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► **To cite this version:**

Saikat Mukherjee, Mario Barbatti. A Hessian free method to prevent zero-point energy leakage in classical trajectories. *Journal of Chemical Theory and Computation*, In press, 10.1021/acs.jctc.2c00216 . hal-03693785

HAL Id: hal-03693785

<https://hal.science/hal-03693785>

Submitted on 13 Jun 2022

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A Hessian free method to prevent zero-point energy leakage in classical trajectories

Saikat Mukherjee ^{a,1*}, Mario Barbatti ^{a,b,2*}

^a Aix Marseille University, CNRS, ICR, Marseille, France

^b Institut Universitaire de France, 75231 Paris, France

¹ ORCID: 0000-0002-0025-4735

² ORCID: 0000-0001-9336-6607

* saikat.mukherjee@univ-amu.fr, mario.barbatti@univ-amu.fr

This is the accepted version of the paper published at <https://doi.org/10.1021/acs.jctc.2c00216>

Keywords: zero-point energy, prevent zero-point energy leak, Hessian free method, classical trajectory simulation

Abstract

The problem associated with the zero-point energy (ZPE) leak in classical trajectory calculations is well known. Since ZPE is a manifestation of the quantum uncertainty principle, there are no restrictions on energy during the classical propagation of nuclei. This phenomenon can lead to unphysical results, such as forming products without the ZPE in the internal vibrational degrees of freedom (DOFs). The ZPE leakage also permits reactions below the quantum threshold for the reaction. We have developed a new Hessian-free method, inspired by the Lowe-Andersen thermostat model, to prevent energy dipping below a threshold in the local-pair (LP) vibrational DOFs. The idea is to pump the leaked energy to the corresponding local vibrational mode, taken from the other vibrational DOFs. We have applied the new correction protocol on the ab initio ground-state molecular dynamics simulation of the water dimer (H₂O)₂, which dissociates due to unphysical ZPE spilling from the high-frequency OH modes. The LP-ZPE method has been able to prevent the ZPE spilling of the OH stretching modes by pumping back the leaked energy into the corresponding modes while this energy is taken from the other modes of the dimer itself, keeping the system as a microcanonical ensemble.

1 Introduction

Zero-point energy (ZPE) is a consequence of the quantum uncertainty principle, and thereby, an inherent error creeps into the propagation of classical trajectories in mixed quantum-classical (MQC) methods by neglecting it. The classical nuclear motion approximation permits reactions below the quantum threshold of energy leading to unphysical results where products can be formed with less energy than ZPE in the internal vibration degrees of freedom. The problem becomes serious if the ZPE flows out of several modes and pumps into a specific weak bond to make it unphysically hot. This ZPE leakage phenomenon is well discussed in the literature,¹⁻⁷ and few strategies have been designed to reinforce ZPE maintenance during quasi-classical trajectories (QCT).

Independently, Bowman et al.⁸ and Miller and Hase^{9,10} proposed a method to constrain the ZPE spilling by time-reversal of the momentum of any normal mode undergoing ZPE leakage. In other words, they imposed a hard-wall

sphere in the phase space, inside of which the energy is less than the ZPE of the corresponding normal mode. Whenever a mode loses energy and the resultant trajectory tends to enter the hard-wall sphere, it is forced to bounce back. This protocol was achieved by monitoring normal harmonic modes at each timestep and reversing the sign of the momentum of the particular mode, which drops its energy below the corresponding ZPE. However, this treatment is valid only when the system is not far from the well-defined equilibrium region. The same algorithm should be applied at any arbitrary nuclear configuration outside the equilibrium region on instantaneous normal modes. However, the method has some apparent shortcomings as the impulsive kicks produce discontinuous linear momenta and vibrational phase of the altered mode.

Lim and McCormack modified¹¹ the hard-sphere model by incorporating a rigid but inelastic wall sphere, where the trajectory is repelled from entering the quantum forbidden zone and is made to “skid” along the ZPE orbit. This prescription, named trajectory projection onto the ZPE orbit

(TRAPZ), was achieved by applying a non-Newtonian force in holonomic constraints dynamics, which showed that each corrected mode's momentum and vibrational phase are continuous. The TRAPZ method was used to study the dissociation of the Al_3 cluster and found a highly vibrationally excited molecular fragment of Al_2 .¹² The overestimation can be rationalized because each mode has to conserve its ZPE even if all the other modes have energy much higher than their ZPE. mTRAPZ¹³ is a softened version of TRAPZ, where the linear momentum transformation is only performed when the total instantaneous vibrational energy drops below the total local ZPE. In other words, now the checking of ZPE leakage is carried out not for individual modes but for the total local vibrational energy of the system to prevent excess addition of vibrational energy at the expense of translational energy.

