

An *ad hoc* improvement to ring polymer molecular dynamics

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Two of the most successful methods that are available for simulating the quantum dynamics of condensed phase systems are ring polymer molecular dynamics (RPMD) and centroid molecular dynamics (CMD). Despite their conceptual differences, practical implementations of these methods differ in just two aspects: the choice of the Parrinello-Rahman mass matrix and whether or not a thermostat is applied to the internal modes of the ring polymer during the dynamics. Here we explore a method which is in a sense ‘half-way’ between the two approximations: we keep the path integral bead masses equal to the physical particle masses but attach a path integral Langevin equation (PILE) thermostat to the internal modes of the ring polymer. The justification for this is that the inclusion of an internal mode thermostat does not affect any of the wholesome features of RPMD: because of the choice of bead masses, the resulting method is still optimum in the short-time limit, and the transition state approximation to its reaction rate theory remains closely related to the semiclassical instanton approximation in the deep quantum tunneling regime. In effect, there is a continuous family of methods with these properties, parameterised by the coupling strength of the PILE thermostat, that equally well preserve the short-time limit of RPMD, which depends on the choice of the mass matrix but is not sensitive to thermostating of the internal modes. Here we explore numerically how the approximation to quantum dynamics depends on this coupling strength, with a particular emphasis on vibrational spectroscopy. We find that a broad range of values around the critical damping chosen for the original PILE thermostat give very similar results, that give a reasonable albeit arguably *ad hoc* approximation to quantum effects, while being immune to both the resonance problem of RPMD and the curvature and time step problems of CMD. We find that the critical damping chosen for the original PILE thermostat is close to optimum, and that the resulting dynamical approximation is immune to both the resonance problem of RPMD and the curvature problem of CMD.

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The quantum nature of light nuclei has a very significant impact on the behaviour of molecules and materials, not only at cryogenic temperatures, but also at room temperature and above. Well-established techniques exist to perform atomistic simulations that accurately and rigorously include nuclear quantum effects (NQEs) on static, time-independent configurational and thermodynamic properties^{1–4}, and efforts are concentrated on making them less demanding, with some success^{5?}

For what concerns dynamical properties, however, the situation is much less clear. Exact techniques are extremely complex, and impractical for anything but the simpler molecules⁷. Approximate techniques are restricted to either quasi-harmonic perturbative expansions⁷ or one of few approximate, semi-classical techniques, most notably the linearized semi-classical initial value representation (LSC-IVR), centroid molecular dynamics (CMD)^{6,7}, and ring-polymer molecular dynamics (RPMD). LSC-IVR can be derived rigorously starting from quantum mechanical expressions, but the approximations that are practically affordable are affected by severe zero-point energy leakage, which makes it very hard to collect satisfactory statistics and casts shadows on the applicability to long-time properties of anharmonic systems. CMD and RPMD both can be regarded as real-time versions of imaginary-time path integrals, CMD being essentially classical molecular dynamics on the centroid potential of mean force, RPMD being classi-

cal molecular dynamics based on the ring polymer Hamiltonian. Both are to an extent arbitrary, *ad hoc* approximations, even though recent efforts have put them on somehow more robust grounds^{8?–11}. They are only exact for linear operators in the harmonic limit^{11,12}, and both are known to exhibit artefacts that are most evident when computing vibrational spectra of molecules^{13–15}, that are related to the so-called curvature problem for CMD (that we will interpret as a consequence of adiabatic separation between the centroid and the internal modes of the ring polymer) and resonance between physical modes of the system and internal modes of the ring polymer for RPMD.

Here we will discuss the effect of thermostating the internal modes of the ring polymer while using the physical ring polymer mass matrix, thereby obtaining a method that can be regarded as a “hybrid” of RPMD and CMD. We will show that both the short-time limit accuracy of RPMD and the analogy between RPMD and the instanton in the study of rates are not affected by the use of stochastic thermostats for the internal modes of the ring polymer. This means that there is a whole family of methods, differing by the details of the thermostating, that are not more *ad hoc* than RPMD, and offer a way to improve upon the existing approximations. While we cannot at this stage suggest a way to exploit this additional freedom to obtain a more rigorous method for quantum dynamics, we show that for a broad range

of thermostat parameters, this stochastic term cures the resonance problem of RPMD without triggering the curvature problem. Furthermore, this method can be used with much larger time steps than CMD, as it uses the RPMD mass matrix and does not rely on adiabatic separation.

