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Keywords: X-ray_diffraction, serine, dynamic_charge_density

MS41.P09

The Transferability of Atomic Multipoles in Amino Acids and Peptides

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Popular force fields usually employ point charges. Supplementing atomic charges with higher electrostatic multipole moments leads to more accurate charge distribution models. New generation force fields based on multipole models require high level of transferability of atomic multipoles. The aim of this work was to analyze the level of transferability achievable with the use of different methods of molecular density partitioning.

Molecular densities (MDs) were calculated for selected natural amino acids as well as di- and tripeptides in geometries as observed in X-ray diffraction experiment. The MDs were obtained through Fourier space fitting of pseudoatom model to the electron densities resulting from *ab initio* DFT calculations at B3LYP/6-31G** level. Such procedure was selected in order to be compatible with the idea of building a pseudoatom database [1-3] pursued in the charge density crystallography. Atomic multipole moments expressed in local coordinate system were calculated on the basis of three density partitions: directly from pseudoatoms, from atomic densities computed via stockholder partitioning and from atomic basins derived via topological analysis. Standard deviations from averaging over multipole moment components of atoms that are considered equal in their chemical environments (atoms representing the same atom type) were chosen as a measure of transferability.

The advantage of stockholder partition as yielding the best transferability within considered atom types was observed. The results were compared to the calculations of atomic multipoles directly from molecular wave functions (in atomic basins partition).

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Keywords: multipole moments, amino acids, transferability

MS41.P10

Bond Characterization of trans-4,4'-azo-1,2,4-triazole: A Combined Experimental and Theoretical Charge Density Study

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The experimental charge density distribution of a planar centrosymmetric molecule, trans-4,4'-azo-1,2,4-triazole, has been investigated in terms of a pseudo-atomic multipolar expansion

(Hansen-Coppens formalism) using high resolution single-crystal X-ray diffraction data at 100K. A parallel computation based on DFT calculation at the B3LYP level using 6-31G(d,p) basis set was performed on the molecule in gas phase. The electron density will be presented in terms of deformation density as well as the Laplacian distribution. Bond characterizations are expressed in terms of topological properties at the bond critical points; typical covalent character on N−N, N−C bonds are observed. The π bonding-delocalization of the molecule will be further illustrated by the Fermi-hole distribution. A π−π interaction with the inter-planar distance of 3.2 Å is allocated through the BCP and the associated bond paths. The agreement between experiment and theory is good on all intra-molecular interactions; the atomic charges, molecular electrostatic potentials, and natural bond orbital analyses will also be presented.
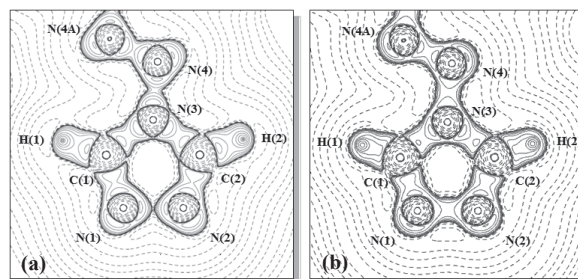

Figure. Laplacian map, $\nabla^2\rho(r)$ in the plane of N1-N2-N4 from (a) the experimental (b) the theoretical charge density.

Keywords: charge density, multipole model, π−π interaction

MS41.P11

New version of UBDB databank and LSDB program, verification and applications

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The theoretical databank of aspherical pseudoatoms (UBDB) has been designed as a set of parameters to be used in standard refinement of crystal structures, as a starting point in high-resolution studies, or also in reconstruction of molecular densities and the evaluation of a number of electrostatic properties of studied molecules. The UBDB consists of all atom types found in peptides, proteins and some other biologically relevant molecules [1]. It had been already shown that the databank corresponds very well to the electron density in a number of amino acids, when compared to conventional *ab initio* methods at the B3LYP/6-31G** level, and also, reproduces the electrostatic interaction energies quite well (~1kcal per mole).

The UBDB was recently extended by over 100 new atom types present in RNA, DNA and in other molecules of great importance in biology and pharmacy. The atom types' definitions were modified and new atom keys added to provide more precise description of the atomic charge distribution. H-X bond lengths were updated according to Allen et al. (2010) [2] and implemented in the LSDB program as well as used for modelling the appropriate atom types. The new version of LSDB and databank is available on the website [3].

UBDB databank was extensively tested. Electrostatic interaction energies calculated on the basis of databank of aspherical atom models (EP/MM method) [4] were compared to the corresponding results obtained directly from wave functions at the same level of theory (B3LYP/6-31G**) (SPDFG program) [5] and to some other theoretical methods [6]. Various small complexes were analysed to cover most of different interaction types and to test the newly added

atoms, *i.e.* adenine- thymine (AT), guanine- cytosine (GC)- hydrogen bonding, guanine- adenine (GA)- stacking, and a group of charged species. The energetic tendencies are very well preserved, however, the energy values differ between the two methods of about 5 kcal/mol on average.