Varandas and Marques modified the Bowman-Hase-Miller approach of constraining ZPE in quasi-classical trajectory calculations by compensating the amount of energy leak of a bound vibrational mode from the remaining modes of the molecular system.¹⁴ The protocol is the following: at each time step, the local normal mode coordinates (instantaneous normal modes) are determined, and the amount of energy leak for each vibrational mode is calculated. This leaked energy will be given to the local normal mode and withdrawn from the energy pool constructed by the sum of energy in the remaining vibrational modes.

Keeping in mind that the intermode coupling terms in a multimode Hamiltonian govern the energy transfer between the modes, Xie and Bowman proposed¹⁵ a method of annihilating mode coupling by introducing a smooth switching function when the energy of the corresponding mode drops below the ZPE. In principle, this method can be applied to the on-the-fly dynamics of a general polyatomic system. However, it has not yet been tested in this context.

In the past decade, the quantum thermal bath (QTB) model¹⁶ was introduced to quantify the ZPE leakage in molecular simulations using colored-noise Langevin dynamics. In this framework, temporal prevention of the ZPE leakage could also be achieved by increasing the damping coefficient value, but the simulation's accuracy

will be questionable. Recently, an adaptive QTB model (adQTB) has been proposed^{17,18} to suppress the ZPE leakage phenomenon, where the quantum fluctuation-dissipation criterion is actively enforced by adjusting the system-bath coupling parameter during the simulation. In other words, instead of a constant coupling, an "on-the-fly" tuned frequency-dependent coupling parameter is used to construct the Langevin equation of motion. As a result, each vibrational mode of the system is thermalized at an effective temperature that includes the appropriate ZPE, and thereby, the dynamics always accounts for the quantum ZPE effect.

A different approach¹⁹ was taken to conserve the total ZPE throughout a trajectory by constructing an effective potential by adding an estimate of harmonic ZPE at an arbitrary nuclear configuration to the Born-Oppenheimer (BO) molecular potential energy surface (PES). Thus, an effective ZPE-corrected PES was constructed for the H_2CO molecule, and QCT simulations on this modified PES yielded good product state distributions for the roaming reaction.

Apart from the above discussed active ZPE constraint models, few passive techniques have been suggested to overcome the ZPE leakage problem in classical trajectory calculations.²⁰⁻²³ These methods do not alter the dynamics but discard unphysical trajectories from the statistics that either form products with less than their ZPE or form products where the sum of the product vibrational energies is less than the total product ZPE. Although passive methods have been successfully used,²⁴⁻²⁷ they waste an extraordinary amount of computational effort. For example, while studying the roaming dynamics in acetaldehyde, Shepler et al. discarded almost 85% of the products violating ZPE conservation.²³ Therefore, while passive methods may be an alternative when running dynamics on pre-computed potential energy surfaces, they are unaffordable in on-the-fly dynamics, where a single trajectory may cost thousands of CPU hours.

All active ZPE constraint models discussed above (except adQTB) are based on calculating instantaneous normal modes and Hessians. Because the dynamics of realistic molecules is usually based on on-the-fly calculation of electronic quantities and potential energy surfaces are not

pre-computed, to require knowing the Hessian during propagation becomes an insurmountable hurdle even for medium-sized molecules. Moreover, we miss a method that could also be adapted to mixed-quantum classical methodologies based on Born-Oppenheimer molecular dynamics (BOMD), like surface hopping.²⁸ Thus, the conclusion of Guo et al.⁵ that no satisfactory solution to the infamous ZPE spilling problem in classical dynamics has been found to date remains somewhat true 25 years later. Novel techniques devoid of Hessian calculations, tailored to on-the-fly dynamics, and generally adaptable to different dynamics algorithms must be developed if we aim for long-timescale simulation.²⁹

This article takes the first steps to close this methodological gap. We present a new Hessian-free method for correcting the ZPE leakage in a molecule during classical or MQC dynamics in Section 2. Named local-pair (LP) ZPE correction, it is applied on the water dimer (H₂O)₂ system, where the dimer dissociates due to unphysical ZPE spilling from the high-frequency OH modes. The computational details are given in Section 3. We discuss the results obtained from unconstrained and constrained (LP-ZPE corrected) trajectory simulations in Section 4. Finally, we conclude in Section V.