The Langevin RPMD approach we introduce (which we refer to as *PILE*) is a practical solution to explore the role of NQEs on dynamical properties, even though we cannot claim that there is a universal choice of the damping that gives a rigorously better approximation to quantum dynamics. It is quite possible that by exploring the additional degrees of freedom that are associated with stochastic dynamics of the internal modes of the ring polymer future research may eventually fulfill this arduous goal.

I. ALL SECTIONS FROM DAVID

II. MODEL MOLECULES: OH AND CH₄

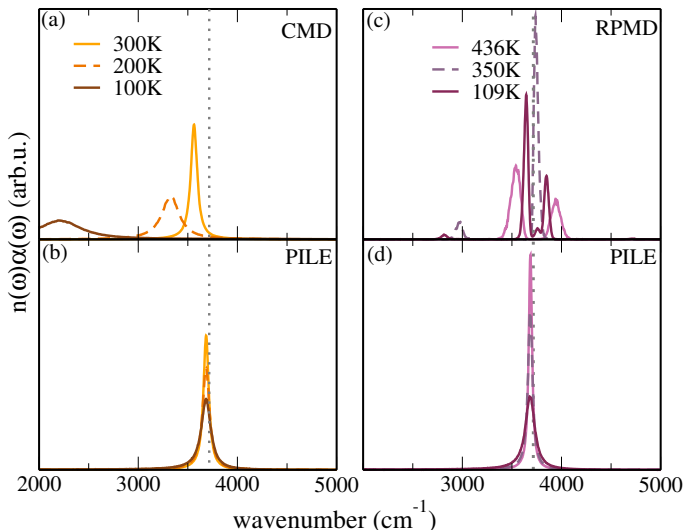


FIG. 1: Dipole absorption cross section for the OH model molecule: (a) and (b) CMD and PILE methods at 100, 200, and 300K ; (c) and (d) RPMD and PILE methods at 109, 450, and 436 K. The dotted grey line corresponds to the classical vibrational frequency predicted for this model.

In this section we study two model molecules, already treated in Ref.¹³. They are the OH and the CH₄ molecules, for which the interatomic potential is given by

$$\phi = \sum_{\text{bonds}} \frac{k_b}{2} (r - r_{eq})^2 + \sum_{\text{angles}} \frac{k_a}{2} (\theta - \theta_{eq})^2, \quad (1)$$

These model molecules are especially interesting because they are known cases where both the curvature and

the resonance problems have been well studied by Witt and coworkers¹³. As in Ref.¹³, we chose $k_b = 0.49536$ Ha/bohr² and $r_{eq} = 1.0\text{\AA}$ for the OH molecule, and $k_b = 0.30345$ Ha/bohr², $k_a = 3.1068 \times 10^{-5}$ Ha/deg², $r_{eq} = 1.09\text{\AA}$, and $\theta_{eq} = 107.8\text{deg}$ for the CH₄ molecule. For these models, we calculate the dipole absorption cross section given by

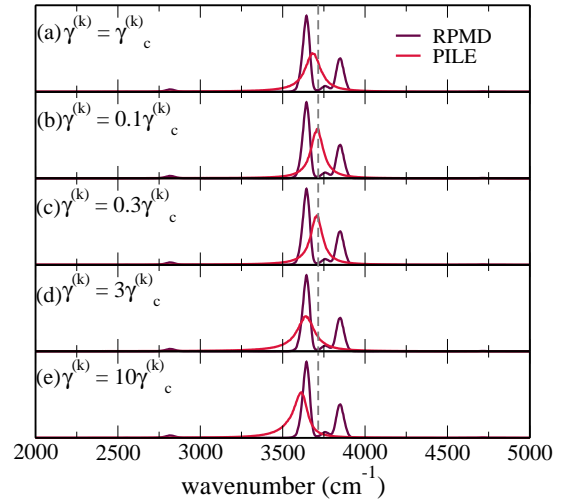


FIG. 2: Dipole absorption cross section for the OH model molecule at 109K. The various plots show the RPMD spectrum compared to the PILE methods with different $\gamma^{(k)}$ parameters.

$$n(\omega)\alpha(\omega) = \frac{\pi\beta\omega^2}{3cV\epsilon_0} \tilde{I}(\omega), \quad (2)$$

where $\tilde{I}(\omega)$ is the Fourier transform of the Kubo-transformed dipole autocorrelation function. It is this autocorrelation function that we approximate with CMD, RPMD, and the PILE method. We here also filter out translations and rotations of the molecule using the scheme proposed in Ref.¹³.

