Moving quantum crystallography from sub-atomic XRD to near-atomic 3D ED

P.M. Dominiak, M. L. Chodkiewicz, B. Gruza, K. K. Jha, M. Kulik, P. Rybicka, A. Sypko

Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, ul. Zwirki i Wigury 101, Warsaw, 02-089, Poland,

pdomin@chem.uw.edu.pl

One of the kinds of information gained from high resolution (sub-atomic) structures is the observation that electron density parameters are transferable between atoms having similar chemical topology. This stimulated creation of databases of multipolar pseudoatoms (Invariom [1], ELMAM2 [2], MATTS – successor of UBDB [3], etc.) and their applications in (a) structure refinements on standard (atomic) resolution data for small-molecule crystals, and (b) electrostatic properties and non-covalent bonding characterisations for macromolecules.

Transferable Aspherical Atom Model (TAAM) of scattering built from a pseudoatom database proved to be advantageous in refining the structure on X-ray diffraction (XRD) data compared to the Independent Atom model (IAM) [4], leading to better fit of the model to the data and improved localization of hydrogen atoms. We have recently showed [5] that also for small-molecule 3D electron diffraction (3D ED) data, a better model-to-data fit and more accurate structures should be expected from TAAM.

To improve its usability, we further extended the MATTS bank to cover 98% of atoms found in all the structures deposited in the Cambridge Structural Database [6] composed of chemical elements like C, H, N, O, P, S, F, Cl and/or Br. It is planned that the remaining 1% will be covered by the more general atom types resulting from multidimensional cluster analysis.

Some benefits of TAAM over IAM refinements were also reported for macromolecular XRD data of 0.9 Å resolution and better [7]. As most macromolecular crystals diffract to lower resolutions, we recently moved our investigation towards near-atomic resolutions. We quantified the differences between the macromolecular electron density Fourier maps obtained with TAAM and IAM, calculated with a resolution of 1.8 Å. We did the same for electrostatic potential maps, a key property in the context of 3D ED.

TAAM refinements affect not only the positions of the atoms, but also the atomic displacement parameters (ADPs) [8]. ADPs appears to be less resolution dependent with TAAM than with IAM. With IAM, ADPs increased for XRD and decreased for 3D ED by about 30%, when the resolution was reduced from 0.6 Å to 0.8 Å [5]. From modified Wilson plots we recently predicted, and then verified by TAAM refinements on macromolecular XRD or 3D ED data, what will happen with ADPs (B-factors) with a further resolution worsening, up to 1.8 Å.

All the above helps to understand if there will be any benefits of TAAM refinements on lower than atomic resolutions.

[1] Dittrich, B., Hübschle, C. B., Pröpper, K., Dietrich, F., Stolper, T. & Holstein, J. (2013). *Acta Crystallogr. B* **69**, 91.

[2] Domagała, S., Fournier, B., Liebschner, D., Guillot, B. & Jelsch, C. (2012). *Acta Crystallogr. A* **68**, 337.

[3] Kumar, P., Gruza, B., Bojarowski, S. A. & Dominiak, P. M. (2019). *Acta Crystallogr. A* **75**, 398.

[4] Jha, K. K., Gruza, B., Kumar, P., Chodkiewicz, M. L. & Dominiak, P. M. (2020). *Acta Crystallogr. B* **76**, 296.

[5] Gruza, B., Chodkiewicz, M., Krzeszczakowska, J. & Dominiak, P. M. (2020). *Acta Crystallogr. A* **76**, 92.

[6] Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Crystallogr. B* **72**, 171.

[7]. Malinska, M. & Dauter, Z. (2016). *Acta Crystallogr. D* **72**, 770.

[8]. Sanjuan-Szklarz, F. W., Woińska, M., Domagała, S., Dominiak, P. M., Grabowsky, S., Jayatilaka, D., Gutmann, M., Woźniak, K. (2020). *IUCrJ*, **7**, 920.

Keywords: quantum crystallography; structure refinement; X-ray diffraction, electron diffraction; 3D ED, microED, aspherical scattering factors; multipolar model; TAAM; MATTS; UBDB; ELMAM2

Support of this work by the National Centre of Science (Poland) through grant OPUS No.UMO-2017/27/B/ST4/02721 and PL-Grid through grant plgubdb2020 is acknowledged.