2 Theory

The LP-ZPE correction method is a collisional model inspired by the Lowe-Andersen thermostat.³⁰ It monitors the local vibration of hydride modes (AH), where A is any atom without losing any generality. When the kinetic energy of such vibration drops below the zero-point energy of the AH mode, the kinetic energy difference is added to the AH bond. This addition is compensated by removing the same energy amount from an energy pool constructed by the other atoms of the molecule. In contrast with the thermostat model, the energy is taken from the molecule itself, and the velocity change conserves the total energy, keeping the system as a microcanonical ensemble. In this sense, LP-ZPE is less intrusive than the use of a thermostat algorithm.

LP-ZPE shares with the Varandas-Marques approach¹⁴ mentioned in the Introduction the general idea that the mode undergoing ZPE leakage can be corrected by pumping energy from the remaining modes. However, this is the only

common point between the two methods. From there, they diverge entirely in terms of concept and implementation. The core difference is that LP-ZPE correction does not require Hessian matrices, making it tailored for correcting ZPE leakage in long-timescale excited-state dynamics simulations based on on-the-fly calculation of the ab-initio electronic structure.²⁹

The LP-ZPE workflow can be described as follows:

(1) The atom pairs of the molecule are classified into two groups: (a) the high-frequency modes built from the atom pairs, mainly prone to ZPE leakage (such as hydride bonds), are named as AH bonds. These AH bonds will be monitored for ZPE leakage, and if necessary, energy will be added to them. (b) All the other atom pairs, not necessarily bonded, are named BC pairs. These atom pairs will donate energy to the energy pool from where energy will be pumped to the leaked bond.

(2) The average parallel component of the A and H velocities to the kinetic energy for each AH bond is calculated at the beginning of the dynamics over time τ .

$$\bar{\varepsilon}_k^0 = \frac{1}{N} \sum_{t=0}^{\tau} \frac{1}{2} \mu_{AH} \left[v_H^{\parallel}(t) - v_A^{\parallel}(t) \right]^2, \quad (1)$$

where N is the number of steps. μ_{AH} is the reduced mass of AH bond defined as $\mu_{AH} = m_A m_H / (m_A + m_H)$ with $m_{A(H)}$ being the mass of the A(H) atom. The parallel component of the velocity of A atom is $v_A^{\parallel} = \mathbf{v}_A \cdot \hat{\mathbf{u}}_{AH}$, and $\hat{\mathbf{u}}_{AH} = \mathbf{R}_A - \mathbf{R}_H / \|\mathbf{R}_A - \mathbf{R}_H\|$. We use bold letters for vectors and matrices throughout the article.

(3) At a later time t_c , the mean contribution of the parallel velocity components to the kinetic energy for each AH bond is again calculated over the same time period τ ,

$$\bar{\varepsilon}_k^c = \frac{1}{N} \sum_{t=t_c}^{t_c+\tau} \frac{1}{2} \mu_{AH} \left[v_H^{\parallel}(t) - v_A^{\parallel}(t) \right]^2. \quad (2)$$

(4) If the mean kinetic energy drops below a pre-defined critical threshold value ε ,

$$\delta\varepsilon = \bar{\varepsilon}_k^0 - \bar{\varepsilon}_k^c > \varepsilon, \quad (3)$$

the leaked energy is added to the AH bond in terms of the velocities of A and H atoms as

$$\mathbf{v}_{H_{new}} = \mathbf{v}_{H_{old}} + \frac{\mu_{AH}}{m_H} \Delta_{AH} \hat{\mathbf{u}}_{AH}, \quad (4)$$

$$\mathbf{v}_{A_{new}} = \mathbf{v}_{A_{old}} - \frac{\mu_{AH}}{m_A} \Delta_{AH} \hat{\mathbf{u}}_{AH},$$

where

$$\Delta_{AH} = \left[\left(v_{H_{old}}^{\parallel} - v_{A_{old}}^{\parallel} \right)^2 + \left(\frac{2\delta\mathcal{E}}{\mu_{AH}} \right) \right]^{1/2} - \left(v_{H_{old}}^{\parallel} - v_{A_{old}}^{\parallel} \right). \quad (5)$$

(5) The same amount of pumped energy is removed from each of the BC atom pairs (not containing an H atom) by adjusting the velocities of B and C atoms as

$$\mathbf{v}_{B_{new}} = \mathbf{v}_{B_{old}} + \frac{\mu_{BC}}{m_B} \Delta_{BC} \hat{\mathbf{u}}_{BC}, \quad (6)$$

$$\mathbf{v}_{C_{new}} = \mathbf{v}_{C_{old}} - \frac{\mu_{BC}}{m_C} \Delta_{BC} \hat{\mathbf{u}}_{BC},$$

where

$$\Delta_{BC} = \left[\left(v_{B_{old}}^{\parallel} - v_{C_{old}}^{\parallel} \right)^2 - \left(\frac{2\delta\mathcal{E}}{\mu_{AH}} f_{BC} \right) \right]^{1/2} - \left(v_{B_{old}}^{\parallel} - v_{C_{old}}^{\parallel} \right). \quad (7)$$

