ENTROPIC INDICES OF CHEMICAL BONDS FROM INFORMATION THEORY

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Introduction

Communication Theory of Chemical Bonds (CTCB) has been recently formulated as a part of works on application of Information Theory to analysis of electronic structure of molecular systems. Within the former theory a molecule is interpreted as a communication system. The aim of present work was implementing of CTCB for computing the entropic bond indices based on typical Hartree-Fock results and testing the method on both molecular systems of well known bond structure and systems which still are subject to discussion in literature.

Communication Theory of Chemical Bonds

Within the CTCB a molecule is interpreted as a communication system of Information Theory. The source of input signal is defined through a set of atomic orbits of atoms forming the reference pro-molecule and a set of input probabilities $P_k$ of finding an electron on orbit $k$. Similarly, an output of a communication channel is defined through a corresponding set of atomic orbits with related output probabilities $P'_k$. The information flow through a communication channel is attributed to changes in electron occupations of particular atomic orbits in the molecular system. Information is scattered in the communication channel, and the noise in the CTCB is related to delocalization of electrons. The conditional entropy $S$ is measuring the amount of such scattering, thus it may be treated as a "covalency" index of molecular system:

$$ S = S(\gamma|\psi) = -\sum_{k=1}^{N} \sum_{l=1}^{N} P_k P'_l \log(\frac{P_k P'_l}{P'_k P_l}) $$. 

In such a communication channel the conditional entropy and mutual information are both functions of the so called binary entropy $H(P)$ and $I(P;Q)$:

$$ S = H(P) = -\sum P \log P - (1 - P) \log(1 - P) $$

$$ I = I(P;Q) = \sum P \log \frac{P}{P'}. $$

The sum of both indices is constant and equal 1.

Entropic covalence and ionic components of chemical bond

In order to compute the entropic components of chemical bond the communication channel has been defined in which the binary 2-AO channels are connected in parallel. The contributions of particular sub-channels to propagation of information was assumed to be proportional to the squares of the corresponding elements of the charge- and bond-order matrix (no need for extra computing the reference pro-molecule data) and easy interpretation of results (they provide both the ionic and covalent components of the chemical bond).

Degree of entropic covalency and ionicity of a chemical bond

In the case of highly polarized bonds the total IT bond indices assume small, fractional values; in such cases it is recommended to compute the relative shares of IT covalency and ionicity of the total entropic bond index:

$$ \delta_{AB} = \frac{\delta_{IT}^{covalent}}{\delta_{IT}^{covalent} + \delta_{IT}^{ionic}} \quad \gamma_{AB} = \frac{\gamma_{IT}^{covalent}}{\gamma_{IT}^{covalent} + \gamma_{IT}^{ionic}} = 1 - \delta_{AB}. $$

Results

The proposed entropic covalency and ionicity IT bond indices and related degrees of informational covalency and ionicity, based on the 2-AO model, have been tested on several simple molecular systems. The RHF one-electron density matrices in orthogonalized OAO bases were obtained using the familiar GAMESS quantum chemical package.

Analysis of degree of the IT covalency and ionicity in diatomic molecules

Figure 1. Panel a) The values of ion and covalent components of entropic bond indices and the Wiberg bond index are shown for the series: HF, HCl, HBr and HI. "covalency" denotes the degree of covalency. Panel b) Similar data for the series NeH, NaF, NaCl, NaBr, NeI.

Bond order indices in simple hydrocarbons

Figure 2. Values of the IT bond indices for the series: ethene, ethylene, hydrocarbons. Blue: the entropic covalency component of the bond; green – the ionic component; black – Meyer and red – Nalewajski-Mrozék bond indices.

Analysis of bond orders in small propellanes

Figure 3. Values of the IT bond indices for the series of small propellanes. Blue: the entropic covalency component of the bond; green – the ionic component; black – Meyer and red – Nalewajski-Mrozék bond indices. have been added for comparison in the case of the bonds between the bridgehead atoms.

Conclusions

The results obtained show that the concepts of entropic covalency and ionicity well correspond to their classical counterparts. One may assume that entropic effects are playing an important role in process of forming chemical bonds and may be used in evaluation of reactivity in molecular systems. The proposed entropic bond indices are an interesting alternative to the other methods used for direct studying the character of chemical bonds in the molecules, due both to the computational simplicity (no need for extra computing the reference pro-molecule data) and easy interpretation of results (they provide both the ionic and covalent components of the chemical bond).

Literature

- N. Abramson, "Teoria informacji i kodowania" 1969, PWN.