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Structural Homeomorphism between Structural Descriptors and Relation between Corresponding Structures: A Mathematical Picture

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Abstract

A rigorous definition of the structural descriptors and structural homeomorphism between them are studied. It is shown that the structural homeomorphism is an equivalence relation on the family of structural descriptors. An exact relation between molecular structures corresponding to the homeomorphic descriptors is derived. Thereby, the average properties of the molecular structures are compared.

1. Introduction

Roughly speaking, molecular structure, as a generic property of system, is described by the combination of molecular geometry and electronic properties of the network of bounds. In practice, various kinds of methods may be applied to determination of molecular structure that includes X-ray diffraction, electron diffraction, optical spectroscopy, mass spectroscopy, nuclear magnetic resonance, and so on. Similarly, molecular and structural descriptors may be described in many ways. An important class of molecular descriptors is calculated based on the molecular graph and is usually called as topological indexes. During the last half century, several scholars [1-16] have paid their attention to this kind of molecular descriptors and several versions of them, namely topological information content, chromatic information, Hosoya index, Wiener index, and so on, are proposed.

Recently, some scalar fields have been considered to be "descriptors of the coulombic system” [17-20]. Such a descriptor is referred to as the scalar field containing all information regarding to the quantum system, i.e., the descriptor uniquely determines the number of electrons, N , and provides the external potential to within an additive constant and consequently determines the Hamiltonian of system. For instance, shape function, Fukui function, Kohn-Sham effective potential and local softness are some examples of this kind of descriptor.

Within this paper, the mathematical definition of the molecular structure is regarded as a part of the Quantum Theory of Atoms in Molecule (QTAIM) [21,22]. This theory is based on the quantum variational approach and provides a modern tool for understanding atoms in molecules. Although QTAIM is now routinely used by chemists for identification and computational consideration of quantum atoms within molecules, however, less attention has been paid to mathematical foundation of this approach [23-27]. This is particularly true for the mathematical properties of the molecular structures, forms and structural homeomorphisms [28,29].

Briefly, within QTAIM, the one-electron density ρ_x of a molecular system may be partitioned into open quantum subsystems with well-defined energy, so-called topological atoms. [30] each of which bounded by the local zero flux surfaces $\partial\Omega$, i.e.,

$$\nabla\rho_x\left(r\right)\cdot n\left(r\right)=0 \qquad r\in\partial\Omega \qquad (1)$$

where n(r) is the unit vector perpendicular to $\partial\Omega$ at the point r and x is a parameter belonging to the nuclear configuration space associated with Born-Oppenheimer approximation. This equation is the result of a rigorous procedure based on Schwinger‘s principle of quantum stationary action [31] and implies that each trajectory of $\nabla\rho_x\left(r\right)$ (gradient path) of the electronic charge density originating from the core of an atom will not cross the atomic surface $\partial\Omega$. In this manner, QTAIM should be regarded as a method for the topological analysis (TA) of scalar field ρ_x .

Bader [21,33]and Collard and Hall [32] pioneered the employ of gradient paths of electron charge density in order to gain a deeper insight into molecular structure. Subsequently, the study of the topological structure of scalar fields found an increasing number of applications throughout computational and theoretical chemistry.

The mathematical framework of TA is not confined to analysis of the electron charge density. In general, a physical system should be investigated based on analysis of the various scalar fields. For such fields that describe physical observations, the number, place and type of critical points can be invoked to elucidate the different properties of the system under the study. For instance, TA of electron localization function (ELF)

$$\lambda(r)=\left[1+\left(D(r)/C_F\rho^{5/3}(r)\right)^2\right]^{-1} \tag{2}$$

provides the bounding evolution theory (BET) [34-36], i.e., a precise description of the bounding associated with a chemical reaction. Where, $\lambda(r)=\left[1+\left(D(r)/C_F\rho^{5/3}(r)\right)^2\right]^{-1}$ $D(r)$ and C_F are local kinetic energy density due to Pauli repulsion and Fermi constant, respectively. Gradient vector field of the Laplacian of the electron density, $\nabla^2\rho_x$, tends to sound justification for valance-shell electron pair repulsion models [37-41].

