

Extensions and Foundations of the Continuous Symmetry Measure

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Abstract

A quantum mechanical extension of the continuous symmetry measures (CMS) proposed by Avnir et al. is described. The theoretical framework is essentially based in a simple extension of the HMO approach, leading to compute molecular CSM energy spectra, constituting a useful step for construction of first and higher order CSM terms. This permits in turn to connect the general CMS theoretical framework with the fundamentals of structure-property relationships and allows the evaluation of statistical mechanics CMS partition functions and the deduction of CMS thermodynamical functions as well.

1 Introduction

The symmetry of an object is usually described as a binary measure, i. e., an object is either symmetric or not. However, it is very intuitive to think that the symmetry can be treated as a continuous scale where some objects are more symmetric than others. This idea has been under development by Avnir et al. [1, 2] (for reviews see [3, 4]) since the beginning of the 90's of the XX century. They have proposed that given a molecule and a symmetry group G it is possible to evaluate quantitatively the "amount" of G -symmetry contained by such molecule. The situation is also found in different contexts where yes-or-not concepts are better expressed in the form of quantitative scales. One of such examples is the bipartivity of a set of relations, usually determined to be either bipartite or not-bipartite. However, the

practical necessity has obligated to define scales in which the “amount” of bipartivity of the relationships can be quantified [5-7].

The continuous symmetry measure put forward by Avnir et al. have found numerous applications across several fields of chemistry [8-16]. This approach can be resumed in the following. Let Ω be the space of all molecular shapes of a given dimension, where each shape P is represented by a sequence of n points $\{P_i\}_{i=1}^n$. Let d be a metric on this space defined as follows:

$$d : \Omega \times \Omega \rightarrow R$$

$$d(P, Q) = d(\{P_i\}, \{Q_i\}) = \frac{1}{n} \sum_{i=1}^n \|P_i - Q_i\|^2$$

Then, this metric defines a distance function between every two molecular shapes in Ω . Now, let a symmetry transform (ST) represent the symmetric shape closest to P in terms of the metric d . Then, the symmetry distance of a shape P has been defined as the distance between P and its corresponding ST :

$$S(sym) = d(P, ST(P))$$

which can be evaluated by finding the $ST \hat{P}$ of P and computing

$$S(sym) = \frac{1}{n} \sum_{i=1}^n \|P_i - \hat{P}_i\|^2 \quad (1)$$

The measure given in (1) is known as a *continuous symmetry measure* (CSM), $S(sym)$ and represents the square deviation of the shape P from a perfect symmetry (sym). The CMS can be considered as a *first order measure* of the deviation from perfect symmetry of a given object. The definition of the symmetry distance implies invariance to rotation and translation and a normalization of the original shape allows for invariance of scale.

Here it is proposed to interpret this approach in a wider of quantum chemical context, as well as to extend this approach to a series of measures, which in some way quantify the “distribution” of continuous symmetry across a molecule.

2 CSM Graphs

It is evident that in order to represent the CSM process there are needed two graphs for every studied object. For every “real” object P for which the deviation from perfect symmetry is to be studied, one can employ the object P and a “virtual” object \hat{P} , which represents the perfect symmetry for which the CSM will be computed. For instance, in the CSM process shown in Fig. 1A there are present two objects: a “real” one, represented by solid lines and a “virtual” one with perfect C_6 -symmetry depicted by dotted lines. An abbreviated representation of the CSM process can be carried out by means of the CSM graph. The CSM graph of a CSM process is formed by joining the nodes of the “real” and “virtual” nodes into pseudo-nodes, in such a way that two pseudo-nodes are adjacent in the CSM graph if, and only if, the corresponding nodes are adjacent in the real and virtual object [17]. Fig. 1B represents the CSM graph for the previously mentioned CSM process.

