New Theoretical Tool for Modeling and Analyzing Two-Photon Absorption Processes

Kaushik D. Nanda[1] and Anna I. Krylov[1]

[1]Department of Chemistry, University of Southern California, Los Angeles, California 90089-1062, United States of America

Understanding two-photon absorption (2PA) transitions at the molecular level in terms of molecular orbital theory is critical not only for characterizing the experimental 2PA spectra but also for designing novel organic materials with enhanced/tunable 2PA activity for many applications in chemical, biological, and materials sciences. Elucidating the orbital picture, however, has been difficult for nonlinear processes such as 2PA for which the experimental observables are given by the familiar sum-over-states expressions. We will present a quantitative wave-function analysis tool for characterizing 2PA transitions in terms of orbitals. By extending the concepts of transition density and natural transition orbitals to 2PA transitions, we will demonstrate that this tool provides a rigorous black-box alternative to traditional qualitative few-states analysis of 2PA cross sections. We will highlight the utility of this tool by considering 2PA transitions in benchmark systems. We will present our perspective on extending this toolkit for understanding other nonlinear processes and the impact of intermolecular interactions on nonlinear properties.