The term f_{BC} is a weight factor, which determines how much energy is taken from the corresponding BC atom pair among all the $B'C'$ atom pairs to construct the energy pool. There is some methodological freedom to choose this function. In this first application of the LP-ZPE method, it is defined as

$$f_{BC} = \frac{\frac{1}{2} \mu_{BC} \left(v_{B_{old}}^{\parallel} - v_{C_{old}}^{\parallel} \right)^2}{\sum_{B'C'} \frac{1}{2} \mu_{B'C'} \left(v_{B'_{old}}^{\parallel} - v_{C'_{old}}^{\parallel} \right)^2}. \quad (8)$$

(6) A problematic situation may arise when there is not sufficient kinetic energy available in a BC atom pair, that is

$$\left(v_{B_{old}}^{\parallel} - v_{C_{old}}^{\parallel} \right)^2 - \left(\frac{2\delta\mathcal{E}}{\mu_{AH}} f_{BC} \right) < 0, \quad (9)$$

then, the velocities of that particular BC pair are not changed. In that case, the weight factor f_{BC} is recomputed, excluding the BC pair with the imaginary component, and the same amount of pumped energy ($\delta\mathcal{E}$) is removed from the other BC pairs to maintain energy conservation.

$$\mathcal{E}_{removed} = \sum_{B'C'} (\delta\mathcal{E} f_{B'C'}), \quad (10)$$

where the sum excludes the BC pair with imaginary components.

The LP-ZPE correction is constructed to cause minimum impact on the dynamics. First, we keep the number of adjustable parameters to a minimum, only three (τ , t_c , and ε), independently of the system size. Moreover, the system's total energy, the system's total linear momentum, and the atom pairs' total angular momentum are perfectly conserved.

It is instructive to inspect Eq. (4) in more detail. It alters the velocity of A and H in the direction parallel to the vector connecting these two atoms ($\hat{\mathbf{u}}_{AH}$). The change in velocity is determined by Δ_{AH} defined in Eq. (5). It first removes the parallel component of A and H velocities (rightmost parenthesis in Eq. (5)) and then adds it again but summed to the correction energy $\delta\mathcal{E}$ (bracket in Eq. (5)). The result of the operation is that the kinetic energy stored in the AH pair is increased by $\delta\mathcal{E}$. This kinetic energy increase is explicitly derived in Eq. SI-9 of the Supporting Information (SI). Because the velocity changes are carried out only in the parallel direction, it works as a central force, with the advantage of conserving the linear and angular momenta of the AH pair (see Eqs. SI-16 and SI-17).³¹

The effect of changing the velocities of the BC pair through Eq. (6) is similar. The velocity is changed in the direction parallel to the vector connecting B and C ($\hat{\mathbf{u}}_{BC}$). Δ_{BC} removes the velocity parallel component and adds it again, subtracting $\delta\mathcal{E}$. Thus, the kinetic energy stored in the BC pair is reduced by $\delta\mathcal{E}$, compensating for the kinetic energy addition to AH. In the SI, we discuss the energy conservation (Eqs. SI-12 and SI-13). Once more, constraining the changes to the parallel component of the velocity leads to linear and angular momentum conservation (Eqs. SI-18 and SI-19).

The main advantage of the LP-ZPE correction over most other approaches is that it does not require the computation of Hessian matrices because the ZPE leakage is monitored for local AH pairs, not normal modes. We can justify using local AH stretching vibrations as the basis for applying ZPE corrections by noticing that the high-frequency normal modes can be well described in terms of local fragment modes. For instance, Huix-Rottlant and Ferré³² showed that the high-frequency normal modes of benzene are combinations of single internal local oscillators (the local

oscillator matrix appears as a Huckel-like structure), where each local stretching oscillator couples only to the nearest neighbor with a fixed, small coupling value. Thus, the eigenvectors of such a local oscillator matrix lead to a spectrum that closely matches the six highest normal modes of benzene, obtained by the full Hessian-matrix diagonalization. These results make us confident that using the LP-ZPE correction method to cool down weak bonds that are artificially hot due to leakage while neglecting minor vibrational couplings in the high-frequency modes is a worthwhile trade-off to avoid the harsh artifacts that ZPE leakage may cause.

