# A Hessian-free method to prevent zero-point energy leak in classical trajectory simulation

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The problem associated with zero-point energy (ZPE) leakage in classical trajectory calculations is well-known. Methods based on classical dynamics of the nuclei may present artefacts due to ZPE leakage. This phenomenon can lead to unphysical results, such as forming products without the ZPE in the internal vibrational degrees of freedom (DOFs). It may also permit reactions below the quantum threshold for the reaction.

This talk will be started by discussing a few previously prescribed solutions to rectify the ZPE spilling. Nevertheless, most of them require the calculation of Hessian matrices during the dynamics, which is unaffordable in the ab initio molecular dynamics framework. Moving on, I shall present a new Hessian-free method, namely, local-pair ZPE correction [1], to prevent energy leakage below a threshold in the internal vibrational DOFs during classical propagation. The idea is to pump the leaked energy to the corresponding internal DOF, taken from the other internal DOFs. Thus, the energy is redistributed over the DOFs conserving the total energy of the system.

This talk will finish with an abrupt jump to nonadiabatic dynamics. The direction of velocity adjustment in the fewest switch surface hopping dynamics should be along the nonadiabatic coupling (NAC) vector. The unavailability of such a quantity forces us to perform the rescaling along the momentum vector, which may lead to bias dynamics. I shall show a newly developed size-extensivity correction scheme for velocity rescaling [2].

[1] S. Mukherjee et al., *J. Chem. Theory Comput.* 18, 4109 (2022);
DOI: 10.1021/acs.jctc.2c00216

[2] G. Braun et al., *J. Chem. Phys.* 157, 154305 (2022);
DOI: 10.1063/5.0113908