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Properties of molecular structures by quantum energy density analysis

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The chemical system is characterized by electronic distribution (determined by wave function) that links and unites the net of atomic nuclei. Such molecular connectivity possessing electronic origin may exhibit different (covalent or non-covalent) nature.

It is needed to evaluate interaction properties in order to better understanding of mechanisms that rule our experiments. This knowledge helps to interpret experimental results and planning new experiments. For example, does the hydrogen bond (h-bond, for short) is not covalent but rather physical interaction (like vdW)? There have been distinguished several types of h-bond like interactions: usual h-bonds involving lone pairs of O and N atoms, other involving halogen ions, or noble gases[1], or as extraordinary as interaction with π -electrons (or similar interactions although without proton bridge [2]) and dihydrogen bonds. They all seem to have slightly different origin. How to generalize the model for such interactions to make clear and unify definition as in case of covalent, ionic or metallic bonds? Some phenomena related with h-bond (covalency in ice [3], existence of cooperative effects due to charge flow between h-bonds [4], electron transfer, dipole models) cause difficult questions for modeling. There are opponents of electrostatic character as well as partial covalency of hydrogen bond. Although many concepts have been applied to explain the mechanism of formation of this particular interaction (i.e. Coulson “ionic resonance”, Lewis donor-acceptor concept, Pauling’s model or Bader atoms in molecules theory) many doubts remain. As benzene molecule has its own structure and can not be composed of structural elements from other molecules in exact way, in the same fashion hydrogen bond needs its own idealized, working model. Many correlations between h-bond energy and other parameters are known [5]. However, before the generalized model might be obtained, the common points have to be extracted for all interaction patterns, from leading terms in interaction energy to electronic properties and quantum effects.

The electronic interactions expressed in terms of the new quantum energy density analysis provide reliable evaluation of inter-atomic and inter-molecular bonding. Rational utilization of properties of “hard” and “soft” molecular structures leads to cheaper and more efficient chemistry and opens way to new materials and technologies.

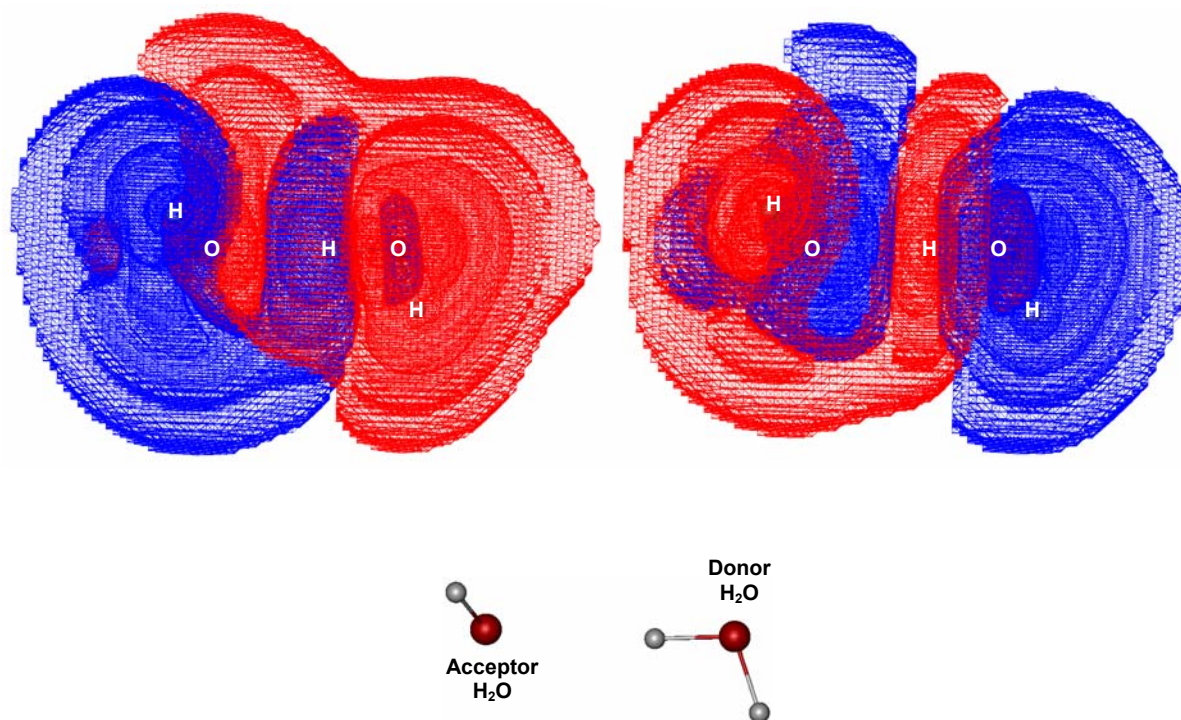


Figure 1. Hydrogen bond in water dimer: a) electron density change in system as a difference of dimer electron density and densities of monomers; blue corresponds to regions of decreased electron density (hydrogen atoms of acceptor water molecule and bridging proton), while red indicates increase of electron density (lone pairs of oxygen atoms and O-H bond between donating O atom and bridging H atom); b) Stabilization Energy Density; blue areas denote local stabilization and red – local destabilization of bonding interaction; destabilization is mainly caused by withdraw of electrons from the local area.

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