Development and Application of Constrained Hirshfeld-based Atoms in Molecules Partitioning Schemes

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Abstract: Experimental chemists have developed a toolbox of concepts such as the chemical bond, charge, electrophilicity, or aromaticity. Despite the absence of a rigorous mathematical definition, these concepts have been successfully applied to rationalize and enhance our understanding of various chemical phenomena. The application of this chemical toolbox within a quantum mechanics framework often requires defining an atom within a molecule from its wavefunction. Nonetheless, because atomic properties do not correspond to a quantum mechanical observable, there is an inherent ambiguity in calculating them. However, their effectiveness and practical utility have driven the development of various methods for decomposing computationally calculated molecular properties into atoms or fragments. In this seminar, I will present my work on developing and applying novel methods for partitioning real-space electron density into atomic regions. Specifically, I will discuss two methods for deriving constrained atomic properties within the variational Hirshfeld framework: charge-constrained Hirshfeld-Iterative (c-HI) and dipole-constrained Additive Variational Hirshfeld (d-AVH). The charges generated by these schemes can improve force fields used in molecular mechanics simulations and improve the description of non-convalent interactions in macromolecules. Lastly, I will present the application of one of these methods to a new approach for the atomic decomposition of static polarizability and hyperpolarizabilities for the study of non-linear optical properties.