

MS14 P05**Atomic Surface Modeling and AIM Charges**

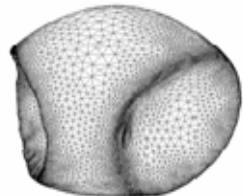
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Keywords: topology of the electron density, AIM charges, divergence theorem

The quantum theory of “Atoms in Molecules” (AIM)^[1] is a powerful method to get a molecular partitioning having a physical meaning. The zero flux electron density gradient surfaces define the atomic sub-volumes within chemical systems. Therefore, intrinsic atomic properties like charges and electric moments can be estimated from a 3D integration over the atomic basins. Nowadays, several softwares are available for this purpose and are frequently used in theoretical or experimental topological electron density studies. However, the analytical representation of the atomic boundaries requires sophisticated interpolations and is computationally expensive. Recently, a fast and robust numerical algorithm based on the steepest-ascent method was proposed by Henkelman *et al.*^[2] for the computation of the AIM charges. In this method, every mesh point in the cube containing the studied molecule is assigned to the atom to which the corresponding electron density belongs to. Therefore, surfaces encompassing the atomic basins can be defined numerically as a cloud of points. Popelier was the first who proposes the calculation of the IAM charges by using the Gauss divergence theorem on the flux of the electric field.^[3] However, particular interpolations were used in his method to delimitate the atomic boundaries which are defined analytically in spherical geometries. In the present work, the atomic surfaces are treated numerically from the Henkelman method^[2] as a cloud of points. In order to calculate the flux of the electric field, these points are taken as vertices of Delaunay triangles and exact reconstructions of the atomic boundaries are carried out.^[4] Advantages and generalizations of this new approach to small and larger molecules will be discussed.



triangulated surface of the oxygen atom in water molecule

[1] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*. Oxford University Press, Oxford, 1990.

[2] E. Sanville, S. Kenny, R. Smith, G. Henkelman, *J. Comput. Chem.* 28 (2007) 899.

[3] P.L.A. Popelier, *Theor. Chem. Acc.* 105 (2001) 393.

[4] Gamma Project. INRIA, Rocquencourt, France.

MS14 P06

Can crystal structure prediction predict whether a salt or a cocrystal will be formed? Katarzyna E. Hejczyk^a, Graeme M. Day^a, William Jones^a; ^a*The Pfizer Institute for Pharmaceutical Materials Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. E-mail: keh49@cam.ac.uk*

Keywords: crystal structure prediction, organic molecular crystals, energy

An estimated about 75% of all drug molecules used in medicinal therapy are formulated as salts. The solid-state properties of a drug, as well as its properties in solution, can be modified by salt formation. Therefore, molecular modelling and successful structure prediction can open new opportunities, not only in the design of drugs but also in the study of their solid-state properties [1].

We are studying the contrasting crystallisation behaviour of some acids:base combinations in terms of salt or cocrystal formation. It has been reported by Haynes *et al.*[2] that succinic acid forms only cocrystals with the lutidines, while fumaric acid forms salts with some isomers, but cocrystals with others. We are investigating whether computational methods can explain whether a cocrystal or a salt will be formed when an acid and a base are combined and what factors determine the nature of the observed crystal structure.

Our study is based on comparison of energies (molecular and lattice) between the observed and corresponding hypothetical systems (cocrystals and salts). Crystal structure prediction calculations are presented for selected systems; these calculations successfully locate the observed structure in the vicinity of the lowest energy calculated structure.

[1] Handbook of Pharmaceutical Salts: Properties, Selection and Use, ed. P.H. Stahl and C. G. Wermuth, Wiley-VCH/VHCA, Weinheim/Zürich, 2002

[2] D. A. Haynes, W. Jones and W. D. S. Motherwell, *CrystEngComm*, (2006), 8, 830 – 840.

