^+(\omega) d\omega, \quad I^- = \int_0^{\omega_{max}} \beta^-(\omega) d\omega. \quad (8)$$

Then the difference

$$\chi_{rot} = I^+ - I^- \quad (9)$$

makes the new positive chirality measure. Unlike $|R^+ - R^-|$, this index correctly differentiates all chiral and achiral species. The above procedure transforming the pseudoscalar sets to positively defined quantities can be easily extended to other pseudoscalar chirality measures.

4. Chirality index χ_{rot} within EHT

Now we describe in more detail the proposed scheme for chirality characterization of electronic systems from which many molecular materials are composed, in particular biomaterials. However, in this work we restrict ourselves by carbon-containing systems. There are no technical restrictions for extending our program code to treat molecules which include heteroatoms.

The EHT model [32] is used here to simply produce all-valence molecular orbitals (MO) needed at the electronic level of the problem. The underlying EHT one-electron Hamiltonian is easy to compute for very complex molecules. Thus, we assume that the Hamiltonian matrix is constructed semiempirically, and one-electron coordinate matrices $\{X, Y, Z\}$ are calculated in the

standard valence Slater-type AO (atomic orbital) basis [37]. The eigenstates of h^0 are MOs which will be denoted by kets $|\varphi_k\rangle$. Eigenvalues of h^0 correspond to orbital energies ε_k . With this, the momentum matrices $\{P^x, P^y, P^z\}$ are obtained by the usual commutation relations:

$$P^x = -i(h^0X - Xh^0). \quad (10)$$

Accordingly, angular momentum matrices in the AO representation are computed, e.g., $L^x = ZP^y - YP^z$ etc. If so doing the usual Hermitization procedure should be additionally applied by computing $L^x \Rightarrow [L^x + (L^x)^\dagger]/2$ etc.

In the Huckel-like one-electron approximation, excited states are trivially formed by promoting occupied MO $|\varphi_i\rangle$ to vacant (virtual) MO $|\varphi_a\rangle$, so excitation energies are

$$\lambda_{i \rightarrow a} = \varepsilon_a - \varepsilon_i. \quad (11)$$

Then the working expression for rotatory polarizability (4) is

$$\beta(\omega) = \sum_i^{\text{occ}} \sum_a^{\text{vac}} \beta_{i \rightarrow a}(\omega), \quad (12)$$

$$\beta_{i \rightarrow a}(\omega) = \frac{\lambda_{i \rightarrow a}^2 (\lambda_{i \rightarrow a}^2 - \omega^2)}{[(\lambda_{i \rightarrow a}^2 - \omega^2)^2 + (\Gamma_{i \rightarrow a} \omega)^2]} R_{a \rightarrow i}, \quad (13)$$

with $R_{i \rightarrow a}$ being the rotatory strength for one electron transition $i \rightarrow a$:

$$R_{i \rightarrow a} = \text{Im}[P_{ai}^x L_{ai}^x + P_{ai}^y L_{ai}^y + P_{ai}^z L_{ai}^z] / \lambda_{a \rightarrow i}, \quad (14)$$

where one-electron matrix elements $P_{ai}^x = \langle \varphi_a | P^x | \varphi_i \rangle$ and so on. Moreover, $\Gamma_{i \rightarrow a} = \sigma \lambda_{i \rightarrow a}$ and σ is a damping factor (in practical computations we put $\zeta = 0.2$). Eqs. (10)–(14) are easily programmed, and the computations on rather large systems can be efficiently performed even by using laptops.

An important point is concerned with the numerical integration procedure needed for obtaining index (9) numerically. In our work, the trapezoidal method of integration is utilized. This method should only be used with a sufficiently large number of nodes for integration. Indeed, in practice the functions $\beta^+(\omega)$ and $\beta^-(\omega)$ turn out to be rather highly oscillatory, exhibiting a great number of extreme peaks.

