

## Microsymposium

MS89.O06

### *Applications of X-ray Wavefunction Refinement*

S. Grabowsky<sup>1</sup>, M. Woinska<sup>1,2</sup>, J. Bak<sup>1,2</sup>, D. Jayatilaka<sup>1</sup>

<sup>1</sup>*The University of Western Australia, School of Chemistry and Biochemistry, Perth, Australia,* <sup>2</sup>*University of Warsaw, Faculty of Chemistry, Warsaw, Poland*

X-ray wavefunction refinement (XWR) is a way of modeling the total aspherical electron density from an X-ray diffraction experiment on a single crystal of a molecular compound. It is a combination of existing quantum-crystallographical techniques: In the first step, geometry is determined using Hirshfeld atom refinement,[1] 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 minimize the molecular energy.[2] The XWR protocol involves embedding the molecule into a field of point charges and dipoles as well as termination strategies to avoid overfitting.[3] 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 suitable 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 (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 at various synchrotron facilities. 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 modeling. Moreover, we will discuss the contribution of the experimental data to the final constrained wavefunction (defect density) and demonstrate how the experimentally derived orbital-based descriptors assist in solving fundamental chemical problems.

[1] D. Jayatilaka, B. Dittrich, *Acta Cryst. A*, 2008, 64, 383-393, [2] D. Jayatilaka, D. Grimwood, *Acta Cryst. A*, 2001, 57, 76-86, [3] S. Grabowsky, P. Luger, J. Buschmann, et al., *Angew. Chem. Int. Ed.*, 2012, 51, 6776-6779

**Keywords:** electron density, high-resolution single-crystal diffraction