



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

Paul Niklas Ruth, Regine Herbst-Irmer, Dietmar Stalke

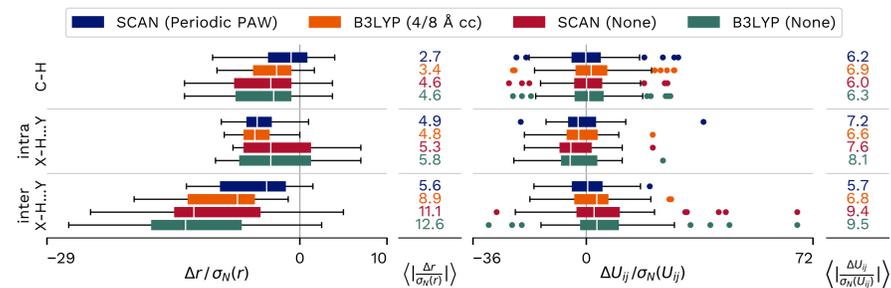
Institute of Inorganic Chemistry, University of Göttingen, paul-niklas.ruth@chemie.uni-goettingen.de



## Introduction

So far, Hirshfeld atom refinement has been conducted using non-periodic theoretical approaches to calculate the density, which is subsequently split up into aspherical atomic form factors. We have demonstrated the application of the method with densities from periodic projector augmented wave DFT [1].

The method particularly benefits from the fact that no fragment needs to be chosen. In an evaluation against neutron bond lengths and ADPs for five structures, this was demonstrated by comparing X-H distances of hydrogen bonds, where the acceptor is not located within the calculated fragment (inter X-H...Y) for the non-periodic calculation. The effect was below the significance threshold for H atoms outside hydrogen bonds (C-H) and non-existent for hydrogen bonds, where the acceptor is located within the calculated fragment (intra X-H...Y).

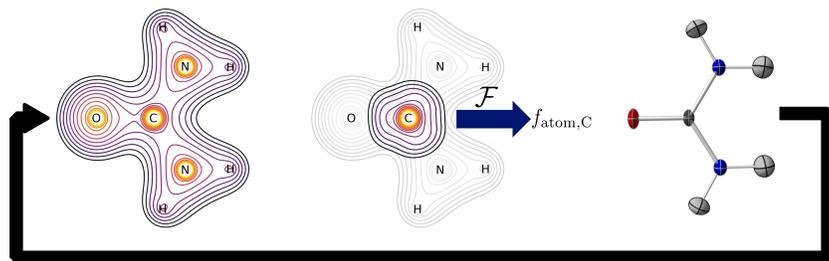


Evaluation of X-H distances and hydrogen ADPs for five structures against neutron values. Differences are divided by the estimated standard deviations from the neutron refinement Calculation methods: SCAN (Periodic PAW), XHARPy/GPAW; B3LYP (4/8 Å cc), NoSpherA2/Tonto; SCAN/B3LYP (None), NoSpherA2/ORCA. Figure was first published in [1].

## Basic principle

The refinement follows the conventional Hirshfeld Atom Refinement Scheme [2].

1. Calculate a density
2. Hirshfeld partitioning for atomic densities, Fourier transform for atomic form factors
3. Crystallographic refinement with calculated aspheric atomic form factors

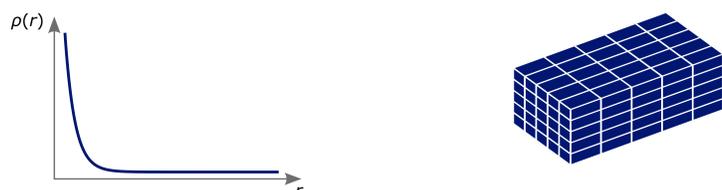


Repeat until atomic positions are converged

## Separation of density

As the core density is highly localised near the atomic positions, it would require a more thinly spaced regular grid. In accordance with the treatment within the DFT calculation, the core density is therefore treated separately from the valence density.

$$f_{0j}(\mathbf{S}) = f_{0j,\text{core}}(|\mathbf{S}|) + f_{0j,\text{valence}}(\mathbf{S})$$



The core atomic form factors are calculated by discrete Fourier-Bessel transform of the frozen core density on a spherical grid. Core density is completely assigned to the respective atom.

The valence density of the unit cell is evaluated and partitioned on a regular grid. Atomic valence form factors are calculated by FFT.

