Recent developments in energy decomposition analysis: From components to observables and back again.

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Abstract:

Energy decomposition analysis (EDA) is increasingly used for applications such understanding non-covalent interactions, chemical bonds, and even aspects of chemical catalysis and reactivity. Yet EDAs themselves cannot be considered entirely mature themselves. With this in mind, I will discuss the current status of the Absolutely Localized MO (ALMO) EDA, which attempts to decompose supermolecular calculations on molecular clusters into underlying physical driving forces, such as Pauli repulsions, permanent and induced electrostatics, dispersion, and charge-transfer [1]. Recent developments to refine the DFT-based ALMO-EDA and to rigorously extend successful SCF-level ideas to a post-SCF ALMO-EDA will be discussed. An important frontier is linking EDA components to observable properties, and I will discuss examples of how this can be accomplished, with a focus on the newly introduced Force Decomposition Analysis (FDA).

[1] Y. Mao, M. Loipersberger, P. R. Horn, A. Das, O. Demerdash, D. S. Levine, S. P. Veccham, T. Head-Gordon, and M. Head-Gordon, "From intermolecular interaction energies and observable shifts to component contributions and back again: A tale of variational energy decomposition analysis", *Annu. Rev. Phys. Chem.* **72**, 641–666 (2021).