

*Introducing Iterative X-ray wavefunction refinement*Rumpa Pal¹, Emanuel Hupf¹, Dylan Jayatilaka², Simon Grabowsky¹

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Hirshfeld atom refinement (HAR)[1] is a structural refinement method of single-crystal X-ray diffraction data by using an aspherical atom partitioning of tailor-made ab initio quantum mechanical molecular electron densities, in contrast to spherical scattering factor used in the Independent Atom Model (IAM). The original HAR has been extended by implementing an iterative procedure of successive cycles of electron density calculations, Hirshfeld atom scattering factor calculations and structural least-squares refinements, repeated until convergence.

X-ray constrained wavefunction (XCW)[2] fitting as a separate technique overcomes the shortcomings of the theoretical ansatz used by including experimental observations (such as electron correlation or the crystal effect) into the wavefunction. In X-ray wavefunction refinement (XWR)[3] HAR is followed by an adjustment of the electronic wave function through XCW fitting. Similar to the implementation of an iterative procedure within HAR itself, a natural forward step of sophistication for XWR would be to directly incorporate the fitted wavefunction into a new HAR, obtain an improved geometry and improved ADPs and use this as input for another XCW fitting, and so on, until convergence in both energy and geometry: iterative XWR = HAR + XCW + HAR + XCW + ...

In this study we have introduced the above sequence by benchmarking against experimental and theoretical results on the well-studied systems urea and L-alanine. We are interested in investigating to which extent the geometrical results and the atomic displacement parameters improve relative to a simple HAR, and to which extent the information extracted from the wavefunction such as electron correlation and the crystal effect (polarization) are enhanced relative to a simple X-ray constrained wavefunction fitting.

We will furthermore present preliminary applications of the iterative XWR procedure to study rare and subtle chemical features, such as the presence of a non-nuclear attractor in a stable molecular species, the dimeric Mg(I) molecule, resonance in an organolithium complex, 2-Picolylithium (PicLi), or the relationship between hypercoordination and hypervalency in molecular compounds.

[1] Capelli, S. C. et al. (2014). *IUCrJ*. 1, 361-379.

[2] Jayatilaka, D. & Grimwood, D. J. (2001). *Acta Cryst.* A57, 76-86.

[3] Grabowsky, S. et al. (2012). *Angew Chem.* 51, 6776-6779.

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