Continuous Symmetry Measure using the electron density

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Abstract

In this contribution we address the problem of near symmetry and present a Continuous Symmetry Measure (CSM) based on the electron density function. In particular we propose an algorithm which generalizes the formalism proposed by Avnir[1, 2] toward an exploitation of point symmetry groups properties. Correlations with existing definitions of CSM are discussed and an implementation which uses a simplified electron density of the proposed approach is presented. Advantages and disadvantages of the different approaches are reported.

1

I. INTRODUCTION

Continuous Symmetry Measure (CSM) in chemistry has been introduced by Avnir and coworkers[1, 2] and subsequently reproposed by Grimme[3] via a wave function approach. Wales[4] used pure energetic considerations to present a near symmetry concept and Bellarosa and Zerbetto[5] proposed a measure which combines the ideas proposed by Avnir and Grimme. If the CSM is limited to inversion and mirror symmetry it determines a continuous chirality measure. Recent works aiming to quantify chirality are presented by Smirnov *et al.*[6] and by Capozziello and Lattanzi[7–10]. They define a measure closely related to the CSM proposed in this contribution. A recent paper[11] by M.Petitjean reviews the symmetry and chirality measures proposed since 1890 in different scientific fields and underlines the importance of the subject for the scientific community.

The concept at the base of CSM is that symmetry can be treated as a continuous rather than a discrete property of an object. Potential applications of this concept have been foreseen by its authors and later successfully applied in biology[12] as well as in fields completely different from natural sciences[13]. Applications of the CSM as a correlation parameter for the study of several properties are getting more and more frequent in the literature and yield promising results[14–16]. Inclusion of CSM as a standard parameter in QSPR (quantitative structure-property relationship) approaches should be a growing trend in particular for those area where chirality and enantiodifferentation are investigated.

Reactivity, dynamic properties of molecules, allowed and forbidden transitions in electronic and vibrational spectra are only a few of the fields of possible application in chemistry of a near symmetry concept. Allowing for a quantitative measure of chirality, CSM opens very interesting prospectives in stereochemistry and asymmetric synthesis. A review on CSM and chirality measures appears in Encyclopedia of Computational Chemistry (1998)[1].

In this paper we will present an algorithm which defines a CSM for a molecular electron density function for every point symmetry group. We argue that the proposed algorithm has a more general validity and in this respect we will present a comparison of the proposed procedure with two others definitions of CSM. In particular we formalize within point symmetry group theory the approach proposed by Avnir and coworkers[1]. We shall also show that the approaches proposed by Avnir and Grimme can be both included as particular cases of our proposition and that molecular chirality measures in the framework of the Quantum

Similarity Approach (QSA)[17, 18] can be easily derived from our proposed formalism.

The success of density functional theory (DFT)[19–21] in the last decade in the study of electronic structure of molecules justifies the use of the electron density as a basic object to refer to for a CSM analysis.

In order to compete in terms of computer time with Avnir's definition and propose an implementation able to handle large molecules we define an approximated electron density which we will use in a computer program.

The next section presents the new CSM definition. Section III briefly reviews the previous definitions and discuss similarities and differences from the presently proposed one. Before concluding we report selected examples.

II. DESCRIPTION OF THE CSM MODEL

We introduce a model that allows the implementation of the calculation of CSM starting from the electron density function. At present there is no mean to relate CSM with the Hamiltonian of any molecular system but we would like to underline that the electron density is one of the few parameters which is connected directly to the molecular Hamiltonian and is at the same time subject to a direct experimental measure. These properties make the electron density a unique parameter for the application of pure geometrical considerations.

We define the CSM as the minimal distance between an object (the electron density) and a symmetrized one which is used as a reference. This requires the definition of two quantities: the symmetrized object and a distance.

A symmetrized density $\tilde{\rho}(\mathbf{r})$ with respect to a symmetry group G is constructed from a given electron density $\rho(\mathbf{r})$ using the following equation

$$\tilde{\rho}(\mathbf{r}) = \frac{1}{n_G} \sum_{\mu}^{n_G} S_{\mu}\rho(\mathbf{r}) \tag{1}$$

where n_G is the order of the symmetry group G, and S_{μ} runs over all the distinct symmetry operations of the group.