For the OH molecule we calculate the RPMD spectra at the same temperatures and number of beads discussed in Ref.¹³, namely 109 K and 64 beads (resonant case), 350K and 16 beads (non-resonant case), and 436K and 16 beads (resonant case). We used a time step of 0.25 fs for these simulations. In Figure 4(c) and (d), we compare these spectra with the corresponding PILE spectra (critical damping). The classical frequency of vibration for this molecule and the parameters chosen here would lie at 3715.6 cm⁻¹ [check!](#). As in Ref.¹³, the vibrational frequencies of the ring polymer in the RPMD method split the peak at the resonant temperatures. The PILE spectra yield a single peak, which is at the same place at all temperatures and slightly red-shifted with respect to the classical vibrational frequency. Also, the non-resonant frequencies of the ring polymer cannot be observed in the PILE spectra. We also notice that the PILE spectrum

gets broader as the temperature is lowered. This effect arises from the fact that at lower temperatures there are more internal frequencies of the ring polymer which interact with the physical frequency ... [comment: must discuss!].

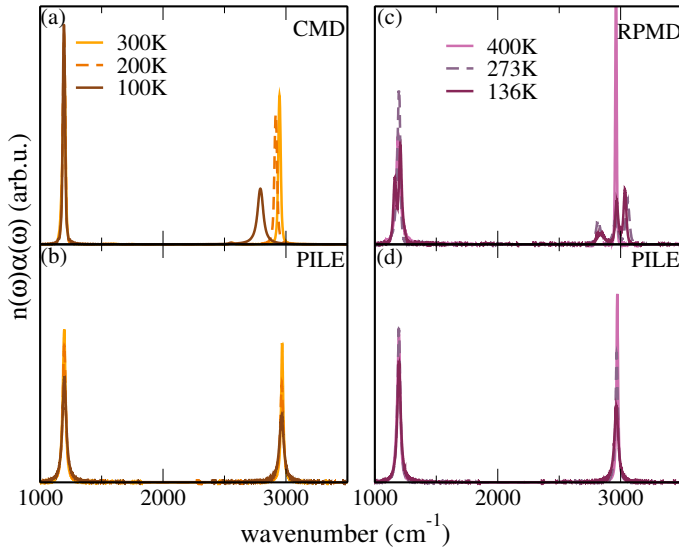


FIG. 3: Dipole absorption cross section for the CH_4 model molecule: (a) and (b) CMD and PILE methods at 100, 200, and 300K; (c) and (d) RPMD and PILE methods at 136, 273, and 450 K.

In Fig. 4(a) and (b) we compare the CMD and PILE spectra for the OH molecule at 100K, 200K, and 300K. The CMD simulations were run with a time step of 0.01 fs, while the PILE simulations were run with a time step of 0.25 fs. We used 64 beads at 100K, and 16 beads at 200 and 300K. The curvature problem is clear for the CMD spectra: at 100K the peak is red-shifted to as low as 2200 cm^{-1} and massively broadened. Even at 300K some of the curvature problem is still observed. The PILE method does not show this effect. Although the PILE peak broadens slightly as the temperature lowers, the peak stays at the same position for all temperatures. The severe curvature problem seen in CMD is thus closely related to the choice of the dynamic mass matrix.

In Figure 2 we compare different values of the $\gamma^{(k)}$ parameters in the PILE method, both in the underdamped and overdamped regimes for the IR spectrum of the OH molecule at 109K. The position and width of the peaks are affected by changing this parameter, but not substantially - similar to what we observe for the quartic potential. Going as high as ten times the critical damping, or as low as one tenth of it, does not change the peak position by more than 3% of its wavenumber. Since we do not find a mathematical criterion to fix these parameters, this uncertainty will be intrinsic to this method.