## Literature and Funding

- [1] P. N. Ruth, R. Herbst-Irmer, D. Stalke, *IUCrJ* **2022**, *9*, 286.  
 [2] S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky, D. Jayatilaka, *IUCrJ* **2014**, *1*, 361.  
 [3] H. Birkedal, D. Madsen, R. H. Mathiesen, K. Knudsen, H.-P. Weber, P. Pattison, D. Schwarzenbach, *Acta Cryst.* **2004**, *A60*, 371.  
 [4] F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327.  
 [5] F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschnann, S. Grabowsky, *Chem. Sci.* **2021**, *12*, 1675.  
 [6] A. E. Whitten, M. A. Spackman, *Acta Cryst.* **2006**, *B62*, 875.  
 [7] S. Swaminathan, B. M. Craven, R. K. McMullan, *Acta Cryst.* **1984**, *B40*, 300.  
 We are grateful for the scientific and financial support by the research training group 2455 "Benchmark experiments for numerical quantum chemistry", which is funded by the DFG.

## The XHARPy Python library

This custom refinement library was built from scratch in pure Python, using JAX for automatic gradient generation. Currently available are atomic form factor generators using GPAW and experimental implementations using Quantum Espresso and NoSpherA2/Orca.



Available at:  
<https://github.com/Niolon/XHARPy>

Current crystallographic features include:

- Refinement of SHELXL style extinction
- Special position constraints from a .lst file
- Manual entry of special position constraints
- Gram-Charlier refinement up to fourth order

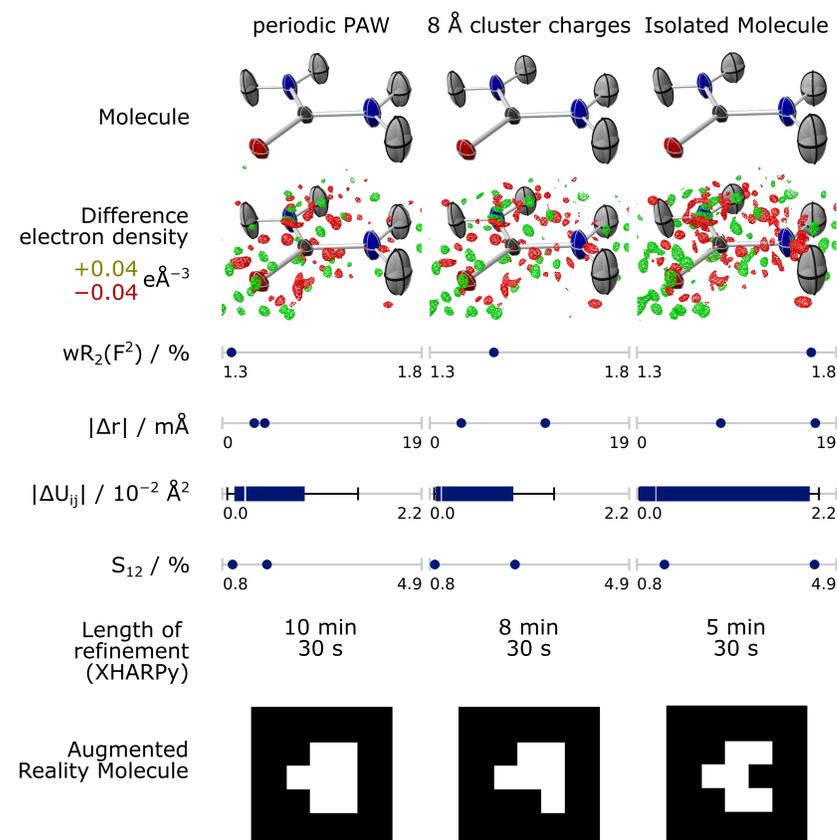


## Refinement of Urea

Within the XHARPy library we refined against the same literature urea data [3] three times. Periodic PAW used the SCAN functional at the  $\Gamma$ -point and a real-space grid size of 0.175 Å, which was interpolated to one fourth for the partitioning and atomic form factor calculation. The cluster charge and isolated molecule calculation used the B3LYP functional with a def2-TZVPP basis set in ORCA [4] and NoSpherA2 [5] for Hirshfeld partitioning and Fourier Transform.

All structures showed the typical Gram-Charlier "Shashlik" pattern and therefore have been refined with fourth order Gram-Charlier parameters for nitrogen and oxygen.

$|\Delta r|$ ,  $|\Delta U_{ij}|$  and  $S_{12}$  [6] have been calculated in comparison to the neutron values from literature [7].



## Augmented reality on this poster



To access the augmented reality structures on this poster, go to the website behind this barcode and point the camera onto the square markers. Tested with Safari on iOS and Chrome/Firefox on Android.

Works with JavaScript using a-frame/ARjs and ShelXle .obj file export.

The following structures are examples of refinement results of the PAW-HAR method with the XHARPy package.

Sodium chloride



L-Alanin



Hexaqua magnesium maleate