TA was also applied to other 3D scalar fields, namely, bare nuclear potential (BNP) [8]

$$V_{nuc}(r;x)=\sum_{\alpha} Z_\alpha\left(|r-x_\alpha|\right)^{-1} \tag{3}$$

molecular electrostatic potential (MESP) [42,43]

$$V_{mes}(r;X)=V_{nuc}(r;X)-\int\frac{\rho_X(\xi)d^3\xi}{|r-\xi|} \tag{4}$$

and virial field [29]

$$v(r;X)=\hbar^2/m\left\{-\nabla_\xi\cdot\nabla_r\rho_X^{(1)}(\xi,r)\Big|_{r=\xi}+(1/4)\nabla^2\rho_X(r)\right\}=Tr\sigma_X(r) \tag{5}$$

Where Z_α is the charge of the nucleus located at x_α, $\rho^{(1)}(r,\xi)$ is the one-electron density matrix and

$$\ddot{\sigma} = \left(\hbar^2/4m\right)\left(\nabla' - \nabla\right) \otimes \left(\nabla' - \nabla\right) \rho^1\left(r; r'\right)\Big|_{r=r'} \tag{6}$$

is the Pauli stress tensor [21].

TA of these three latter fields can be compared with TA of the electron charge density. Tal et al.[28] studied the topological relationship between scalar functions, electron charge density and BNP for a molecular system. Popelier et al. [44] compared the topology of the BNP of just over 130 molecules and molecular complexes with the topology of electron density and revealed the existence of a “geometrically faithful” homeomorphism between them. Keith et al. [29] exhibited a structural homeomorphism between the virial field and electron density for a small number of test cases. Gadre et al. [42] compared the topological properties of MESP with BNP and charge density and deduced that MESP has more structural similarity to electron density than BNP. Besides the computational and theoretical chemistry, the literature in quantum biology and quantum pharmacology is rich with the study of the topological properties of MESP of various molecular systems [45-49]. More recently, TA of the “joint density” for the positronic system LiH,e+ , the simplest positronic species, has been investigated by Nasertayoob et al. [50]. Moreover, the electronic and positronic structure of this positronic system has been compared. TA was also applied to multi-dimensional scalar fields. For instance, TA of BNP as a functions of nuclear position permits the partitioning of the potential energy hypersurface into catchment regions [51,52].

TA of the scalar fields provides a useful tool for offering the rigorous definition of the molecular structure. We call such a scalar field as structural descriptor. Comparison between the TA of different structural descriptors leads to the definition of the structural homeomorphism between them.

In this paper, we are concerned with mathematical foundations of the structural homeomorphisms and their properties. Appealing to a rigorous definition of structural homeomorphism between structural descriptors, it is demonstrated that the homeomorphism property propone an equivalence relation on the family of structural descriptors. Also, an explicit relationship between the corresponding structures and structural averages over them associated to the homeomorphic structural descriptors is determined.

2. Structural Descriptors and their Corresponding Structures

Let M be a specific molecular system. In general, one may assign a set of parameters, say Π, to this molecular system so that by varying the parameters the result of measurement varies. For instance, the set Π may be regarded as the nuclear configuration space. In this case, the different fixed points x and y belong to Π correspond to two different nuclear configurations in Born-Oppenheimer approximation and consequently leads to the different purely electronic Hamiltonians, namely H_x and H_y. This immediately cause different chemical bonding pattern, different electronic charge densities, and so on. At all, for $x \neq y$, these two molecular systems, denoted by M_x and M_y, differ in the quantum measurement sense and are called as two different *forms* [21, 27, 62] of the molecular system $\mathrm{M} \equiv \{\mathrm{M}_z\}_{z\in\Pi}$. In this manner, the molecular system M together with parameter space Π should be regarded as a family of the forms, namely $\{\mathrm{M}_z\}_{z\in\Pi}$ [27].

We emphasize that two different forms, M_x and M_y, of a specific molecular structure may be considerably different even if the parameters x and y are considerably close. In other words, a continuous change in the parameters x, leads to a discontinuous change in molecular form. In such a case, x, customarily, called as catastrophe point [21,2 4, 53].