For the CH_4 molecule we calculate the same data as we did for the OH molecule. We use all the same simulation settings as for the OH molecule. The results are reported

in Figure 3. In Fig. 3(c) and (d), it is clear that the resonance problem of RPMD is healed by the PILE method for the double resonant case (136K) and single resonant case (273K). In Fig. 3(a) and (b), it is also shown that the PILE method predicts the bending peak ($\approx 1200 \text{ cm}^{-1}$) at the same position as CMD, while the stretching peak at high frequencies does not show the curvature problem in the PILE method. For the higher temperatures (300K and 400K), where both the curvature problem of CMD and the resonance problem of RPMD are not severe, both spectra agree very well with the PILE one. Overall, we again observe a broadening of the stretching peak in the PILE method as the temperature is lowered. All observations are consistent with the OH case.

Next, we investigate a non-empirical potential energy surface in order to see how these methods compare.

III. REAL OH

We consider the real OH molecule with the interatomic potential given by a Morse-type potential of the form

$$\phi = D_e \left[1 - e^{-\alpha(r-r_e)} \right]^2 \quad (3)$$

where $D_e = \omega_e^2/4\omega_e\chi_e$, $\alpha = \sqrt{2\mu_{OH}\omega_e\chi_e}$. The parameters $\omega_e=3737.76 \text{ cm}^{-1}$, $\omega_e\chi_e=84.881 \text{ cm}^{-1}$, and $r_e = 0.96966 \text{ \AA}$ were obtained from the parameters measured for the real OH molecule, as reported in Ref. [HERZBERG].

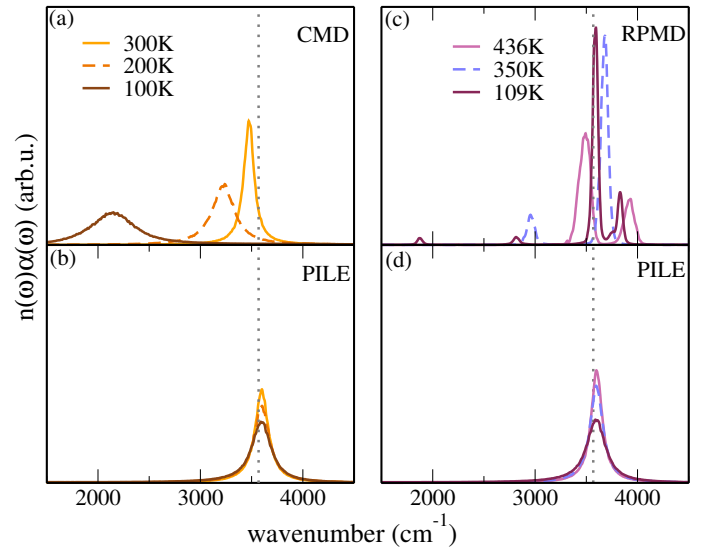
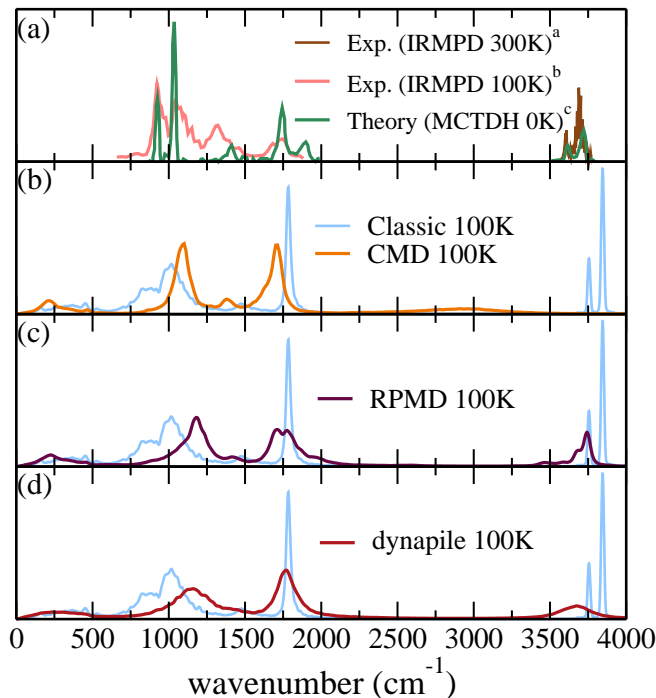


FIG. 4: Dipole absorption cross section for the real OH molecule: (a) and (b) CMD and PILE methods at 100, 200, and 300K ; (c) and (d) RPMD and PILE methods at 109, 450, and 436 K. The dotted grey line corresponds to the anharmonic (exact) vibrational frequency predicted for this model.

