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Refining Structures of Molecular Crystals through Modern Methods of Quantum Crystallography

Wednesday, 14 September 2022 14:30 (30 minutes)

Quantum crystallography is an emerging field of science having the goal of investigating properties and phenomena of the crystalline state that can be explained only if one uses the laws of quantum mechanics [1]. To accomplish this task, several methods have been developed over the years [2]. They range from the traditional multipole model techniques for the determination of experimental electron densities through X-ray diffraction data to the more recent X-ray restrained wavefunction (XRW) approach and Hirshfeld atom refinement (HAR) strategy, which are characterized by a stricter relationship with the methods of quantum chemistry [3].
In this presentation, the focus will be on the Hirshfeld atom refinement [4], a technique that requires a quantum chemical calculation at each step of the procedure and that, using only X-ray diffraction data, allows the determination of hydrogen atom positions with the same precision and accuracy usually attained by means of neutron diffraction measurements. After a general introduction on the main features and capabilities of HAR, recent methodological advancements in this research field will be presented and discussed.
First of all, we will consider the extension of HAR to large molecules (e.g., macromolecules of biological interest) through its coupling with libraries of extremely localized molecular orbitals (ELMOs) [5], namely with databanks of molecular orbitals that are strictly localized on small molecular fragments (i.e., atoms, bonds and functional groups) and that allow instantaneous reconstructions of wavefunctions and electron densities of biosystems. The validation tests of the recently proposed HAR-ELMO method on small polypeptides and proteins will be shown and analyzed in detail [6].
In the second part of the talk, we will consider the coupling of HAR with the new multiscale embedding technique QM/ELMO [7], a quantum chemistry approach where only the chemically relevant region of the examined system is treated at fully quantum mechanical level, while the remaining part is described through transferred and frozen extremely localized molecular orbitals. In this context, we will present the development of the novel HAR-QM/ELMO strategy and we will show how the method has been already successfully exploited to accurately refine structures of molecular crystals characterized by strong intermolecular interactions [8].

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