5. Chirality characterization of typical molecular structures

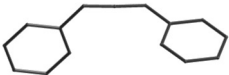
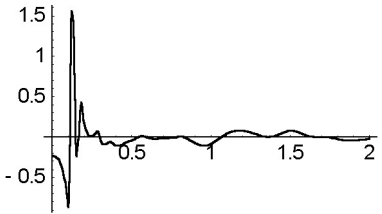

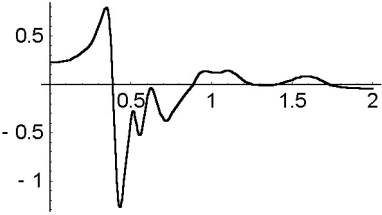

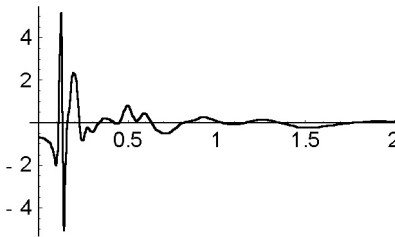
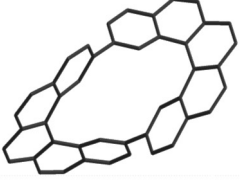
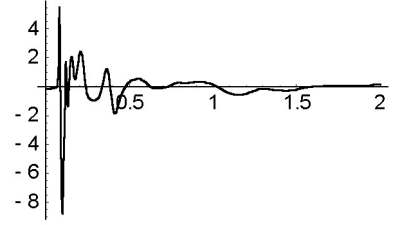

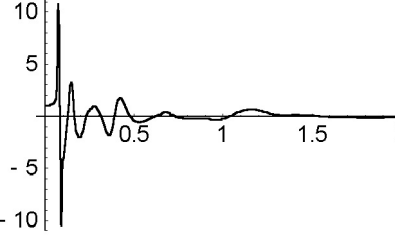
In this section we present several illustrative examples of computing chirality measure (9) (see Tables 1–3). The examples are mainly taken from [21, 31] and structural chemistry literature [38, 39]. Among them, carbo[n]helicenes are of significant interest as unusual molecular materials [40].

For all our computations, AM1 optimized geometrical data are used. The values of χ_{rot} in the tables are expressed in relative units of $\chi_{rot}[\text{C}_6\text{H}_{12}]$, that is the chirality measure for the cyclohexane molecule in the D_2 symmetric conformation (explicitly, $\chi_{rot}[\text{C}_6\text{H}_{12}] = 12.64$ atomic units (a.u.)). In Table 1, together with χ_{rot} , we give plots of the dependency of $\beta(\omega)$ versus ω (all in a.u.). Within the EHT approximation, they present the modelled ORD curves in the wide excitation energy (ω) range [0,2] where, in fact, all active one-electron excitations are lumped. For convenience, ordinate values in plots of Table 1 are scaled by a factor of 10^{-2} .

Referring to the data of Tables 1–3, it seems that the proposed chirality index provides a quite reasonable chirality discrimination if judging from the geometrical shape of molecules in question. At the same time one must keep in mind that χ_{rot} , as defined by Eq. (9) from $\beta(\omega)$, reflects, first of all, the electronic rather than geometrical chirality. For instance, χ_{rot} is varying due to various nongeometrical factors, e.g., under electronic excitation.

In order to describe molecular chirality in pictorial terms we use the additional technique of visualization which allows us to approximately assign to each atom A a certain local quantity χ_{rot}^A . The visualization method is explained in Appendix B. From the results presented in Tables 2 and 3 where atomic distributions $\{\chi_{rot}^A\}$, are given we see that in all system, even in the fully asymmetric butylethylmethylpropylmethane (BEMPM) [41] molecule, the chirality is delocalized over almost all carbon atoms of the molecule. As expected, the contribution of hydrogen atoms is small, especially in unsaturated systems, and in Table 3 we suppress the hydrogen atoms in the respective distributions. However, certain regions of the carbon backbone can be significantly more involved in the chirality formation than others. It is quite well seen in the BEMPM molecule (the first system in Table 2). Notice

Table 1. Chirality measure χ_{rot} (in units of $\chi_{rot}[\text{C}_6\text{H}_{12}]$) for dissymmetric structures with C_n and D_n spatial symmetry and modelled ORD curves within EHT