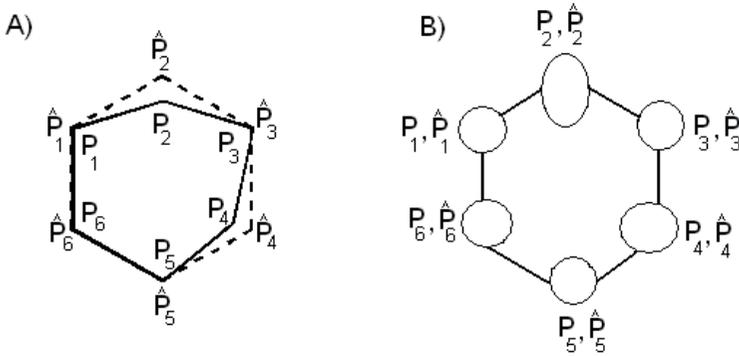


Figure 1. A) Illustration of the symmetry transform of $\{P_1, P_2, \dots, P_6\}$ to $\{\hat{P}_1, \hat{P}_2, \dots, \hat{P}_6\}$ with perfect C_6 -symmetry. B) The CSM graph representing the symmetry transform given in Fig. 1A.

The necessity for this kind of representation will be evident in the following section. An object P can be represented by means of a weighted graph: $G = (V, E, W, \phi)$. Here the sets V and E are the set of nodes (vertices) and links (edges) of the object P , characterizing its connectivity or discrete topology. The cardinality of these sets are $\#|V| = n$ and $\#|E| = m$, respectively. The set $W = (\gamma_1, \gamma_2, \dots, \gamma_n)$, where $\gamma_i = \|P_i - \hat{P}_i\|^2$, accounts for the deviations from perfect symmetry for every node of the object P . Such deviations are quantified by

means of the CSM approach. The surjective mapping $\phi: V \rightarrow W$ assigns a value of γ_i to each node.

The graph $G = (V, E, W, \phi)$ can be represented through the use of the matrix: $\Gamma(G) = \mathbf{A} + \mathbf{W}$, where \mathbf{A} is the *adjacency matrix* [18] of the simple graph, whose elements $\mathbf{A}_{ij} = 1$ if the nodes i and j are adjacent, or zero otherwise, and \mathbf{W} is a diagonal matrix whose diagonal entries are the values of the deviation from perfect symmetry for the corresponding node $\mathbf{W} = \text{diag}(\gamma_1, \gamma_2, \dots, \gamma_n)$.

3 Quantum-mechanical formulation

From now on one can consider that P represents a quantum object. In the particular case of a molecule one can consider an AO basis set associated to each atom, which only depend on the deviation of a given atom from the perfect symmetry as accounted by the CSM approach. However, in the CSM graph each pseudo-node is formed by two orbitals, one representing the atom deviated from the perfect symmetry and the other the atom in the perfect symmetry. Then, the CSM orbitals, which are the orbitals in the CSM graph, can be supposed as a set of localized orbitals: $\{\varphi_i^{CSM}\}$, which can be constructed as the bond orbitals introduced by Hall and Lennard-Jones and used in a linear combination of bond orbitals (LCBO) approach. A similar approach to the present, although in a different context was proposed many years ago by Paoloni et al. [19]. They proposed for the first time the p-type AO's in aromatic molecules like benzene to be substituted by spherical s-type functions. A more elaborated approach has been also employed in describing approximate promolecular first order density functions [20-[24] . A parent approach has been successful in order to compute topological indices, which explicitly include molecular structure [25],[26]. More recently, the idea has been also successfully employed to compute multicenter aromaticity indices [27]. In fact the present approach amounts the same as to use both spherical and elliptically distorted s-type functions. Such distortion in GTO's has been early described and even employed to compute AO integrals [28-[30].

