Poster

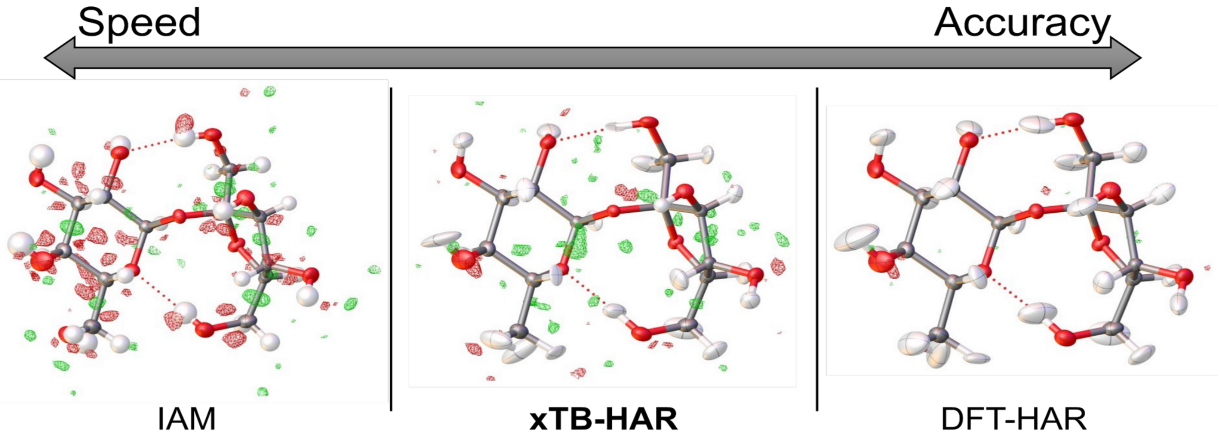
First implementation of tight-binding methods (xTB) for quantum crystallographic refinement

B. Ebel*[1], F. Kleemiss[1]

[1]*Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, Aachen, Germany*

ben.ebel@ac.rwth-aachen.de

Due to the computational cost of quantum mechanical simulations for large and electron-rich systems, semiempirical methods have been developed to provide a better compromise between accuracy and computational cost. The *xTB* program package [1] is a collection of semiempirical quantum chemical methods based on the tight-binding approximation. The methods are designed to be computationally efficient and can provide accurate results for a wide range of chemical systems. The *xTB* methods have been implemented in the *NoSpherA2* [2] software package, which is a tool for the calculation of non-spherical atomic form factors for Hirshfeld atom refinement (HAR) in *Olex2* [3].



IAM	**xTB-HAR**	DFT-HAR
R_1: 3.20%, wR_2: 7.54%	R_1: 2.71%, wR_2: 5.60%	R_1: 2.39%, wR_2: 4.27 %
0.21/-0.19 eÅ^{-3}	0.16/-0.18 eÅ^{-3}	0.12/-0.16 eÅ^{-3}
Level of theory	GFN-2	R2SCAN, cc-pVTZ
Calculation time	0.060 s	17.463 s
Partitioning time	8 s	15 s

Figure 1: Comparison of the difference maps (0.120 eÅ^{-3}) for the available methods.

Fig. 1 shows that for both HAR methods only statistically distributed residual densities are observed while the IAM model shows significant residual electron density on the bonds. However, while DFT-HAR yields the most accurate results, the xTB calculation proofs to be significantly faster with retention of the HAR advantages, like realistic hydrogen distances and ADPs. Since xTB was parametrized for geometry optimization, which is irrelevant for the HAR, it does not yield good results for structures containing heavier elements. Nevertheless, this implementation serves as a proof of concept for the use of tight-binding methods in quantum crystallographic refinement and the implementation of a new method called *pTB*[4] is already being developed.. This method is parametrized to yield accurate electron density matrices and should be ideal for calculating structure factors.

[1] C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher, S. Grimme, *WIREs Comput. Mol. Sci.* **2021**, *11*, e1493.

[2] 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. Puschmann, S. Grabowsky, *Chem. Sci.* **2021**, *12*, 1675–1692.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[4] S. Grimme, M. Müller, A. Hansen, *J. Chem. Phys.* **2023**, *158*, 124111.