

Dynamical Information Content of the Molecular Structures: A Quantum Theory of Atoms in Molecules (QTAIM) Approach

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Abstract

How may one assign information to a molecular structure? This question is answered based on the definition of regional information on the space of the molecular forms. It is shown that, this quantity is invariant under structural homomorphism.

1 Introduction

Within the present report, the mathematical definition of the molecular structure is regarded as a part of the Quantum Theory of Atoms in Molecule (QTAIM) [1]. 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 [2-5]. This is particularly true for the mathematical properties of the molecular structures, forms and structural homeomorphisms [6]. Briefly, within QTAIM, the one-electron density, say ρ , of a molecular system may be partitioned into subsystems (topological atoms) each of which bounded by the local zero flux surfaces $\partial\Omega$, i.e.,

$$\nabla\rho_x(r).n(r) = 0 \quad \forall r \in \partial\Omega \quad (1.1)$$

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where $n(r)$ is the unit vector perpendicular to $\partial\Omega$ at point r and x is a parameter belonging to the nuclear configuration space associated to Born-Oppenheimer approximation. This equation is a result of a rigorous procedure based on Schwinger's principle of quantum stationary action [7] and implies that each trajectory of $\nabla\rho_x(r)$ (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 the one-electron charge density. Of course, TA of various scalar functions is now routinely employed in the computational chemistry. For instance, TA of electron localization function [8-10], the nuclear potential energy field [11], the virial field [6] and Laplacian of charge density [12-14]. These applications indicate that mathematical framework of TA is not confined to charge density. Collard and Hall also briefly considered TA of potential energy hyper-surface [15]. These are multi-dimensional scalar functions. Subsequently this program was fully realized by Mezey [16, 17].

The main steps of the static aspects of TA of the one-electron charge density, within QTAIM, may be enumerated as follows:

- 1 Constructing the gradient dynamical system with respect to the one-electron charge density in a given nuclear configuration (not necessarily the equilibrium configuration).
- 2 Searching for the critical points of ρ_x , i.e., $\nabla\rho_x(z) = 0$.
- 3 Classification of critical points, namely, repulsions, attractors and saddle points, based on the spectrum of ρ_x -Hessian matrix.

Since the spectrum of ρ_x -Hessian matrix precisely determines the dynamical behavior of $\nabla\rho_x$ -gradient vector field, one should classify the configuration space of a molecular system based on the TA above. Such a classification is the origin of the mathematical definition of structure, structural stability and instability of molecular structure within QTAIM [1, 4].

In this report, we turn our attention to the dynamical aspects of TA, i.e., the dynamics on the configuration (or control) space. In this manner, a weight (probability measure) can be associated to each structure. This is the essence of our strategy to assign an invariant quantity, referred to as structural information, to each molecular structure.

2 The nature of the problem

Studying the concept of form, structure and structural stability is one of the most fundamental problems for scientists. In particular, an explicit and authoritative definition of molecular structure is the desire of chemists. Although researchers in different branches of science have more or less the same intuitive perception concerning the concept of form and structure, it seems to be impossible to acquire a common belief regarding an explicit definition of form. Nevertheless, in the most general case, if $(G, *)$ is a group (or a pseudo-group) acting on a topological space Ω , the triple $(G, \Omega, *)$ may be posed as the mathematical definition of form [19]. In this account, and for our goal, it suffices to consider a topological space Ω as the space of forms and to replace the action of the group G by a dynamical system on Ω . In order to elucidate the connection between this abstract definition of form and QTAIM one should regard the topological space Ω as the nuclear configuration space. In fact, for a chemist, different molecules have different forms, i.e., different molecules possess different charge density distribution functions ρ . In accordance with this delineation a molecular system also possesses different forms, i.e., different nuclear geometries x or equivalently different charge density distributions ρ_x , where x arises from Born-Oppenheimer approximation. This correspondence, namely $x \mapsto \rho_x$, indicates that the nuclear configuration space is in fact a *space of forms*.

