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Advanced tools for charge density refinement and estimation of errors

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A review of some new advanced tools available within the MoProSuite [1] software for electron density refinement will be given.
For instance an alternate model to multipoles is proposed to describe the electron density using spherical scatterers on the covalent bond and lone pairs sites [2]. The Hansen & Coppens multipoles yield better R-factor values and residual electron densities than the spherical virtual atoms as the larger number of parameters gives more flexibility. Electrostatic properties are however well reproduced by the spherical atoms and additional charges model.
A database describing the electron density of common chemical groups using combinations of real and virtual spherical atoms is proposed. It is based on 38 crystal structures of small molecules for which theoretical structure factors were computed from periodic density functional theory calculations and the charge density was subsequently refined
The spherical charges modeling can allow for calculation of electrostatic energies as fast as for the point charges model. Fitted exponential functions a.exp(-b.r) which reproduce well the interaction energy between pairs of spherical charges are used for this purpose.

The implementation of spherical harmonics beyond hexadecapoles up to level l = 6 allows for the more flexible treatment of d and f-electron systems and can improve the accuracy of multipolar models for heavy elements. Such modelling has been applied on the electron density distribution of [PPh4][UF6] which was obtained from high-resolution X-ray diffraction data measured at 20 K [3]. Additionally, refinement of the anomalous dispersion coefficients has been implemented and tested on the uranium compound because these terms have been shown to vary in heavy elements depending on the chemical environment.

Application of the MoProViewer software to the analysis of crystal contacts and electrostatic fingerprint plots by the Hirshfeld surface methodology will be discussed.

Finally, a new methodology to determine errors based on perturbed structures and charge density models is proposed within the MoPro software [1]. Sets of random numbers R for all structural and charge density parameters are generated to create molecular models at standard deviation. The perturbed models X' are obtained by equation: X' = A R,
where A is a definite positive square root of the inverted normal matrix.
Sample standard deviations (ssd) of values can be computed from, for example, typically 20 altered models. Reliability of topological properties at the critical point, electrostatic potential and interaction energy can be fully assessed this way.
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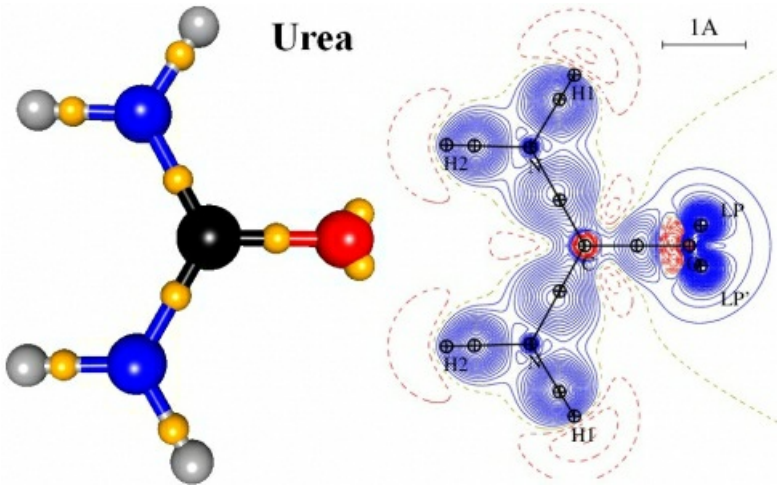

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