Poster Presentations

[MS29-P01] X-ray Wavefunction Refinement – Introduction, Examples, Validation

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Electron-density analysis performed after multipole modelling (MM) [1] is the primary source of chemical information from an X-ray diffraction experiment beyond pure geometry. But it is known that there are problems with the used basis functions, so that, in particular, heavier atoms and polar bonds cannot always be described satisfactorily.[2] There are promising efforts to improve MM.[3]

Here, we present an alternative way to improve the electron-density modelling that does not need multipoles. We term this novel way "X-ray wavefunction refinement (XWR)". XWR is a protocol that defines how to combine existing techniques to arrive at a final electron-density model that reconstructs the measured data. In the first step, the geometry is determined using Hirshfeld atom refinement,[4] which is based on a stockholder partitioning of quantum-mechanical aspherical electron densities. In the second step, the same wavefunction is fitted to the experimental data to reproduce the diffraction pattern and simultaneously minimise the molecular energy.[5] The XWR protocol involves embedding the molecule into a field of point charges and dipoles as well as termination strategies to avoid overfitting.[6]

Results from an X-ray wavefunction refinement are not restricted to the analysis of electron density: the full reconstructed density matrix is available. Therefore, chemical problems can be tackled with the optimum tools for any given question including, e.g., experimentally derived bond orders, electron-pair localisation information, or energetics.

We will present first applications of this protocol for a selection of organic (amino acids, tripeptides, hydrogen maleate salts, sulfur-containing protease inhibitors) and inorganic (siloxanes, sulfur dioxide) compounds, for which we measured high-resolution low-temperature X-ray diffraction data. We will show geometry improvements, anisotropic displacement parameters for hydrogens, anharmonic motion parameters for sulfur and chlorine atoms, and improved total electron-density distributions in comparison to results from multipole modelling. Moreover, we will discuss the contribution of the experimental data to the final constrained wavefunction (experimental exchange-correlation interaction density) and demonstrate how the experimentally derived orbital-based descriptors assist in solving fundamental chemical problems.

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