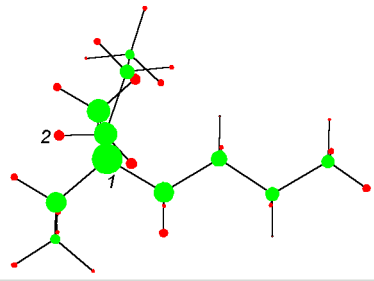
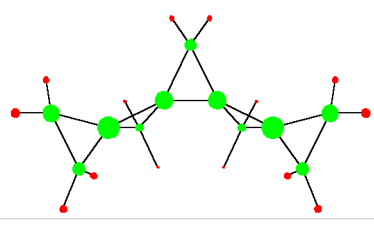
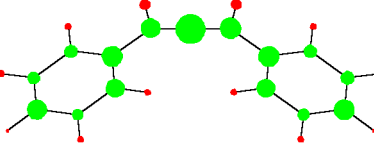
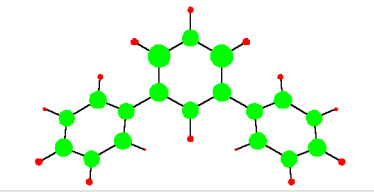
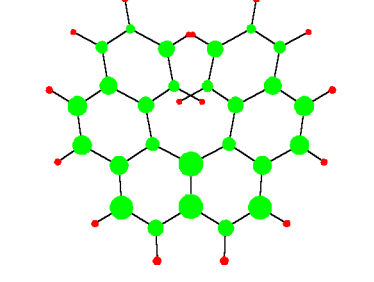
Structure (symmetry)	χ_{rot}	ORD
1,3-Diphenylallene (C_2) 	1.4	
Tritwistane (D_3) 	3.2	
5-Layered Cyclophane (D_2) 	5.3	
Propellicene (D_2) 	7.2	
[12]Helicene (C_2) 	8.4	

that this molecule is fully saturated (no double bonds), and has a small chirality index. Another example is given in Table 3 where the results for the partially conjugated α -carotene molecule are presented. In this case we also observe a preferable localization of chirality — on the left cyclohexene ring of the carotene.

Much more chiral are specifically curved and twisted conjugated hydrocarbons (rest

of the systems in the Tables). In the case of the *m*-terphenyl (see Table 2), the central ring is more chiral. The example of 1,3-diphenylallene in Table 2 is interesting as a typical case of the molecule with chiral axis (in the present case, it goes through carbon atoms of the allene subunit). We observe that the central atom of the chiral axis is just the atom which is markedly more "chiral" than other ones. However, for more

Table 2. Chirality measure χ_{rot} (in units of $\chi_{rot}[\text{C}_6\text{H}_{12}]$) and the full atomic chirality diagram $\{\chi_{rot}^A\}$

Structure (symmetry)	χ_{rot}	$\{\chi_{rot}^A\}$
BEMPM	0.7	
[5]Triangulane (C2)	0.8	
1,3-Diphenylallene (C2)	1.5	
<i>m</i> -Terphenyl (C2)	2.7	
Hexahelicene (C2)	2.7	

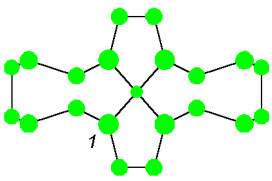
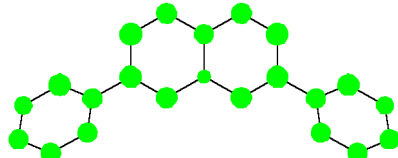
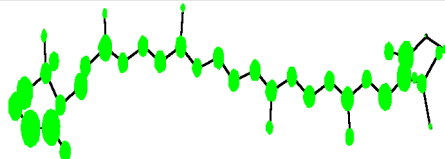
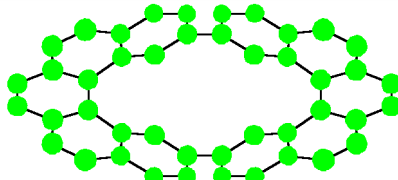
complex systems, such as the propellicene molecule (Table 3), chirality distribution is rather delocalized over the whole molecule.