3 Computational Details

As reviewed by Bowman et al., the absence of ZPE in classical MD simulations involving water can be severely

erroneous.³³ With this motivation, we applied our LP-ZPE correction method to prevent the ZPE leakage in BOMD of the water dimer system. We have employed the MP2/aug-cc-pVDZ level of theory in this work for ground-state optimization of the dimer, normal mode analysis at the optimized ground state geometry, and ground-state BOMD. The dimer dissociation energy obtained in this work is 0.225 eV (Table 1), which is much larger than the ZPE (0.012 eV) of the stretching mode (the harmonic frequency is 189 cm⁻¹; see Table S1), causing dissociation of the water dimer. Therefore, any dissociation of the dimer during the classical dynamics should occur only due to the unrealistic ZPE leakage from the high-frequency OH stretching modes.

Table 1. Geometric properties (Angstrom, degree) and dissociation energy (eV) of the water dimer in this present calculation are compared with previously reported results.

	Present result MP2/aug-cc-pVDZ	Previous theoretical results		Previous expt. results ³⁴
		^a CCSD(T)- F12b/CBS ³⁵	^b CCSD(T)(FULL)/ IO275 ³⁶	
R(O ₁ O ₄)	2.90758	2.91278	2.912	2.976 (+0.0000, -0.030)
R(O ₁ H ₂)	0.96617	0.95902	0.9583	
R(O ₄ H ₅)	0.97249	0.96464	0.9639	
R(O ₄ H ₆)	0.96427	0.95744	0.9569	
θ(H ₂ O ₁ H ₅)	104.136	104.892	104.87	
θ(H ₅ O ₄ H ₆)	104.450	104.801	104.83	
α	7.402	5.703	5.5	6 ± 20
β	113.506	123.379	124.4	123 ± 10
^c Dissociation energy (D_e)	0.225	0.216	0.2177	^d 0.236 ± 0.03

^aCCSD(T)-F12b/CBS extrapolation scheme with the aug-cc-pVQZ/aug-cc-pV5Z basis sets.

^bCCSD(T)(FULL)/IO275 (IO275: interaction optimized basis set with 275 basis functions for the H₂O dimer. O: 7s5p5d3f2g1h; H₃: 2s4p1d, H: 2s3p, BF: 3s3p2d1f).

^c D_e is the total bond energy (BSSE corrected) from the bottom of the well.

^dReference³⁷. D_e was estimated by adding the ZPE calculated at the HF/4-21G level.

We have sampled 125 initial conditions from a correlated quantum-harmonic-oscillator distribution such that the total energy of the system remains fixed at its ZPE value (1.26 eV). While keeping the total energy fixed at the ZPE value, Figure S2 in SI depicts the distribution of the kinetic and potential energy for the 125 sampled initial conditions that are to be fed in the dynamics simulation. Ground-state classical trajectory simulations are carried out with these 125 initial conditions by a homegrown newly written Newton-X suit of codes^{29,38,39} (Newton-X NS) in two ways:

(a) without any constrain or ZPE leakage correction and (b) applying the LP-ZPE correction in the dynamics. In both cases, BOMD trajectories are propagated via Newtonian equations of motion up to 20 ps with the velocity-Verlet algorithm with a timestep of 0.25 fs. The forces acting on the nuclei are proportional to the gradient of the ground state BO potential energy surface, where the latter is calculated on the fly by MP2/aug-cc-pVDZ theory using the TURBOMOLE (version 7.3) suite of quantum chemistry programs.^{40,41} The outputs for LP-ZPE corrected and

without LP-ZPE corrected (unconstrained) dynamics for 125 trajectories are stored in H5MD files and available for download.⁴²

In the LP-ZPE correction scheme on the water dimer, we identified the four OH bonds as local AH pairs, and all the other 11 atom pairs (even those not bonded) are considered BC atom pairs. Hence, the four local AH pairs are (O₁-H₂), (O₁-H₃), (O₄-H₅), and (O₄-H₆), and the eleven BC atom pairs are (O₁-O₄), (O₁-H₅), (O₁-H₆), (H₂-H₃), (H₂-O₄), (H₂-H₅), (H₂-H₆), (H₃-O₄), (H₃-H₅), (H₃-H₆), and (H₅-H₆) as shown in Figure 1. Since non-bonded atom pairs are considered in the BC pair ensemble, energy is pumped from all types of vibrations (and not only stretching modes) into the leaked modes.

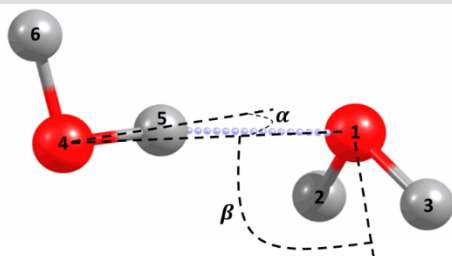


Figure 1. The equilibrium structure of the water dimer.

