Trajectory-dependent cellularized frozen Gaussians, a new approach for semiclassical dynamics: Theory and application to He–naphtalene eigenvalues

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A semiclassical cellular method is proposed. Signals generated by semiclassical techniques generally deteriorate over time as trajectories become chaotic. One approach to remedy this problem has been to have each trajectory weighted by an entire cell of nearby trajectories (Filinov transform). But even in this approach the exponential part of the propagator typically becomes large and positive over time. Here the cellularization (Filinov) parameter is subject to constraints which make it time dependent and trajectory dependent. It also depends on dimensionality, so it ends up as a matrix. Physically, the Filinov transform is done differently in different directions associated with the stability matrix for the phase—essentially a more confined integration in directions where the matrix diverges and a wider integration in other directions. This squelches the contribution from any part of a trajectory that becomes excessively chaotic. A trajectory-dependent cellurized frozen Gaussian is applied here within the Herman–Kluk semiclassical approach. It is tested by looking at a single-particle three-dimensional problem, He attached to a rigid immovable naphtalene, where it is shown to be more accurate than the original HK approach, without the divergence of the correlation function common in the usual cellular dynamics (HK) formulation, and is able to separate a low-lying excited state from the ground state.
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I. INTRODUCTION

Semiclassical methods for wave packet propagation have recently been an area of rich research because of the ability to treat quantum effects in heavy-particle motion.[1–9] These methods offer the hope of being numerically more feasible than full quantum calculations for very large systems and are potentially accurate enough to properly describe quantum observables.

The basis of semiclassical methods is that the full Green's function in the Feymann path integral formulation is replaced by classical paths, with a preexponential term that contains phase information of the nonclassical trajectories around each classical path. An additional improvement has been a substitution of integration variables, so that each integration is done over initial position and momentum.[10–12] This area—initial variable representation (IVR)—has been a focus of substantial research. Within this area, the Herman–Kluk (HK) propagator has proved to be exceptionally useful.[1] In the HK method, the coherent wave function is represented by a swarm of frozen Gaussians,[13] so that each classical path has an associated term weighting the contribution of nearby trajectories. This method has the correct asymptotic behavior in the limit of $\hbar \to 0$. Unfortunately, many trajectories become chaotic over time and can contribute to a calculated correlation function that becomes larger than 1. A large number of trajectories is required to compensate for this.

Two possible categories of approaches to counteract this deficiency are using a signal processing method that requires only a short-time signal or filtering to improve the sampling of phase space. (A third set of approaches, the backward–forward or interaction-picture method, is complementary to the methods suggested here and can be used in conjunction with them.[9])

The first approach has been effectively done using signal processing tools, such as filter diagonalization with a correlation matrix C_{ij},[7,14] which extracts a large amount of information about a short-time signal.[15,16]

The approaches to remove the difficulties associated with problematic trajectories have evolved. One possibility is a method in which any chaotic trajectory is removed, an *ad hoc* procedure.[5] Alternately, a stationary phase approach was developed that weighted chaotic trajectories through a Monte Carlo truncation method.[8] This method is not related to the HK approach.

Approaches that deal with modifying the original HK integral have also been developed.[2,17] Many of these methods involve using the Filinov transform. The idea of these approximations is that a ''cell'' of trajectories is averaged and each of these cells is propagated. In this case, the chaotic part is hopefully suppressed. The cell is determined by a parametrized size which is equally applied to all trajectories at all times in all dimensions. This can prolong the length of

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the signal. In cases where trajectories in different dimensions have very different chaotic behavior, this method also breaks down. For one dimension the phase is well behaved, but in another it can become chaotic. In the usual cellular dynamics equations, both dimensions would be equally damped and one must choose between losing useful information or keeping a wildly chaotic trajectory.

A further problem is that the Gaussian integral which enters the cellularization can become either very large (for scattering systems) or, even worse, formally divergent.

In this paper, we present a method that changes the averaging parameter of the cellularization over time and dimension for each trajectory. The advantages of this are twofold. The damping can be adjusted for each trajectory at each time step so that the cellularization only damps the dimension that becomes problematic at the time it is problematic. Simultaneously, we check and ensure that the Gaussian which enters the cellularization is never formally divergent or large.

