A Periodic Density Source for a Periodic System: Using PAW-DFT for Hirshfeld Atom Refinement

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In 2008 Jayatilaka and Dittrich proposed the method of Hirshfeld Atom Refinement [1]. The method relies on calculating a density by theoretical methods and subsequently splitting it up by Hirshfeld stockholder partitioning [2]. The partitioned atomic densities are then used to calculate the atomic form factors for the refinement of positions and displacement parameters against X-ray diffraction data. Previous implementations used non-periodic calculations to obtain the density, which is subsequently partitioned into the individual atomic contributions.

We have implemented Hirshfeld Atom Refinement using partitioned periodic densities calculated in the projector augmented wave DFT method using the NUMPY/JAX/GPAW libraries in PYTHON. To our knowledge, this is the first implementation of an iterative approach for the Hirshfeld Atom Refinement scheme using periodic DFT calculations as the source of the atomic form factors. The scripted approach allowed us to evaluate twelve DFT functionals on five different structures for their performance in the reproduction of X-H distances and hydrogen displacement parameters from neutron data and identify the SCAN/revSCAN functionals to perform favourably for the evaluated X-ray datasets. Additionally, we could show that the more sophisticated source for the density did reveal anharmonic vibration patterns in a refinement of the urea molecule, which were fitted with Gram-Charlier parameters for oxygen and nitrogen (Figure 1).

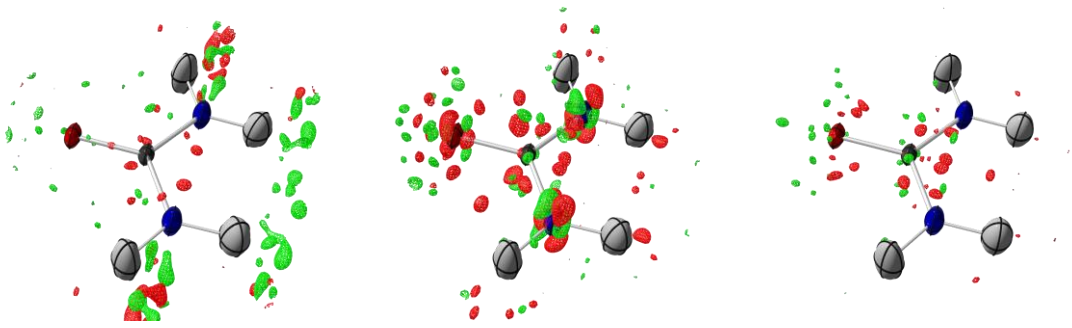

Fig. 1: Results of Hirshfeld Atom Refinement with different models for the crystal field. Cluster charge embedding / B3LYP (left), periodic PAW-DFT / SCAN (centre) and periodic PAW-DFT / SCAN with Gram-Charlier parameter refinement (right).

[1] D. Jayatilaka, B. Dittrich, X-ray structure refinement using aspherical atomic density functions obtained from quantum-mechanical calculations, Acta Cryst., A64, 383, (2008). doi: 10.1107/S0108767308005709.

[2] F. Hirshfeld, Difference densities by least-squares refinement, Acta Cryst., B27, 769, (1971). doi: 10.1107/S0567740871002905.

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