Here a tight-binding approach similar to the one used in the Hückel molecular orbital (HMO) approach is employed. This is so, because in the present approach, the use of adjacency matrices as a basic tool precludes the theoretical association with the HMO wave function simplification. Therefore, such a choice permits the immediate use of MO's instead of the implicit Hartree wave function. First, the MO's are built as linear combinations of the

pseudo-atomic orbitals by considering that the CSM orbitals are orthonormalized, in order to obtain an easily manageable set of application algorithms. Of course that this is not compulsory and the method can use non orthogonal CSM orbitals, without needing a considerable change. The Coulomb integral H_{ii} of a CSM orbital ϕ_i is assumed to depend only on the deviation from perfect symmetry of the atom i . As it is customary in HMO procedures, such an integral is set equal to $H_{ii} = a + \gamma_i b$, while the resonance integral H_{ij} between CSM orbitals ϕ_i and ϕ_j is assumed to be zero, unless i and j are adjacent atoms in the molecule, in which case it is set $H_{ij} = b$. After normalizing each element of the CSM Hamiltonian by b the main diagonal, the entries are given by $x + \gamma_i$, where

$$x = \frac{a - \varepsilon}{b} \quad (3)$$

The non-diagonal entries of this matrix are unity if, and only if, the corresponding atoms are adjacent. Thus, the orbital energy is determined by the eigenvalues of the matrix \mathbf{H} , which are the eigenvalues of the weighted matrix $\Gamma(G)$ representing the CSM graph,

$$\varepsilon_j = a - bx_j \quad (4)$$

where x_j is an eigenvalue of the matrix $\Gamma(G)$. The total electronic ‘‘CSM’’ energy is given by

$$E_{CSM} = 2 \sum_{j=1}^n \varepsilon_j = na - 2b \sum_{j=1}^n x_j, \quad (5)$$

where $b < 0$.

From now on the value $p = na \equiv 0$ is used without loss of generality, since p simply sets the origin of the energy scale. This makes the CSM energy expression equal to:

$$E_{CSM} = 2|b| \sum_{j=1}^n x_j, \quad (6)$$

It is well known that the sum of the eigenvalues of any Hermitian matrix is equal to its trace. Then, it is straightforward to realize that the CSM is the total energy of the symmetry deviation for a molecule under the previous tight-binding assumptions,

$$E_{CSM} = 2|b| \sum_{j=1}^n \gamma_i = S(sym) = \frac{1}{n} \sum_{j=1}^n \gamma_i, \quad (7)$$

for $2|b| = \frac{1}{n}$.

4 Higher order CSM

The CSM, corresponding in the present scheme to the total energy of the symmetry deviation for a given molecule, does not account for the differences in symmetry between pairs of structures having the same sum of the γ_i values. In other words, the CSM total energy appears to be a first order measure for the CS deviation of a molecule. However, in the previous section it has been discussed that the CS total energy is given by the trace, the sum of diagonal elements, of the matrix $\Gamma(G)$:

$$E_{CSM} = tr\mathbf{H} = tr\Gamma(G) \quad (8)$$

This expression can be generalized in order to account for higher-order contributions of the deviations from perfect symmetry. Let μ_k be the k -th spectral moment of the Hamiltonian matrix, which represents a weighted closed walk of length k between the pseudo-nodes of the CSM graph, where the weight associated with the walk is the product of the $H_{1a,ib}$ interaction elements,

$$\mu_k = tr\mathbf{H}^k = \sum_{i_1, i_2, \dots, i_k} H_{i_1, i_2} H_{i_2, i_3} \cdots H_{i_k, i_1}. \quad (9)$$

It is evident that the energy is just the first moment of the Hamiltonian. Then, the consideration of the higher-order moments differentiate the structures not distinguished by the first order measure. The higher-order terms can be accounted for in a more efficient way in a further section.

5 Higher-order CSM in structure-property relationships

One of the principal objectives of developing the CSM has been its use in describing quantitatively many different properties. Let P be an experimental property which can be expressed as a linear combination of the higher-order CSM,

$$P = \sum_k b_k \mu_k + \alpha, \quad (10)$$

where b_k are the coefficients of the correlation model and α is the error. Then, the following result can be easily set:

Theorem: Any property P expressed quantitatively by means of the higher-order CSM can be expressed as an atomic additivity function.