On the other hand, each point in Ω can be associated to a gradient dynamical system as in the following steps (see section 4 or [1, 19] for details):

$$\begin{aligned} x &\rightarrow \text{molecular form } \rho_x \rightarrow \text{gradient vector field } \nabla \rho_x \\ &\rightarrow \text{corresponding dynamical system } \xi_x. \end{aligned} \tag{2.1}$$

In this manner, each two points x and y in Ω , as two different forms, are related based on the following equivalence relation:

$$"x \sim y \text{ if and only if two dynamical systems } \xi_x \text{ and } \xi_y \text{ are conjugate.}"$$

The definition of such an equivalence relation on the space of forms automatically leads the definition of the molecular structure and structural stability, i.e., each equivalence class is called a *molecular structure* and each open class (as a topological set) referred to as a *structural stable* class. Other classes show the catastrophic properties [20].

A significant question concerning these equivalence classes or equivalently stable chemical structures is: can one assign a quantitative measure to each molecular structure? Such

measures are usually called *topological indices* and several versions of them are proposed during the time [21-29]. Studying this area states the fact that Shannon information theory is one of the important tools in describing different structures. In particular, it provides an efficient tool to present a quantity, namely, *information content of a molecular system*, as a part of mathematical chemistry. It was first introduced by Rashevsky [30, 31] in the language of graph theory, namely, *topological information content*. The mathematical framework of this definition was precised using automorphism group of the graphs by Trucco [32]. Mowshowitz [33-36] and Bonchev *et al* [37-40] introduced *chromatic information* and *information content of molecules* respectively, which led to the analysis of the relationship between topological information and symmetry of molecules.

In all works, mentioned above, a molecular system is considered as a structure consisting of vertices and wedges of a graph whereas, the present approach is based on the definition of forms and molecular structures within QTAIM. On the other hand, since the molecular structures may be exhibited based on the gradient paths of the different structural descriptors [6, 11], can one assign this quantitative measure so that be invariant under structural homeomorphisms? In this report, it is demonstrated that the answer, in the sense of information contained in structures, is affirmative. In order to do so, we define the *regional information* as a set function on the space of forms which is invariant under topological conjugacy.

3 Definition of regional information: Mathematical foundations

The Shannon information [41] for a discrete distribution (p_1, \dots, p_k) is defined as follows:

$$S(\{p_i\}) = - \sum p_i \log p_i \quad (3.1)$$

wherein, p_i is the probability of the i th event. The quantity $-\log p_i$ may be regarded as the surprise associated with the outcome i . To see this, note that if p_i is small, one would be quite surprised if the outcome is explicitly i . Accordingly, $-\log p_i$ is large for small p_i . Also, if p_i is large, one perceives that the surprise is small. In this manner, (3.1) may be interpreted as the expectation value of the surprise for a system of a random variable with discrete distribution (p_1, \dots, p_k) .

Now, let Ω be a compact metric space and $\Phi : \Omega \rightarrow \Omega$ be a continuous dynamical

system. In conformity with probability p_i above, one can offer the following quantity:

$$\tau_{\Phi}(x, A) := \limsup_{n \rightarrow \infty} \frac{1}{n} \text{card}(\{k \in \{0, 1, \dots, n-1\} : \Phi^k(x) \in A\}) \quad (3.2)$$

where the $\text{card}(B)$ denotes the cardinality of the set B . This quantity is the average time in which $x \in \Omega$ spends in the arbitrary region $A \subset \Omega$ under the dynamic of Φ . Since $\tau_{\Phi}(x, A)$ may play the role of p_i in (3.1), $-\log \tau_{\Phi}(x, A)$ may be regarded as the measure of how encountering the orbit of x in A surprises an observer. In this regard, if $\xi = \{A_1, \dots, A_n\}$ is a Borel partition of Ω , a primary counterpart for relation (3.1) may be defined as follows:

$$S_{\Phi}(x; \xi) := - \sum_{j=1}^n \tau_{\Phi}(x, A_j) \log \tau_{\Phi}(x, A_j). \quad (3.3)$$

The map $x \mapsto S_{\Phi}(x; \xi)$ is called the *local information map with respect to ξ* . That is the average of information attained by observing the orbit of x in each fragment of the specific partitioning ξ .

