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Improving Density Functional Tight Binding Predictions of Free Energy Surfaces for Slow Chemical Reactions in Solution MATTHEW KROONBLAWD, NIR GOLDMAN, Lawrence Livermore National Laboratory — First principles molecular dynamics using highly accurate density functional theory (DFT) is a common tool for predicting chemistry, but the accessible time and space scales are often orders of magnitude beyond the resolution of experiments. Semi-empirical methods such as density functional tight binding (DFTB) offer up to a thousand-fold reduction in required CPU hours and can approach experimental scales. However, standard DFTB parameter sets lack good transferability and calibration for a particular system is usually necessary. Force matching the pairwise repulsive energy term in DFTB to short DFT trajectories can improve the former's accuracy for reactions that are fast relative to DFT simulation times (<10 ps), but the effects on slow reactions and the free energy surface are not well-known. We present a force matching approach to improve the chemical accuracy of DFTB. Accelerated sampling techniques are combined with path collective variables to generate the reference DFT data set and validate fitted DFTB potentials. Accuracy of force-matched DFTB free energy surfaces is assessed for slow peptide-forming reactions by direct comparison to DFT for particular paths. Extensions to model prebiotic chemistry under shock conditions are discussed. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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