294 - Extended Hirshfeld: Atomic charges that combine accurate electrostatics with transferability

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Non-polarizable force fields usually model the molecular electrostatics as the interaction between a set of atomic partial charges. A myriad of population analysis schemes can be found in the literature to derive atomic charges from a wavefunction computed with an electronic structure method. Such methods are convenient tools to parameterize the electrostatic energy term in a force-field model. For the development of a force field, the atomic charges must satisfy two criteria: (i) the charges should accurately describe the electrostatic interactions and (ii) the charges must be transferable from (small) model systems to the actual application of interest. Each charge definition makes a specific compromise between these two criteria. For example, ESP fitted charges obviously reproduce the ESP very well but are heavily geometry and environment dependent. The opposite behavior is found with QTAIM charges, which are very transferable but typically overestimate the electrostatic interactions. (For QTAIM, one must include higher atomic multipoles to converge the ESP.) We recently proposed the Extended Hirshfeld scheme with an improved trade-off between both criteria. New benchmarks reveal that Extended Hirshfeld also works well for intra-molecular electrostatic interactions, outperforming ESP fitted charges, which are easily over-fitted to reproduce the ESP outside the molecular van der Waals surface.

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Location: OmniDallas Hotel
Room: Dallas Ballroom D/H

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