In conformity, a one-parameter family of scalar fields;

$$F : R^3 \times \Pi \to R,\ F(r\,;x) \equiv F_x(r) \tag{7}$$

is called as a *"Structural Descriptor"* (S-descriptor) of the molecular system M, provided that for any fixed $x \in \Pi$ the scalar function $F_x : R^3 \to R$, $F_x(r) = F(r\,;x)$ comprises the adequate information concerning the structure of the molecular form M_x. In other words, a S-descriptor is a family of scalar field such that for any $x \in \Pi$ geometrical and topological properties of F_x, in the sense of information contained in the Hessian matrix $\nabla \otimes \nabla F_x$, is in conformity with the structural character, namely, bond paths, stability, and so on, of the molecular form M_x (see 1 and 4 for details). For instance, one-electron charge density [21], bear nuclear potential [28], molecular electrostatic potential [42,43] and virial field [29] have been introduced as the S-descriptors.

Let $F = \{F_x\}_{x\in\Pi}$ be the S-descriptor of the given molecular system. Let for any $x \in \Pi$ the scalar function F_x be *smooth* almost everywhere. i.e., for each $x \in \Pi$, $F_x(r)$ has continuous derivative except for a finite point in R^3 (for instance, charge density $\rho_x(r)$, for a coulomb system is smooth except at the nuclei positions [54]). Then, there is a one-parameter family of three-dimensional *flows* (gradient dynamical systems), denoted by $\xi^F = \{\xi_x^F\}$, in correspondence to the family $F = \{F_x\}_{x\in\Pi}$. Relation between the flow ξ_x^F and the S-descriptor, F_x, is provided through the equating the velocity field of the flow with the gradient vector field of the S-descriptor, i.e., [24]

$$\frac{dr(t)}{dt} = \partial_t \xi_x^F(r,t) = \nabla_r F_x\left(\xi_x^F(r,t)\right) \qquad \forall x \in \Pi \tag{8}$$

Where, the trajectories are given by $r(t) = \xi_x^F(r,t)$. In other words, the flow ξ_x^F is a gradient system in which its associated scalar field is F_x. All extremas of the S-descriptor are fixed points of this gradient system.

The evolution rule of the flow, $\xi_x^F : R^3 \times R \to R^3$, satisfies:

$$\xi_x^F(r,0) = r(0) = r_0 \tag{9}$$

$$\xi_x^F(r,t+s) = \xi_x^F\left(\xi_x^F(r,t),s\right). \tag{10}$$

In this way, for a given S-descriptor F, there exists a one-to-one correspondence Ω_F from the parameter space onto the family of gradient system $\{\xi_x^F\}$:

$$\begin{aligned} \Omega_F : \Pi &\to \{\xi_x^F\} \\ z &\to \xi_z^F \end{aligned} \tag{11}$$

Two flows ξ_x^F and ξ_y^F are called *conjugate* if there is a homeomorphism (see section 3 or Ref. [36]) $J : R^3 \to R^3$ that satisfies following *commutative relation* [24, 55]

$$J \circ \xi_y^F - \xi_x^F \circ J = 0 \tag{12}$$

This means that the flows ξ_x^F and ξ_y^F are equivalent in the behavioral sense. In other words, there is a correspondence between attractors, saddle (hyperbolic) points and basins of these two gradient systems. One may easily investigate that the conjugate relation is an equivalence relation on the family $\{\xi_x^F\}$ and consequently partitions it into the k non-overlapping equivalence classes, namely, $[\xi_{x_1}^F]$, $[\xi_{x_2}^F]$,…, and $[\xi_{x_k}^F]$ [21,24]. In this manner, one should partitions the parameter (control) space Π, through the inverse of the correspondence (11), into the non-overlapping class, i.e.,

$$[x_j]_F = \Omega_F^{-1}\left([\xi_{x_j}^F]\right), \qquad 1 \le j \le k \quad (13)$$

where, for $i \neq j$, $[x_i]_F \bigcap [x_j]_F = \phi$ and $\bigcup_j [x_j]_F = \Pi$. We briefly denote the conjugate relation (12) by $\xi_x^F \leftrightarrow \xi_y^F$. Vividly, the partitioning of Π is the result of the following induced equivalence relation, denoted by $\leftrightarrow$, on this space:

