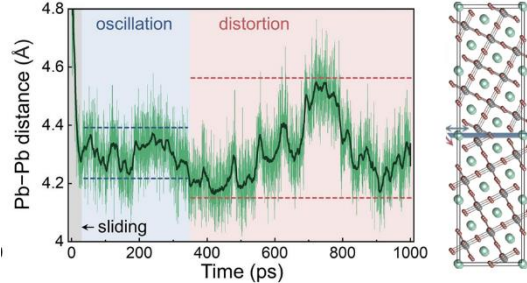


Nonadiabatic Molecular Dynamics with Machine Learning

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$$G_i^{\text{mod}} = 2^{1-\zeta} \sum_{j,k \neq i}^{\text{atoms}} (1 + \cos(\theta_{ijk} - \theta_s))^\zeta \times \text{el} \left[-\eta \left(\frac{R_{ij} + R_{ik}}{2} - R_s \right)^2 \right] f_c(R_{ij}) f_c(R_{ik})$$

$$I(X, Y) = \iint dx dy p(x, y) \log \left(\frac{p(x, y)}{p(x)p(y)} \right)$$

Machine learning (ML) provides tools to both accelerate [1-4] and analyze [5-7] nonadiabatic (NA) molecular dynamics (MD) simulations.

Ab initio quality ML force fields (FF) allow us to perform long MD simulations and observe rare atomic rearrangements. A 100 ps structural rearrangement of a metallic particle on a 2D substrate creates a long-lived hot-electron state that can rationalize plasmon driven photochemistry commonly catalyzed by metallic nanocrystals [1]. Fluctuations of structure of metal halide

perovskites (MHPs) around point defects lead to appearance of very deep trap levels that can be both detrimental and beneficial for optoelectronic performance [2]. Sliding and distortions of grain boundaries in MHPs take nanoseconds and have a significant influence on charge carrier lifetimes [3].

To accelerate NA-MD simulation we use the MD trajectory generated with a ML force field, to compute NA couplings for a small fraction (2%) of geometries along the trajectory and interpolate the NA coupling for the remaining 98% geometries. This is particularly important for MHPs that exhibit complex MD with strongly anharmonic motions and many timescales. The method generates accurate NA-MD results with over an order of magnitude computational saving. [4]

We use unsupervised ML to analyze NA-MD and uncover nontrivial correlations [5-7]. The I-I angle is the key structural parameter in MAPbI₃ [6] and CsPbI₃ [7], the most popular MHPs, governing the NA coupling and the bandgap, although the Pb-I-Pb angle is discussed most. We discover that, surprisingly, MHP structure is much more important than motions, even though the NA coupling depends explicitly on atomic velocity. Also surprisingly, the MA⁺ and Cs⁺ cations strongly influence charge carrier dynamics, even though they do not contribute to electron and hole wavefunctions.

Combining supervised and unsupervised ML [5], we show that mutual information can be used for feature selection and significant reduction of dimensionality of ML models of NA Hamiltonians. Focusing on CsPbI₃ we uncovered that chemical environment of a single element is sufficient in predicting the NA Hamiltonian. The analysis allows us to reduce a typical 360-parameter model used for a ML force-field to just a 12-parameter NA Hamiltonian model.

NA-MD is a valuable tool for studying excited state processes. Overcoming its high computational cost through simple ML models allow us to streamline NA-MD simulations, and expand accessible system size and simulation time.

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