MS21.02.03 EXPERIMENTAL DETERMINATION OF TOPOLOGICAL FEATURES IN METALS AND INORGANIC MATERIALS.

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Accurate X-ray diffraction data allow the electron density distribution (ED) of crystals to be determined. Recently, Iversen et al. (1) derived the ED in metallic Be using both the maximum entropy method and the multipole refinement method. The high resolution of the ED allowed a critical point network for the beryllium hcp structure to be proposed. The detailed information about the topology of beryllium suggested new explanations for some of the interesting physical properties of hcp metals. To see if these findings were general properties of hcp metals we have subsequently determined the ED of metallic Mg from 8 K AgKα X-ray diffraction data. Overall the topology resembles that of Be, but the valence features are sharper. This corroborates, according to the theory of atoms in molecules (2), the fact that Mg is a poorer conductor than Be. If accurate diffraction data are measured at very low temperatures detailed topological features of transition metal complexes can also be mapped. We have studied $Ni(ND_3)_4(NO_2)_2$ from 9 K AgKα X-ray diffraction data, and based on the properties of the Laplacian at the bond critical points the interaction between the metal and the ligands can be studied. As an example the topological analysis reveals a larger pi contribution to the bonding for the nitro group than for the amine group, but overall the metal-ligand bonding is dominated by electrostatic interactions.

1. B.B. Iversen, F.K. Larsen, M. Souhassou, M. Takata. Acta Cryst. B51 (1995) 580592.
2. R.F.W. Bader. Atoms in Molecules. A Quantum Theory. Oxford University Press (1991).

MS21.02.04 TOPOLOGY AND QUANTUM THEORY OF ATOMS IN MOLECULES AND CRYSTALS

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The topological definition of an atom in a molecule is extended to generalize the defintion of a Wigner-Seitz cell in a solid. The topological definition of molecular structure identifies all the atomic interactions that determine a crystal structure, the identification providing a firm physcial basis for a new crystal classification scheme and for establishing structure-property relationships. The identification of the atoms in a crystal with proper open systems enables one to define their conributions to all of the properties of a crystal and to determine the local properties of specific micro-structures such as defects and surface adsorption sites.

MS21.02.05 AN EFFICIENT LOCAL ANALYTIC REPRESENTATION OF ELECTRON DENSITY MAPS: THE SPECTRAL SPLINE APPROXIMATION.

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The analysis of molecular crystals frequently requires an accurate functional representation of the electron density so that basic mathematical operations, such as differentiation or integration, can be performed analytically before resorting to complicated numerical methods. A prime example is the location of the critical points which describe the topology of the map — others appear in phase refinement by non-crystallographic symmetry averaging, and resampling of maps in different coordinate systems.

The spectral spline approximation, first introduced by Eric Gross (Approximation Theory V. 1986), generates such a representation by a single Fast Fourier Transform of the (scaled) structure factors. The output of the FFT is a unique set of coefficients that describe the entire map as a basis expansion in terms of "basis spline" functions of an arbitrarily specified order k. The spline representation is a smooth, k - 1 differentiable polynomial function. The map is local in the sense that only k^3 coefficients are needed to specify the density at any point in the crystal, however each coefficient contains information from the entire space of Fourier coefficients. Furthermore, the approximation does not rely on any a priori information concerning atomic or molecular structure.

This paper presents applications of the spectral spline approximation recently implemented in the XtalView software package for macromolecular crystallography.

MS21.02.06 TRANSFERABILITY AS A PRINCIPLE IN CHEMISTRY - THE CHARGE DENSITY OF $CH_3NH_3^+$ IN TWO SALTS.

