

DFT-D and the validation of crystal structures from XRPD

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Although single-crystal X-ray diffraction has established itself as the gold standard for the determination of the structures of molecular compounds, crystal structures determined from X-ray powder diffraction (XRPD) data have a more questionable reputation. Especially the peak overlap in XRPD data substantially reduces the information content of an XRPD pattern, limiting the reliability and accuracy of crystal structures determined from XRPD data.

The solution to this problem is the use of external information, increasingly often in the form of dispersion-corrected density functional theory (DFT-D) calculations. The scientific basis for this solution is the observation that DFT-D is able to reproduce high-quality molecular single-crystal structures with great accuracy[1], and is therefore able, through mere energy minimisation, to provide us with a pseudo-single-crystal version of a powder structure. The pseudo-single-crystal structure can then be used to verify the correctness of the powder structure and to create a set of highly accurate restraints for bond lengths and valence angles for the Rietveld refinement. In most cases, the DFT-D calculations are able to locate all hydrogen atoms with great accuracy. The rapid development of hardware and software over the past decade have already made DFT-D calculations on molecular crystal structures routine, and such calculations will only become cheaper and faster in the future.

Although peak overlap is generally considered the main weakness of powder diffraction data, our statistics on 215 crystal structures from XRPD data suggest that the negative effects of preferred orientation are underestimated[2].

Recently, we have validated how DFT-D can be used to check the space-group symmetry of organic crystal structures[3].

In total, we have now collected data from energy minimisations of over 600 organic crystal structures, enabling us to outline a protocol that maximises the reliability and accuracy of molecular crystal structures from powder diffraction data.

[1] Van de Streek, J. & Neumann, M. A. (2010). *Acta Cryst.* B66, 544-558.

[2] Van de Streek, J. & Neumann, M. A. (2014). *Acta Cryst.* B70, 1020-1032.

[3] Hempler, D. et al. (2017). Submitted.

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