A Free Energy Decomposition Analysis

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In the pursuit of understanding the nature of the chemical bond, many energy decomposition analyses (EDA) have been developed. The most widely used of these are the Morokuma-Ziegler EDA in the Baerends-Bickelhaupt implementation (MZ-EDA) [1], the Natural Energy Decomposition Analysis (NEDA) [2] and the Localised Molecular Orbital EDA (LMO-EDA) [3], but many other approaches exist [4]. A common goal of these EDA is the rationalization of the driving forces behind bond-braking and bond-formation as well as the classification of individual chemical bonds in terms of common heuristics that are widely used in chemistry.

However, when these EDA are used to describe the driving forces of chemical reactions, important thermal contributions to the enthalpic and entropic changes along the reaction pathway are completely ignored. This is most acutely problematic for the description of endothermic reactions, but still of major importance in exothermic processes. Here, we present an analysis that decomposes the Gibbs Free Energy of Reaction into components of electronic origin, the bond-braking and bond-formation, as well as other thermochemical contributions that can be derived from statistical mechanics.

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