Application of Orbital Communication Theory of Chemical Bond

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ABSTRACT: *Communication Theory of Chemical Bond* (CTCB) has recently been formulated as a part of work on using *Information Theory* (IT) in probing molecular electronic structure. This IT-approach to chemical bond is based on the Shannon theory of communication and provides tools for describing bonding patterns in both the ground and exited electron configurations.

The key concept of CTCB is the molecular information system, in which a molecule is interpreted as a communication system of Information Theory. The source of input signal is defined through a set of atomic orbitals, atoms or fragments, $\boldsymbol{a} = \{a_i\}$, and vector of input probabilities of finding an electron on particular orbital (or atom/fragment), $\boldsymbol{p} = \{p_i\}$. Similarly, an output of a communication channel is defined through a corresponding set of atomic orbitals, atoms or fragments, $\boldsymbol{b} = \{b_j\}$, and its probability vector, $\boldsymbol{q} = \{q_j\}$. The communication channel in the CTCB is uniquely determined by conditional probability matrix $\boldsymbol{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(b_j|a_i)\}$, where element $P(b_j|a_i)$ denotes probability of finding on b_j (output) electron derived from a_i (input).

In the CTCB the information flow through a communication system is attributed to changes in electron occupations of particular atomic orbits in the molecule. Information is scattered in the communication channel, and the noise in the CTCB is related to delocalization of electrons. The conditional entropy, $S(\boldsymbol{b}|\boldsymbol{a})$, measures the amount of such scattering (in bits), thus in CTCB it is treated as a IT covalency index of molecular system and the mutual information, $I(\boldsymbol{a}:\boldsymbol{b})$, is measuring the amount of information which passes through the communication channel, thus it is specifying to what a degree electrons are attributed to particular atoms. Then, one may assume that it reflects the IT ionicity of the communication channel. The special case of CTCB in which input/output events and related probabilities are defined in basis-set orbital resolution is called the *Orbital Communication Theory* (OCT).

HF/DFT one-electron density matrices in orthogonalized bases were obtained using the familiar GAMESS quantum chemical package. 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. Novel information descriptors 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).

KEYWORDS: chemical bond · entropic bond descriptors · communication systems · atom-inmolecule · information theory · bond covalency · bond ionicity · electronic structure · bond multiplicity · bond order · molecular fragments · reduced molecular channel · bond entropy

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