Excited-state machine learning molecular dynamics simulations on nanosecond time scales

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Many important processes in nature and life on earth are photo-induced. To unravel fundamental mechanisms at the basis of these processes, excited-state ab-initio molecular dynamics simulations can be carried out, that describe the motion of a molecule after its excitation with light. As undoubted as the importance of this method is its limitation to short time scales, which is due to the unfortunate cost of the underlying on-the-fly quantum chemical calculations [1]. In this work, we circumvent this bottleneck by machine learning algorithms, that speed up simulations up to a factor of 4000 and make nanosecond molecular dynamics simulations possible within only a couple of days [2]. As an example, we show the surface hopping molecular dynamics simulations of the methylenimmonium cation. We also treat spin-orbit and nonadiabatic couplings of additional molecules with up to 66 degrees of freedem, for which we generated reference data by random grid sampling and an adaptive sampling scheme [2,3]. In order to render the reference data learnable, we apply a phase correction algorithm that tracks the phase of the electronic wavefunctions from one reference point to every other configuration inside of the training set. For dynamics simulations and the computation of wavefunction overlaps we utilized the program suite SHARC (Surface Hopping including ARbitrary Couplings)[1,4]. To further guarantee that our machine learning models predict the potential energy surfaces and corresponding properties correctly, we apply an active learning approach similar to reference [5] by using two models and comparing their outputs on-the-fly. As machine learning models we use multi-layer feed forward neural networks [2] and the deep learning model SchNet [6] that show the scopes and possibilities for treating different excited-state characteristics with high efficiency and on long time scales.

References

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