Proof. The spectral moments of the CSM Hamiltonian can be expressed in terms of local moments for the atoms of the molecule $\mu_k[a]$

$$\mu_k = \sum_{a=1}^n \mu_k[a], \quad (11)$$

where the atomic moments are expressed in terms of the MO coefficients and energies as follows,

$$\mu_k[a] = \sum_{j=1}^m [c_j(a)]^2 \varepsilon_j^k. \quad (12)$$

Then, substituting (11) in (10) the property under study can be expressed in terms of the atomic moments,

$$P = \sum_k \sum_{a=1}^n b_k \mu_k[a] + \alpha. \quad (13)$$

Summing up all the local moments corresponding to a given atom a multiplied by their respective coefficients, calling $P(a)$ the CSM contribution of the atom a to the property P , then the following expression is deduced:

$$P(a) = \sum_k b_k \mu_k[a]. \quad (14)$$

Consequently, one can express the global property as a sum of atomic contributions,

$$P = \sum_{a=1}^n P(a) + \alpha \quad (15)$$

which proves the theorem,

6 Statistical mechanics approach to higher-order CSM

First, it can be defined a CSM partition function, associated to the previously defined CSM energies,

$$Z(CSM) = \sum_{j=1}^n e^{-\beta \varepsilon_j}, \quad (16)$$

where $\beta = 1/kT$ is the inverse temperature (T) and k is the Boltzmann constant. Using this partition function one can define the entropy of the CSM electronic distribution as

$$S(CSM) = -k \sum_{j=1}^n p_j \ln p_j = k \sum_{j=1}^n p_j [\beta \varepsilon_j + \ln Z], \quad (16)$$

where

$$p_j = \frac{e^{-\beta \varepsilon_j}}{Z}, \quad (17)$$

is the probability of finding the system in the state having energy ε_j and $Z \equiv Z(CSM)$. Eq.

(16) can be rewritten in the following way

$$S = k\beta \sum_{j=1}^n \varepsilon_j p_j + k \ln Z \sum_{j=1}^n p_j. \quad (18)$$

Then, by multiplying by T and reordering the terms it is obtained

$$-\frac{1}{\beta} \ln Z = \sum_{j=1}^n \varepsilon_j p_j - TS, \quad (19)$$

which by using the known expression $F = H - TS$, permits to identify the CSM enthalpy

H and the CSM free energy F , as the expressions

$$H(CSM) = \sum_{j=1}^n \varepsilon_j p_j \quad (20)$$

$$F(CSM) = -\frac{1}{\beta} \ln Z \quad (21)$$

In order to establish a connection between the statistical mechanics parameters and the higher-order CSM parameters previously defined, the spectral moments of the Hamiltonian matrices can be easily used. First, the partition function (16) can be rewritten as the trace of the exponential of the Hamiltonian matrix, which can be immediately interpreted in terms of the spectral moments of the corresponding Hamiltonian,

$$Z = \text{tr} \left[e^{-\beta \mathbf{H}} \right] = \sum_{k=0}^{\infty} (-\beta)^k \frac{\text{tr} \mathbf{H}^k}{k!} = \sum_{k=0}^{\infty} (-\beta)^k \frac{\mu_k}{k!}. \quad (22)$$

Thus, the CSM partition function is a weighted sum of all the higher-order CS measures accounted by the spectral moments of the corresponding CSM Hamiltonian. Because the Hamiltonian here is simply the adjacency matrix of a weighted graph, the partition function is the CSM version of the “subgraph centrality” or the Estrada index of the graph (see [31-35] and references therein).

7 Summary

The concept of continuous symmetry measure (CSM) of Avnir et al. has been extended within a quantum mechanical background, employing a simple modification of HMO and the attached topological adjacency matrices. This permits to easily compute first and higher order CSM terms, which can be applied in turn to describe the partition of molecular properties as a sum of atomic contributions in structure-property relationships. Finally, CMS energy spectra can be employed to develop statistical mechanics partition functions and hence this permits to compute CMS related thermodynamic functions.

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