The function $\tilde{\rho}(\mathbf{r})$ is then totally symmetric with respect to the point group G and can be therefore used as the symmetrized reference object. The demonstration that $\tilde{\rho}(\mathbf{r})$ is totally symmetric follows a standard group theory technique which makes use of the rearrangement theorem and is reported in the appendix.

We should stress that in this case the function $\rho(\mathbf{r})$ can have no symmetry properties. Because of this we cannot define any specific position and orientation of the symmetry elements belonging to the group G with respect to the $\rho(\mathbf{r})$. We solve this problem with a minimization procedure which is discussed later in this paper. Nevertheless equation (1) is our master equation for the following development.

The second step in our procedure is to define a distance function. We define it to be a pure Euclidean geometrical distance:

$$D = \int |\tilde{\rho}(\mathbf{r}) - \rho(\mathbf{r})|^2 d\mathbf{r} \tag{2}$$

where D is the distance and ρ and $\tilde{\rho}$ are the quantities previously defined.

The distance proposed in equation 2 is for example used in most of the density fitting tools for quantum chemistry applications for the reproduction of coulomb potentials[22]. The Avnir's definition of CSM makes use of the same Euclidean distance for discrete terms. More interesting is the fact that an ongoing discussion exists[23] (and references therein) about the concept of Quantum Similarity Measure (QSM) which is defined by integrals of the type:

$$Z_{AB} = \int \int \rho_A(\mathbf{r}_1)\Omega(\mathbf{r}_1, \mathbf{r}_2)\rho_B(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{3}$$

where the electron densities of a molecules A and a molecule B are introduced and Ω is a given positive definite operator. If the two densities are of the same molecule then the measure is defined as quantum self-similarity measure.

If the Ω operator is the Dirac delta and we substitute our $\tilde{\rho}$ and ρ for ρ_A and ρ_B respectively we obtain:

$$Z_{CSM} = \int \tilde{\rho}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \tag{4}$$

which, we shall see later, is the discriminating term in equation 2 as discussed also in the QMS approaches[23, 24].

These arguments clearly identify the proposed distance as the best candidate. There are obviously other possible definition for the distance function. For example we will make use of a different one in the context of a wave function approach. There is a further possible definition which will not be investigated in this work but nevertheless we would like to introduce in this context.

We can define a symmetry constrained energy minimization. In the framework of DFT $E = E[\rho]$ is the total energy defined via a functional of the density ρ. We can define a sym-

metrized energy $\tilde{E}$ by minimizing the energy functional $E[\tilde{\rho}]$ with the additional constrain of having $\tilde{\rho}$ total symmetric with respect a given group G

$$\tilde{E} = \min E[\tilde{\rho}] \tag{5}$$

The variational principle will assure $\tilde{E} - E \geq 0$ and a CSM can be defined in the form:

$$E_{CSM} \propto \tilde{E} - E \tag{6}$$

This measure seems to be promising expacially in cojunction with concepts arising from superpositon states of chiral molecules[25] but has not been chosen for the context of this paper because it will need a more detailed formal description expecially in conjunction with the symmetry constrained minimization procedure. It would be possible to follow our procedure described in the following text (summarized by equations (1) and (7)) but it will give rise to expensive calculation in terms of computer time (which is not in the spirit of the presented CSM), technical problems in the implementation (due to nuclei cusps) and while an equation like (1) whould be a wanted feature in order to obtain correlations it is not guarrantied that a minimization of the type of equation (7) as proposed also by other authors[2, 2] is suited for a DFT approach.

because it will result expensive in terms of computer time (which is not in the spirit of the presented CSM) and it gives rise to some technical problems in the implementation (due to nuclei cusps). Moreover it will need a more detailed formal description expecially in conjunction with the symmetry constrained minimization procedure

which is out of the scope of this contribution.

