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 states that the properties of a molecule can be considered as simple sums of the properties of its constituent atoms. Although a precise definition of an AIM remains elusive, an impressive amount of insight has, over the years, been gained through its usage. The central question in the AIM concept is how one should divide the electrons of the system over its constituent "atoms". Such a division can be done either in Hilbert-space (e.g. Mulliken population analysis) or in real space (e.g. Bader's QTAIM). Over the years, many different partitioning schemes have been developed and have been employed in the study of molecules. In recent years, the solid state community has started to show an increasing interest in using the AIM concept for the investigation of solids. Bader's QTAIM approach has received much interest in this context, since this approach is well suited for the close packed nature of solids. Recently, also 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 allowing for overlap between neighboring 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,[23] since these can easily be obtained from standard solid state codes. This makes the implementation independent of the basis set 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. $\mathrm{Ce}^{\mathrm{III}}$ and $\mathrm{Ce}^{\mathrm{IV}}$ in ceria, and $\mathrm{V}^{\mathrm{III}}$ and V^{IV} in different metal organic frameworks (MOFs)) and inequivalent atomic sites (e.g. graphite and O in $\mathrm{Ce_2O_3}$).[23] We also investigate the propagation of charge transfer due to the presence of dopants (e.g. in $\mathrm{CeO_2}$) 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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