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Prediction of unknown crystal structures with evolutionary algorithms

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Crystal structure prediction on the basis of just the chemical formula has long been considered a formidable or even insoluble problem. Being able to solve this problem would open the possibilities to find new phases of planetary materials at extreme conditions [1,2], to solve structures where experimental data are insufficient, and to design new materials entirely on the computer (once the structure is known, it is relatively easy to predict many of its properties - e.g., [3]). Essentially, the problem can be reduced to the problem of global optimization of the free energy of a crystal with respect to structural parameters. Recently, we addressed this problem and devised a new method based on a specifically devised and carefully tuned *ab initio* evolutionary algorithm, which we implemented in the USPEX code (Universal Structure Predictor: Evolutionary Xtallography, [4-6]). At given *P-T* conditions, USPEX finds the stable structure and a number of robust metastable structures. USPEX uses *ab initio* free energy as evaluation function and features local optimization and spatial heredity, as well as further operators such as mutation and permutation. This method has been widely tested and applied to solve a number of important problems. It turns out to be extremely efficient for predicting crystal structures with very different geometrical features and types of chemical bonding.
In this talk I will discuss some of the applications of this method to a number of interesting materials (C, N, O, S, H_2O, $MgSiO_3$, $CaCO_3$, $MgCO_3$). Possible industrial applications will be discussed as well. Future developments of the method will be outlined.

[1] Oganov A.R. & Ono S. (2004). Theoretical and experimental evidence for a post-perovskite phase of $MgSiO_3$ in Earth's D″ layer. *Nature* 430, 445-448.
[2] Oganov A.R., Ono S. (2005). The high pressure phase of alumina and implications for Earth's D'' layer. *Proc. Natl. Acad. Sci.* 102, 10828-10831
[3] Oganov A.R., Brodholt J.P., Price G.D. (2001). The elastic constants of $MgSiO_3$ perovskite at pressures and temperatures of the Earth's mantle. *Nature* 411, 934-937.
[4] Glass C.W., Oganov A.R. & Hansen N. (2006). USPEX: a universal structure prediction program. *Submitted.*
[5] Oganov A.R. & Glass C.W. (2006). Crystal Structure Prediction using *ab initio* evolutionary techniques: principles and applications. *Submitted.*
[6] Oganov A.R., Glass C.W., Ono S. (2005). High-pressure phases of $CaCO_3$: crystal structure prediction and experiment. *Earth Planet. Sci. Lett.* 241, 95-103.

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CrystalExplorer: A Tool for Displaying Hirshfeld Surfaces and Visualising Intermolecular Interactions in Molecular Crystals

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The classification and visualisation of interactions in molecular crystal structures is an important precursor to understanding why they adopt specific morphologies, and hence for the rational design of molecular crystal structures. CrystalExplorer [1] is a graphical user interface which facilitates such a classification and visualisation in a novel way. The primary purpose of CrystalExplorer is to display and manipulate *Hirshfeld surfaces* [2] in three dimensions, and to generate the corresponding *fingerprint plots* [2]. The Hirshfeld surface for a molecule in a crystal is simply the dividing surface inside which more than half of the electron density comes from the molecule itself. The shape of the Hirshfeld surface is characteristic of the molecule and its crystalline environment. The Hirshfeld surface can be coloured to highlight close contacts of the surface with neighbouring atoms, and the curvature of the surface can be used to determine the overall coordination of the molecule in the crystal. Both distance and curvature are remarkably sensitive to the type of interaction present: for example, pi-pi and CH-pi type interactions are immediately and clearly visible as imprints on the Hirshfeld surface. The fingerprint plot is a two-dimensional representation of the Hirsheld surface: distances to the nearest atoms outside and inside the surface are plotted for evenly space points on the Hirshfeld surface. The resulting distance-pair points in the plane can also be coloured according to their density, and, like the Hirshfeld surface, these fingerprint plots are also unique for a symmetry unique molecule in the crystal. With training, simple interaction motifs can be recognised almost immediately without resorting to a detailed examination of the crystal structure itself. A new feature of the software is the ability to produce fingerprint plots for specific interactions between molecules, allowing a more detailed comparison. In this presentation I will outline some applications of the Hirshfeld surface and the corresponding fingerprint plots to polymorphs, and to systems of related compounds.

[1] CrystalExplorer, S.K. Wolff, D.J. Grimwood, J.J. McKinnon, D. Jayatilaka, M.A. Spackman, University of Western Australia (2005). CrystalExplorer is available for all major computer platforms. For download information see *http://www.theochem.uwa.edu.au/CrystalExplorer.*
[2] See, for example, 'Novel tools for visializing and exploring intermolecular interactions in molecular crystals', J.J. McKinnon, M.A. Spackman and A.S. Mitchell, *Acta Cryst*. B60, 627-668 (2004) and references therein.