A partition $\xi = \{A_1, \dots, A_m\}$ may be regarded as listing the possible outcomes of an experiment. Consequently, if we consider the dynamic Φ as a passage of one day of time then

$$\bigvee_{i=0}^{n-1} \Phi^{-i} \xi = \{A_{i_0} \cap \Phi^{-1}(A_{i_1}) \cap \dots \cap \Phi^{-(n-1)}(A_{i_{n-1}}) : A_{i_k} \in \xi, 0 \leq i_k \leq m\}$$

represents the combined experiment of performing the original experiment ξ on n consecutive days.

In analogy to the standard definition of the information of a partition [42] (more precisely, the information of a dynamical system with respect to a partition) we define

$$\bar{S}_{\Phi}(x; \xi) := \limsup_{n \rightarrow \infty} \frac{1}{n} S_{\Phi}(x; \bigvee_{i=0}^{n-1} \Phi^{-i} \xi). \quad (3.4)$$

For any $x \in \Omega$, the quantity $\bar{S}_{\Phi}(x; \xi)$ could be interpreted as the average local information of per day that one gets from performing the original experiment daily forever.

Now we are in a position to define the information of a Borel set.

Definition 3.1 (*Information of a Borel set*) Suppose that $\Phi : \Omega \rightarrow \Omega$ is a continuous dynamical system on the compact metric space Ω , μ is a Borel measure and A is a Borel subset of Ω . The information of A is defined as follows:

$$\mathcal{I}_{\Phi, \mu}(A) := \sup_{\xi} \int_A \bar{S}_{\Phi}(x; \xi) d\mu(x) \quad (3.5)$$

where the supremum is taken over all Borel partitions of Ω .

Since this quantity depends on μ and the dynamical system Φ , the map $\mathcal{I}_{\Phi,\mu} : \mathfrak{B}(\Omega) \rightarrow [0, \infty]$, given by $A \mapsto \mathcal{I}_{\Phi,\mu}(A)$ is called the Φ -regional information map with respect to μ , wherein, $\mathfrak{B}(\Omega)$ is the family of Borel subsets of Ω . Theorem 3.4 reveals that for $A = \Omega$, $\mathcal{I}_{\Phi,\mu}(\Omega)$ coincides with the well known measure theoretic entropy (information) of Φ . In this regard $\mathcal{I}_{\Phi,\mu}(A)$ may be interpreted as the contribution of the Borel subset A of the measure theoretic information of the dynamical system Φ .

Note that since we do not deal with a dynamical system on the phase space in general, we invoke the term "Information" instead of "Entropy". Theorem 3.4 (*infra*) justifies why we offer the term "information of A " for the expression (3.5).

Before going any further, we recall the Choquet's Theorem and its corollary [43]. Note that, if Ω is a compact metric space and $\Phi : \Omega \rightarrow \Omega$ is a continuous dynamical system, then the space of all Borel probability measures on Ω is denoted by $\mathcal{M}(\Omega)$. In addition, $\mathcal{M}(\Omega, \Phi)$ denotes the space of all invariant measures of Φ . We also write $E(\Omega, \Phi)$ for the space of ergodic measures of Φ . One can see that $\mathcal{M}(\Omega)$, equipped by the weak* topology, is a compact metrisable space and $E(\Omega, \Phi)$ equals the extreme points of the compact convex set $\mathcal{M}(\Omega, \Phi)$ [44].