$x \leftrightarrow y$ *if and only if* $\xi_x^F \leftrightarrow \xi_y^F$

It is important to note that notation $\xi_x^F \leftrightarrow \xi_y^F$ is more complete than $x \leftrightarrow y$ since the first one involves the S-descriptor of molecular system, namely, F. Each equivalence class $[x]_F$ comprises all parameters in which their corresponding gradient systems have the same dynamical behavior. This means that there is a correspondence between attractor, repulsion and saddle points of the gradient systems ξ_x^F and ξ_y^F while x and y belong to the same class. Since the molecular structure of a given molecular system should be characterized through the number, place and type of such critical points, this is reasonable to name each equivalence class in the parameter space as F*-structure* while F is the S-descriptor of the molecular system. The diagram illustrating these F-structures, as the partitioning of the parameter space Π, is called as F*-diagram*.

3. Homeomorphism between S- descriptors

In mathematical textbooks [56], a function $\eta : A \rightarrow B$ is called as *Homeomorphism* if η is *bijective* and *bicontinuous* , i.e.,

i) η is injective (one-to-one)

ii) η is into surjective (onto)

iii) η is continuous

iv) $\eta^{-1} : B \rightarrow A$ is continuous0

A homeomorphism from set A to itself is called as automorphism. The space of all automorphisms on A is denoted by $Aut(A)$. We emphasize that this mathematical definition of homeomorphism between sets A and B is subtly different from concept of homeomorphism between two S-descriptors F and G. Hereafter, we denote such a structural homeomorphism by *S- homeomorphism* or (F, G)*-homeomorphism*. Let F and G be two different S-descriptors of the given molecular system and z be an arbitrary point belong to the parameter space Π. In general, there is not well-known relationship between F-structure, $[z]_F$ and G-structure, $[z]_G$. In other words, there is not any particular relation between F- diagram and G-diagram. Nevertheless, one should classify the family of all S-descriptors of this molecular system such that the members of each class possess the diagrams with the similar topological (in mathematical sense [28, 44, 56]) properties.

To clarify, consider a given molecular system within the Born-Oppenheimer approximation with the nuclear configuration $x \in \Pi$. Based on Hohenberg-Kohn theorem [57] there exist an unknown functional relationship between the ground state charge density, $\rho_x(r)$, and external potential, $V_{nuc}(r; x)$. This means that the external potential determines uniquely the charge density, and the charge density determines uniquely (to within an additive constant) the external potential. Therefore, it is anticipatable that two family of the scalar fields, namely, $\rho \equiv \{\rho_z\}_{z\in\Pi}$ and $V_{nuc} = \{V_{nuc}(r; z)\}_{z\in\Pi}$, as the two S-descriptors of a particular molecular system, have the similar diagrams. In fact, Tal *et al*

[28] indicated that there exists a one-to-one correspondence between ρ-diagram and V-diagram.

Each pair of the S-descriptors F and G, like ρ and V, with the corresponding structures, are referred to as Homeomorphic [26,29]. Unfortunately, this definition is not explicit and useful enough. In ref. [28] authors defined two S-descriptors F and G to be homeomorphic if there exist two homeomorphisms η and ω such that the following diagram is commutative

$$\begin{tikzcd}
\Pi \arrow[r, "F"] \arrow[d, "\eta"'] & C^{\infty}(R^3,R) \arrow[r, "grad"] & \mathrm{T}(R^3) \arrow[d, "\omega"] \\
\Pi \arrow[r, "G"] & C^{\infty}(R^3,R) \arrow[r, "grad"] & \mathrm{T}(R^3)
\end{tikzcd} \tag{14}$$

That means

$$\omega \circ grad \circ F = grad \circ G \circ \eta \tag{15}$$

Where the parameter space is the nuclear configuration space, $\Pi = R^q$, and the gradient operator, $grad$, from the space of the almost everywhere smooth functions $C^{\infty}(R^3,R)$ onto the 6D-tangent bundle $\mathrm{T}(R^3)$ [58] of 3D Euclidian space R^3 is defined as follows

$$\begin{aligned} grad &: C^{\infty}(R^3,R) \to \mathrm{T}(R^3) \\ & F_x(r) \to \nabla_r F_x(r) \end{aligned} \tag{16}$$

Relation between η and ω is given by

$$\omega \circ \nabla F_x = \nabla G_{\eta(x)} \tag{17}$$

Based on the commutative diagram above it may be deduced that the origin of the definition of the S-homeomorphism between S-descriptors, F and G, goes back to the fact that for each arbitrary point z belong to the nuclear configuration space (parameter space) there exists the point $z' = \eta(z)$ such that gradient vector fields ∇F_x and $\nabla G_{\eta(x)}$ are equivalent.

