Energy Decomposition Analysis for Systems Involving Excited State Molecules

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An energy decomposition analysis (EDA) method is developed for unraveling the nature of intermolecular interactions in systems involving excited state molecules, which is compatible with methods based on linear response theory such as CIS and TDDFT. The EDA utilizes absolutely localized molecular orbitals (ALMOs) to define the frozen and polarized intermediate states, and the shift in excitation energy when an excited molecule interacts with the environment is partitioned into frozen (FRZ), polarization (POL), and charge transfer (CT) contributions. These terms can be added to their counterparts obtained from the ground state ALMO-EDA to achieve a decomposition of the total interaction energy. For excimers (dimers strongly bound in their excited states), an extra intermediate state is introduced between the frozen and polarized states to characterize the excitonic coupling effect between local excited states, and its energy difference relative to the frozen state is defined as the excitonic-splitting (EXSP) term. This EDA scheme is utilized to study a variety of systems, including exciplexes (e.g. excited pyridine/pyrimidine-water complexes) and excimers formed by noble gas atoms and aromatic compounds. Useful insights can be obtained regarding the role that each term plays in the formation of these excited intermolecular complexes.