Theorem 3.2 (*Choquet [43]*) *Suppose that Y is a metrisable compact convex subset of a locally convex space E , and that x_0 is an element of Y . Then there exists a probability measure λ on Y which represents x_0 and is supported by the extreme points of Y , i.e., $\mathcal{L}(x) = \int_Y \mathcal{L}d\lambda$ for every continuous linear functional \mathcal{L} on E .*

For $\mu \in \mathcal{M}(\Omega, \Phi)$ and a bounded measurable function $f : \Omega \rightarrow \mathbb{R}$, applying Theorem 3.2 for $E = \mathbf{M}(\Omega)$, the space of all finite Borel regular measures on Ω , $Y = \mathcal{M}(\Omega, \Phi)$ and the linear functional $\mathcal{L} : \mathbf{M}(\Omega) \rightarrow \mathbb{R}$ given by $\mathcal{L}(\mu) = \int_{\Omega} f d\mu$, we have the following corollary:

Corollary 3.3 *Suppose that $\Phi : \Omega \rightarrow \Omega$ is a continuous map on the compact metric space Ω . Then for each $\mu \in \mathcal{M}(\Omega, \Phi)$ there is a unique measure λ on the Borel subsets of the compact metrisable space $\mathcal{M}(\Omega, \Phi)$ such that $\lambda(E(\Omega, \Phi)) = 1$ and*

$$\int_{\Omega} f(x)d\mu(x) = \int_{E(\Omega,\Phi)} \left(\int_{\Omega} f(x)dm(x) \right) d\lambda(m)$$

for every bounded measurable function $f : \Omega \rightarrow \mathbb{R}$.

Under the assumptions of Corollary 3.3 we write $\mu = \int_{E(\Omega,\Phi)} md\lambda(m)$ and it is called the ergodic decomposition of μ .

The following theorem indicates that in case of $A = \Omega$ and while μ is an invariant measure, i.e., the dynamic is taken on the phase space, the quantity (3.5) coincides with the measure theoretic information (entropy). Therefore, in some sense, the quantity (3.5) may be regarded as the contribution of A to the measure theoretic information of the dynamical system Φ .

Theorem 3.4 *Suppose that $\Phi : \Omega \rightarrow \Omega$ is a continuous dynamical system on a compact metric space Ω and $\mu \in \mathcal{M}(\Omega, \Phi)$. Then*

$$\mathcal{I}_{\Phi, \mu}(\Omega) = h_{\mu}(\Phi)$$

where $h_{\mu}(\Phi)$ is the measure theoretic information (entropy) of Φ .

Proof. First, let m be ergodic. For any Borel set A and $x \in \Omega$, by Birkhoff ergodic Theorem, one can easily show that $\tau_{\Phi}(x, A) = m(A)$ for almost all $x \in \Omega$, and consequently, if ξ is any Borel partition then $S_{\Phi}(x; \xi) = H_m(\xi)$ for almost all $x \in \Omega$, where $H_m(\xi)$ is the entropy of ξ . Therefore, if ξ is any Borel partition of Ω then $\bar{S}_{\Phi}(x; \xi) = h_m(\Phi, \xi)$ for almost all $x \in \Omega$. Integrating both sides on Ω yields $\int_{\Omega} \bar{S}_{\Phi}(x; \xi) dm(x) = h_m(\Phi, \xi)$. The result follows by taking supremum over all Borel partitions of Ω .

Now let $\mu \in \mathcal{M}(\Omega, \Phi)$. Let ξ be a Borel partition of Ω and let $\mu = \int_{E(\Omega, \Phi)} m d\lambda(m)$ be the ergodic decomposition of μ . Then, as was stated before, one obtains

$$\int_{\Omega} \bar{S}_{\Phi}(x; \xi) dm(x) = h_m(\Phi, \xi)$$

for all $m \in E(\Omega, \Phi)$. For $n \geq 1$, let $S_n := \min\{\bar{S}_{\Phi}(\cdot; \xi), n\}$. Then $\{S_n\}_{n \geq 1}$ is an increasing sequence of bounded maps such that $S_n \rightarrow \bar{S}_{\Phi}(\cdot; \xi)$ on Ω . Applying Corollary 3.3, Jacob's Theorem and Monotone Convergence Theorem one obtains

$$\begin{aligned} \int_{\Omega} \bar{S}_{\Phi}(x; \xi) d\mu(x) &= \lim_{n \rightarrow \infty} \int_{\Omega} S_n(x) d\mu(x) \\ &= \lim_{n \rightarrow \infty} \int_{E(\Omega, \Phi)} \left(\int_{\Omega} S_n(x) dm(x) \right) d\lambda(m) \\ &= \int_{E(\Omega, \Phi)} \left(\int_{\Omega} \bar{S}_{\Phi}(x; \xi) dm(x) \right) d\lambda(m) \\ &= \int_{E(\Omega, \Phi)} h_m(\Phi, \xi) d\lambda(m) \\ &= h_{\mu}(\Phi, \xi). \end{aligned}$$