In conformity with our notations within this paper, we extend the diagram (17) to the following one

$$\begin{tikzcd}
\Pi \arrow[r, "\tilde{F}"] \arrow[d, "\eta"'] & C^{\infty}(R^3,R) \arrow[r, "grad"] & \mathrm{T}(R^3) \arrow[r, "\xi"] & \Im_F(R^3) \arrow[r, "\Phi"] & \Im_F/\Re \arrow[d, "\omega"] \\
\Pi \arrow[r, "\tilde{G}"] & C^{\infty}(R^3,R) \arrow[r, "grad"] & \mathrm{T}(R^3) \arrow[r, "\xi"] & \Im_G(R^3) \arrow[r, "\Phi"] & \Im_G/\Re
\end{tikzcd} \tag{18}$$

That means

$$\omega \circ \Phi \circ \xi \circ grad \circ \widetilde{F} = \Phi \circ \xi \circ grad \circ \widetilde{G} \circ \eta \tag{19}$$

Where, the notation $\hookrightarrow$ referred to as embedding map:

$$\begin{aligned} \tilde{F} : \Pi &\to C^{\infty}\left(R^3, R\right) \\ z &\longrightarrow F_z \end{aligned}, \tag{20}$$

The $\Im_F\left(R^3\right)$ is the space of the smooth (almost everywhere) gradient systems and the map ξ is given by

$$\begin{aligned} \xi : \mathrm{T}\left(R^3\right) &\to \Im_F\left(R^3\right) \\ \nabla F_z &\xrightarrow{\xi} \xi_z^F\left(q,t\right) \end{aligned} \tag{21}$$

While the flow, $\xi_Z^F(q,\tau)$, defines via $\partial_t \xi_z^F(q,t) = \nabla_q F_z\left(\xi_z^F(q,t)\right)$.

The space $\Im_F/\Re$ is the quotient space [56] of the space $\Im_F\left(R^3\right)$ with respect to the conjugate relation (12), i.e.,

$$\begin{aligned} \Im_F/\Re &= \left\{\left\{\xi_z^F \in \Im_F\left(R^3\right) : \xi_z^F \leftrightarrow \xi_x^F\right\} \ : \ \xi_x^F \in \Im_F\left(R^3\right)\right\} \\ &= \left\{\left[\xi_z^F\right] : \ z \in \Pi\right\} \equiv \left\{\left[x_j\right]_F = \Omega_F^{-1}\left(\left[\xi_{x_j}^F\right]\right) \quad , i = 1,2,\ldots,k\right\} \end{aligned} \tag{22}$$

In this regard, map Φ is defined by

$$\begin{aligned} \Phi : \Im_F\left(R^3\right) &\to \Im_F/\Re \\ \xi_z^F &\xrightarrow{\Phi} \left[\xi_z^F\right] \end{aligned} \tag{23}$$

In this manner, one should define the "*S-homeomorphism*" between S-descriptors via the following rigorous way:

Definition 3.1 *Two S-descriptors F and G of a molecular system with the parameter space Π are S-homeomorphic if there exists automorphism $\eta : \Pi \to \Pi$ and homeomorphism $\omega : \Pi \to \Pi$ such that the diagram (18) is commutative.*

Theorem 3.2 *The S-homeomorphism relation defined through the commutative diagram (18) is an equivalence relation on the space of S-descriptors.*

Proof: Setting, $\alpha = \Phi \circ \xi \circ grad \circ F$ and $\beta = \Phi \circ \xi \circ grad \circ G$ and acting both side of the commutative relation (19) on the arbitrary configuration z one obtains

$$\beta \circ \eta \circ \alpha^{-1}\left(\left[\xi_z^F\right]\right) = \left[\xi_{\eta(z)}^G\right] \qquad \forall z \in \Pi \tag{24}$$

