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Communication: HK propagator uniformized along a one-dimensional manifold in weakly anharmonic systems

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A simplification of the Heller-Herman-Kluk-Kay (HK) propagator is presented that does not suffer from the need for an increasing number of trajectories with dimensions of the system under study. This is accomplished by replacing HK's uniformizing integral over all of phase space by a one-dimensional curve that is appropriately selected to lie along the fastest growing manifold of a defining trajectory. It is shown that this modification leads to eigenspectra of quantum states in weakly anharmonic systems that can outperform the comparatively computationally cheap thawed Gaussian approximation method and frequently approach the accuracy of spectra obtained with the full HK propagator. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901301]

INTRODUCTION

Semiclassical quantum wave packet evolution is a powerful method to evolve quantum states using classical trajectories. Many efficient methods exist.

Perhaps the most widely used semiclassical method of quantum propagation is the Heller-Herman-Kluck-Kay (HK) propagator.[1–5] In brief, this method is a stationary phase approximation of the quantum coherent state propagator evaluated in an uniformized initial value representation. When applied to finding autocorrelations and from the perspective of phase space, every timestep requires the calculation of the overlap of a swarm of "frozen" Gaussians, often selected by Monte Carlo-based sampling dependent on the initial state. The propagation of every such Gaussian is governed by its central classical trajectory and each Gaussian's contribution to the propagator's value at a timestep is dependent on the classical action of its central trajectory as well as elements of its stability matrix. In practice, computation of these elements, first order differentials of final position and momenta with respect to initial position and momenta, is the most intensive part of the procedure.

Unfortunately, HK suffers from the necessity of calculating an increasing number of trajectories as the number of degrees of freedom increases. The calculation of every trajectory's associated stability matrix elements is doubly confounded; not only do the number of matrix elements scale unfavorably with degrees of freedom ($4d^2$ for d degrees of freedom), the number of times these elements must be calculated also proliferates (frequently exponentially) with the number of trajectories. Efforts have been made to address this issue, the most notable of which is cellular dephasing[6] or Filinov filtering.[7] However, these methods have proven ineffective in many systems and only reduce the growth of trajectories necessary to a point.[8]

One way around this unfavorable growth in the number of trajectories is to take a more targeted approach in selecting only the most important trajectories. In this paper, a simplification to the HK formulation is presented referred to as "directed" HK (DHK), wherein the uniformizing integration is performed along a one-dimensional manifold instead of all of phase space regardless of the dimension of the system under study. This curve is chosen to lie along the eigenvector with the largest eigenvalue of the stability matrix associated with a defining trajectory. In a test set of chemically relevant anharmonic systems, it is shown that this approach eliminates the scaling in the number of trajectories with dimension and produces results that are frequently more accurate than the computationally cheaper method of the thawed Gaussian approximation (TGA).[9]

METHOD

The uniformization present in the HK propagator involves an integration over all the degrees of phase space where the quantum state of interest resides (see Fig. 1(a)). In the case that a dominant eigenvector of the stability matrix governing the dynamics of the state exists, such isotropic sampling is redundant from the perspective that all the trajectories tend towards this one-dimensional manifold. Sampling solely along this manifold reduces the integration over initial states dramatically while still accomplishing a good sampling of the time-evolved state (Fig. 1(c)).

As an exposition of the accuracy and efficiency of such one-dimensional sampling, we calculate the autocorrelation of a coherent state Ψ_β centered at $(\boldsymbol{p}_\beta, \boldsymbol{q}_\beta)$ with width γ_β in position space. The DHK method is based on the full HK propagator and is presented below:

$$\langle \Psi_\beta(0) \mid \Psi_\beta(t) \rangle_{\mathrm{DHK}} = \mathcal{N}^{-1} \int_{\mathcal{L}} dl \mathcal{A}(l,t) g(l,0) g^*(l,t) e^{\frac{i}{\hbar} S(\boldsymbol{p}_0(l), \boldsymbol{q}_0(l), t)}, \quad (1)$$

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where

$$g(l,0)=\exp\left[-\frac{1}{2}\frac{\gamma\gamma_\beta}{\gamma+\gamma_\beta}(\boldsymbol{q}_\beta-\boldsymbol{q}_0(l))^2-\frac{1}{2\hbar^2(\gamma+\gamma_\beta)}(\boldsymbol{p}_\beta-\boldsymbol{p}_0(l))^2+\frac{i}{\hbar(\gamma+\gamma_\beta)}(\boldsymbol{q}_0(l)-\boldsymbol{q}_\beta)(\gamma\boldsymbol{p}_\beta+\gamma_\beta\boldsymbol{p}_0(l))\right], \quad (2)$$

