Some Remarks on the Concept of Molecular Topology

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Some general aspects of the concept of molecular topology are delt with. The role of the separability of topological and non-topological factors that determine molecular properties, as well as the "holistic" behaviour of certain classes of compounds are discussed. A suggestion regarding a deeper understanding of the role of molecular topology is made.

The *topology* of a molecule can be described as a neighbourhood (Hausdorff) topology defined in the vertex set of a (connected) molecular graph. The vertex set together with its neighbourhood topology forms the *molecular topological space*. It contains the totality of information about the mutual connectedness of all pairs of atoms of the molecule but it does not contain any information about the kind of atoms present and the geometry of the molecule (bond lengths and angles) [1].

It is now a well-established (but not at all trivial) fact that the physical and chemical properties of many chemical substances are related to the topological spaces associated with the molecules (see e.g. [2]). – In the present communication some more general considerations regarding the concept of molecular topology are presented.

All kinds of structural characteristics of a molecule that are not topological in nature will be termed *material* characteristics, i.e. kind of atoms present, bond lengths and angles, charge, etc. For sets of compounds three cases can be distinguished:

Case A: The material characteristics are constant within the set but topology varies ("isomaterial" sets of compounds, e.g. polynuclear benzenoid hydrocarbons [3]).

Case B: The material characteristics are different within the set but topology is constant ("isotopological" sets of compounds [1], e.g. the tricyclic spezies $P_7^{3\ominus}$ and PS_3As_3 [4, 5]).

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Case C: For pairs of compounds material characteristics are constant, topological characteristics are different, but the *topological relation* within a pair of compounds is always the same one ("topomeric" pairs of compounds [2, 6], e.g. o-benzoquinodimethane/p-benzoquinodimethane; phenanthrene/anthracene).

From the study of the three cases it has been concluded that topology determines significantly molecular properties. However, the evidential value of the three approaches is different and increases in the order $A < C < B$.

The main reason for the success of topological approaches in chemistry lies in the fact that for "related" molecules the influences of the material factors on molecular properties are *topology-invariant*. (The other way round, we can define "related" molecules as those where the influences of material factors on properties are topology-invariant.) In sets of molecules that meet this condition the influence of material and topological factors, respectively, on molecular properties must be regarded as independent from each other, i.e. as separable. For various kinds of molecular properties (including chemical reactivity, for a detailed discussion see [7]) the *separability of topological and material influences on properties* has been experimentally confirmed.

The application of purely topological quantum chemical methods (e.g. Hückel MO theory, Free-Electron Network model [8], Valence Bond Structure Resonance Theory [9]) to certain classes of compounds, e.g. polynuclear benzenoid hydrocarbons, has revealed (in agreement with experiment) that in many cases the electronic properties of the *individual atoms* of a molecule are directly related to the topology of the *entire molecule*. This well-established fact indicates that certain (predominantly large) molecules show the behaviour of "*holistic*" systems (for a profound discussion of the meaning of the term "holistic" in natural science see [10]). Although the holistic behaviour that the systems reveal in theory is simply a consequence of the algebra used in topological quantum chemistry, the amazement remains that the results obtained are in agreement with experimental findings.

The concept of molecular topology is clearly related to the idea that molecules have a molecular structure that determines the molecular properties. Despite their high degree of abstraction, the topological

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spaces associated with molecules (and being one of the factors that determine molecular properties) correspond to the pattern of electronic interaction in a "classical" molecule, i.e. a molecule (i) having a structure, (ii) with the electrons localized to a high degree (near to the nuclei), and (iii) without electronic interactions between non-neighboured centres. It seems now to be well-established that these features of classical molecule description cannot be derived (not even justified) by a quantum physical treatment starting from first principles [10–14] (although there are controversial views with regard to details [13]). On the other hand, chemistry provides an overwhelming amount of experimental evidence that at least larger molecules (roughly, systems containing ≥ 6 nuclei [11]) exhibit these classical (non-quantum physical) features. To "create" the classical features of molecules, quantum mechanics affords the introduction of superselection rules acting on the Hilbert space of state vectors [10, 14]. However, these superselection rules, derived from asymptotic approximations (the Born-Oppenheimer approximation being a well-known example) cannot be rigorously justified within the frame of quantum mechanics [10, 14].

Provided, the assumption is correct that the significance of the topological space for molecular properties cannot be explained in terms of quantum physics, then the following suggestion may be conceivable: The behaviour of molecules is governed by both quantum physics and a complementary "*Topological Principle*" that is related to the notion of coherence and order. If these speculations are relevant, some kind of relation should exist between the "Topological Principle" and the particular asymptotic approximation that formally would lead to the corresponding superselection rule.

A similar role of topology has been suggested in other fields of natural science, e.g. nuclear physics [15] and biology [16]. N. Rashevsky [16] in an article on "Topology and Life" says: "*Living systems manifest themselves through processes that are obeying all laws of physics, yet they seem to possess relational properties* (in another place of the article termed "relational or topological properties") *which while not contradicting them, do not follow necessarily from those laws*". Substitution of the term "living systems" in this sentence by "molecules" leads to the suggestion made in the present paper.

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