One should represent this expression in the more practicable form

$$\xi_z^F \leftrightarrow \xi_{\eta(z)}^G \qquad \forall z \in \Pi \tag{25}$$

We briefly denote this by $\xi^F \xleftrightarrow{\eta} \xi^G$ and denote the S-homeomorphic relation on the space S-descriptors by notation $\approx$. In this regard, all mentioned above should be re-expressed, in short, as follows:

$F \approx G$ *if and only if there exists* $\eta \in Aut(\Pi)$ *such that* $\xi^F \xleftrightarrow{\eta} \xi^G$ Where $Aut(\Pi)$ is the space of all automorphism on the parameter space Π. We assert that the relation $\approx$ is an equivalence relation on space of S-descriptors. To see this, note that identity map, id, belongs to $Aut(\Pi)$ and clearly $\xi^F \xleftrightarrow{id} \xi^F$, consequently relation $\approx$ is reflective. On the other hand, suppose that $F \approx G$, this means that there exist $\eta \in Aut(\Pi)$ such that $\xi^F \xleftrightarrow{\eta} \xi^G$. Since $\eta^{-1} \in Aut(\Pi)$, one immediately obtains $\xi^G \xleftrightarrow{\eta^{-1}} \xi^F$ or $G \approx F$, i.e., relation $\approx$ is symmetry. Finally, suppose that $F \approx G$ and also $G \approx L$. This means that $\xi^F \xleftrightarrow{\eta} \xi^G$ and $\xi^G \xleftrightarrow{\gamma} \xi^L$ for appropriate automorphisms η and γ. Since $Aut(\Pi)$ is closed under combination of functions, i.e., $\gamma \circ \eta \in Aut(\Pi)$, one obtains $\xi^F \xleftrightarrow{\gamma\circ\eta} \xi^L$ which indicate that relation $\approx$ is transitive. Proof is completed.

In accordance with definition 3.1, two S-descriptors F and G of a given system are called *"isomorphic"* if $\eta : \Pi \to \Pi$ is identity map, that is

$$\xi_z^F \leftrightarrow \xi_z^G \qquad \text{for any } z \in \Pi \tag{26}$$

This means that F-diagram coincide with G-diagram.

For instance, shape function (the density per particle [59]) $\sigma = \{\sigma_z\}_{z \in \Pi}$ and charge density $\rho = N\sigma$ as two S-descriptors are isomorphic, where

$$\sigma_z(r) = \sum_{spin} \int_{space} \Psi^*(\tau_1, \ldots, \tau_N; z)\delta(r - r_1)\Psi(\tau_1, \ldots, \tau_N; z) dr_1 \ldots dr_N, \tag{27}$$

N is the number of electrons, $\Psi(\tau, z)$ is a pure quantum state of the system and z is the nuclear geometry in Born-Oppenheimer approximation. Since for any fixed parameter z

we have, $\nabla\rho_z = N\nabla\sigma_z$, scalar fields σ and ρ have the same gradient pattern (with different speeds), i.e.,

$$\xi_z^{\rho} \leftrightarrow \xi_z^{\sigma} \qquad \text{for any } \; z \in \Pi \qquad (28)$$

With due attention to definition 3.1 and theorem 3.2 one may determine the exact relation between corresponding structures associated to the S-homeomorphic S-descriptors.

Theorem 3.3 *Let F and G be two S-descriptors of the specific molecular system and diagram (19) be commutative (i.e., $F \approx G$). Then for any $z \in \Pi$ the following equality is satisfied*

$$\eta([z]_F) = [\eta(z)]_G \qquad \text{for any } \; z \in \Pi \qquad (29)$$

Proof: Let x be an arbitrary system parameter belong to the F-structure $[z]_F$. Since $F \approx G$ we obtain $\xi_x^F \leftrightarrow \xi_{\eta(x)}^G$ and $\xi_x^F \leftrightarrow \xi_z^F$. Therefore $\xi_z^F \leftrightarrow \xi_{\eta(x)}^G$. As such, condition $F \approx G$ tends to relation $\xi_z^F \leftrightarrow \xi_{\eta(z)}^G$ for arbitrary point z. Combining these two latter relations yield $\xi_{\eta(x)}^G \leftrightarrow \xi_{\eta(z)}^G$ or equivalently reveals that $\eta(x) \in [\eta(z)]_G$. Therefore, one obtains $\eta([z]_F) \subseteq [\eta(z)]_G$. Taking the symmetry of problem into account one obtains the equality $\eta([z]_F) = [\eta(z)]_G$ and proof is completed.