$$g(l,t)=\exp\left[-\frac{1}{2}\frac{\gamma\gamma_\beta}{\gamma+\gamma_\beta}(\boldsymbol{q}_\beta-\boldsymbol{q}_t(l))^2-\frac{1}{2\hbar^2(\gamma+\gamma_\beta)}(\boldsymbol{p}_\beta-\boldsymbol{p}_t(l))^2+\frac{i}{\hbar(\gamma+\gamma_\beta)}(\boldsymbol{q}_t(l)-\boldsymbol{q}_\beta)(\gamma\boldsymbol{p}_\beta+\gamma_\beta\boldsymbol{p}_t(l))\right], \quad (3)$$

$$\mathcal{A}(l,t)=\sqrt{\det\left[\frac{1}{2}\left(\frac{\partial\boldsymbol{p}_t(l)}{\partial\boldsymbol{p}_0(l)}+\frac{\partial\boldsymbol{q}_t(l)}{\partial\boldsymbol{q}_0(l)}-i\gamma\hbar\frac{\partial\boldsymbol{q}_t(l)}{\partial\boldsymbol{p}_0(l)}+\frac{i}{\hbar\gamma}\frac{\partial\boldsymbol{p}_t(l)}{\partial\boldsymbol{q}_0(l)}\right)\right]}, \quad (4)$$

and

$$\mathcal{N}=\int dl\, g(l,0)g^*(l,0). \quad (5)$$

The differences between this simpler relation and the full HK propagator are the contour integral over the curve $\mathcal{L}$ and the addition of the global normalization $\mathcal{N}$ so that the expression is 1 at $t=0$.

No effort is made to formally justify these simplifications aside from pointing out the following observations. Grossman and Xavier have shown that the uniformization integral in HK can be formulated as the result of inserting a coherent state identity operator into a primitive semiclassical propagator to be evaluated fully[10] (as opposed to by stationary phase). Herein this identity operator is the one-dimensional manifold of coherent states which is not a complete basis set (in any dimension except with proper modification in one dimension) and so, at the very least, requires an overall normalization with $\mathcal{N}$. The amplitudes and phases from the coherent states that are neglected by this one-dimensional manifold seem to be proportionally accounted for by the central manifold's values.

It is important to notice that when applied to dimensions greater than one, the fluctuations in the magnitude of the $\mathcal{A}(l,t)$ can cause the magnitude of DHK's autocorrelation to exceed 1, especially for ill-chosen manifolds $\mathcal{L}$. In practice, this was found to be uncommon in the systems studied here though a ceiling of 1 was forced in all numerical simulations.

NUMERICAL EXAMPLES

A series of test runs were conducted on progressively larger molecular systems obeying the coupled Morse vibrational Hamiltonian

$$H=\sum_{i=1}^{N}\left\{\frac{1}{2\mu}p_i^2+D[1-\exp(-\alpha q_i)]^2\right\}+g_{qq'}\sum_{i<j}^{N}p_ip_j+f_{qq'}\sum_{i<j}^{N}q_iq_j. \quad (6)$$

Numerical tests were performed for a parametrization of HCl ($N=1$),[11,12] SO_2 ($N=2$),[13] GeH_4 ($N=4$),[14] and $^{184}WF_6$ ($N=6$).[15] Initial states were chosen to be displaced coherent states in one vibrational degree of freedom and ground states in all the others. DHK's one-dimensional manifold $\mathcal{L}$ was chosen to lie along the dominant stability matrix eigenvector for the coherent state's central trajectory during either its first or second quasi-periodic return to the region near its initial state. For a list of parameters used see the Appendix.

Figure 2 shows the eigenspectra of these states—the Fourier transforms of their autocorrelations. Comparison with

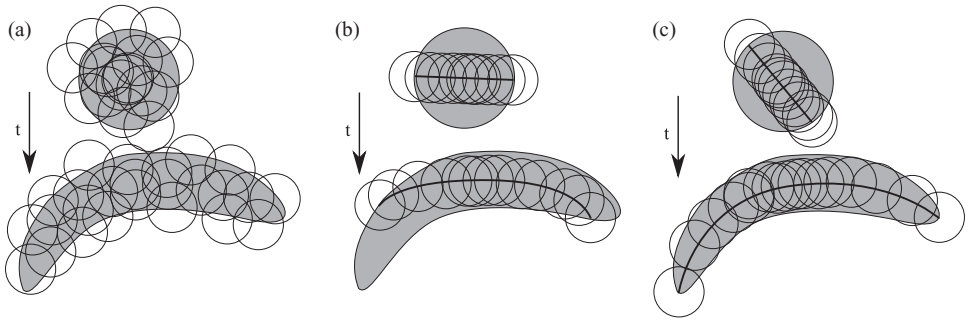

FIG. 1. Cartoon of the effect of the uniformization integral in HK as it appears in phase space. (a) Sampling the initial state based on its absolute density in all dimensions, as frequently performed with the Metropolis-Hastings algorithm for integration. Though initially isotropic, such a distribution of "frozen" Gaussians propagates to become a distribution that stretches out along a dominant stability matrix eigenvector. (b) Replacing this isotropic distribution which is slow to converge with one along an ill-chosen one-dimensional manifold will lead to a poor representation of later distributions. (c) However, if the proper axis is used, a similar distribution to the one obtained with the full HK propagator can be formed (especially at later times) without initially sampling the full dimensional space since all trajectories tend to that dominant manifold.

