Independent Gradient Model: a new approach for probing strong and weak interactions in molecules from wave function calculations


Abstract: Extracting the chemical interaction signature from local descriptors based on electron density (ED) is still a fruitful field of development in chemical interpretation. In a previous work using promolecular ED (frozen ED), the new descriptor δ\(\gamma\) was defined. It represents the difference between a virtual upper limit of the ED gradient (\(\nabla P\)) and the true ED gradient (\(\nabla \rho\)). It can be seen as a measure of electron sharing brought by ED contragradience. A compelling feature of this model is to provide an automatic workflow that extracts the signature of interactions between selected groups of atoms. As with the NCI (Non Covalent Interaction) approach, it provides chemists with a visual understanding of interactions present in chemical systems. \(\nabla P\) is achieved simply by using absolute values upon summing the individual gradient contributions making up the total ED gradient. Hereby, we extend this model to relaxed ED calculated from a wave function. To this end, we formulate the Gradient-Based Partitioning (GBP) to assess the contribution of each orbital to the total ED gradient. We highlight these new possibilities across two prototypical examples of organic chemistry: the unconventional hexamethylenediamine dication involving a hexa-coordinated carbon atom and the \(\beta\)-thioaminoacrolein. It will be shown how a bond-by-bond picture can be obtained from a wave function opening the way to monitor specific interactions along reaction paths.

Introduction

A number of tools have been derived from the analysis of the electron density \(\rho\) in a molecular system, e.g. QTAIM[1] (Quantum Theory of Atoms in Molecules), ELF[2] (Electron Localization Function) and LED[3] (Localized Electron Detector). Such techniques are useful for the interpretation of quantum chemical computations by extracting pieces of information that may be connected to simple concepts used by chemists such as atoms linked by bonds. The implementation of such analysis may also provide a valuable theoretical support to challenging experimental electronic structures. The NCI[4] approach, another local ED-based descriptor developed by one of the present authors, is one of the modern tools for chemical bonding analysis. It is exclusively given in terms of electron density \(\rho\) (ED) and its gradient. Although NCI is able to reveal covalent bonding patterns,[5] it is usually devoted to the visualization of weak interactions where previous tools were conspicuously failing. This approach provides a direct three-dimensional representation in the form of closed domains that highlight the spatial localization of the interactions within the chemical system. In these pictures, through the application of the NCI index, the nature of the interaction can be visually associated in practice to a color code directly related to electron density derivatives: red for strongly repulsive, green for van der Waals, and blue for strongly attractive interactions. Amongst others, NCI applications cover organic chemistry,[6] inorganic chemistry,[7] biomolecules,[8] solids[9] and crystallography.[10] The original formulation of NCI, although very useful to detect the existence of non-covalent interactions, has only a semi-quantitative value. One of the present authors has previously published results where the integration of an ED function over non-covalent regions reproduces rather well the hydrogen-bonding potential of selected dimers along the whole energy potential (infinite distance, equilibrium distance and repulsion wall).[11] More recently, G. Saleh et al.[12] have obtained good correlations between complex stabilization energies and kinetic energy densities integrated within reduced density gradient isosurfaces. However, these relations are limited to dimer interactions having a similar physical origin. In a very recent development,[13] considering a frozen electron density (promolecular density), we have proposed a supplementary tool, denoted “IGM” (Independent Gradient Model), which leads to another non-interacting reference. It has been also associated to the ED gradient, leading to the new descriptor \(\delta\gamma\) that identifies and quantifies the ED gradient softening due to interaction. Compared to NCI, an attractive feature of this new methodology is to provide a workflow that automatically extracts the signature...