Estimating ADP's of Hydrogen Nuclei for Charge Density Analysis

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Charge density analysis of X-ray diffraction data requires accurate treatment of the motion of all nuclei in order to deconvolute nuclear motion from the electron distribution. Presently, nearly 80% of charge density studies on molecular crystals assume isotropic motion of hydrogen nuclei, in large part due to the difficulty of performing accurate neutron diffraction studies on all systems of interest. However, failure to model the motion correctly not only alters the topology of the electron density close to the nuclei where the thermal motion has been simplified, but also in the vicinity of neighbouring nuclei [1].

Methods for approximating hydrogen atom ADP's based on a combination of rigid-body analysis and allowances for internal modes have been shown to be quite successful [1,2]. We have recently developed a new method for estimating hydrogen atom ADP's from first principles, using two layer "ONIOM" calculations [3] which mimic the effects of the crystal field and yield internal (high frequency) and external (low frequency) contributions to the nuclear motion. Results obtained for small molecules are consistent with neutron experiments at a variety of temperatures.

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