In equation 1 we assumed a predefined space orientation and position of the symmetry elements (inversion center, mirror planes or rotational axis) associated with each given symmetry operation S_i of the given point symmetry group G. The distance will also be a function of the position and orientation of these symmetry elements. With this in mind we define the CSM as:

$$CSM = min_{R_g,\theta,\phi,\psi}D = min_{R_g,\theta,\phi,\psi}\left\{\frac{1}{N}\int |\tilde{\rho}[R_g,\theta,\phi,\psi] - \rho|^2 d\mathbf{r}\right\} \tag{7}$$

Where we introduced the dependency of $\tilde{\rho}$ on the θ, ϕ, ψ, R_g which are respectively the Eulerian angles and the vector identifying the origin of a Cartesian reference frame fixed

5

to the symmetry elements of the point symmetry group G with respect to the cartesian molecular frame. A normalization factor N is also introduced in order to define proper limits for the CSM. A symmetric object will be characterized by a CSM value of 0.

The whole procedure is summarized by these steps:

- Define a symmetrized object using equation 1.

- Choose a suitable distance measure (equation 2 in our case).

- Define the CSM as the minimum distance as in equation 7.

This three steps definition of CSM is valid for all point symmetry groups. In the next sction we will also show that we can apply the procedure to quantities different from the electron density.

III.   RELATION WITH PREVIOUS CSM DEFINITIONS

As mentioned above there are other approaches to CSM which use different quantities to define a CSM. One of these definitions uses the coordinate vectors in the CSM equation as basic parameters. A second definition instead applies symmetry operators to the wave function.

In this section we relate these CSM to our three steps procedure.

The approach which uses geometrical points for the CSM definition has been developed by D. Avnir and coworkers[2]. For simple cases this CSM definition can be summarized with this equation

$$CSM_P = \frac{1}{M} \sum_i^N |\tilde{p}_i - p_i|^2 \tag{8}$$

where the p_i are vectors indicating the position of the nuclei and the $\tilde{p}_i$ are a symmetrized set of vectors obtained from the original p_i set. The summation runs over the total number of points N and M is a normalization factor. In Avnir's formalism equation 8 defines directly the CSM due to the particular procedure used to define the set of points $\tilde{p}_i$.

We will apply the method proposed in section II to a set of N Cartesian points $p_i(i = 1, N)$. We propose here a simplified procedure which is valid for cyclic point symmetry groups C_n.

In equation (7) there is an implicit averaging of the electron density ρ due to the presence of the integral. In the case of discrete points we are bound to develop an assignment procedure from the set $\{p_i\}$ to the set $\{\tilde{p}_i\}$ in order to obtain an equivalent averaging.

We divide the set of $\{p_i\}$ position vectors in partitions considering $n_\gamma > 0$ partitions of n_G vectors of the set $\{p_i\}$ plus 1 partition with the $N - n_\gamma \cdot n_G$ remaining vectors up to include all the vectors of the $\{p_i\}$ set. γ labels the possible different partitioning. An equivalent partitioning scheme is defined for the set of symmetric vectors $\{\tilde{p}_i\}$.

For each possible partitioning scheme the set of symmetrized vectors $\{\tilde{p}_i\}$ is determined by

$$\tilde{p}_i^\gamma = \frac{1}{n_G} \sum_\mu^{n_G} S_\mu p_{j(\mu,i)}^\gamma \tag{9}$$

for vectors in the first n_γ partitions and

$$\tilde{p}_i^\gamma = \frac{1}{n_G} \sum_\mu^{n_G} S_\mu p_i^\gamma \tag{10}$$

for the other vectors belonging to the last partition.

In equation 9 the special index $j(\mu, i)$ is used to select vectors in the partition containing the vector p_i and identify the μ-th vector cyclically counted within the partition elements index starting from the vector p_i.

For example assuming the partitioning $\{p_1, p_2, p_3\}\{p_4, p_5, p_6\}\{p_7\}$ the index $j(\mu = 3, i = 6) = 5$ determines the point p_5. The index $j(\mu, i)$ will be completely determined only once we define an order for S_μ symmetry operators with respect to the index μ. We use the convention that $S_1 = E$ (identity) and that $S_n = C_n^{(n-1)}$.