MS14 P07

Structure and Magnetism in Prussian Blue Analogues: Theory and Experiment. L. M. Lawton, D. S. Middlemiss and C. C. Wilson, *Department of Chemistry and WestCHEM Research School, University of Glasgow, UK. E-mail: Lorrla@chem.gla.ac.uk*

Keywords: Prussian Blue Analogues, Magnetism, Pressure

The Prussian Blue Analogue (PBA) structure is a three-dimensional lattice of magnetic ions that interact via intermediate cyanide ligands. The structure directing property of these particular ligands and the flexibility of the structure allow ions of specific spin and oxidation states to be selected, so that the exchange interactions behave as predicted from fundamental orbital rules. The most important corollary of this fact is it has proved possible to synthesise PBAs with specific structure and properties, obtained primarily by inclusion of varying ratios of the magnetic ions, but also by application of external perturbations.

Ohkoshi and Hashimo [1] studied the saturation magnetisation as a function of x in the $\{Ni_x^{II} Mn_{x-1}^{II}\}_{1.5} [Cr^{III} (CN)_6] \cdot nH_2O$ family and at $x \sim 0.4$ this was found to switch from antiferro-ferromagnetic ordering. Pressure

has also been used to tune the interaction strength and pole orientation in the bulk magnetisation of a series of recently synthesised PBA's [2]. We have commenced a theoretical study of the effects of change in pressure and composition parameter, x , upon the trimetallic PBA $\text{KNi}_x\text{Mn}_{1-x}[\text{Cr}(\text{CN})_6]$. We apply the same 35% HF functional and basis sets as were used in our recent study of the $\text{KM}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$ ($\text{M} = \text{V}, \text{Mn}, \text{Ni}$) [3] system. Our initial optimisations of structures at different Mn/Ni ratios indicate an adherence to Vegard's Law, which postulates a linear relationship between the lattice constant of substitutional alloys and their composition. We note that similar behaviour has also been observed in mixed oxide lattices [4].

Experimentally, PBAs often prove difficult to crystallise, are generally highly insoluble, contain large numbers of water molecules and $\text{M}^{\text{III}}(\text{CN})_6$ vacancies and possess low crystal symmetries. While the first two issues clearly offer no impediment to theoretical approaches, the presence of the disordered water molecules and $\text{M}^{\text{III}}(\text{CN})_6$ vacancies necessitate the use of idealised models containing charge-balancing cations. Efforts to synthesise high quality $\text{CsM}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$ crystals with minimal water content are currently under way, with the aim of permitting a direct comparison between experimental and theoretical properties both at equilibrium and under pressure. Experimental findings of early results from the synthesis will be presented.

[1] (a) S. Ohkoshi, O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Inorg. Chem.* 1997, 36, 268-269. (b) S. Ohkoshi, T. Iyoda, A. Fujishima and K. Hashimoto, *Physical Review B*, 1997, 56, No. 18. (c) S. Ohkoshi and K. Hashimoto, *Physical Review B*, 1999, 60, No. 18. (d) S. Ohkoshi, Y. Abe, A. Fujishima and K. Hashimoto, *Physical Review Letters*, 1999, 82, No. 6. (e) S. Ohkoshi, T. Hozumi, M. Utsunomiya, M. Abe, K. Hashimoto, *Physica B*, 2003, 329-333, 691-692.

[2] (a) S. Ohkoshi, S. Yorozu, O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Appl. Phys. Lett.*, 1997, 70, 1040. (b) L. Egan, K. Kamenev, D. Papanikolaou, Y. Takabayashi and S. Margadonna, *J. Am. Chem. Soc.* 2006, 128, 6034-6035.

[3] L. M. Lawton, D. S. Middlemiss, A. Harrison, and C. C. Wilson, in preparation.