6. Conclusion remarks

In this paper we have presented a rather general scheme that transforms pseudosca-

alars (which are not always reliable for indicating chirality) into a positive chirality measure. The scheme is specified here for the case of pseudoscalar rotatory strengths which determine optical activity of chiral molecules. We analyze several typical dissymmetrical systems having proper rotation groups C_n and D_n , and fully asymmetri-

Table 3. Chirality measure χ_{rot} (in units of $\chi_{rot}[\text{C}_6\text{H}_{12}]$) and the complete atomic chirality diagram $\{\chi_{rot}^A\}$ for selected structures (hydrogen atoms are suppressed)

Structure (symmetry)	χ_{rot}	$\{\chi_{rot}^A\}$
[2,2]Vespirene (D2)	2.2	
2,7-Diphenylnaphthalene (C2)	3.1	
α -Carotene	4.8	
Propellicene (D2)	7.7	

cal systems. Overall, results suggest that the new degree of chirality χ_{rot} serves as a suitable measure of molecular chirality treated at an electronic level. This feature distinguishes the index from many other existing measures which are normally based on formal geometric or topological reasoning. The additional analysis provides a pictorial representation in form of diagrams showing approximately the distribution of the chirality over atoms in molecule. We see that the frequently used notion of the local chirality is not appropriate to describe generally too complicated and globalized features of the molecular chirality. It is especially valid for the dissymmetric π -conjugated structures which are the main illustrative focus of this paper.

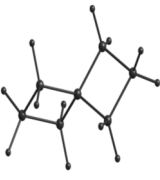
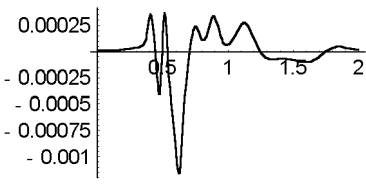
Some critical points should be made about the used computational scheme. Here the basic scheme has been implemented within EHT, that is the simplest semiempirical approximation for valence shells. Much more reliable results are likely to be obtained by the standard ab initio Hartree-Fock model even with a modest basis set, say, the computationally not too expensive 6-31G. However,

for this we need bring in more powerful computational tools. Another point where further improvement should be made is using more precise numerical integration technique needed for Eqs. (8) (as well as for Eq. (23) in Appendix B). The Gauss-Kronrod scheme is the technique that our preliminary study points to as a more viable. At last, additional pseudoscalar quantities, such as considered in [25, 26, 42], are worth being investigated in the same manner as rotatory strengths (2). These issues will be a subject of future work.

Appendix A. Snags of using absolute values of rotatory strengths

This appendix aims to elucidate the difficulties of using the auxiliary index R_+ , Eq. (5). We will see that the difficulties are closely related to computing rotatory strengths R_j , Eq. (2), for high-symmetry systems. For these systems, degenerate states occur, and the situation is formally the same as in the case of usual optical transitions and corresponding oscillator strengths (see p.98, Eq. (2) in [43]). In our case we assume the ground state $|\Psi_0\rangle$ to be nondegenerate, and the j th excited state to

Table 4. Auxiliary index R_{+-} and chirality index χ_{rot} for the spiro[3.3]heptane molecule taken with approximate D_{2d} geometry. The R_{+-} value is given in a.u.

Spiro[3.3]heptane)	R_{+-}	χ_{rot}	ORD
	46.3	0.00002	

be degenerate. Then, instead of a single excited state $|\Psi_j\rangle$ we must take into account the whole degenerate set $\{|\Psi_j^{(\alpha)}\rangle\}_{1 \leq \alpha \leq v_j}$ with v_j being a degree of degeneracy. The correct formula (see also Eq. (24) in [44]) is

$$R_j = \sum_{\alpha=1}^{v_j} R_j^{(\alpha)} \quad (15)$$

where

$$R_j^{(\alpha)} = \text{Im}[\langle \Psi_0 | P | \Psi_j^{(\alpha)} \rangle \cdot \langle \Psi_0 | L | \Psi_j^{(\alpha)} \rangle / \lambda_j]. \quad (16)$$

A stumbling block here is that in the numerical computations over a large array of states we cannot beforehand know whether the given rotatory strength belongs to the "degenerate" set, say a set $\{R_j^{(\alpha)}\}$, or not. Indeed, in finite precision computations, the excitation spectrum is only approximately degenerate (quasidegeneracy). For sufficiently large molecules, the problem is aggravated due to lumping energy levels very densely together, thus preventing their unambiguous identification. That is why we prefer using rotatory polarizability (4) which automatically gives correct contributions of all degenerate excitations. In practice, not all degenerate states are source of troubles, but the difficulties are quite possible even for simple symmetric molecules.