We have assumed a one-to-one correspondence between the vectors $\{p_i\}$ and the newly generated vectors $\{\tilde{p}_i\}$. Once a given γ partitioning is determined we can relax this constraint by considering all possible permutations of the vectors $\{p_i\}$ while leaving the index i in place. We call $P^\chi(\{p_i\})$ all the possible permutations indexed by χ and assume that $P^0(\{p_i\})$ ($\chi = 0$) is the permutation that leaves the $\{p_i\}$ points in place. With this in mind we can introduce the γ index of the partitions and the χ index of the permutations within the $j(\ldots)$ index. We define a new index $j(\gamma, \chi, \mu, i)$ as follow: j determine a γ partition and a $P^\chi(\{p_i\})$ permutation and identifies the element in the μ-th position of the partition which contain the element $P^\chi(\{p_i\})$ (identified by i after the permutation operator P^χ has been applied)

cyclically counted from the $P^\chi(\{p_i\})$ element itself.

For example assuming $P^0(\{p_i\}) = \{p_1, p_2, p_3\}\{p_4, p_5, p_6\}\{p_7\}$ and $P^{\chi=6}(\{p_i\}) = \{p_2, p_3, p_5\}\{p_6, p_1, p_4\}\{p_7\}$ of a given $\gamma = 1$ partitioning, the index $j(\gamma = 1, \chi = 6, \mu = 3, i = 6) = 1$ determines the point p_1. The symmetric points are then determined by:

$$\tilde{p}_i^{\gamma,\chi} = \frac{1}{n_G} \sum_{\mu}^{n_G} S_{\mu} p_{j(\gamma,\chi,\mu,i)} \tag{11}$$

The distance function is defined as:

$$D_P^{\gamma,\chi} = \frac{1}{M} \sum_{i=1}^{N} |\tilde{p}_i^{\gamma,\chi} - p_i|^2 \tag{12}$$

Performing the minimization we define the CSM_P as

$$CSM_P = min_{R_g,\theta,\phi,\psi,\gamma,\chi} \left\{ \frac{1}{M} \sum_{i=1}^{N} |\tilde{p}_i^{\gamma,\chi} - p_i|^2 \right\} \tag{13}$$

With these last equations we have reformulated Avnir's CSM definition within our three steps scheme and we have introduced the additional mapping index $j(\gamma, \chi, \mu, i)$ which summarize Avnir's scheme.

A complete description of this approach for all the point symmetry groups require a more detailed treatment which will be the subject of a second paper[26].

A completely different approach was proposed by Grimme[3]. This method uses the wave function as a basic quantity for the CSM.

Grimme's definition is based on the expectation value of a symmetry operator. Summarizing the work of Grimme in an equation we have

$$CSM_W = 1 - |\langle \Phi | S | \Phi \rangle| \tag{14}$$

where Φ is the a normalized wave function obtained via an *ab-initio* method, S is a given symmetry operator and CSM_W labels a CSM definition based on the wave function.

As in the previous case we follow the steps described in section II using the wave function of a molecule as basic quantity for the CSM.

Grimme's approach does not extend the symmetry measure to all the symmetry groups but it is limited to a single symmetry operator and in order to compare the two measures we apply our procedure to symmetry groups defined by only two symmetry operations: the identity and a symmetry operation S.

8

A symmetrized wave function is then defined by

$$\left|\tilde{\Phi}\right\rangle = \frac{1}{n_G} \sum_{\mu}^{n_G} S_\mu |\Phi\rangle = \frac{1}{n_G} \left(E|\Phi\rangle + S|\Phi\rangle \right) \tag{15}$$

In the Hilbert space a natural distance is the scalar product and we define the measure of symmetry as:

$$D_W = \left\langle \Phi | \tilde{\Phi} \right\rangle \tag{16}$$

Introducing the definition 15 in this last equation we obtain:

$$D_W = \frac{1}{2} \left(1 + \langle \Phi | S | \Phi \rangle \right) \tag{17}$$

where we used $\langle \Phi | E | \Phi \rangle = \langle \Phi | \Phi \rangle = 1$. The two distances CSM_W and D_W respectively from equations 14 and 17 are in linear relation.

