Additive Variational Hirshfeld Atoms-in-Molecules Partitioning

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It is common to use the electron density to partition a system into atomic regions. The necessity for such a partitioning scheme is rooted in the unquestionable role of atoms in chemistry. Nevertheless, atomic properties are not well-defined concepts within the domain of quantum mechanics, as they are not physical observables. One of the most popular families of atoms-in-molecules models is the Hirshfeld partitioning schemes. [1-2] The various flavors of the Hirshfeld scheme mainly differ in choosing the reference proatomic density that is being used to define the fuzzy atomic densities.

To resolve the ambiguity in choosing the reference proatomic density, we first justify the pervasiveness of Hirshfeld atoms-in-molecules partitioning. [3-5] Specifically, we prove that the family of *f*-divergence measures is necessary and sufficient for deriving Hirshfeld partitioning, and realize that among all possible *f*-divergences, only the extended Kullback-Leibler information measure is a suitable choice. This motivates our new partitioning method, called the Additive Variational Hirshfeld (AVH) partitioning which defines the proatomic density as a convex linear combination of the spherically-averaged charged atomic electron densities. The AVH method is implemented in the ChemTools software package [6], and its robustness is confirmed by testing it on chemically diverse datasets. Considering its unique mathematical properties and our favorable numerical results, we believe that AVH has the potential to supplant other partitioning methods, and is a suitable choice for machine learning local atomic properties.

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