

Energy Decomposition Analysis in an “Adiabatic” Picture: Theory and Application

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Energy decomposition analysis (EDA) of electronic structure calculations enables quantitative understanding of various intermolecular interactions. One limitation of most existing approaches is that they usually perform the analysis at a single geometry and thus decompose a “single-point” interaction energy. As a result, the influence of each physically meaningful interaction component on the molecular structure and other properties are not directly obtained.

To address this gap, we reformulate the absolutely localized molecular orbital (ALMO)-EDA in an “adiabatic” picture, where the frozen, polarization, and charge transfer (CT) energy contributions are defined as energy differences between the stationary points on different potential energy surfaces (PESs), which are accessed by performing geometry optimizations at the frozen, polarized, and fully relaxed levels of density functional theory (DFT). The structural change at each level is thus directly characterized, and the shifts in other properties such as multipole moments, vibrational frequencies can also be obtained at the stationary point on each PES. This method provides a complementary and more “panoramic” view of intermolecular interactions than conventional EDA methods, and is especially useful in interpreting the changes in molecular properties induced by intermolecular interactions.

Besides proof-of-the-concept applications, we utilized the “adiabatic” EDA to study the red- and blue-shift phenomenon in hydrogen-bonding systems and metal-carbonyl complexes. New insights into the origins of these vibrational frequency shifts are obtained. In addition, by extending this approach to the constrained DFT (CDFT)-based definition of “CT-free” state, the observable consequences of CT calculated using the ALMO and CDFT definitions are compared. The results suggest that the former is more compatible with the well-accepted role of CT in non-covalently bound intermolecular complexes.