The method for observation of the bond reorganization on the reaction path

Mateusz Jędrzejewski

Streszczenie (EN)

The starting point of the research were the concepts of Ordon and Tachibana for determining the evolution of supermolecule reactivity along the IRC trajectory. The first extension of these ideas was to represent the reaction force and reaction force constant at atomic resolution. Assigning atomic contributions to the reaction force allowed to identify atoms that travel the longest distance during a chemical change but did not allow for identification the accompanying variations in electron density. Also, extending the method to the second derivative of the reaction progress number ξ (the reaction force constant) did not bring the expected effect. The interesting results obtained in this way were limited only to global quantities, i.e., those characterizing the supermolecule as a whole; this point of view is of little use for structural analysis in chemistry.

The most important element of this work is the numerical implementation of the concept of reaction fragility of atoms and bonds. This computational scheme allows for tracking the mechanism of a chemical reaction, i.e. the sequence of breaking and forming bonds along the IRC trajectory, additionally providing the value of the reaction coordinate for which a specific transformation occurs. The representations of the reaction susceptibility spectrum at atomic resolution and bond resolution are unambiguous because they result from the definition of the Hellmann-Feynman force.

The second logical step was to recognize the properties of the DFT connection matrix, i.e., a square matrix of dimension n (the number of atoms in the system), whose expressions are the divergences of H-F forces acting on the nuclei, which depend directly on the electron density function. These divergences, as scalar products, are independent of the transformation of the coordinate system (shift or rotation); the evolution of the elements contained in the density matrix along the reaction path directly carries information about the changes in electron density around each atom at the next step of the reaction.