

Chemistry in Solids; Extending the Hirshfeld-I method.

Danny E. P. Vanpoucke, Patrick Bultinck, Isabel Van Driessche

*Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan
281-S3, 9000 Ghent, Belgium. Danny.Vanpoucke@Ugent.be*

ABSTRACT The concept of “atoms in molecules” (AIM), is probably one of the most successful concepts in chemistry. It states that the properties of a molecule can be seen as simple sums of the properties of the molecules’ constituent atoms. This shows that the concept of AIM is strongly linked to the concept of transferability. Since both are central in chemistry, and chemists mainly focus on molecules, they are generally used to investigate molecules. There is, however, no reason why these concepts should not hold for solids. Even more, if these concepts are truly valid, they should work equally well for solids as for molecules and thus provide additional insight in the chemical properties of defects such as dopants and interfaces.

The AIM concept is centered around the question of how one should divide a molecule, or more general a system, into “atoms”. Practically, this means dividing the electrons. In real-space one divides the charge density distribution, either using non-overlapping regions (*e.g.* Bader’s approach) or overlapping regions (*e.g.* Hirshfeld and derived methods).[1, 2, 3]

We have implemented an extension of the iterative Hirshfeld-I approach to periodic systems.[4] This implementation makes use of precalculated pseudo-potential based charge density distribution grids. We show how the accuracy is influenced by the used grid spacings, and that the use of pseudo-potentials has no negative influence on the results. We identify a delocalization problem due to the use of plane waves and periodic boundary conditions, and present a simple and satisfactory solution.

This extension of the Hirshfeld-I method allows for the easy calculation of atomic charges and charge transfer in periodic systems, such as wires, surfaces and bulk materials.

References:

- [1] Bader, R. F. *Chem. Rev.*, 91 (1991) 893–928
- [2] Hirshfeld, F. L. *Theoret. Chim. Acta* 44 (1977) 129-138
- [3] Bultinck, P., Alsenoy, C. V., Ayers, P. W., and Carbo-Dorca, R. *J. Chem. Phys.* 126 (2007) 144111
- [4] Vanpoucke, D. E. P., Bultinck, P., and Van Driessche, I.
Extending Hirshfeld-I to bulk and periodic materials
submitted to J. Chem. Theory Comp. (2011)