Grimme introduces in his equation the absolute value to account for antisymmetric wave functions. It is possible to include antisymmetry in our definition using a different approach.

In particular we can introduce the representations Γ of the group G and their characters χ_μ^Γ and use the projector to define a Γ symmetrized wave function as:

$$\left|\tilde{\Phi}^\Gamma\right\rangle = \frac{1}{n_G} \sum_{\mu}^{n_G} \chi_\mu^\Gamma S_\mu |\Phi\rangle \tag{18}$$

assuming again that the group G is bidimensional and that it has two irreducible representations, a total symmetric one and an antisymmetric one, for example $\Gamma = A$ and $\Gamma = B$, it is possible to write a second measure for the second representation:

$$D_W^B = \frac{1}{2} \left(1 - \langle \Phi | S | \Phi \rangle \right) \tag{19}$$

where for the characters χ_μ^B the values of 1 and -1 have been used for the E and the generic S operations parts respectively.

The minimization procedure will not be considered since it is equivalent in both measures.

Instead we should argue that in our development we explicitly used a symmetrized wave function which justifies the use of a minimization procedure. The equivalence of our definition of CSM and the one proposed by Grimme seems to suggest the presence of a symmetrized wave function hidden in Grimme's definition which would justifies the required minimization.

This doesn't complete a CSM definition which uses the wave function and much space is left for discussion.

We have shown that the proposed algorithm includes the CSM proposed by Avnir and Grimme once the proper quantity are used. We shall now present an implementation which will preserves the advantages of both Avnir and Grimme's CSM. It will allow for fast evaluation and it will include electronic contribution.

IV. IMPLEMENTATION

We now present a simplified and fast version of the CSM proposed in this contribution. Equation 2 can be written as:

$$D' = \int |\rho - \tilde{\rho}|^2 d\mathbf{r} = \int \rho^2 d\mathbf{r} - 2 \int \rho \tilde{\rho} d\mathbf{r} + \int \tilde{\rho}^2 d\mathbf{r} \tag{20}$$

We can recognize three different terms on the right hand side of this equation. The first one depend completely on the original density ρ while the other two have a dependency on the symmetrized density $\tilde{\rho}$. In particular we can expand the third term of the r.h.s. and write:

$$\int \tilde{\rho}\tilde{\rho} d\mathbf{r} = \frac{1}{n_g^2} \int \left(\sum_n S_n \rho \right) \left(\sum_m S_m \rho \right) d\mathbf{r} = \tag{21}$$

$$= \frac{1}{n_g} \sum_n \left[\frac{1}{n_g} \int (S_n \rho) \left(\sum_m S_m \rho \right) d\mathbf{r} \right] \tag{22}$$

The integral in equation 22 is an integral of the product of two function (namely $S_n \rho$ and $\sum_m S_m \rho$) over the whole space and its value doesn't change if both function are rotated by the same symmetry operator. Applying the rotation S_n^{-1} to both functions we can write for the integral in square braket of equation 22:

$$\left[\frac{1}{n_g} \int S_n^{-1} S_n \rho \left(S_n^{-1} \sum_m S_m \rho \right) d\mathbf{r} \right] = \tag{23}$$

$$\left[\frac{1}{n_g} \int S_n^{-1} S_n \rho \left(\sum_m S_n^{-1} S_m \rho \right) d\mathbf{r} \right] = \tag{24}$$

$$\left[\frac{1}{n_g} \int \rho \left(\sum_p S_p \rho \right) d\mathbf{r} \right] = \left[\int \rho \tilde{\rho} d\mathbf{r} \right] \tag{25}$$

10

where we used again the rearrangement theorem. Equation 22 can now be written as:

$$\int \tilde{\rho}\tilde{\rho}d\mathbf{r} = \frac{1}{n_g}\sum_n \left[\int \rho\tilde{\rho}d\mathbf{r}\right] = \int \rho\tilde{\rho}d\mathbf{r} \tag{26}$$

and substituting in the main distance equation (20) we obtain

$$D' = \int \rho^2 d\mathbf{r} - \int \rho\tilde{\rho}d\mathbf{r} \tag{27}$$

After normalization we have

$$D = 1 - \frac{\int \rho\tilde{\rho}d\mathbf{r}}{\int \rho^2 d\mathbf{r}} \tag{28}$$

which gives a more practical approach for the calculation of the distance. Moreover we can see that this distance is related to the indexes used in QMS[24] which uses quantities of the type of equation 4.