Besides, this definition immediately demonstrate that the structural characters (bond paths, stability, instability, ring and cage structures, and so on) of the molecular system are invariant under the replacing a S-descriptor by another isomorphic one.

Let Δ be the space of S-descriptors of a specific molecular system. Based on Theorem 3.2 , relation $\approx$ is an equivalence relation on Δ. Therefore, $\approx$ partitions Δ into the equivalence classes, say $\Delta/_{\approx}$. Partitioning of the descriptor space and partitioning of control (configuration) space of a molecular system must not be confused. The control space is a particular Euclidian space and each fragment is referred to as molecular structure, whereas each fragment of $\Delta/_{\approx}$ is a set of homeomorphic descriptors. Vividly, partitioning of space of S-descriptors depends on the intrinsic properties of the molecular system. For instance, electronic charge density ρ, nuclear potential V_{nuc}, and virial field

v are belong to the same class for H_2O system, whereas these are not true for B_2H_6 system [28,29].

4. Average Property of a Structure

According to what mentioned in previous sections a molecular structure is essentially a class of molecular forms. In analogy to language of graph theory, this means that each molecular structure is in correspondence to a class of molecular graphs. More precisely, we attribute a one-parameter dynamical system to each molecular graph or equivalently a conjugate class to each one. The parameter depends on the position of vertices in 3D-space. For each specific parameter the dynamical properties namely attractors, repulsions and saddle points are in conformity with the network of bounds of the corresponding molecular graph (see [28], where BNP has been investigated as a S-descriptor of 130 molecules and molecular complexes). Each class contains the family of similar molecular graphs with the same bound paths. It is possible to categorize these equivalent classes into two fundamental sets namely stable and unstable (see [24] for details). Every unstable class has the property that a small perturbation may render the molecular form into a new class. In other words, the molecular graph is transformed into the new molecular graph with the same vertices and different network of bounds. Since, in some sense, each molecular structure is a measurable set in control space, this prompts us to assign a specific quantity to each one. Somehow, it may be regarded as the topological index counterpart in this new approach. In fact, one can define the "dynamical information content" [27] as a new index based on this procedure.

Measurement of a property of a molecular form M_x, generally, is depend on the corresponding parameter x. Let $P(x)$ stand for the probability of finding the molecular system $\mathrm{M} \equiv \{\mathrm{M}_z\}_{z\in\Pi}$ in the particular form M_x. By definition, $P(x)$ is a nonnegative, continuous and integrable map [60]. Let F be a S-descriptor of this system. The probability of finding M in a molecular form M_x belong to the particular structure $[z]_F$ is given by

$$P[F,z]\equiv \int_{[z]_F} P(x)dx\,. \qquad (30)$$

Let $F \approx G$ and $\eta \in Aut(R^q)$ be the corresponding homeomorphism such that diagram (18) to be commutative. Let $x=(x_1,\dots,x_q)\in R^q$ and

$$(x_1,\dots,x_q)\xrightarrow{\eta}(\eta_1(x_1,\dots,x_q),\dots,\eta_q(x_1,\dots,x_q))=(\eta_1,\dots,\eta_q).$$

Let $dm=dx_1\dots dx_q$ be the standard (Lebesgue) measure on R^q. Combining theorem 3.3 and change of variable theorem [60], one obtains

$$\begin{aligned}
P[F,z] &= \int_{[z]_F} P(x)\,dm \\
&= \int_{[z]_F} P\left(x_1,\dots,x_q\right)dx_1..dx_q = \int_{\eta([z]_F)} P\circ\eta^{-1}\left(\eta_1,\dots,\eta_q\right)\frac{\partial\left(x_1,\dots,x_q\right)}{\partial\left(\eta_1,\dots,\eta_q\right)}d\eta_1..d\eta_q \\
&= \int_{[\eta(z)]_G} P\circ\eta^{-1}\left(\eta_1,\dots,\eta_q\right)\frac{\partial\left(x_1,\dots,x_q\right)}{\partial\left(\eta_1,\dots,\eta_q\right)}d\eta_1..d\eta_q = \int_{[\eta(z)]_G} \tilde{P}\left(\eta_1,\dots,\eta_q\right)dv \qquad ,(31) \\
&= \tilde{P}\left[G,\eta(z)\right]
\end{aligned}$$

