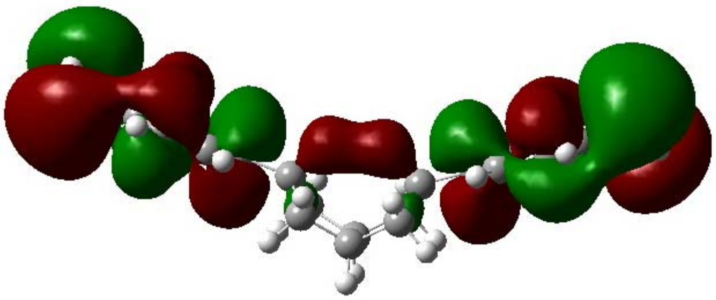
Electron Transfer and Electronic Coupling

Professor Robert J. Cave, Harvey Mudd College, CHE-0353662

Research Experiences for Undergraduates

Many chemical and biological systems involve electron transfer reactions. Therefore there is significant interest knowing the rate (k_{et}) of these reactions. The distance and orientation dependence of these reactions are predominantly based on the magnitude of the electronic coupling element (H_{DA}). In electron transfer reactions in proteins, electrons tunnel from a donor to an acceptor by traversing three different broad categories of contact. The electron can pass through covalent bonds, hydrogen bonds, or Van der Waals contacts. In the Pathways model, each of these paths are given a decay constant which is a measure of how much the magnitude of H_{DA} will decay if the electron travels through that junction.

Undergraduate Student Westin Kurlancheek (HMC) demonstrated the feasibility of obtaining the electronic coupling element using a variety of computational methods to gather all the relevant information with which to calculate H_{DA} using Generalized Mulliken-Hush. Calculations were done on small model systems designed to imitate the three types of coupling interactions mentioned in the Pathways model. Results show that the Pathways model overestimate the importance of hydrogen bonds and underestimates the importance of Van der Waals contacts. Furthermore, our results indicate that there is little difference between these two types of weak interactions, which is contrary to popular belief.



System in which the through-space contact contributes greatly to the electronic coupling