Quantum Effects In Hydrogen Transfer Reactions

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Protein motion is an essential component of enzyme catalysis. When small particles like hydrogens are transferred, quantum effects such as tunneling and zero-point energy play an important role in their motion. In order to interpret experimental results, an effective theoretical model must thus incorporate nuclear quantum effects and the influence of protein motion on the transfer reaction. Here, an adaptable simplified model is used to simulate hydrogen transfer in various regimes. The model includes a hydrogen-transfer coordinate with a double-well potential whose barrier is attenuated by a donor-acceptor coordinate with a Lennard-Jones-type potential (Figure 1). Both coordinates are coupled to dissipative baths. Nuclear quantum effects of hydrogen transfer are modeled using ring polymer molecular dynamics, which provide accurate quantum dynamics while still allowing for the use of classical equations of motion. Dynamical sampling from the dividing surface and free energy sampling are used to understand the relationship between donor-acceptor gating motion and quantum effects during hydrogen transfer. Use of this model will allow for a more complete examination of hydrogen transfer reactions and in the interpretation of kinetic-isotope effects in other chemical systems.

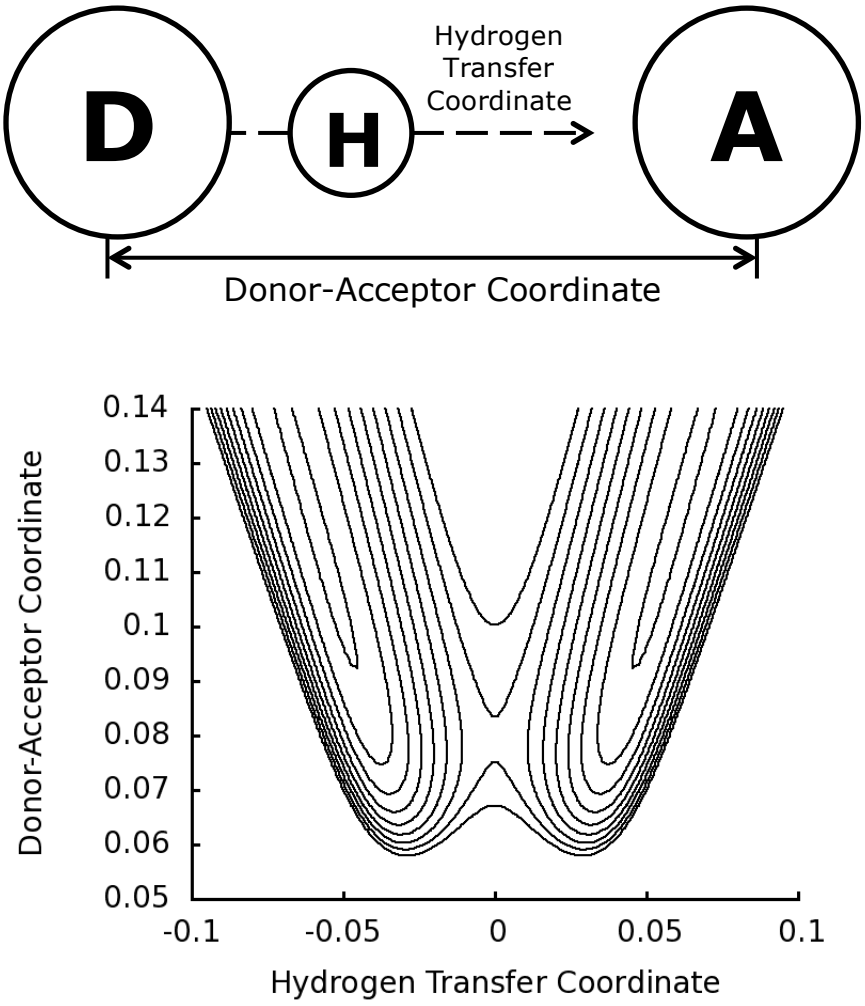

Figure 1. (top) A hydrogen atom (H) is transferred from a donor site (D) to an acceptor site (A). The progress of the reaction is measured along the hydrogen transfer and donor-acceptor coordinates. (bottom) Contour map of the two-dimensional potential energy surface. Minimum contour is at -10 kJ/mol in the basins and maximum contour is at 80 kJ/mol at the edges. Contour increments are 10 kJ/mol.