where, $\tilde{P}=P\circ\eta^{-1}$ is a nonnegative, continuous and integrable map on R^q, as well as,

$$dv=\frac{\partial(x_1,\dots,x_q)}{\partial(\eta_1,\dots,\eta_q)}d\eta_1\dots d\eta_q=\frac{\partial(x_1,\dots,x_q)}{\partial(\eta_1,\dots,\eta_q)}dm, \qquad (32)$$

is the measure on the $\eta(R^q)$ as a deformed body (deformed F-diagram). In other words, $dm=dx_1\dots dx_q$ is the measure on F-diagram, whereas dv is the measure on the deformed F-diagram, that is referred to as G-diagram.

Similarly, let F be the S-descriptor of the system. If the dependence of some property Γ of the molecular form M_x on the parameter, x, is described by $\Gamma(x)$, then the average property of the structure $[z]_F$ is given by

$$\begin{aligned}
\Gamma[F,z] &= \int_{[z]_F} \Gamma(x)P(x)\,dm \\
&= \int_{[\eta(z)]_G} \tilde{\Gamma}\left(\eta_1,\dots,\eta_q\right)\tilde{P}\left(\eta_1,\dots,\eta_q\right)dv = \tilde{\Gamma}\left[G,\eta(z)\right],
\end{aligned} \qquad (33)$$

where, $\tilde{\Gamma}=\Gamma\circ\eta^{-1}$.

Equation (33) may be employed as a powerful tool for calculation of the structural properties and relation between them, when corresponding descriptors are homeomorphic. Very recently, one of the authors introduced the “Dynamical information content of the molecular structure” based on relation (33) [27],. In Ref. [27] it has been demonstrated that information content of a specific molecular structure is invariant under structural homeomorphism, where $\Gamma(x)P(x) \equiv \overline{S}_{\phi}(x)$ is the average local entropy (information) of per experiment.

We may assume that the role of nuclear excursions could be simulated with a nuclear distribution function. In this way, one should attribute a weight to every point of parameter (configuration) space. This weight discriminate the relative importance of different parameters. A typical form of such a weight function may be offered by considering the quantum treatment of the nuclear vibrations as well as the statistical consideration (assuming the thermodynamics equilibrium) [24], that is

$$P(x,\beta) = \frac{1}{Q}\sum_j f_j(x)\exp\left(-\beta E_j^{vib}\right) \qquad (34)$$

Where, $f_j(x) = \chi_j^{vib^*}(x)\chi_j^{vib}(x)$ is the quantum probability density attributed to each vibrational normal mode and $Q = \sum_j \exp\left(-\beta E_j^{vib}\right)$ is partition function. In such a case, we obtain,

$$\Gamma_j[F,z] = \int_{[z]_F} \Gamma(x) f_j(x)\, dm, \qquad (35)$$

and

$$\begin{aligned} \Gamma[F,z\ ;\beta] &= \sum_j \Gamma(x)P(x,\beta) \\ &= \frac{1}{Q}\sum_j \Gamma_j[F,z]\exp\left(-\beta E_j^{vib}\right). \end{aligned} \qquad (36)$$

5. Summary and Conclusions

In this paper, a rigorous definition of the structural descriptors and homeomorphisms between them, based on the commutative diagram, has been investigated. Based on this definition, the structural homeomorphism relation provides an equivalence relation on the family of structural descriptors. Consequently, the space of the structural descriptors is partitioned into nonoverlapping equivalence classes. Clearly, this partitioning depends on the properties of the molecular system under consideration. For instance, two scalar fields ρ and V_{nuc} as structural descriptors of BH_3 are belong to a class, whereas this is not true when they are regarded as the structural descriptors for B_2H_6 [44]. An explicit relationship may be derived between corresponding structures associated to the Structural homeomorphic descriptors. This allows us to compare the average properties of the molecular structures and exhibit an exact relation between them.

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