Applications of the CSM are usually correlations with other properties and we should not expect strong variation of a given correlation for small variation of the symmetry measure. In general we should not seek for high accuracy in the calculation of CSM but instead we need fast evaluation.

In this respect we can approximate the electron density with a superposition of Gaussian functions.

The electron density is then given by:

$$\rho = \sum_i g_i \tag{29}$$

where g_i is a simple Gaussian function.

The denominator of the second term of equation 28 is then:

$$\int |\rho|^2 d\mathbf{r} = \int \left|\sum_i g_i\right|^2 d\mathbf{r} = \sum_i \sum_j \int g_i g_j d\mathbf{r} \tag{30}$$

while the numerator reads:

$$\int \rho\tilde{\rho}d\mathbf{r} = \frac{1}{n_g}\sum_m \sum_i \sum_j \int g_i S_m g_j d\mathbf{r} \tag{31}$$

11

One of the S_m operations in the summation in m is the identity and we can extract it out from the sum in m obtaining:

$$\int \rho\tilde{\rho}d\mathbf{r} = \frac{1}{n_g}\left(\sum_i\sum_j\int g_ig_jd\mathbf{r} + \sum_{m'}\sum_i\sum_j\int g_iS_{m'}g_jd\mathbf{r}\right) \qquad (32)$$

where the index m' runs over all the symmetry operators but the identity. Substituting equations 30 and 32 into 28 we obtain a simplified equation for the distance

$$D = \frac{n_G - 1}{n_G} - \frac{\sum_{m'}\sum_i\sum_j\int g_iS_{m'}g_jd\mathbf{r}}{n_G\sum_i\sum_j\int g_ig_jd\mathbf{r}} \qquad (33)$$

These equations are valid for any decomposition of the density of the type of equation 29 but if the functions g_i are Gaussian functions it is clear that all the integrals in equation 33 are easily evaluated.

V.   APPLICATION

In section IV we have seen a simplified decomposition of the density.

The functions g_i can be obtained fitting the density calculated via quantum mechanical methods but this approach is computationally demanding. Instead we can use a very simplified approach.

We can generate an approximated density using a single Gaussian function for each nuclear center. The exponents and coefficients of the Gaussian functions can be simply evaluated constraining the half height width of the Gaussian functions to match the atomic radii and normalizing their integrals to the atomic charges.

A simple example reported by Grimme[3] is the butadiene. This molecule can present chirality depending on the spatial conformations. We can measure the Chirality content of the molecule at different geometries evaluating the CSM for groups containing improper symmetry operations. In particular the C_i and C_s groups are related to the inversion symmetry operation i and mirror plane σ respectively.

In figure 1 are presented the results of the two CSM measure. The measures have been performed with a variation of the torsional angle defined by the four carbon chain keeping all the other geometrical parameter fixed. In particular all the geometrical parameters were
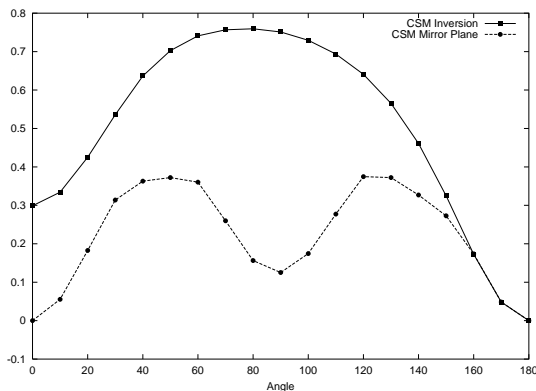
12

FIG. 1: CSM in % for butadiene at different dihedral angles. The measure is performed against the C_i and C_s symmetry groups.

obtained as medium bond values. We obtained the atomic radii from the periodic table and fixed the charges to 0.