The new version of databank has also been applied to the refinement of selected nucleic acid bases and their modifications as the source of aspherical atomic scattering factors (transferred aspherical atom refinement, TAAM). It significantly improved the final geometries of molecules in the crystal, R factors and ADPs. Several other calculations were performed for the aforementioned solved structures *i.e.* periodic calculations in CRYSTAL06 [7], energy calculations with PIXEL package [8]. The results were compared to the energy values obtained with the aid of a number of force fields in order to get an idea of the accuracy and limits of all the methods [9].

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Keywords: nucleic acids, aspherical pseudoatoms, electrostatic interaction energy

MS41.P12

Comparison of electrostatic energies between selected DNA-ZnF complexes

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Zinc Fingers (ZnF) are small protein domains widely present mostly in *Eucaryota*. Among other structural subgroups of ZnF, the most relevant is C2H2-like family, with zinc ion tetrahedrally coordinated by two cysteine and two histidine residues. Such ZnF domain consists of 24 aminoacids folded into two anti-parallel beta-strands and an alpha-helix and recognizes DNA via hydrogen bonding with outer side of helix. ZnF can be combined with an effector domain e.g. transcriptional activator, transcriptional represor, methylation domain or nuclease. Especially ZFNs have the greatest role in molecular biology and medicine: their ability to recognize (ZnF) and cut DNA sequence (nuclease) is widely used in gene therapy.

Several structures of ZnF interacting with DNA were deposited in PDB databank. The structures with the best resolution were chosen for further studies and the UBDB databank [1] was extended with a set of new atom types.

The theoretical approach applied in this study is based on transferability of electron density parameters between atoms in chemically equivalent environments. It allows to reconstruct the unperturbated, static electron density of larger systems on the basis of experimentally obtained geometry. The electrostatic energy of interaction was calculated with EPMM method developed by Volkov [2] including Exact Potential for overlapping charge distributions and Buckingham-type multipole approximation for non-overlapping charge distributions. The quantitative characterization of particular electrostatic interactions for selected structures of interest will be presented and discussed.

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Keywords: electrostatic, protein, zinc

MS41.P13

Experimental charge density study and bond characterization on [Cu(I)(4-pytH)₂](HC₄O₄)

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TThe title compound, $[Cu(I)(4-pytH)_2](HC_4O_4)$ (4-pyt = pyridine-4-thiolate), can be obtained by the in-situ generation of 4-pytH ligand obtained from the 4-dpds (4,4'dipyridyldisulfide) precursor through the reductive cleavage of the disulfide bond of 4-dpds under solvothermal conditions. The structural analysis reveals that the tetrahedral Cu(I) ion is bonded to four sulfur atoms of the 4-Hpyt ligands forming a 1D cationic chain-like framework, $[Cu(I)(4-pytH)_2]^+$, and further extended to a pseudo-3D supramolecular architecture via the intermolecular $\pi-\pi$ interactions and the hydrogen bonds between cation and monohydrosquarate, The Cu(I) ion is coordinated to sulfur atoms with four different Cu−S distances, 2.2458(2), 2.2793(1), 2.2983(1) and 2.8023(2)Å. A $HC_4O_4^-$ dimer is formed through two strong O−H··O hydrogen bonds with the O··O distance of 2.500 Å. The experimental charge density distribution of $[Cu(I)(4-pytH)_2](HC_4O_4)$ has been investigated in terms of a pseudo-atomic multipolar expansion (Hansen-Coppens' multipole model) using high resolution single-crystal X-ray diffraction data at 100(2) K with sinθ/λ up to 1.0 and synchrotron data at 10(2) K with sinθ/λ up to 1.3. The electron density will be presented in terms of deformation density as well as the Laplacian distribution. Bond characterizations are expressed in terms of topological properties associated with the bond critical points including the dative covalent Cu−S bonds and typical covalent character on N—N, N—C and C—C bonds. The detail comparison between in house and synchrotron data sets will be performed and the topological properties of those intra- and inter-molecule interactions will also be discussed in details.

Keywords: Cationic chain, Charge density analysis, Bond characterization

MS41.P14

MoProViewer: a molecular viewer for the MoPro charge density analysis program

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The MoPro program suite [1] is a crystal structure and charge density refinement package which includes two main modules: the MoPro least-squares refinement program and VMoPro, a tool dedicated to the computation of properties derived from the electron density. MoPro already possesses its own graphical user interface, but VMoPro was still a text-based program.

P.MS.41