A periodic calculation for a periodic system: Using projector augmented wave densities as basis for Hirshfeld Atom refinement.

Paul Niklas Ruth

Durham University, Chemistry Department, Durham, UK
panikruth@gmail.com

Keywords: Hirshfeld atom refinement, hydrogen atom positions, periodic calculations

In 1993 Peter Blöchl proposed the projector augmented wave method [1], which combines the convergence properties of pseudo-potential based methods with the benefits of projector based methods. Of major interest in this context is the availability of the all-electron density. I want to present the applicability of this method as a basis for the calculating the atomic form factors in Hirshfeld atom refinement.

Having been originally proposed in 2008, Hirshfeld atom refinement [2-3] uses atomic densities derived by Hirshfeld partitioning [4]. So far the calculation has so far mainly conducted using densities from non-periodic calculations. After one initial non-iterative publication by Wall [5], the potential of projector augmented waves remained largely unexplored.

I want to remedy this fact, as the periodic calculation yields hydrogen bond distances with superior agreement to X-H distances derived from neutron diffraction [6]. While the computation time is higher than neglect of the crystal environment or a classical description in the form of charges surrounding the calculated molecules, it is still significantly faster than describing even one shell of surrounding molecules fully quantum mechanically. This can clearly be seen with the comparison of different refinements of the L-Alanin molecule presented in Figure 1.

In addition to refinement results I want to introduce a software which interested viewers can use to apply the method to their own crystallographic structures.

Figure 1. Results of the Hirshfeld atom Refinement of already published X-ray diffraction data [7] of the L-Alanin molecule using the PBE functional. Naming of the individual rows is composed of the quantum mechanical software used for the calculation of the density. Following in the brackets is the approximation of the crystal environment where: pbc: periodic boundary conditions using PAW; None: no description of the crystal environment. 4 Å cc: 4 Å of cluster charges and QM: Cluster of molecules, which were calculated using a full quantum mechanical calculation. Finally the last entry denominates the basis, where GPAW uses a real-space grid spacing and Quantum Espresso uses a plane wave basis with the given energy cut-off and ORCA uses the given basis set. Agreement to neutron values [8] is given as box-whisker plot.