Limitations of reaction barrier benchmarks with fixed geometries

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A sizable fraction of the advancements in accuracy for density functionals over the last two decades have been due to insights from benchmarking studies. These studies are usually done at frozen geometries due primarily to computational cost. This works extremely well for some properties such enthalpy of formation, for example; a given density functional will give about the same error bar in ΔH_f if the molecules in question are optimized with that functional or not. However, fixed geometries are not very good when benchmarking barrier heights except at the high end of the accuracy range. Functionals with high accuracy in predicting barrier heights with frozen geometries tend to produce good transition state geometries, so optimization is not required for functional ranking at the low error end of the scale. At the lower accuracy end of the spectrum, this is not the case, and we demonstrate here that in some cases the functionals when used to optimize the geometries actually do significantly worse in predicting barrier heights, including a few cases where transition states disappear completely, which makes numerical value for these errors inappropriate. This work emphasizes the necessity of using high accuracy functionals for reaction modeling in spite of the slightly higher expense.