Accurately determining the transition temperature of metal halide perovskites via RPA calculations and phase-transferable machine learning potentials

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In the past decade, metal halide perovskites (MHPs) have shown great potential for various optoelectronic applications. However, their spontaneous transition to an inactive yellow phase impedes the widespread adoption of, e.g., $CsPbI_3$ and $FAPbI_3$. Herein, we present a detailed first-principles procedure to obtain accurate insight in this phase stability by computationally predicting the Helmholtz free energy, which is challenging due to the MHPs' flexible and anharmonic behavior. Using high-level RPA+HF calculations as benchmark for the ground-state energy, we validate the performance of different exchange-correlation functionals and dispersion methods, with SCAN+rVV10 showing the best results. Moreover, we show that including spin-orbit coupling only has a minor effect on the ground state energy. The vibrational density of states is derived using molecular dynamics simulations to account for the MHPs' anharmonicity, and a phase-transferable machine learned potential is trained to speed up the calculations and assess size effects. This procedure is then validated on MHPs, which are challenging materials as their phase stability changes slowly with varying temperature. We demonstrate that our procedure is quintessential to reproduce the experimental transition temperature, as choosing an inadequate functional can easily shift the transition temperature with more than 100 K. This validated protocol can now be adopted to understand the factors influencing the phase stability for a wide range of MHPs.

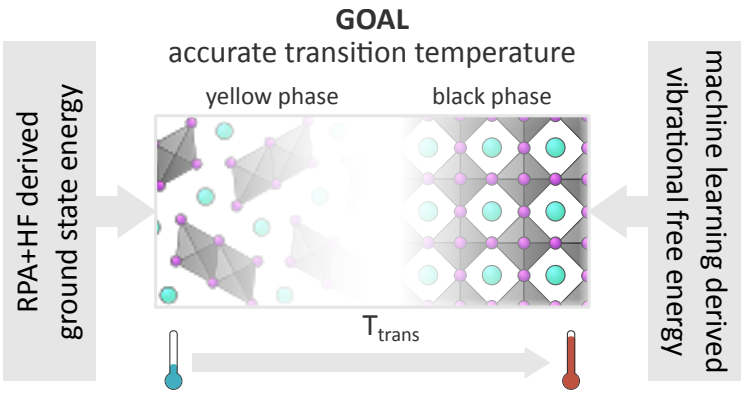

Figure 1. Schematic depiction of our approach to accurately determine the transition temperature in MHPs.