The numerical example of the achiral spiro[3.3]heptane molecule (D_{2d} symmetry) helps to clarify the point. In Table 4 we present the corresponding numerical results for the auxiliary index R_{+-} , Eq. (5), and the main chirality index (9). We see that in practice R_{+-} cannot universally serve the chirality quantification. The cause is that the individual R_j values may be really incorrect, as stated above (if no exact grouping of states, $\{R_j^{(\alpha)}\}$, is involved). For instance, take only the lowest one-electron excitation

HOMO→LUMO of the molecule in question (HOMO and LUMO are acronyms for highest occupied MO and lowest unoccupied MO, respectively). Within the EHT model, the non-degenerate HOMO is of symmetry B_2 , whereas the doubly degenerate LUMO is of symmetry E . Thus, we have here two HOMO→LUMO contributions, $R^{(1)}$ and $R^{(2)}$. Numerically they, being almost the same by the absolute value, are opposite in sign:

$$R^{(1)} = -0.0684436, \quad R^{(2)} = 0.0684438.$$

Of course, Eq. (15) provides the correct numerical result $R^{(1)} + R^{(2)} = 2 \cdot 10^{-7}$. However, if we take the sum $|R^{(1)}| + |R^{(2)}| = 0.1368874$ (as our program performs computations on Eq.(5)), then the wrong conclusion about chirality of the achiral spiran is drawn. At the same time, by using Eq.(9) we avoid such incorrect results.

We must also add that above troubles (with nonzero R_{+-} for achiral systems) are rare, and in principle the R_{+-} index could be used for surely chiral systems. However, for the sake of completeness, another drawback of R_{+-} should be stressed. It is a scaling property of this index. Let n_o is the number of the occupied MOs, and n_v is that of the vacant MOs. Then R_{+-} is scaled, approximately, as $n_o n_v \sim N^2$, where N is a total number of electrons. We see that generally R_{+-} can increase too quickly with increasing size of chiral systems, and such a behavior makes the index not well suitable for quantification purposes.

Appendix B. An approximate technique for computing local contributions

In order to compute local (atomic) chirality contributions $\{\chi_{rot}^A\}$, we adopt the previously given scheme for electronic excitation localization [45]. This allows us to decompose each term $\beta_{i>a}(\omega)$ into atomic contributions. Thus we can represent an atomic structure of the overall $\beta(\omega)$ values

(13), from which the resulting index χ_{rot} is computed. More exactly, we start with a quite understandable formula describing the excitation indices of one-electron transition $i \rightarrow a$. We define the usual atomic localization distributions for occupied MO $|\varphi_j\rangle$ and vacant MO $|\varphi_a\rangle$

$$L_A[\varphi_i] = \sum_{\mu \in A} |\langle \chi_\mu | \varphi_i \rangle|^2, \quad (17)$$

$$L_A[\varphi_a] = \sum_{\mu \in A} |\langle \chi_\mu | \varphi_a \rangle|^2, \quad (18)$$

where $|\chi_\mu\rangle$ is taken from the full orthonormal set of AOs, and subscript A denotes the selected atom in molecule. The corresponding excitation index $L_A(i \rightarrow a)$ is identified with the evident expression (see Eq. (19) in [45] and Eq. (6.9) in [46]):

$$L_A(i \rightarrow a) = (L_A[\varphi_i] + L_A[\varphi_a]) / 2. \quad (19)$$

Then we can introduce the related atomic contribution $\beta_{(i \rightarrow a)}(\omega) L_A(i \rightarrow a)$ for each term $\beta_{(i \rightarrow a)}(\omega)$ in Eq. (12). From here it follows that for rotatory polarizability the atomic localization index, $\beta_A(\omega)$, is of the form

$$\beta_A(\omega) = \sum_i^{occ} \sum_a^{vac} \beta_{i \rightarrow a}(\omega) L_A(i \rightarrow a), \quad (20)$$

