PRINCIPLES AND APPLICATION OF THE SELF-CONSISTENT HIRSHFELD ATOMS-IN-MOLECULES METHOD.

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The view of molecules as combinations of atoms being held together by chemical bonds is prominent and successful in all fields of chemistry. It is not surprising that the partitioning of the electron density of molecules into atomic contributions has been much discussed in literature[1]. One of the most straightforward and clear-cut schemes for partitioning the electron-density is the Hirshfeld population analysis[2].

Several difficulties, among which the arbitrariness in the choice of the reference- or pro-molecule is the most important[3], are analyzed and a solution for these difficulties is found in an alternative, iterative version of the Hirshfeld scheme. This iterative Hirshfeld scheme will be explained and its ability to overcome the difficulties that occur with the 'classical' Hirshfeld are demonstrated[4]. Furthermore, it is shown that iterative Hirshfeld charges are less basis set dependent than the classical' Hirshfeld method[5].

The iterative Hirshfeld method has been used to calculate atom condensed Fukui functions. The different procedures to obtain atom condensed Fukui functions are described. It is shown how the resulting values for atom condensed Fukui functions differ, depending not only on the partitioning method used, but also by the way we define the atom condensed Fukui function. The condensed Fukui function can be computed using either the fragment of molecular response approach (FMR) or the response of molecular fragment (RMF) approach. The two approaches are non-equivalent, only the RMF approach corresponds with the widespread method of calculating the difference in atomic populations. The different resulting expressions are tested for a wide set of molecules. In practice one must make an seemingly arbitrary choice about how to compute condensed Fukui functions, which might questions objectivity of these indicators in conceptual density-functional theory[6].

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