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Transferability in chemistry has for some years been demonstrated on theoretical charge densities[1]. We have compared topological features of the experimental charge densities of the $CH_3NH_3^+$ ion in two different salts, methyl ammonium hydrogen succinate monohydrate (MAHS)[2] and methyl ammonium deuterium maleate (MADMA). For the latter neutron and X-ray diffraction data were measured at 122 K to resolutions of 0.732 Å^{-1}, and 1.08 Å^{-1} respectively. Parameters for the hydrogen atoms obtained from the refinement of the neutron data were used in the multipole refinement of the X-ray data with the program VALRAY[3]. The bond critical points (bcp's) in the experimental charge density were found, and the bond paths determined. The MADMA crystallizes in space group Pnam with the cation in a general position and two different anions on crystallographic mirror planes perpendicular to the double bonds. The bcp's in the two very short (2.40Å) symmetric intramolecular hydrogen bonds both have negative Laplacians (equal within the uncertainty) indicating the covalent character of these interactions. The chemically equivalent bcp's for the $CH_3NH_3^+$ ion in MADMA and MAHS have been compared. This showed that equivalent bcp's have identical ρ, and $\nabla^2 \rho$ within the uncertainty, the only exception being the C-N bcp, which is in a crystallographic mirror plane in MAHS and in a general position in MADMA. These results show that transferability may also be applicable to experimental charge densities. Further studies to determine the charges and volumes of the atoms will be attempted to make definitive conclusions.

[1]Chang, C. and Bader, R. F. W. (1992), J. Phys. Chem. 96, p. 1654-1662. [2]Flensburg, C. et al. (1995), J. Phys. Chem. 99, p. 10130-10141. [3]Stewart, R. F. and Flensburg, C. (1996), Personal Communication.

PS21.02.07 TOPOND : A PROGRAM FOR THE APPLICATION OF THE QUANTUM THEORY OF ATOMS IN MOLECULES TO PERIODIC SYSTEMS.

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The TOPOND program implements the Quantum Theory of Atoms in Molecules[1] (QTAM) to periodic systems in N (N=0-3) dimensions. The program is interfaced to CRYSTAL-92[2] (and CRYSTAL-95 pre-release) package. A preliminary version of TOPOND has been described elsewhere[3], together with its first application to the urea[3] and ice VIII[4] molecular crystals. TOPOND is presently divided in five sections. The first two implement the topological analysis of the electron density (ρ) and of its Laplacian ($\nabla^2\rho$) scalar fields. An option for an automated search of critical points (Cps) is provided and two different search algorithms can be exploited (Newton Raphson or eigenvector following

techniques). Analytic representations of the *atomic interaction lines* may be evaluated and the associated *bond path* lengths determined. The fourth section of TOPOND computes atomic properties which may be obtained either following an indirect[3] determination of the zero-flux surfaces or using a combination of the indirect with the standard[5] direct methods. The last section performs the grid evaluation of ρ, $\nabla^2\rho$, $|\nabla\rho|$ functions and traces out molecular graphs, or generically, $\nabla\rho$ trajectories in selected crystalline planes. The electron localization function (ELF), along with other local and integral properties (kinetic energy densities) which depend on the non-diagonal elements of the first order density matrix, can now also be computed.

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(2) R. Dovesi, V.R. Saunders, C. Roetti, CRYSTAL-92 - An ab-initio Hartree-Fock LCAO program for periodic systems, User manual 1992
(3) C. Gatti, V.R. Saunders, C. Roetti, *J. Chem. Phys.* 101, 10686 (1994)
(4) C. Gatti, B. Silvi, F. Colonna, *Chem. Phys. Lett.* 247, 135 (1995)
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PS21.02.08   A TOPOLOGICAL ANALYSIS OF CHARGE DENSITIES OF THE DIAMOND, SILICON AND GERMANIUM CRYSTALS.

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The Hansen-Coppens multipole model of charge density has been fitted to published [1,2] highly accurate experimental and theoretical structure factors for diamond, silicon and germanium crystals. Careful consideration was given to the choice of variable parameters and to their significance. Analysis of both model experimental and model theoretical charge densities has been performed in terms of Bader's topological theory using the obtained model parameters. The general topology of the charge density appeared to be identical for all crystals, displaying the four possible types of critical points of rank three and showing no non-nuclei atractors between nearest-neighbour atoms. Properties of the charge density at the bond critical points (3,-1) and of the Laplacian distribution reflect the strong covalent bond in diamond crystal and its dramatic weakening on descending that series of crystals. This correlates with the change in semiconducting behaviour and increase in atomic displacement amplitudes at room temperature. Values of the Laplacian of charge density at the cage critical points, (3,+3), exhibit the same trend as those of the bulk modulus B.

1. Lu, Z.W. et al. (1993) *Phys. Rev.* B47, 9385, and references therein
2. Lu, Z.W. et al. (1995) *Phys. Rev.* B52, 11904, and references therein.