

*Wavefunction refinement derived spin density of two cAAC-SiCl<sub>3</sub> polymorphs*Birger Dittrich<sup>1</sup>, Marion Flatken<sup>1</sup>, Dylan Jayatilaka<sup>2</sup><sup>1</sup>Heinrich-Heine Universität Düsseldorf, Anorganische Chemie Und Strukturchemie, Düsseldorf, Germany, <sup>2</sup>School of Molecular Sciences, The University of Western Australia (M313), Crawley WA6009, Australia  
E-mail: dittrich@hhu.de

When in 1998 wavefunction fitting was introduced [1a], it emerged that the evaluation of single crystal x-ray diffraction experiments permits to extract spin density. Procedures require fitting coefficients of a quantum chemical basis set. These coefficients are adjusted to best reproduce the electron density of a crystallographic structural model, which is in turn obtained via Fourier transform of measured structure factors. In the same time the resulting wavefunction is energy-minimized.

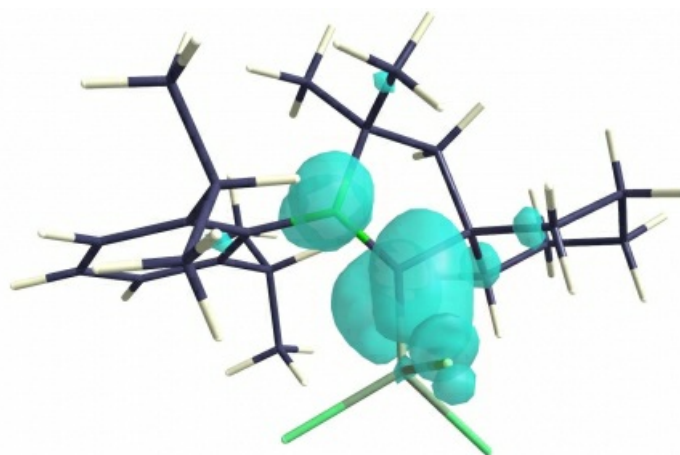
In 2008 technical feasibility of the approach was significantly improved by introduction of Hirshfeld atom refinement (HAR) [2a,b] where more accurate structural models can be refined by relying on aspherical scattering factors of the whole molecule; scattering factors are obtained by sequences of single-point energy computations of structures adjusted to experimental Bragg data. The combination of wavefunction fitting after successful HAR has been termed wavefunction refinement [1b]. The ability to extract a minimal energy wavefunction that is in best agreement with crystallographic measurements gives access to many properties formerly only accessible by theory.

From a solid-state chemistry point of view non-disordered stable radicals are required for trying out the new capabilities to extract spin density. We show first results of two polymorphs of a stable radical of the type cAAC Si R<sub>3</sub> [3]. Both data sets were measured at the Petra III synchrotron at a temperature of 23 K with hard X-rays to high resolution. Theoretical calculations have also been performed on these systems. Theory and experimental results are compared for judging on the success of the experimental spin density determination and the reliability of the theoretical computation.

[1] D. Jayatilaka, Phys. Rev. Lett. 1998, 80, 798–801; S. Grabowsky, P. Luger, J. Buschmann, T. Schneider, T. Schirmeister, A. N. Sobolev, D. Jayatilaka, Angew. Chem. Int. Ed. 2012, 51, 6776–6779.

[2] D. Jayatilaka, B. Dittrich, Acta Cryst. A 2008, 64, 383–393; S. C. Capelli, H. B. Bürgi, B. Dittrich, S. Grabowsky, D. Jayatilaka, IUCrJ. 2014, 1, 361–379.

[3] K. C. Mondal, H. W. Roesky, A. C. Stückl, F. Ehret, W. Kaim, B. Dittrich, B. Maity, D. Koley, Angew. Chem. Int. Ed. 2013, 52, 11804–11807.



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