Scaling and thickness optimization in dynamic refinement of 3D ED data using cubic spline interpolation.

H. Chintakindi[1], L. Palatinus[1]

[1]*Department of Structure Analysis, Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic*

chintakindi@fzu.cz

With the advent of 3D Electron diffraction (3D ED) data acquisition and processing techniques, electron crystallography has emerged as a powerful method for accurate atomic-level structure determination [1], particularly when combined with dynamical refinement to account for multiple scattering effects [2]. A key aspect of this refinement involves optimizing structural parameters while refining the crystal thickness and individual scale factors for each frame. These scale factors exhibit significant variation across frames due to changes in the irradiated area of the sample as the crystal tilts, along with other experimental uncertainties. The variation of the scale factors in dynamical refinement is such that it cannot be compensated in the data processing step, like in the case of kinematical treatment. Therefore, it is necessary to refine the scale factors in the refinement stage. This, however, leads to significant increase of refinement parameters, a decrease of the data to parameter ratio, and a possible introduction of noise in the refined parameters.

To address this issue, we propose a strategy to limit the number of refined parameters while maintaining the flexibility of the frame scale refinement. The strategy uses natural cubic splines. Instead of refining a separate scale factor for each frame, scale factors are refined only at selected node frames, spaced at regular intervals defined by a parameter called node spacing (h). The scale factors for the remaining frames are then interpolated using natural cubic splines, ensuring smooth and continuous variation up to the second derivative. This approach significantly reduces the number of refined parameters, thereby minimizing the risk of overfitting. The interpolated scale factors are expressed as explicit linear combinations of the refined node values, with interpolation weights determined by the cubic spline equations based on the selected node spacing. The method was implemented and tested in Jana2020[3], where these equations can be entered in the equations window and used as constraints in the dynamical refinements. We note that the method does not neglect the scale factors outside of the nodes. The equations ensure that all data are taken into account in the refinement, and thus even if, technically, only some scale parameters are refined, they are refined to such values that ensure the best overall fit of all scales.

We evaluated this method on two experimental quartz datasets collected using continuous-rotation (C.ROT) and precession-assisted (PEDT) 3D ED techniques. As shown in Table 1, the interpolation approach resulted in a substantial reduction in the number of refined parameters from 69 to 19 for the C.ROT dataset and from 265 to 19 for the PEDT dataset, with only a minimal increase in R-factors. The method also improved the smoothness of scale variation and enhanced the data-to-parameter ratio, demonstrating its effectiveness for the dynamical refinement of 3D ED data.

Table1: Dynamical refinement statistics for cubic spline interpolation of scale factors for Quartz (C.ROT and PEDT)

C.ROT (continuous rotation dataset); N(obs)-2543, N(all)-3050				
h (Node spacing)	**Refined Scales (# of nodes)**	**No of Refined parameters**	**R(all)**	**wR(all)**
1	**All Scales (54)**	**69**	**5.76**	**6.48**
6	10	25	5.88	6.76
18	4	19	6.08	7
PEDT (Precession dataset); N(obs)-8907, N(all)-12107				
1	**All scales (250)**	**265**	**5.4**	**5.51**
40	8	23	5.52	5.78
100	4	19	5.52	5.83

[1] Gemmi, M., Mugnaioli, E., Gorelik, T., Kolb, U., Palatinus, L., Boullay, P., Hovmöller, S. & Abrahams, J. (2019). ACS Cent. Sci. **5**, 1315–1329.

[2] Palatinus, L., Petricek, V. & Correa, C. A. (2015). Acta Cryst. A71, 235-244.

[3] Petříček, V., Palatinus, L., Plášil, J., Dušek, M. (2023). *Z. Krist.*, **238**, 271-282.

This research was funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 956099 (NanED – Electron Nanocrystallography – H2020-MSCAITN