Global Conceptual DFT Reactivity Indexes Redefined

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Classical organic chemistry is built around the concepts of electrophilicity and nucleophilicity. These kinetic notions define the propensity of molecules to undertake certain chemical reactions. Understanding and predicting the reactivity of various electrophiles and nucleophiles is of critical relevance. From the conceptual DFT perspective, notable attempts have been made to establish global electrophilic indices, such as the electrophilic index,[1] electrodonating and electroaccepting powers,[2] and net electrophilicity.[3] Defining a nucleophilic index, on the other hand, proved to be more difficult than defining an electrophilicity index. All of the reactivity descriptors introduced so far are based on the quadratic expansion of energy in some way. In the present work, a new definition for reactivity indices is proposed based on a cubic interpolation of the energy. The proposed index depends on the definition of chemical potential: $\mu = \alpha I + (1-\alpha) A$, where I is the ionization potential, A is the electron affinity and α is some parameter between 0 and 1. As usual the frozen orbital approximation is used to obtain I and A. Therefore, the result depends on the quality of the respective I and A. Numerical support for this descriptor were presented for 316 electrophiles (149 charged and 167 neutrals) and 386 nucleophiles taken from the Mayer's database of reactivity parameters. Furthermore, the current index can generalize previous works.

References
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