[4] M. Königstein, F. Cora, C. Richard and A. Catlow, *Journal of Solid State Chemistry*, 137, 261-275, 1998

MS14 P08

Validation of "Kick maps". Jure Pražnikar^a, Pavel Afonine^b, Dušan Turk^a, ^a*Jozef Stefan Institute, Department of Biochemistry, Molecular and Structural Biology, Ljubljana, Slovenia.* ^b*Lawrence Berkeley National Laboratory, Berkeley, USA.* E-mail: jure.praznikar@ijs.si

Keywords: model building, electron density, maximum likelihood

The concept of Kick map has been in use for a while as a part of MAIN [1] distributions. However, apart from occasional comparisons, kick maps have not been systematically analyzed and compared against $2F_{\text{obs}}-F_{\text{calc}}$ least square and maximum likelihood maps calculated with unit or likelihood-weighted weights. The kick map is an average of a series of $2F_{\text{obs}}-F_{\text{calc}}$ maps, where each F_{calc} set was calculated from kicked atomic positions generated with a different random number seed. Kick of an atomic position is a random displacement along X, Y, and Z coordinate.

Validation involved convergence of a map as results of different number of repeats, kick size and resolution. The

resulting maps were compared with maximum likelihood weighted maps, LSQ weighted maps among themselves and against the F_{calc} map of the final model. The tests were carried out with the initial structures of the phospholipaseA2 [4] and stefin B tetramer [5]. Tests with phospholipaseA2 shows that maximum likelihood and kick maps are better than traditional least square map. Linear correlation for both maps was 0.69 when compared with F_{calc} map of final model. Local differences reveal that both maps have their virtues and "weak" points. Tests with stefin B tetramer show that the kick map gave better correlation than traditional least square and maximum likelihood map (stefin B initial structure required partial model rebuilding due to conformational change). The linear correlation coefficient of kick map against "true" map was 6% higher than that of the maximum likelihood map.

The kick map is comparable to maximum likelihood map and is occasionally closer to the "true" map. Therefore it can be successfully applied as an alternative approach on map calculations based on molecular models especially during the early stages of model building and refinement, when model bias plays a crucial role.

[1] Turk, D., *Ph.D. Thesis*, 1992, Technische Universitaet, Muenchen.

[2] Urzhumtsev A. G., Skovoroda T. P. and Lunin V. Y., *J. Appl. Cryst.*, 1996, 29, 741.

[3] Turk D., et al., *manuscript in preparation*.

[5] Jenko K. S., Gunčar G., Štern I., Morgan G., Rabzelj S. Kenig M., Staniforth R. A., Waltho J. P., Žerovnik E., Turk D., *J. Mol. Biol.*, 2007, 366, 1569.

MS14 P09

Crystallochemical design of langasite family compounds and information technology Tyunina E., Kuz'micheva G. *Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia*

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Keywords: langasite, crystallochemical design, information technology

Langasite family is one of the most attractive single crystals in promising piezoelectric materials. These crystals with general formula $\text{A}_3\text{B}_1\text{C}_3\text{D}_2\text{O}_{14}$ have $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ($\text{La}_3\text{GaGa}_3(\text{Ga}_{0.5}\text{Si}_{0.5})_2\text{O}_{14}$) structure and belong to the sp.gr. P321. There are four kinds of cation sites in the structure. A and B atoms are located on a dodecahedral (CN=8) sites and an octahedral (CN=6) ones, respectively. C and D atoms occupy tetrahedral (CN=4) and trigonal-pyramidal (CN=3+1) sites. There are three crystallographic positions for oxygen atoms. The most interesting part of material design is how to improve piezoelectricity by the substitution of other metal one.

In this work, we demonstrate relationship between composition, structural peculiarities and some properties of langasite family compounds and suggest an information technology for prediction new compositions with required properties set.

Well-known 216 compounds of $\text{A}_3\text{B}_1\text{C}_3\text{D}_2\text{O}_{14}$ general composition were divided into four groups. Compounds of the I-st (26.3 %) and the II-nd (27.6 %) groups have langasite structure confirmed and unverified by the structural analysis, respectively. Compounds of the III-rd group (23.5 %) have not langasite structure. Samples of the IV-th group (22.6 %) contain both langasite phase and impurities. According to crystallochemical analysis, the