We have chosen the three parameters needed to set up this model as $\tau = 10$ fs (time period for averaging the parallel component of the kinetic energy of the AH bond), $t_c = 10$ fs (checking of ZPE leakage), and $\varepsilon = 0.001$ a.u. (maximum allowed deviation of the mean kinetic energy at the correction time from the reference value obtained at the beginning of the dynamics (Eq. (2)).

A judicious and careful parameter setting is needed to apply the LP-ZPE correction scheme. The time period for averaging the parallel component of the kinetic energy of the AH bond (τ) should allow the OH stretching to complete at least one oscillation, and the energy can deliver a reasonable estimate of the ZPE value of the local vibration mode. It can be decently assumed that there should not be much ZPE leakage at the beginning of the dynamics. The parameter t_c —also controlling the correction time during the dynamics—should not be too short. Otherwise, unnecessary corrections could hamper the inherent dynamics. On the other hand, if t_c is too long, it would lose the essence of the correction. Similarly, a very low threshold

for the parameter ε would force the method to interfere much with the inherent dynamics, and a high value does not allow the correction to occur. This work allowed $\sim 10\%$ energy loss from the corresponding ZPE value of the high-frequency AH bonds. Although more tests concerning the parameters will be carried out in the future, we expect that a moderate set of parameters chosen in this work is adequate to demonstrate the workability of the LP-ZPE corrections in classical trajectory calculation.

To validate our ground state classical dynamics, we have simulated the power spectra from the classical trajectories by Fourier transform and the velocity autocorrelation function using TRAVIS software,^{43,44}

$$P(\omega) = m \int \langle \dot{\mathbf{r}}(\tau) \dot{\mathbf{r}}(t + \tau) \rangle_{\tau} e^{-i\omega t} dt, \quad (11)$$

where m is the reduced mass of the oscillator and $\dot{\mathbf{r}}$ is the velocity vector.

We have codified the LP-ZPE correction scheme in a Fortran 2008 written module, which can be interfaced readily with any classical trajectory propagator. The LP-ZPE correction code mainly requires the nuclear geometries to determine the AH bond and BC atom pairs, and velocities to add and remove energies from AH bond and BC atom pairs, respectively, at the correction timestep. The code can be freely downloaded from GitLab [<https://gitlab.com/saikat.mukherjee/lp-zpe-correction>].

4 Results and Discussion

Water dimer, a prototypical hydrogen-bonded complex, has been serving as a classic testbed for benchmarking the electronic structure methods for more than twenty years, not only because of its small size but also its fundamental physical properties and important role in atmospheric chemistry. The interested readers are referred to the detailed chronological reviews of experimental⁴⁵ and theoretical⁴⁶ studies on the water dimer by Mukhopadhyay *et al.* Since a detailed discussion⁴⁷⁻⁵⁰ on the electronic structure calculation of water dimer is outside the scope of this article, we limit ourselves by comparing only the geometry, harmonic normal mode frequencies, and the dissociation energy of our optimized cluster with previously reported theoretical and experimental findings (Table 1 and Table S1). As expected, compared to the sophisticated electronic

structure methods with high basis sets, our results obtained by the MP2/aug-cc-pVDZ level of theory are not the best estimates⁴⁹ but fall within the margin of error. Hence, we can safely proceed with the present level of theory and apply our LP-ZPE correction during the propagation of the classical trajectories.

The total energy conservation during the dynamics is checked in both types of simulation, with and without applying the LP-ZPE correction scheme. The distribution of total-energy variation from time zero considering all the 125 trajectories (20 ps propagation with a timestep of 0.25 fs; a total of 10^7 entries) has the mean value of 0.0013 eV with a 0.0022 eV standard deviation in the case of the uncorrected simulation. Applying the LP-ZPE correction on the 125 trajectories yields a distribution of total-energy variation with -0.00003 eV mean and a 0.0031 eV standard deviation (see Figure S3 in the SI). Hence, the numerical errors associated with the correction scheme are negligible.

On average, LP-ZPE corrects 1.5 OH bonds every time it is applied (set as every 10 fs by parameter t_c). A histogram of the added energy to each OH bond obtained for all the trajectories and considering each correction time (see Figure S5 in SI) attains a half-normal distribution peaked at 1 meV (the value of the parameter ε) with a 2.8 meV mean and a 1.4 meV standard deviation. This energy is removed from a pool of 11 atom pairs, implying that each pair contributes with only 0.26 meV to correct an OH bond at each application. These tiny energy values (near to or even smaller than the uncorrected dynamics' accuracy) ensure that the LP-ZPE correction minimally impacts the dynamics.