Even if the presented example implement a simple approach with strong approximations the final picture is qualitatively close to the evaluation of CSM using the wave function[3].

A second example makes clear the advantage of a density based approach if compared with a geometrical points approach. We evaluate the CSM for H_2O_2 and H_2S_2 molecules. In figure 2 is presented the plot of CSM for the C_s group at different dihedral values.
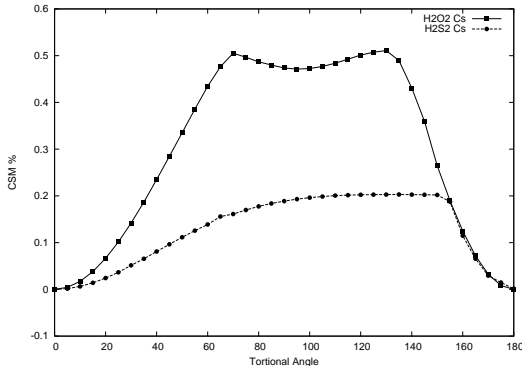

FIG. 2: CSM in % for H_2O_2 and H_2S_2 at different dihedral angles.

The equilibrium geometries for both molecules are obtained via Density Functional Theory using the program ADF[27] and the other geometries are obtained following a constrained variation of the $HOOH$ dihedral angle (all other geometrical parameter fixed to the DFT equilibrium values). The Gaussian functions where determined using periodic table atomic radii and considering a polarization of the $X - H(X = O, S)$ bonds of 0.3 electrons. The

numerical value 0.3 is a crude approximation of the Mullikan charges obtained in the DFT calculations of the equilibrium structures. A CSM using the geometrical points approach would determine identical measures for these systems.

In this examples we used simple parameters for the Gaussian functions. In principle we can define different atom types and build a database of Gaussian function parameters in the same way molecular mechanic methods define force fields.

VI.   CONCLUDING REMARKS

This contribution described a CSM definition which we claim to have general validity. This general validity has been undelined by the application of the definition to different quatities.

It is also proposed an approximation which allow for a "fast" CSM implementation and still includes electronic contribution.

In the case of the chirality measure we can regard our distance function as a distance of the original chiral object from an achiral reference (deviation from achirality) as well as a distance of the original object from its mirror image (similarity measure). This is intrinsic in our definition of symmetrized object and an a priori classification of the measure into chirality measure of the first or of the second kind[11] is not possible.

When the CSM is limited to a Chirality Measure by considering only the C_s point symmetry group out definition reduces to the chirality measure defined within the framework of Quantum Similarity Approach[18] including it in a more general picture.

A true connection with the hamiltonian of a molecule has not been presented in this contribution. Nevertheless it has been introduced an approach which uses point group theory as starting equations. Preliminary work for a future contribution show that a symmetric decomposition of a molecular wave function within the Hilbert space can lead to a consisted approach and it is worth for exploration. The simple DFT example of $H_2X_2(X = O, S)$ seems to recover part of the electron orbit contribution which is present in high quality parity violation calculation[25]. This approach is a possible "way to go" for a future symmetry measure.

The computer program used for the evaluation of the CSM using the electron density will be made available free of charge at http://www.scriptsfprscience.com/.

VII. ACKNOWLEDGMENTS

VIII. APPENDIX

We can demonstrate that $\tilde{\rho}(\mathbf{r})$ is a symmetric function with respect to the group G using the rearrangement theorem[28]. The demonstration is part of the standard group theory techniques but we reproduce it here for sake of clarity. In particular we stress that the initial molecular ρ density does not need (and usually has not) any particular symmetry property to justify the use of the projection operator in equation 1.

