We discuss the hydrogen tunneling problem in the active site of the biological enzyme, soybean lipoxygenase-1. Toward this, we utilize quantum wavepacket dynamics [1, 2, 3, 4] performed on potential surfaces obtained by using hybrid density functional theory under the influence of a dynamical active site. By computing the tunneling matrix nuclear orbitals (eigenstates) along the reaction coordinate, we note that tunneling for both hydrogen and deuterium occurs through the existence of distorted, spherical-like proton wave functions and p-type polarized proton wave functions for transfer along the donor-acceptor axis. In addition, there is also a significant population transfer through distorted p-type proton wave functions directed perpendicularly to the donor-acceptor axis (see intervening at-proton eigenstate interactions) which underlies the three-dimensional nature of the tunneling profile. The quantum dynamical evolution of the complete iron cofactor and complex linoleic acid substrate.

As a model of SLO-1, we used pruned representa- tion of the active site amino acid ligands binding to the central iron atom in addition to a portion of the substrate that contains the r-hydrogen atoms on either side of the donor acceptor axis. The variation of the reaction coordinate (RcR − ROH/ROCO) as a function of the number of steps is displayed in the figure below with the active site geometries in right panel (reactant state: (a), shared proton state: (b), and product state: (c)). In the figure below, the evolution of first three proton (left panel) and deuterium (right panel) eigenstates are displayed. The classical transition state is shown by using a vertical dashed line.

In the figure below, the evolution of first three proton and deuterium eigenstates (d-1) are displayed. It should be noted that if an effective re- sonation action profile were to be constructed that included contributions from the quantum mechanical ground state of the tunneling nucleus, the new profile would display a maximum closer to the reactant. This ef- fect is completely caused by the quantum mechanical nature of the hydrogen nu- clear and the associated potential-energy surface. The classical transition-state localize the hydrogen energy transfer points to the acceptor side (right panel in above figure), and intermediate-state surfaces enforce a double-well character that retains the proton to be partially bound to both donor and acceptor.

For constructing proton potential surface, the electronic-structure calculations at each model geometry were performed using the BLYP density functional and 6-31G Gaussian-type basis set. The classical transition-state is shown by using a vertical dashed line. The classical transition-state localize the hydrogen energy transfer points to the acceptor side (right panel in above figure), and intermediate-state surfaces enforce a double-well character that retains the proton to be partially bound to both donor and acceptor.

In the figure, below, the evolution of first three proton (left panel) and deuterium (right panel) eigenstates are displayed. The classical transition state is shown by using a vertical dashed line. (ac) and deuterium ground eigenstates (d-1) are displayed.