Figure 2 shows the distance between the oxygen atoms of the monomers as a function of time for the 125 trajectories in gray lines for both types of dynamics, with and without the LP-ZPE correction. The monomeric distances are averaged over the 125 trajectories in both cases and shown in thick lines. It is evident that if we do not prevent the ZPE leakage from the AH bonds (in this case, the fast OH stretching modes), the dimer starts to dissociate rapidly after 4 ps. The same phenomenon was reported³³ previously by Bowman and his group. Applying our LP-ZPE correction scheme, most of the trajectories do not dissociate up to the end of the simulation, 20 ps. It can be argued that those few

trajectories still showing large distances between the monomers even after applying the LP-ZPE correction undergo energy leakage from modes other than stretching, such as bending, wagging, and shearing types of motions.

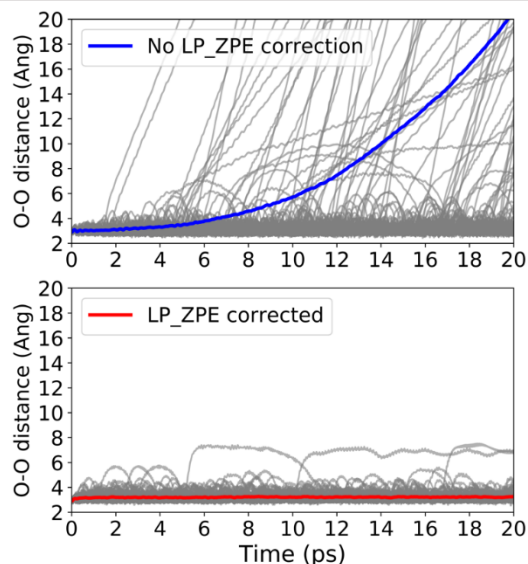


Figure 2. The distances between the two oxygen atoms of the monomers as a function of time (gray lines) for the trajectories without ZPE correction are shown in panel (a). Same quantity is shown in panel (b) for trajectories starting from the same initial conditions but with LP-ZPE correction. The thick lines represent the averaged distances between the two monomers (O_1-O_4) in both cases.

The radial distribution functions (RDFs) of the two oxygen atoms in Figure 3 also show that dissociation of the dimer prevails in the trajectories calculated without applying any ZPE correction. Since the O–O distance of water dimer in equilibrium is 2.91 Å, the RDFs peak around 3 Å in both cases. The O–O RDF obtained from the trajectories without ZPE correction (blue bars) leaves a long tail at higher O–O distances implying dissociation of the trajectories. The O–O RDF generated from the LP-ZPE corrected trajectories is much more localized, maintaining the dimer during the dynamics. The other RDFs of OH and H–H pairs (see Figure S4 in the SI) also vouch for the necessity of applying the LP-ZPE correction to prevent the artificial dissociation of the water dimer due to ZPE leakage from the high-frequency OH modes.

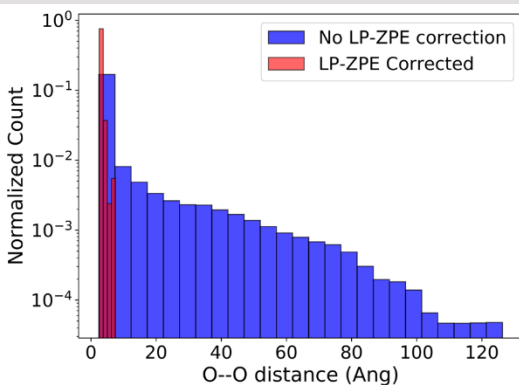


Figure 3. Radial distribution functions (RDFs) of O1–O4 atoms in water dimer are calculated from trajectories with (red) and without (blue) the LP-ZPE correction. Each RDF is normalized such that the area under each curve is unity.

Figure 4 shows the averaged power spectrum over 125 trajectories with the LP-ZPE correction scheme. The frequencies obtained from the power spectra calculated from ground-state BOMD trajectories lie within the acceptable range of the scaled⁵¹ normal mode frequencies of the water dimer calculated in this work, thereby validating our LP-ZPE correction protocol on classical trajectory simulation. A peak around 3200 cm^{-1} is seen in the power spectrum, which does not correspond to any normal mode frequencies of the water dimer. It approximately matches the frequency of the hydroxyl cation (OH^+), whose experimental value in a solid argon matrix is 2979.6 cm^{-1} , and the scaled value calculated by the MP2/6-31++G(d,p) level of theory is 3110 cm^{-1} .⁵² This peak may indicate some residual artifact from the LP-ZPE correction.