The result follows by taking supremum over all Borel partitions of Ω . □

Another important property of the information of a Borel set is its invariance under topological conjugacy. Recall that two dynamical systems $\Phi, \Psi : \Omega \rightarrow \Omega$ are topologically conjugate, if there is a homeomorphism $h : \Omega \rightarrow \Omega$ such that $h\Phi = \Psi h$.

Theorem 3.5 *Suppose that $\Phi, \Psi : \Omega \rightarrow \Omega$ are topologically conjugate continuous dynamical systems on compact metric spaces via the homeomorphism $h : \Omega \rightarrow \Omega$ and A be a Borel set in Ω . If $\mu \in \mathcal{M}(\Omega, \Phi)$ then*

$$\mathcal{I}_{\Phi, \mu}(A) = \mathcal{I}_{\Psi, \mu h^{-1}}(h(A)).$$

Proof. For $n \in \mathbb{N}$, $x \in \Omega$ and the Borel set $A \subseteq \Omega$ we have $\tau_{\Phi}(x, A) = \tau_{\Psi}(h(x), h(A))$. Now, let $\xi = \{A_1, \dots, A_n\}$ be a Borel partition of Ω and $x \in \Omega$, then

$$\begin{aligned} S_{\Phi}(x; \xi) &= - \sum_{j=1}^n \tau_{\Phi}(x, A_j) \log \tau_{\Phi}(x, A_j) \\ &= - \sum_{j=1}^n \tau_{\Psi}(h(x), h(A_j)) \log \tau_{\Psi}(h(x), h(A_j)) \\ &= S_{\Psi}(h(x); h(\xi)). \end{aligned}$$

For $n \in \mathbb{N}$, replacing ξ by $\bigvee_{i=0}^{n-1} \Phi^{-i}\xi$ yields

$$\begin{aligned} S_{\Phi}(x; \bigvee_{i=0}^{n-1} \Phi^{-i}\xi) &= S_{\Psi}(h(x); h(\bigvee_{i=0}^{n-1} \Phi^{-i}\xi)) \\ &= S_{\Psi}(h(x); \bigvee_{i=0}^{n-1} h\Phi^{-i}\xi) \\ &= S_{\Psi}(h(x); \bigvee_{i=0}^{n-1} \Psi^{-i}h(\xi)). \end{aligned}$$

Dividing by n and letting $n \rightarrow \infty$ yields

$$\bar{S}_{\Phi}(x; \xi) = \bar{S}_{\Psi}(h(x); h(\xi)). \tag{3.6}$$

Note that, if $\mu \in \mathcal{M}(\Omega, \Phi)$ then $\mu h^{-1} \in \mathcal{M}(\Omega, \Psi)$. Thus, for any Borel partition ξ one obtains

$$\begin{aligned} \int_A \bar{S}_{\Phi}(x; \xi) d\mu(x) &= \int_A \bar{S}_{\Psi}(h(x); h(\xi)) d\mu(x) \\ &= \int_{h(A)} \bar{S}_{\Psi}(x; h(\xi)) d\mu h^{-1}(x). \end{aligned}$$

The result follows by taking supremum over all Borel partitions of Ω . \square

Note that the information of a set $A \subset \Omega$ could be attained by integrating of other local information maps on A . For instance, the Brin-Katok and Shannon local information maps which measure the exponential rate of the decrease of the number of orbits around the orbit of x may also be used. In this account, we introduced our regional information $\mathcal{I}_{\Phi, \mu}(A)$ instead of the Brin-Katok [45] and Shannon [41] approach, since they are formulated for dynamics on phase spaces and so depend on the invariant measure with respect to the dynamic on the phase space. However our regional information is indeed independent of the *properties of the measure*, i.e., $\mathcal{I}_{\Phi, \mu}(A)$ may be defined for arbitrary (not necessarily invariant) measures. Consequently, it can be defined on an arbitrary compact metric space which could be the space of the molecular forms as a special case. One may find the generalized form of the mathematical approach given in this section in [46].