If $\tilde{\rho}(\mathbf{r})$ is a total symmetric function with respect the group G the equation

$$\tilde{\rho}(\mathbf{r}) = S_\mu \tilde{\rho}(\mathbf{r}) \tag{34}$$

should hold for every operation S_μ of the group G. Substituting the definition of $\tilde{\rho}(\mathbf{r})$ from equation (1) into equation (34) we obtain

$$\frac{1}{n_G} \sum_\nu^{n_G} S_\nu \rho(\mathbf{r}) = \frac{1}{n_G} \sum_\nu^{n_G} S_\mu S_\nu \rho(\mathbf{r}) \tag{35}$$

that has to be demonstrated. To verify this equality it is sufficient to demonstrate that on the right hand side we do not have duplicated elements in the μ, ν series for any arbitrary μ i.e. that the terms of the sum on the right end side are exactly the same as the terms on the left end side.

Suppose indeed that for a given μ we have common elements for example in the case that ν assumes values $\nu = \nu_a$ and $\nu = \nu_b$ we have:

$$S_\mu S_{\nu_a} = S_\mu S_{\nu_b} \tag{36}$$

Multiplying this equation by S_μ^{-1} we obtain:

$$S_{\nu_a} = S_{\nu_b} \tag{37}$$

Which is in contradiction with the fact that the each ν term is a distinct elements of the operation of the group.

If we follow this procedure we will be able to generate an infinity of symmetric objects starting from the same original one (symmetric or not) just changing the relative spatial position of the density and of the point group axes.

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[1] D. Avnir, H. Z. Hel-Or, and P. G. Mezey, Encyclopedia of Computational Chemistry p. 2890 (1998).

[2] H. Zabrodsky, S. Peleg, and D. Avnir, J.Am.Chem.Soc. **114**, 7843 (1992).

[3] S. Grimme, Chem.Phys.Lett **297**, 15 (1998).

[4] D. J. Wales, Chem.Phys.Lett. **285**, 330 (1998).

[5] L. Bellarosa and F. Zerbetto, J. Am. Chem. Soc. **125**, 1975 (2003).

[6] B. B. Smirnov, O. V. Lebedev, and A. V. Evtushenko, Acta Cryst. **A55**, 790 (1999).

[7] S. Capozziello and A. Lattanzi, Chirality pp. 15227–15230 (2003).

[8] S. Capozziello and A. Lattanzi, Chirality pp. 15466–15471 (2003).

[9] S. Capozziello and A. Lattanzi, Chirality pp. 16162–16167 (2004).

[10] S. Capozziello and A. Lattanzi, Theo Chem **671**, 205 (2004).

[11] M. Petitjean, Entropy **5**, 271 (2003).

[12] S. Keinan and D. Avnir, J. Am. Chem. Soc. **122**, 4378 (2000).

[13] H. Zabrodsky and D. Weinshall, computer vision and image understanding **67**, 48 (1997).

[14] H. Zabrodsky, S. Peleg, and D. Avnir, J.Am.Chem.Soc. **115**, 8278 (1993).

[15] S. Alvarez and D. Avnir, J. Chem. Soc.(Dalton Trans.) **4**, 562 (2003).

[16] S. Alvarez and M. Llunell, J.Chem.Soc. Dalton Trans. pp. 3288–3303 (2000).

[17] P. G. Mezey, R. Ponec, lluís Amat, and R. Carbó-Dorca, Enantiomer **4**, 371 (1999).

[18] G. Boon, C. V. Alsenoy, F. D. Proft, P. Bultnick, and P. Geerlings, J.Chem.Phys.A **107**, 11120 (2003).

[19] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, 1998).

[20] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

[21] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[22] J. Whitten, J. Chem. Phys. **58**, 4496 (1973).

[23] R. Carbó-Dorca and E. Besalú, Theo Chem **451**, 11 (1998).

[24] P. Geerlings, G. Boon, C. van alsenoy, and F. de Proft, International Journal of Quantum Chemistry **101**, 722 (2005).

[25] A. Bakasov, T. K. Ha, and M. Quack, J. Chem. Phys. **109**, 7263 (1998).

[26] F. Mariotti, to be pubblished (2005).

[27] E. Baerends, A. Bèrces, C. Bo, P. Boerrigter, L. Cavallo, L. Deng, R. Dickson, D. Ellis, L.Fan, T. Fischer, et al., *Adf 1999/2000*, http://www.scm.com/ (2000), program.

[28] D. M. Bishop, *Group Theory and Chemistry* (Dover, 1973).