Accurate refinement of hydrogen atoms positions through a quantum mechanical embedding scheme based on extremely localized molecular orbitals

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Several physico-chemical properties of materials and biological molecules crucially depend on the hydrogen atom positions. Therefore, obtaining reliable three-dimensional structures of molecules and materials is a crucial step to have accurate results.

Unfortunately, the weak X-rays scattering power of hydrogen atoms makes them usually very hard to detect accurately. Besides, the choice of the refinement method has also a strong influence. The most widely used approach, the i*ndependent atom model* (IAM), describes the total electron density as the sum of spherical atomic densities centred on the nuclei. This approximation evidently fails when applied to hydrogen atoms because their only electron is delocalized in forming a bond. As a result, bonds lengths involving hydrogen atoms are generally too short.

Over the years, different methods have been proposed to overcome this drawback. Within the field of quantum crystallography, the *Hirshfeld atom refinement* (HAR) approach is one of the most promising strategies [1]. HAR is a technique exploiting fully quantum mechanical calculations to obtain tailor-made *ab initio* electron densities, which are partitioned into aspherical atomic contributions to fit experimental structure factors without further approximations. HAR is able to provide X-H bond distances that are in very good agreement with those obtained from neutron diffraction experiments [1-3]. Moreover, the introduction of crystal environment effects is crucial to carry out better refinements, especially when strong intermolecular interactions are present. This is usually done by adding point charges at symmetry-related atomic positions around the selected reference crystal unit [1-3].

In this contribution, we introduce an improvement to the description of crystal field effects in HAR exploiting the recently developed quantum mechanics/extremely localized molecular orbitals (QM/ELMO) technique [4,5]. In our new modified version of HAR, the reference crystal unit is treated variationally at quantum mechanical level as in the traditional HAR, while the symmetry-related crystal units are described using pre-computed frozen extremely localized molecular orbitals [6]. The ELMOs contribution describing the crystal environment is included in the Hamiltonian of the reference crystal unit through an electrostatic embedding.

Other than discussing the theoretical framework at the basis of the new strategy, we will show test refinements performed on the xylitol crystal, a system characterized by an extended network of strong hydrogen bonds. The results show that the new ELMO-embedded HAR approach gives bond lengths involving hydrogen atoms in optimal agreement with neutron results, outperforming not only the traditional HAR but also the charge-embedded HAR technique in practically all the cases [6].

Given the promising results, we envisage the application of the new ELMO-embedded HAR technique to refine structures of crystals with strong intermolecular interactions. However, further test-bed refinements will be necessary to draw final conclusions, also considering other aspects such as basis-sets and theoretical methods dependence.

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