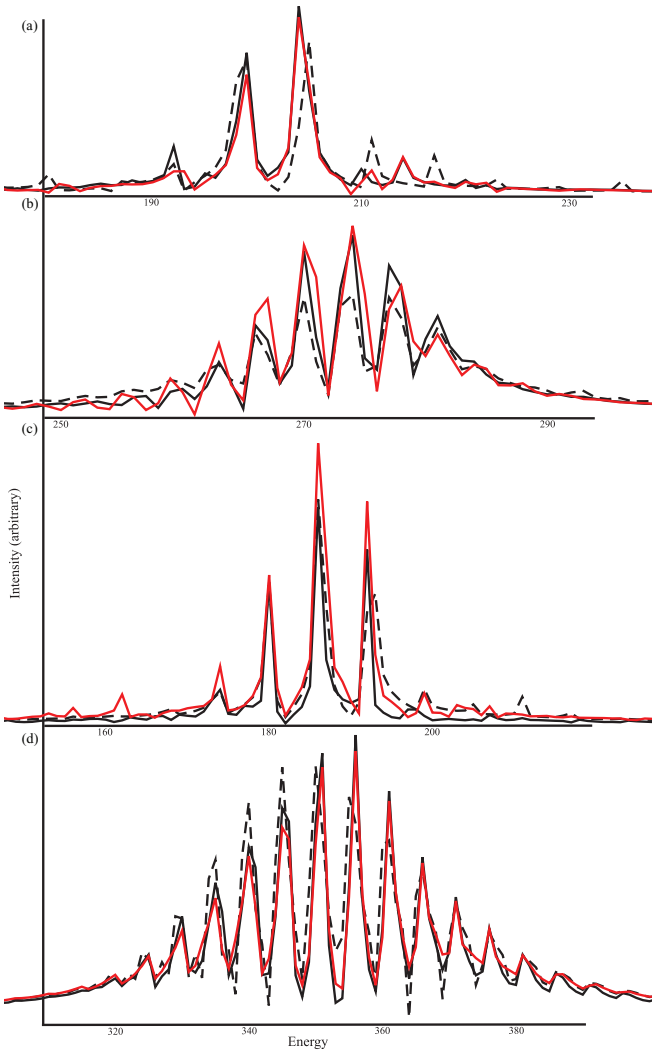

FIG. 2. HK (black), TGA (dashed black), and DHK (red) results are presented for (a) HCl, (b) SO_2, (c) GeH_4, and (d) $^{184}WF_6$. Energy units are 5 THz.

TGA confirms that they quickly explore anharmonic regions of phase space and limit its accuracy. In contrast, the DHK method along the one dimensional manifold is able to maintain very good accuracy with the eigenspectra of the full HK method. Furthermore, it is able to accomplish this without the full HK method's unfortunate scaling with dimension (see Figure 3). Tests with initial states involving more than a single excited degree of freedom produced similar agreement. If the excited states were brought down lower on the Morse potential, agreement with TGA improved, as expected for such a method that is exact for harmonic potentials.

It should be noted that all the trial runs reported here involved strong recurrences in the autocorrelations of the respective systems. In some cases where recurrences were observed to be far smaller, the sensitivity to the selection of the initial manifold seemed to increase (not shown). Indeed, it was found that separate recurrences often required different one-dimensional manifolds to be well brought out in this simplification to HK. This is expected considering that their separate dynamical origins are made more apparent when they

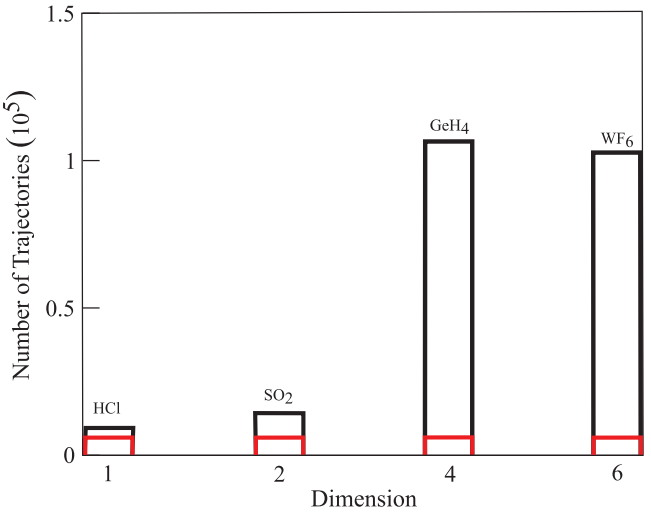

FIG. 3. Number of trajectories necessary for convergence of HK (black) and DHK (red) spectra in Fig. 2 with respect to the dimension of the system.

only produce "glancing" blows with the initial state, leading to weak recurrences.

