

Keynote Lecture

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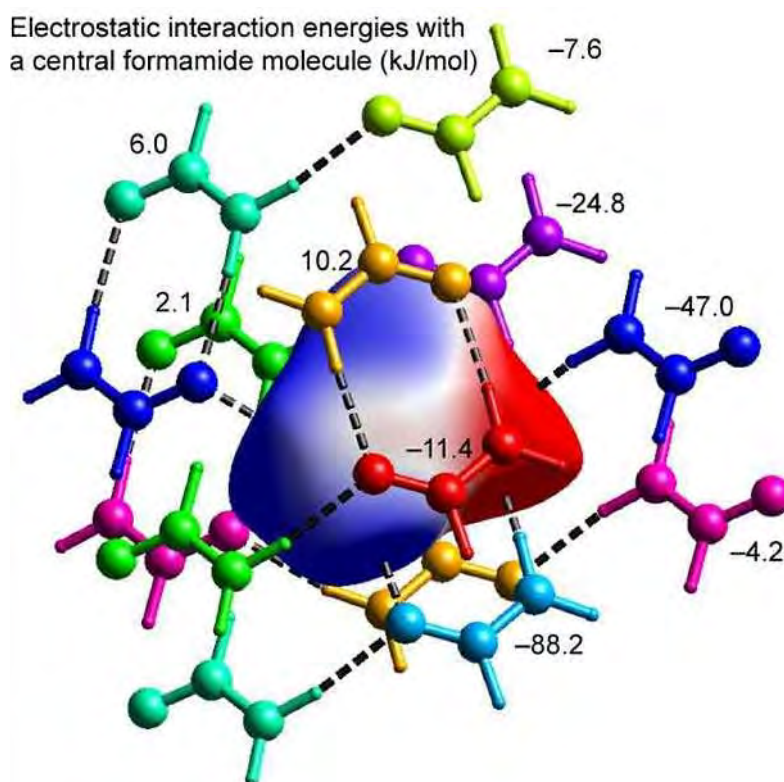
Rationalising molecular crystal structures using Hirshfeld surfaces

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Hirshfeld surface analysis [1] has very quickly become a routine tool for rationalising and visualising intermolecular interactions in crystals. The serendipitous discovery of an intriguing and novel way to identify the space ‘belonging’ to a molecule in a crystal has led to the development of a suite of computational tools that facilitate a deeper understanding of how molecules pack in crystals and why it makes sense that a particular crystal packing occurs [2]. We have previously used the Hirshfeld surface as a vehicle for mapping inherent shape and curvature, surface-mediated distances between closest atoms, as well as quantum mechanical properties such as molecular orbital density, electron density and electrostatic potential. Combining visualisation tools like these with quantum mechanical wavefunctions – and hence properties derived from these wavefunctions – offers a powerful and unique opportunity to investigate intuitive concepts like ‘electrostatic complementarity’ [3]. With this in mind we have been investigating ways to subdivide Hirshfeld surfaces into discrete patches that can be identified with specific pairs of molecules in close contact in crystals, and testing different expressions to quantify our ideas on electrostatic complementarity. Coupled with this appealing visual approach we also compute the electrostatic energy of interaction between the respective molecular wavefunctions. This combination of approaches within an easy to use software package will be powerful enough to not only routinely explore and visualise the patterns of interaction exhibited by molecules in crystals, but also provide meaningful energies of interaction between relevant pairs of molecules. In this way we can readily attach some real significance – energetics – to what are more usually classified as close contacts of various kinds.

[1] M.A. Spackman, D. Jayatilaka, *CrystEngComm*, 2009, 11, 19-32, [2] *CrystalExplorer (Version 3.1)*. S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, University of Western Australia, 2014. <http://hirshfeldsurface.net>, [3] M.A. Spackman, J.J. McKinnon, D. Jayatilaka, *CrystEngComm*, 2008, 10, 377-388



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