4 Information of a molecular structure as an invariant quantity

The regional information, introduced in section 3, is given for an arbitrary measurable region in a compact metric space. We will apply it to the special case of modeling of information for a molecular structure. In this case, since the distance between the nucleus of a molecular system is not violently increased, we may replace Ω by a large compact box, embeded in \mathbb{R}^q , where \mathbb{R}^q is the nuclear configuration space. The Ω may be partitioned into the regions, namely, molecular structures via the structural diagram [1, 4]. These regions are indeed Borel measurable.

The idea of partitioning of the nuclear configuration space is briefly presented in the following steps:

4.1 The structural stability of a dynamical system

We first recall the concept of a dynamical system, based on the ordinary differential equations [47]. Consider an ordinary differential equation

$$\dot{x} = v(x) \tag{4.1}$$

where $x \in \mathbb{R}^m$ and $v : \mathbb{R}^m \rightarrow \mathbb{R}^m$ is a smooth vector field. Equation (4.1) has a solution $\phi : \mathbb{R}^m \times \mathbb{R} \rightarrow \mathbb{R}^m$ determined by the equation

$$\phi(x, 0) = x, \quad \frac{\partial}{\partial t} \phi(x, t) = v(\phi(x, t)). \quad (4.2)$$

For each fixed $x \in \mathbb{R}^m$, the solution of equation (4.2) with initial values x is given by $t \rightarrow \phi(x, t)$. We may also consider the map $\phi_t : \mathbb{R}^m \rightarrow \mathbb{R}^m$ given by $\phi_t(x) = \phi(x, t)$ such that

$$\phi_0 = id, \quad \phi_t \circ \phi_s = \phi_{t+s}.$$

Two dynamical systems $\phi, \psi : \mathbb{R}^m \times \mathbb{R} \rightarrow \mathbb{R}^m$ are said to be conjugate, if there is a diffeomorphism $h : \mathbb{R}^m \rightarrow \mathbb{R}^m$ such that

$$h(\phi(x, s)) = \psi(h(x), s)$$

for all $x \in \mathbb{R}^m$ and $s \in \mathbb{R}$. Based on this conjugacy, we may define an equivalence relation on a family of dynamical systems. This equivalence relation partitions the family of dynamical systems into equivalence classes. Based on this concept one may define the structural stability for a dynamical system.

Let $\phi : \mathbb{R}^m \times \mathbb{R} \rightarrow \mathbb{R}^m$ be a dynamical system. We say that ϕ is structurally stable if there exists $\epsilon > 0$ such that ϕ is conjugate to ψ whenever ψ is a dynamical system on \mathbb{R}^m with $\|\phi - \psi\| < \epsilon$. In other words, the dynamical system ϕ is called structurally stable if it is an interior point of its conjugacy class. In addition, one should interpret the structural stability as follows:

” A dynamical system ϕ is structurally stable if there is a neighborhood such that every dynamical system in this neighborhood behaves like ϕ ,”

or equivalently

” A dynamical system ϕ is structurally stable if a small perturbation does not vary its dynamical behavior.”

