MINIMUM FREE-ENERGY PATHS OBTAINED FROM UMBRELLA SAMPLING

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Transition paths characterize chemical reaction mechanisms. Here we present a new method to find mean reaction paths based on the free energy. A nudged elastic band (NEB) is optimized using gradients and Hessians of the free energy, which are obtained from umbrella integration. The transition state can be refined by a NewtonRaphson search starting from the highest point of the NEB path. Independent molecular dynamics (MD) runs are performed at each image used to discretize the path. This makes the method intrinsically parallel. In contrast to other free energy methods, the algorithm does not become more expensive when including more degrees of freedom in the active space. The method is applied to the alanine-dipeptide as a test case and compared to pathways that have been derived from metadynamics and forward flux sampling.

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