Invited Lecture

The quest for more accurate Hirshfeld atom refinement related methods.

M. Chodkiewicz[1], L. Patrikeev[1], S. Pawlędzio[1,2], K. Woźniak[1]

[1]Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, Warszawa 02-089, Poland, [2]Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ml.chodkiewicz@uw.edu.pl

A modified version of the Hirshfeld partition of the electron density, exponential Hirshfeld, is introduced for use in Hirshfeld atom refinement (HAR)[1]. Its application in HAR (expHAR) sometimes significantly improves the accuracy of hydrogen atom parameters (Fig. 1).

It is demonstrated that reduced accuracy of ADPs of a hydrogen's bonding neighbour may prevent an accurate determination of the hydrogen atom ADPs with HAR. Atomic electron densities partially overlap and the inaccuracies in ADPs of non-H atoms can be partially compensated with modifications to the ADPs of the neighboring H-atoms.

The new partition leads to less overlapping atomic densities. As a result, hydrogen atom parameters are less dependent on the structural parameters of their neighbours and their inaccuracies. The proposed method is parameterized with an adjustable parameter n which allows control of the level of overlap of atomic electron densities and for n=1 it is equivalent to the Hirshfeld partition.

The new partition is also applied in the Transferable Hirshfeld Atom Model (THAM)[2], which uses atomic electron densities that are precalculated and stored in a databank for further use in refinement. THAM avoids the time-consuming step in HAR - wave function calculation – but allows for refinement with similar accuracy as HAR or even higher when used with the exponential Hirshfeld partition.

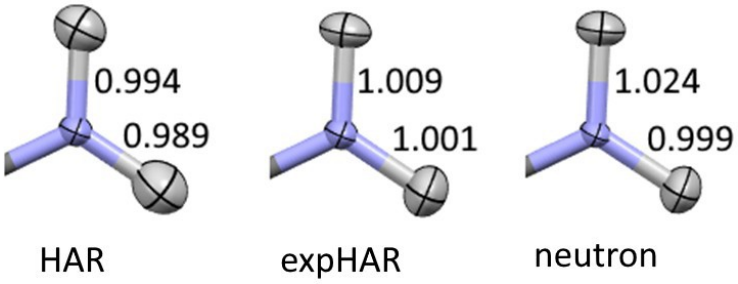

Figure 1. A comparison of carbamazepine structure fragment derived using HAR, expHAR, and neutron refinement (X-ray data and neutron structure taken from [3]). The numbers shown represent bond lengths in Å.

[1] Jayatilaka, D. & Dittrich, B. (2008). *Acta Cryst.* **A64**, 383

[2] Chodkiewicz, M., Patrikeev, L., Pawlędzio, S. & Woźniak, K. (2024). *IUCrJ*, **11**, 249.

[3] Sovago, I., Gutmann, M. J., Senn, H. M., Thomas, L. H., Wilson, C. C. & Farrugia, L. J. (2016). Acta Cryst. B72, 39.

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