4.2 The structural stability of a molecular system

The structural stability was introduced formally within the context of the theory of dynamical systems. We are interested to extend this definition to the molecules. Therefore,

we must find a general way to assign a dynamical system to a molecule. Based on the discussion presented in the previous subsection, we must attribute a differential equation to a molecule. Accordingly, equation (4.3) is the appropriate differential equation [1] (this equation was introduced originally to construct the gradient vector fields of the one-electron charge densities).

$$\frac{dr(s)}{ds} = \nabla\rho(r(s)) \quad (4.3)$$

Note that it is a special case of equation (4.1), replacing the vector field $v(x)$ by $\nabla\rho$. Now, one may establish the formal definition of the structural stability of a molecule. Suppose that M is a molecular system and x is the corresponding nuclear configuration. Then the state function of this molecule is denoted by $\chi = \chi(r; x)$ where r stands for the collection of electronic variables whereas x is introduced to emphasize the parametric dependence of state function to the nuclear coordinates. Accordingly, the one-electron charge density and the corresponding gradient vector field $\nabla\rho_x$ are also dependent parametrically on the nuclear configuration x . Thus, it is possible to rewrite equation (4.3) as follows:

$$\frac{dr(s)}{ds} = \nabla\rho_x(r(s)) \quad (4.4)$$

It is evident that the corresponding dynamical system is also dependent parametrically on the nuclear configuration x which is denoted by ζ_x . Since for every point in the nuclear configuration space there is a certain dynamical system, the equivalence relation \sim on the nuclear configuration space could be introduced as follows:

" $x \sim x'$ if and only if two dynamical systems ζ_x and $\zeta_{x'}$ are conjugate."

Thus, the nuclear configuration space is partitioned into equivalence classes. Every equivalence class is composed of a set of molecular forms and is called as *molecular structure*. Consequently, one may finally define the structural stability for a molecular system: a molecule M with the form x is structurally stable if and only if x is an interior point of its equivalence class.

4.3 Stable structures, unstable structures and structural diagrams

The equivalence relation partitions the nuclear configuration space into separate classes. In order to proceed further, we explicitly suppose that this equivalence relation partitions the space into k (a finite number) different classes. This is denoted by $[x_1], [x_2], \dots, [x_k]$

such that for every $i \neq j$, $[x_i] \cap [x_j] = \emptyset$ and $\cup_{i=1}^k [x_i] = \Omega$. We may categorize these equivalence classes into two fundamental sets, namely, stable and unstable.

An equivalence class $[x]$ is stable if it is open. In other words the equivalence class $[x]$ is stable if for every nuclear configuration $y \in [x]$ there is a neighborhood of y such that it is encompassed within $[x]$. Thus, a small perturbation does not remove y to a new equivalence class (or a small perturbation does not change the molecular structure). Suppose that $[x_1], [x_2], \dots, [x_l]$ ($l \leq k$) are all stable classes. The set $U = \Omega \setminus \cup_{i=1}^l [x_i]$ is called a catastrophe set. It is obvious that U itself is the union of $m = k - l$ classes. These classes are collectively termed unstable classes. Every unstable class $[x_i]$ has the property that for every nuclear configuration y within this class a small perturbation may render the new perturbed nuclear configuration into a new class. In other words, there is no neighborhood around the nuclear configuration y to be completely contained in $[x_i]$. In this regard, the configuration space is partitioned into disjoint regions, bounded by unstable (catastrophe) sets. This pattern is known as structural diagram.

4.4 Information of a structure as an invariant

Based on what mentioned in the last section, the topological analysis of a scalar function may be employed to determine the molecular structure of a molecular system. Since, the topological analysis of various scalar functions can be used to describe the molecular structure, one should consider these scalar functions as "structural descriptors". Suppose that Φ is a continuous dynamical system on the configuration space Ω . If F and G are two homeomorphic structural descriptors (for instance, virial field and charge density [6]) z is a nuclear configuration then based on the correspondence $z \mapsto F_z$ and $z \mapsto G_z$ the structures of the forms F_z and G_z are denoted by $[z]_F$ and $[z]_G$ respectively. The information of the structure $[z]_F$, in accordance with Definition 3.1, is defined as follows:

$$\mathcal{I}_{\Phi, m}([z]_F) := \sup_{\xi} \int_{[z]_F} \bar{S}_{\Phi}(x; \xi) dm \quad (4.5)$$

where $dm = dx_1 \dots dx_q$ is the Lebesgue (standard) measure on \mathbb{R}^q . Let the map

