Final Report

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**"Designing macromolecular electron delivery systems
for artificial biocatalysis."**

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We have made substantial progress in four areas: (1) multi-electron electron transfer processes, (2) coupled quantum/molecular dynamics studies of protein electron transfer, (3) quantum mechanical studies of DNA electron transfer processes, and (4) inverse design of new materials.

Multi-electron electron transfer processes. Chemical, biological, and electrode based electron transfer (ET) processes involve multi-electron events. However, an adequate framework in which to describe these complex reactions does not yet exist. A theory for two-electron transfer reactions in Debye solvents was developed. The theory is formulated by generalizing Zusman's model of ET reactions to those involving three parabolic wells: one for the doubly reduced donor, one for the singly reduced donor/singly reduced acceptor, and one for the doubly reduced acceptor. The ET processes are described in terms of diffusional motion along a one-dimensional reaction coordinate with tunneling transitions at the intersection points of the parabolas. Two competing mechanisms of two-electron transfer arise. One is a process with two sequential single electron steps $D^+=A \rightarrow D^+A^- \rightarrow DA^=$. The other involves ET in one concerted two-electron step ($D^+=A \rightarrow DA^=$). The general rate expressions for two-electron transfer are obtained. When the stepwise mechanism dominates, the free energy of activation is predicted to depend upon the driving forces of the two sequential steps but is independent of the overall driving force of the reaction. When concerted two-electron transfer dominates, the Marcus relation is obtained with a reorganization energy associated with the shift of two electrons. The dynamical solvent effect in two-electron ET processes is predicted to be unusual. Two distinct regimes exist, each with essentially linear τ_L dependence (with τ_L the solvent longitudinal relaxation time): one for slow solvents and one for fast solvents. A combination of solvent and free energy studies could be used to elucidate the mechanism of multi-electron processes in chemical and biological systems.

Coupled quantum/molecular dynamics studies of protein electron transfer. Coupled quantum mechanics and molecular dynamics simulations were performed to investigate the role of secondary structure and small geometrical fluctuations on the long range electronic coupling in peptides. Molecular dynamics simulations were performed to obtain typical relevant conformations of the oligopeptides and self-consistent Hartree-Fock calculations at the semiempirical quantum theory level were performed to extract the long range electronic coupling. α -helical oligopeptides in the initial structure show a dominant contribution due to hole mediation over a long range of tunneling energy, while the initial β -stranded oligopeptides have more equal contributions from both hole and electron mechanisms. Geometrical fluctuations lead to drastic changes in the couplings, including cancellations arising from destructive interference from distinct pathways or between the electron and hole contributions to the coupling. The computations highlight the danger of drawing conclusions from electronic structure calculations of electronic coupling in proteins based upon computations on single geometries.

DNA electron transfer processes. The earliest studies of electron-transfer proteins raised the question of whether or not π -electron residues might facilitate electron transport. Three recent long-range electron-transfer experiments utilizing DNA bridges revisit this provocative, yet unresolved, question. The distance dependence of electron transfer in DNA is not a matter of purely academic concern; it controls the mechanism of DNA damage and repair in cells, and is being exploited in new molecular probes of DNA sequence. We have presented a theoretical analysis based upon very large scale self-consistent-field quantum calculation of all valence electrons (as many as ~ 3300) in these three systems. This computation is the first performed on such large macromolecules, and also the first to extract long-range electronic interactions at this level of theory. DNA electron-transfer is found to be mediated by through-space interactions between the π -electron containing base pairs, but the magnitude of the coupling facilitated by this channel drops rapidly with distance, as a consequence of the ~ 3.4 Å noncovalent gap between base pairs. These predictions are in agreement with most of the experimental data. The rapid decay of electron-transfer rates with distance computed here suggests that biologically controlled DNA electron-transfer events, of importance in DNA repair, must function over relatively short-range. Moreover, the predicted distance dependence of electron-transfer in DNA is strikingly close to that found in proteins.

Inverse design of new materials. An "inverse" molecular design strategy was developed to assist in the development of new molecules with optimized properties. This approach is based on a molecular orbital view and can be used to tailor ground state or excited state properties subject to particular constraints. In this scheme, wave functions are sought that optimize a chemical or electronic property, and then a Hamiltonian is constructed that generates these optimized wave functions. Analysis of the chemical properties in the optimized systems may suggest new synthetic targets. Examples were analyzed in order to optimize certain optical properties in simple structures.

Project output.

The details of this project are well documented in the scientific literature. Reprints are attached. The relevant citations are:

Journal and book articles acknowledging this DOE support:
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