Bowman et al. also applied the hard-wall sphere model to avoid ZPE leak in molecular dynamics on the water dimer system³³ simulating 100 trajectories with a timestep of 0.0484 fs, and the correction was invoked at every 0.242 fs. We have also achieved similar results by applying our proposed method to prevent ZPE leak in classical trajectories with a much longer timestep of 0.25 fs, and the correction is invoked at every 10 fs. Moreover, it is a Hessian-free method making the simulation computationally more effective.

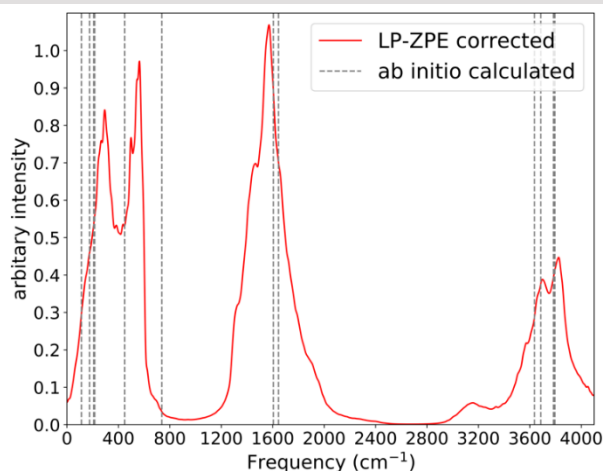


Figure 4. Power spectra are calculated using Eq. (11) and averaged over 125 trajectories with the LP-ZPE correction scheme. The grey dashed lines correspond to the scaled normal mode frequencies of the water dimer calculated in this present work. A scaling factor of 1.0999 is used for the low-frequency normal modes ($< 1000\text{ cm}^{-1}$) and 0.9604 for the high-frequency modes.⁵¹

In the Hase-Miller approach⁹ for correcting ZPE leak by calculating instantaneous normal modes at each correction time step, one must exclude modes with imaginary frequencies from the ZPE constrain. In a similar context, in the present method, a BC atom pair may not have enough kinetic energy to donate, resulting in imaginary terms in Eq. (7). In that case, we ignore the particular pair and try to redistribute the energy in the other BC pairs. If no BC pair is ready to donate energy for constructing the pool from where the energy can be pumped to the leaked modes, we do not change the velocities at that time step, this is, we do not apply the correction and proceed further, hoping that the correction will be applied at the next correction time step (t_c).

5 Conclusions

We have developed a new technique for preventing ZPE leakage in classical trajectory simulations. The method, named local-pair (LP) ZPE correction, works by monitoring the ZPE of local pairs of atoms vibrating at high frequency. Whenever this local ZPE drops below a pre-defined threshold, an energy pool with contributions from all other atom pairs donates the leaked energy back to the local hot pair. The LP-ZPE method is built to have minimum interference in the dynamics. In particular, total energy,

linear momentum, and angular momentum of the center of the mass are explicitly conserved. The LP-ZPE correction does not require Hessian calculations during dynamics, leading to a significant gain in long-timescale dynamics than most other ZPE corrections schemes. Moreover, it can be integrated with any BO-based molecular dynamics scheme.

The LP-ZPE method was tested on the water dimer system, which is well-known for showing artificial dissociation during ab initio BOMD due to ZPE leakage. If no correction is applied, the energy of the OH stretching modes fall below the corresponding ZPE, and the leaked energy is transferred unrealistically to the O₁–O₄ stretching mode causing dissociation of the dimer. The LP-ZPE method has been able to prevent the ZPE spilling of the OH stretching modes by pumping back the leaked energy into the corresponding modes while this energy is taken from the other modes of the dimer itself, keeping the system as a microcanonical ensemble. The LP-ZPE correction scheme interferes less with the dynamics by invoking the correction at a longer timestep interval than previously proposed methodologies for ZPE correction.

A Fortran written module enabling the LP-ZPE correction scheme is distributed freely with this article. This module can be interfaced readily with any trajectory propagator to prevent the ZPE leakage in classical trajectory-guided dynamics.

Acknowledgements

The authors were financially supported by the European Union's Horizon 2020 research and innovation program under grant agreement no. 832237 (project SubNano). They also acknowledge the Centre de Calcul Intensif d'Aix-Marseille for granting access to its high-performance computing resources.

Supporting Information

Derivations of conservation of total energy, linear momentum and angular momentum; Vibrational frequencies of the water dimer system; Kinetic and potential energy distribution of the initial conditions for the BOMD trajectories; Plot of total energy variation during the simulation; The radial distribution functions of H–H and O–H distances obtained from the uncorrected and LP-ZPE

corrected trajectories; The distribution of pumped energy to the OH bonds by LP-ZPE correction. This information is available free of charge via the Internet at <https://doi.org/10.1021/acs.jctc.2c00216>

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