$$(x_1, \dots, x_q) \xrightarrow{h} (h_1, \dots, h_q)$$

be a homeomorphism on the space of forms and let Ψ be the dynamical system conjugate to Φ via the homeomorphism h , i.e., $\Phi h = h \Psi$. Then, combining (3.6) and change

of variables Theorem, one obtains

$$\begin{aligned}
 \int_{[z]_F} \bar{S}_\Phi(x_1, \dots, x_q; \xi) dx_1 \dots dx_q &= \int_{[z]_F} \bar{S}_\Psi(h(x_1, \dots, x_q); h(\xi)) dx_1 \dots dx_q \\
 &= \int_{h([z]_F)} \bar{S}_\Psi(hoh^{-1}(h_1, \dots, h_q); h(\xi)) \left| \frac{\partial(x_1, \dots, x_q)}{\partial(h_1, \dots, h_q)} \right| dh_1 \dots dh_q \\
 &= \int_{[h(z)]_G} \bar{S}_\Psi(h_1, \dots, h_q; h(\xi)) \left| \frac{\partial(x_1, \dots, x_q)}{\partial(h_1, \dots, h_q)} \right| dh_1 \dots dh_q.
 \end{aligned}$$

Now, taking supremum over all partitions ξ and using the notation $d\nu = \left| \frac{\partial(x_1, \dots, x_q)}{\partial(h_1, \dots, h_q)} \right| dm$ we have

$$\sup_{\xi} \int_{[z]_F} \bar{S}_\Phi(x; \xi) dm = \sup_{\xi} \int_{[h(z)]_G} \bar{S}_\Psi(h; h(\xi)) d\nu$$

or equivalently

$$\mathcal{I}_{\Phi, m}([z]_F) = \mathcal{I}_{\Psi, \nu}([h(z)]_G) \tag{4.6}$$

where $\nu = mh^{-1}$.

This is our main result of this section. This exhibits the relationship between the information content of the structures $[z]_F$ and $[h(z)]_G$, where h is the structural homeomorphism between F and G . One may apply (4.5) to define the information content of a form as well. Since $\mathcal{I}_{\Phi, m}([x]_F) = \mathcal{I}_{\Phi, m}([z]_F)$ for all $x \in [z]_F$, we may define the *information of a form* z to be

$$\mathcal{I}_{\Phi, m}^F(z) := \mathcal{I}_{\Phi, m}([z]_F). \tag{4.7}$$

In lights of the latter discussion, "all forms in a specific structure possess the same information content." With this in mind, we may rewrite the relation (4.6) in the following form:

$$\mathcal{I}_{\Phi, m}^F(z) = \mathcal{I}_{\Psi, \nu}^G(h(z)). \tag{4.8}$$

Let F be a structural descriptor of a molecular system and u be a nuclear configuration such that the form F_u is unstable, i.e., the dynamical system ξ_u determined by (2.1), with $\rho_u = F_u$, is unstable. Then, by definition of an unstable structure, there is no q -dimensional ball, centered at u , which is contained in $[u]_F$; so, if m is the standard measure on R^q we have

$$m([u]_F) = \int_{[u]_F} dm = 0.$$

Therefore, for any partition ξ

$$\int_{[u]_F} \bar{S}_\Phi(x_1, \dots, x_q; \xi) dm = 0.$$

Taking supremum over all partitions yields

$$\mathcal{I}_{\Phi,m}([u]_F) = 0.$$

This means that, "the information content of an unstable structure is zero".

5 Summary and discussion

In this report a rigorous definition of the information content of the molecular forms was propounded. The information content, as a function of the space of forms to the extended real line, depends on the structural descriptor of the molecular system, F , and dynamical system Φ on the space of forms (dependence on measure is not drastic since one should fix the standard measure on the space of forms). In this manner, this function may be referred to as Φ -information. Based on this definition all forms belonging to a specific molecular structure possess the same information and information content of each unstable form, independent of the properties of dynamical system Φ , which is zero. The most noteworthy feature of this definition is that the information content of each molecular structure is invariant under structural homeomorphism.

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