MS36 Software development in quantum mechanics-based methods of crystallography

MS36-04

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

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Abstract

Hirshfeld atom refinement was first conceived in 2008, when Jayatilaka and Dittrich proposed using the Fourier Transform of atomic densities, which are obtained by Hirshfeld stockholder partitioning (Hirshfeld, 1971) of theoretically derived densities (Jayatilaka & Dittrich, 2008) source for atomic form factors used in the refinement against X-ray diffraction data. Previous implementations used non-periodic calculations to obtain the density, which is subsequently partitioned into the individual atomic contributions.

Using the Numpy/Jax/GPAW libraries in Python we have built a new refinement library called XHARPy, which enables users to do Hirshfeld Atom Refinement using partitioned periodic densities calculated in the projector augmented wave DFT method (Ruth *et al.*, 2022), in addition to refinement against Hirshfeld densities from non-periodic source via NoSpherA2 (Kleemiss *et al.*, 2021). A basic command line interface is also available.

In an evaluation of the accuracy of the determined atomic displacement parameters and bond lengths of hydrogen from X-ray data (Birkedal et al., 2004) for urea, the periodic description compares favourably to non-periodic descriptions using cluster charges (Figure 1) in the reproduction of results from neutron diffraction (Swaminathan *et al.*, 1984). Evaluated quality indicators were: The crystallographic agreement factor $wR_2(F^2)$, the absolute difference between neutron diffraction and HAR derived X-H bond distances $|\Delta r|$, the absolute difference between atomic displacement parameters $|\Delta U_{ij}|$ and the disagreement of the resulting probability distributions S_{12} (Whitten & Spackman, 2006).

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Comparison of Hirshfeld atom refinement methods