approach. This simulated energy surface is thus only dependent on the charge density. Preliminary calculations seem quite encouraging. This may be of interest for Molecular Dynamics, since such methods rely totally on the assumed energy surface. The method is based on the assumption of central symmetry of the molecules.

We also considered polarization effects in fragments. For example, for simple molecules, we study the evolution of fragments when changing interatomic distances. Simple and general trends appear, that can be empirically modelled and related to polarisabilities or vibrational parameters.

The method can be used either with theoretical or experimental densities.

References


PS09.02.07 PROPERTIES OF THE PROMOLECULE. B. Etschmann, E. N. Maslen. Crystallography Centre, The University of Western Australia, Nedlands, 6907, Australia

The power of the promolecule model, which consists of a (Hartree) product of the free atom wave functions, can be partly attributed to the number of chemical and physical properties that are unique functionals of the one-electron density.

Evaluating atomic charges on overlapping neutral atoms in a promolecule may appear anomalous, but the close relationship between bonding and potential energies makes it physically reasonable to subordinate electron density in proportion to each atom's contribution to the electrostatic potential.

Atomic radii are determined in two stages. An invariant component of the radius associated with the atomic cores is first evaluated to the value at which the integral of the density equals the number of core electrons. The second most significant contribution is from the valence electrons, which must be treated as penetrable. The main requirement when evaluating atomic radii from electron density is to evaluate the penetrability of the valence subshells.

The promolecule also gives a good first order prediction of bonding energies for atoms extending across the whole periodic table. Energies predicted for diatomic molecules containing a monovalent anion are divided by the number of protons at the equilibrium spacing approximating bonding energies more accurately than integral point charges at these locations.

Values for these properties predicted by the promolecule model will be compared with experimentally measured equivalents for the garnet Yb3Al2O12.

Results

1. The difference between the HF and DFT exceeds experimental uncertainty.
2. The description of the atoms is an important part of the discrepancy between HF and experiment.
3. The interaction densities, resulting from HF and DFT calculations, do not differ significantly.
4. Bond structure calculations are not essential for the determination of the interaction density; with well-chosen parts of many-molecule clusters one can construct molecules that hardly differ from molecules in the crystal. Cluster calculations allow the use of larger basis sets.

PS09.02.09 THE CHARGE DENSITY OF DL-ASPARTIC ACID. R. Flaug, T. Koritsanszky, P. Lugter, Z. Zobell, Institute for Crystallography, Freie Universitét Berlin, Germany

A full topological analysis of the electron density of DL-aspartic acid extracted from low temperature (20 K) X-ray data collected with solid state detector and AgKα radiation has been completed and the results compared with those obtained from Hartree-Fock wavefunctions.

The multipole refinement of the diffraction data was performed with the XD program package. The static electron density, its Laplacian and various one-electron properties were derived. All critical points of the electron density and the Laplacian were located to characterize the covalent bonds and intermolecular interactions.

Experimental topological parameters for C-O bonds were found to be sensitive to the refinement model applied in the multipole treatment of the X-ray data. The ab initio calculations at the Hartree-Fock level show considerable basis set dependence of the bond topological parameters. To mimic the intermolecular forces in the crystal calculations on molecular clusters were also carried out. The effect of the inclusion of the surrounding molecules on the topology of the charge density especially in the C-O bond has been analyzed.

A comparative study based on diffraction data collected with solid state detector and MoKα radiation is in progress.

PS09.02.08 QUANTUM CHEMICAL AND EXPERIMENTAL STUDY OF UREA. Dirk Feil and Roelof de Vries, Chem. Phys. Lab, University of Twente P.O. 217, 7500 AE Enschede, Netherlands; Vladimir Tsetrelson, D. Mendeleev University of Chemical Technology, Moscow, Russia

Introduction

In urea crystals one finds a considerable interaction density due to the network of strong hydrogen bonds distorting the molecular electron density distribution. The infinite size of the network requires, strictly speaking, band structure calculations to determine this effect.

Crystal Hartree-Fock calculations (HF) have been carried out by Dovesi et al. while DFT-calculations on clusters and on the crystal were carried out with ADF and the Amsterdam BAND program, respectively, as part of the present study. The outcome of the calculations are compared with the experimental results of Swaminathan et al. and of Zevodnik et al.

Results

1. The difference between the HF and the DFT exceeds experimental uncertainty.
2. The description of the atoms is an important part of the discrepancy between HF and experiment.
3. The interaction densities, resulting from HF and DFT calculations, do not differ significantly.
4. Bond structure calculations are not essential for the determination of the interaction density; with well-chosen parts of many-molecule clusters one can construct molecules that hardly differ from molecules in the crystal. Cluster calculations allow the use of larger basis sets.

References

2. T. Koritsanszky et al.; XD, A Computer Program Package for Multipole Refinement and Analysis of Charge Densities from X-ray Diffraction Data
3. Gaussian 92/DFT, Rev. G. 1, M. J. Frisch et. al., Gaussian Inc., Pittsburgh PA, 1993