Testing various variants of Hirshfeld atom like refinement.

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Hirshfeld atom refinement (HAR)[1,2] is one of the most successful methods for the accurate determination of structural parameters for hydrogen atoms from X-ray diffraction data. It employs atomic scattering factors based on atomic densities obtained via Hirshfeld partition of theoretically determined electron density.

There are various ways of calculating the electron density with theoretical methods. For example, among others, we can independently change (1) a method of quantum chemistry (2) basis set and (3) a representation of molecular environment. This a leads to obvious question – which set of settings is the best for HAR refinement?

An another dimension was recently added to the space of settings by introducing generalization of HAR to other electron density partitions [3] (so called generalized atom refinement (GAR)). This makes the optimal choice of settings even more challenging.

Another factor further complicates the situation – computational cost of GAR. Usually unfavorable scaling of quantum chemical calculations with size of a system may lead to long refinement time for large molecules. While computational chemistry brings here some solutions, we still have to figure out how to handle trade-off between computational cost and accuracy of refinement.

In this contribution we will analyze effects of various settings of GAR on accuracy of the method (assessed by comparison to neutron data). We will also try to find optimal solution for performing accurate refinement with optimized computational cost.

[1] Jayatilaka, D. & Dittrich, B. (2008). *Acta Cryst.* A**64**, 383–393.

[2] Capelli, S. C., Bürgi, H.-B., Dittrich, B., Grabowsky, S. & Jayatilaka, D. (2014). *IUCrJ*, **1**, 361–379

[3] Chodkiewicz, M. L., Woińska, M. & Woźniak, K. (2020). *IUCrJ*, **7**, 1199–1215.

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