CONCLUSION

It is perhaps fulfilling to discover that when the underlying classical dynamics of a state in an anharmonic system exhibit a dominant stability matrix eigenvector, the proliferation of trajectories necessary to compute a semiclassical autocorrelation can be severely reduced. It remains to be seen whether this method can be formalized or if it can be generalized to any submanifold of smaller dimension. The latter is especially important in systems which exhibit more than one dominant eigenvector.

Finally, it is also necessary to examine the robustness of this simplification with regards to weaker autocorrelations and in cases of more anharmonic, mixed, or chaotic dynamics. Future directions also include examining the marriage of this method with Filinov filtering and its usefulness in on-the-fly calculation.

Though many possibilities for speeding up semiclassical evaluation have been examined over the years, few have focused on using the actual dynamics of underlying trajectories to simplify computation with "frozen" Gaussian basis sets. Our findings offer encouraging evidence about the promise of this direction.

APPENDIX: PARAMETERS

HCl: $D = 37\,032\,\mathrm{cm}^{-1}$, $\alpha = 1.63219\,\text{Å}^{-1}$, $\gamma_\beta = 75.7\,\text{Å}^{-2}$, and $q_\beta = 1.87\,\text{Å}$ in excited degree of freedom. SO_2: $D = 57\,116\,\mathrm{cm}^{-1}$, $\alpha = 2.120\,\text{Å}^{-1}$, $\gamma_\beta = 403.3\,\text{Å}^{-2}$, $g_{qq'} = -0.01041\,\mathrm{amu}^{-1}$, $f_{qq'} = 0.0$ and $q_\beta = 1.01\,\text{Å}$ in excited degree of freedom. GeH_4: $D = 34\,716\,\mathrm{cm}^{-1}$, $\alpha = 1.41920\,\text{Å}^{-1}$, $\gamma_\beta = 64.2\,\text{Å}^{-2}$, $g_{qq'} = -0.00463465\,\mathrm{amu}^{-1}$, $f_{qq'} = 581.793\,\mathrm{cm}^{-1}\text{Å}^{-2}$, and $q_\beta = 1.51\,\text{Å}$ in excited degree of freedom. $^{184}WF_6$: $D = 61\,270\,\mathrm{cm}^{-1}$, $\alpha = 1.465\,\text{Å}^{-1}$, $\gamma_\beta = 366.6\,\text{Å}^{-2}$, $g_{qq'} = -0.0014\,\mathrm{amu}^{-1}$, $f_{qq'} = 12\,890\,\mathrm{cm}^{-1}$ for

adjacent bonds, $f_{qq'} = 10810\,\mathrm{cm}^{-1}$ for opposite bonds, and $q_\beta = 2.27$ Å in excited degree of freedom.

$q_\beta = p_\beta = 0.0$ in all other degrees of freedom. One-dimensional manifolds were chosen to be straight lines centered on $(\boldsymbol{p}_\beta, \boldsymbol{q}_\beta)$ with vector $(-1.0, -1.25 \times 10^{-4})$, $(7.02 \times 10^{-1}, 7.12 \times 10^{-1}, 1.61 \times 10^{-5}, 6.53 \times 10^{-6})$, $(0.1, -1.06 \times 10^{-2}, -1.05 \times 10^{-2}, -1.05 \times 10^{-2}, 1.19 \times 10^{-4}, 9.75 \times 10^{-7}, 9.75 \times 10^{-7}, 9.75 \times 10^{-7})$, and $(-9.97 \times 10^{-1}, 3.67 \times 10^{-2}, 3.67 \times 10^{-2}, 3.30 \times 10^{-2}, 3.67 \times 10^{-2}, 3.70 \times 10^{-2}, -2.03 \times 10^{-3}, 7.42 \times 10^{-5}, 7.42 \times 10^{-5}, 6.67 \times 10^{-5}, 7.42 \times 10^{-5}, 7.39 \times 10^{-5})$ for HCl, SO_2, GeH_4, and $^{184}WF_6$, respectively (arbitrary units).

$\gamma = \gamma_\beta$ for all runs. To obtain spectra, Fourier transforms were performed on 1000 timesteps of 0.2 fs.

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