Calculating Hirshfeld-I charges in solids: Implementation, pitfalls and applications

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The concept of ``Atoms in molecules'' (AIM) is one of the most successful concepts in chemistry. It basically assumes that the properties of a molecule are simple sums of the properties of the individual atoms. Although a precise definition of an AIM remains elusive, its usage has provided an impressive wealth of insight over the years. Central to its definition, is the question of how one should divide the electron density of the system over its AIMs. Such a division can be done either in Hilbert-space (*e.g.* Mulliken population analysis) or in real space (*e.g.* Bader's QTAIM). Many such partitioning schemes have been developed and used to study molecules. It is only in recent years that interest has started shifting to also include solids. Recently, the Hirshfeld and Hirshfeld-I (HI) [1] partitioning schemes have been implemented for solids. In this scheme the AIM do not have a sharp boundary, as in the QTAIM case; instead they have a diffuse boundary introducing overlap between neighbouring AIM's.

In this work, we present how the molecular Hirshfeld-I scheme can be extended to (infinite) periodic systems, making use of grid stored charge density distributions only,[2,3] since these can easily be obtained from standard solid state codes. This makes our implementation independent of the particular implementations used in the solid state code.

We will discuss the (conceptual) problem which occurs during the practical generation of the reference anions, and propose several ways to tackle this problem. Using a large set of benchmark molecules, we establish the quality of our implementation, and show the robustness of the partitioning scheme.

With the method established, we turn our attention to actual solids and large periodic systems. We show that the calculated charges allow for the differentiation of oxidation states (e.g. Ce^{III} and Ce^{IV} in ceria, and V^{III} and V^{IV} in different metal organic frameworks (MOFs)) and inequivalent atomic sites (e.g. graphite and O in Ce_2O_3).[2,3] We also investigate the propagation of charge transfer due to the presence of dopants (e.g. in CeO_2) or functional groups (e.g. in the MIL-47 MOF) in the system.[4] These few applications show that the Hirshfeld-I AIM is a useful tool in the study of solids, providing additional insight in the way a system is modified by the presence of defects, interfaces, functional groups etc.

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