Electron transfer pathway control in biomolecular and small molecule systems: the role of fluctuations

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Electron transfer reactions are ubiquitous in biology, chemistry and are central to molecular electronics technologies. In biology they are observed in both protein and DNA systems. Biological electron transfer mechanisms range from tunnelling to thermally activated hopping. Due to the floppiness of biomolecules, molecular motion is an important determinant of the electron transfer rate. The electronic couplings that enable electron transfer in biomolecular systems can be understood in terms of competing and interfering electron transfer pathways that are controlled by structure, dynamics, and initial state preparation. We review the underlying theory and recent theoretical and experimental progress on the effects of conformational distributions, excited-state polarization, and electron-nuclear dynamics on electron transfer reactions in biomolecular and small molecule systems. We discuss electron-transfer-rate control in the presence of a highly fluctuating environment.

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