so that the exact sum rule

$$\sum_A \beta_A(\omega) = \beta(\omega) \quad (21)$$

obeys automatically. However, we encounter difficulties if we try to obtain atomic chirality indices χ_{rot}^A by replicating the algorithm for the whole chirality index χ_{rot} (see Section 4). We can somehow use the mentioned algorithm, but we cannot guarantee that the corresponding sum rule will be exactly satisfied. More or less well working scheme is based on the following expressions. For each atom A , we make up the positive and negative components of $\beta_A(\omega)$:

$$\begin{aligned} \beta_A^+(\omega) &= \beta_A(\omega), \text{ if } \beta(\omega) > 0, \\ &\text{otherwise } \beta_A^+(\omega) = 0, \\ \beta_A^-(\omega) &= \beta_A(\omega), \text{ if } \beta(\omega) \leq 0, \\ &\text{otherwise } \beta_A^-(\omega) = 0. \end{aligned} \quad (22)$$

Thus, having computed the integrals

$$I_A^+ = \int_0^{\omega_{max}} \beta_A^+(\omega) d\omega, \quad I_A^- = \int_0^{\omega_{max}} \beta_A^-(\omega) d\omega, \quad (23)$$

we find an approximate atomic chirality index:

$$\chi_{rot}^A = I_A^+ - I_A^-. \quad (24)$$

In practice, these indices obey only a fairly accurate sum rule:

$$\sum_A \chi_{rot}^A \cong \chi_{rot} \quad (25)$$

(with an accuracy near 5 %). Sometimes, few values in $\{\chi_{rot}^A\}$ (one or two values) can be quite small but negative, and in these cases these small contributions are taken in their absolute value.

The specific calculations are given in Tables 2 and 3, where distributions $\{\chi_{rot}^A\}$ are depicted by the colored circles (green (1) for carbon atoms and red (2) for hydrogen atoms) with radii roughly proportional to $\sqrt{\chi_{rot}^A}$. Notice that we observed a highly delocalized chirality distribution for most molecular systems treated in the present paper. This fact is in concordance with the entirely another study (of other systems) based on a direct partition scheme for rotatory strengths R_j [47, 48].

References

1. Chirality - From Weak Bosons to the α -Helix, ed. by R.Janoschek, Springer, Berlin (1991).
2. Advances in Biochirality, ed. by G.Palyi, C.Zucchi, L.Caglioti, Elsevier, Amsterdam (1999).
3. Chirality in Liquid Crystals, ed. by H.-S.Kitzerow, C.Bahr, Springer, New York (2001).
4. Chirality in Natural and Applied Science, ed. by W.J.Lough, I.W.Wainer, Blackwell/CRC Press, Oxford (2003).
5. Topics in Stereochemistry, Materials-Chirality, vol.24, ed. by M.M.Green, R.J.M.Nolte, E.W.Meijer, Wiley-VCH, New York (2004).
6. Chirality in Drug Research, ed. by E.Francois, W.Lindner, Wiley-VCH, Weinheim (2006).
7. G.H.Wagniere, On Chirality and the Universal Asymmetry: Reflections on Image and Mirror Image, Wiley-VCH, Zurich (2007).
8. Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies & Materials, ed. by H.Amouri, M.Grusselle, Wiley-VCH, Chichester, UK (2008).

