

s2.m2.o3 Application of the theory of atoms in molecules in the critical analysis of the experimental charge density model. A. Volkov, Yu. Abramov, P. Coppens, *Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000, USA.*

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The recent advances in computational technology have made fully periodic *ab initio* calculations of relatively large electronic structures possible, thus allowing the direct comparison of the experimental and theoretical charge density distribution in crystals. The theory of atoms in molecules¹ (AIM) is a natural tool for analysis of the total charge density as it is based on first principles. The great advantage of this method is that it can equally well be applied to both experimental and theoretical charge densities. The AIM properties of the electron density to be analyzed are net atomic charges, atomic volumes, molecular dipole moments and topological properties of the electron density at bond critical points¹.

Experimental charge densities derived from 20 K synchrotron data on several molecular crystals have been compared to theoretical fully periodic and single molecule densities obtained at Hartree-Fock and Density Functional levels of theory, using basis sets of 6-31G** quality or higher. The effect of the experimental multipole model on the primary theoretical density was analyzed through refinement of theoretical static structure factors from crystal calculations.

When the experimental charge density is directly compared to the primary theoretical density, significant differences are observed for net atomic charges, atomic volumes and the positive curvature along the bond path. However, the topological properties of the experimental charge density² strongly depend on the details of the multipole refinement applied. The projection of the primary theoretical density into the multipole density functions reveals the systematic effect of the multipole model (theoretical multipole density). Although the topological properties of the latter are very similar to those of experimental multipole density, they systematically differ from topological properties of a primary theoretical density.

While differences between experiment and theory (isolated molecule calculations) have often been attributed to the effect of the crystalline environment, we find the main origin of the discrepancies to be due to the nature of the radial functions in the experimental multipole model. Improvements in the multipole-model radial functions are being tested using the AIM analysis as a diagnostic tool.

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s2.m2.o4 A Charge Density Study on Vitamin B12 B. Dittrich, A. Wagner, P. Luger, *Institut für Kristallographie, Freie Universität Berlin, Takustr. 6, D-14195 Berlin, Germany* T. Koritsánsky, *Department of Chemistry, University of the Witwatersrand, Private Bag 3. WITS 2050, Johannesburg, South Africa* H.G. Krane, *Mineralog.-Petrolog. Institut, Universität Bonn, Poppelsdorfer Schloß, D-53115 Bonn, Germany* Horst Schmidt, *Mineralog.-Petrolog. Institut, Universität Hamburg, Grindelallee 48, D-20146 Hamburg, Germany*

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A new crystalline modification of Vitamin B12 containing propanol as solvent has been investigated. A fast high resolution X-ray experiment at cryogenic temperature (100 K) with synchrotron radiation and CCD area detection was performed at the HASYLAB/DESY in Hamburg, Germany. The experiment lasted 5 days. Over 500 000 reflections were collected up to a resolution of $\sin \theta / \lambda = 1.5$. Special care was put on the measurement of the low order reflections and on the data reduction, especially the scaling of the synchrotron radiation decrease during one run.

The B12 molecule itself contains about 100 non-hydrogen atoms. It cocrystallizes with twelve water and three propanol molecules of which one is disordered.

A multipolar refinement¹ using the computer package XD² was applied on the dataset. Until now the refinement has been halted at the octapolar level of the multipole expansion for the C,N and O atoms. Here we want to present first results of the electron density and other related properties of Vitamin B12 based on the AIM-theory³.

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