IV. ZUNDEL CATION



^a Ref.²⁰; ^b Ref.²¹; ^c Ref.²²

FIG. 5: (a) Reference data for the IR spectrum of H_5O_2^+ taken from the literature: experimental IRMPD data for the OH-stretch region at 300K from Ref.²⁰, experimental IRMPD data between 650 and 1900 cm^{-1} at 100K from Ref.²¹, and theoretical multi configuration time dependent Hartree (MCTDH) spectrum at 0K from Ref.²². IR spectrum of H_5O_2^+ obtained from the Fourier transform of the dipole autocorrelation from molecular dynamics trajectories in the CCSD(T) parameterised surface of Ref.²³, at $T=100\text{K}$: (b) Comparison between CMD and classical spectra, where the curvature problem is clear especially for the OH stretch peaks; (c) Comparison between RPMD and classical spectra, where the resonances can be seen at all peaks above 1500 cm^{-1} ; (d) Comparison between PILE and classical spectra, where both of the problems mentioned in (a) and (b) are not present, but the peaks are much broader. In (d), substantial shifts due to NQE in the evaluation of the spectra can be identified.

We apply the methods discussed so far to a real and accurate potential energy surface of a real molecule, namely, the Zundel cation H_5O_2^+ . The IR spectrum of H_5O_2^+ has been extensively studied in the literature²⁴, both theoretically^{22,23,25–31} and experimentally^{20,21,32–34}. Particular attention has been given to a doublet structure in the shared proton stretch region

that can be measured at low temperatures^{32,33}. Theoretically, this structure can only be captured by certain levels of theory that include anharmonic effects and nuclear quantum effects, like the multi-configurational time-dependent Hartree (MCTDH) method at 0K²². It is completely absent from any harmonic treatment, and also expected to be absent from the methods used here due to the lack of quantum phase information in any of them. This molecule presents an excellent testing ground for new methodologies also because of the availability of a potential energy and dipole surfaces parametrized with CCSD(T) data that was published by Huang, Braams and Bowman²³, which is both very accurate and inexpensive to evaluate.

For the Zundel cation, we evaluate the classical, CMD, RPMD, and PILE IR spectra at 100K. We chose this temperature because it is a temperature low enough to highlight the issues of RPMD and CMD, and because actual experiments are performed at this temperature²¹. In Fig. 5, these spectra are shown in panels (b), (c), and (d). In panel (a) we show reference data from the literature, both experimental (Refs.^{20,21}) and a high level theoretical spectrum using the MCTDH method (Ref.²²).

It is clear from Fig. 5(b) that the curvature problem of CMD is massive for the OH stretch peaks for this real potential energy surface. For RPMD, the resonant frequencies of the ring polymer split both the OH stretch peaks at high wavenumbers and the shared proton bending mode at around 1700 cm^{-1} . The PILE method, here only reported for critical damping, successfully heals both problems, although especially at higher wavenumbers, the peaks seem to be considerably broadened.

None of the approximate methods investigated here can reproduce the doublet peak at around 1000 cm^{-1} , which is shown in Fig. 5(a). Given that this doublet structure has been interpreted as a Fermi resonance involving a fourth-order coupling between the proton transfer mode, the O-O stretching mode, and the H-O-H wagging mode^{22,24}, it does not come as a surprise that it is not present in the methods investigated here: None of these methods contain the necessary physics to describe such a resonance. However, only extremely computationally expensive methods [CITE?] are able to describe such effects, which also become less important as the system size grows. In the realm of approximate methods for including nuclear quantum effects for dynamical observables, and that can be applied for systems of high dimensionality without an extreme computational cost, the newly proposed PILE method thus emerges as the most promising candidate.

V. CONCLUSIONS

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