9. C.Wolf, *Dynamic Stereochemistry of Chiral Compounds: Principles and Applications*, RSC Publishing, Cambridge, UK (2008).
10. *Comprehensive Chiroptical Spectroscopy, Applications in Stereochemical Analysis of Synthetic Compounds, Natural Products, and Biomolecules*, vol.2, ed. by N.Berova, P.L.Polavarapu, K.Nakanishi, R.W.Woody, Wiley, Hoboken, New Jersey (2012).
11. A.I.Kitaigorodskii, *Organic Chemical Crystallography*, Consultaut Bureau, New York (1961).
12. B.Chion, J.Lajzerowicz, D.Bordeaux, A.Collet, J.Jacques, *J. Phys. Chem.*, **82**, 2682 (1978).
13. G.Gilat, *Found. Phys. Lett.*, **3**, 189 (1990); *J. Math. Chem.*, **15**, 197 (1994).
14. D.Avnir, H.Zabrodsky, P.G.Mezey, in: *Encyclopedia of Computational Chemistry*, vol. 4, ed. by P.v.R.Schleyer, Wiley, Chichester (1998), p.2890.
15. K.Mislow, *Top. Stereochem.*, **22**, 1 (1999).
16. R.Todeschini, V.Consonni, *Handbook of Molecular Descriptors*, Wiley-VCH, New York, (2000).
17. M.Petitjean, *Entropy*, **5**, 271 (2003).
18. P.W.Fowler, *Symmetry, Culture Sci.*, **16**, 321 (2005).
19. A.Pietropaolo, in: *Ideas in Chemistry and Molecular Sciences: Where Chemistry Meets Life*, ed. by B.Pignataro, Wiley-VCH, New York (2010), p.291.
20. C.Dryzun, A.Zait, D.Avnir, *J. Comput. Chem.*, **32**, 2526 (2011); C.Dryzun, D.Avnir, *Phys. Chem. Chem. Phys.*, **12**, 197 (2011).
21. A.V.Luzanov, *Int. J. Quant. Chem.*, **111**, 2196 (2011).
22. A.Pietropaolo, M.Parrinello, *Chirality*, **23**, 534 (2011).
23. C.Dryzun, *J. Comput. Chem.*, **35**, 748 (2014).
24. F.J.Lipinski, J.Cz.Dobrowolski, *RSC Adv.*, **4**, 47047 (2014).
25. A.V.Luzanov, E.N Babich, *Struct. Chem.*, **3**, 175 (1992); A.V.Luzanov, E.N.Babich, *J. Mol. Struct. (Theochem.)*, **333**, 279 (1995).
26. M.A.Osipov, B.T.Pickup, D.A.Dunmur, *Mol. Phys.*, **84**, 1193 (1995).
27. A.B.Harris, R.D.Kamien, T.C.Lubensky, *Rev. Mod. Phys.*, **71**, 1745 (1999).
28. M.Solymosi, R.J.Low, M. Grayson, M.Neal, *J. Chem. Phys.*, **116**, 1 (2002).
29. H.Kamberaj, R.J.Low, M.P.Neal, *Mol. Phys.*, **104**, 335 (2006).
30. N.Weinberg, K.Mislow, *Can. J. Chem.*, **78**, 41 (2000); N.Weinberg, K.Mislow, *Mol. Phys.*, **103**, 2769 (2005).
31. A.V.Luzanov, D.Nerukh, *Functional Materials*, **12**, 15 (2005); A.V.Luzanov, D.Nerukh, *J. Math. Chem.*, **41**, 417 (2007).
32. R.Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
33. J.P.Lowe, *Quantum Chemistry*, Academic Press, New York (1978).
34. A.Moskowitz, *Adv. Chem. Phys.*, **4**, 67 (1962).
35. E.U.Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).
36. J.A.Schellman, *Chem. Rev.*, **75**, 323 (1975).
37. W.C.Hamilton, *J. Chem. Phys.*, **26**, 1018 (1957).
38. V.M.Potapov, *Stereochemistry*, Mir, Moscow (1978).
39. *Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis*, ed. by H.Dodzik, Wiley-VCH, Weinheim (2009).
40. Y.Shen, C.-F.Chen, *Chem. Rev.*, **112**, 1463 (2012).
41. W.T.Hoeve, H.Wynberg, *J. Org. Chem.*, **45**, 2754 (1980).
42. P.Fischer, K.Beckwitt, F.W.Wise, A.C.Albrecht, *Chem. Phys. Lett.*, **352**, 463 (2002); N.Ji, Y.R.Shen, *Chirality*, **18**, 146 (2006).
43. E.U.Condon, G.H.Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge (1959).
44. F.S.Richardson, *Inorg. Chem.*, **19**, 2806 (1980).
45. A.V.Luzanov, *Uspekhi Chimii*, **49**, 1033 (1980).
46. A.V.Luzanov, O.A.Zhikol, *Int. J. Quant. Chem.*, **110**, 902 (2010).
47. R.K.Kondru, P.Wipf, D.N.Beratan, *Science*, **282**, 2247 (1998).
48. R.K.Kondru, P.Wipf, D.N.Beratan et al., *Org. Lett.*, **2**, 1509 (2000).