In the remainder of this paper we first review the Herman–Kluk method and discuss the challenges of the Filinov transformation. Then we show the derivation of the trajectory-dependent cellularized frozen Gaussian (TDCFG) method. We have initially used this method on the naphtalene–helium system and will show results comparing the usual HK method with improvements from the TDCFG method. The last section is a conclusion pointing to further research with this method.

II. METHODOLOGY

A. Herman–Kluk propagator

The time-dependent correlation function associated with a specific initial function is defined as ($\hbar=1$)

$$C(t)=\langle\Psi|e^{-iHt}|\Psi\rangle. \tag{1}$$

To the usual semiclassical propagator, the HK approach adds a swarm of frozen Gaussians which is substituted as a basis set representing the wave function.[1] Using the semiclassical Herman–Kluk propagator, the correlation function can be expressed as

$$C(t)=\left(\frac{1}{2\pi}\right)^N\int\int d^N\mathbf{p}_i d^N\mathbf{q}_i\langle\Psi|g_{\mathbf{q}_f(t),\mathbf{p}_f(t)}\rangle R_{\mathbf{p}_i,\mathbf{q}_i,t}\times\exp(iS_{\mathbf{p}_i,\mathbf{q}_i,t})\langle g_{\mathbf{q}_i,\mathbf{p}_i}|\Psi\rangle, \tag{2}$$

where we introduced the classical initial momentum and position which are scaled by σ, the natural width of the wave function near the potential minimum. (Since the potential has a different curvature near the minimum for z and x,y—where x,y is the plane of the naphtalene—a different σ was used for z and x,y. This amounts to rescaling the coordinates; the modifications needed are straightforward and will not be repeated here.) Also, $g_{\mathbf{q}_i,\mathbf{p}_i}$ are frozen-width Gaussians, $S_{\mathbf{p}_i,\mathbf{q}_i,t}$ is the standard classical action, and $R_{\mathbf{p}_i,\mathbf{q}_i,t}$ is the prefactor that contains the phase information resulting from the interference of the Gaussian wave packets:

$$R_{\mathbf{p}_i,\mathbf{q}_i,t}=\sqrt{\det\left[\frac{1}{2}\left(\frac{\partial\mathbf{p}_t}{\partial\mathbf{p}_i}+\frac{\partial\mathbf{q}_t}{\partial\mathbf{q}_i}-i\frac{\partial\mathbf{q}_t}{\partial\mathbf{p}_i}+i\frac{\partial\mathbf{p}_t}{\partial\mathbf{q}_i}\right)\right]}. \tag{3}$$

Each of terms in $R_{\mathbf{p}_i,\mathbf{q}_i,t}$ is a $N\times N$ matrix that can easily be propagated over time, where N is the dimensionality of the problem. The one challenge with $R_{\mathbf{p}_i,\mathbf{q}_i,t}$ is that we are taking a square root of a complex number, but it can be ensured that it is always continuous.

When the initial (and final) wave function is itself a Gaussian, with initial momentum and position $\mathbf{p}_0,\mathbf{q}_0$, the correlation function with the explicit Gaussian overlaps yields

$$\begin{aligned}C(t)=\left(\frac{1}{2\pi}\right)^N\int\int d^n\mathbf{p}_i d^n\mathbf{q}_i R_{\mathbf{p}_i,\mathbf{q}_i,t}e^{iS_{\mathbf{p}_i,\mathbf{q}_i,t}}&\\ \times\exp\left[-\frac{1}{4}(\mathbf{q}_t-\mathbf{q}_0)^2-\frac{i}{2}(\mathbf{p}_t+\mathbf{p}_0)(\mathbf{q}_t-\mathbf{q}_0)\right.&\\ \left.-\frac{1}{4}(\mathbf{p}_t-\mathbf{p}_0)^2\right]&\\ \times\exp\left[-\frac{1}{4}(\mathbf{q}_i-\mathbf{q}_0)^2+\frac{i}{2}(\mathbf{p}_i+\mathbf{p}_0)(\mathbf{q}_i-\mathbf{q}_0)\right.&\\ \left.-\frac{1}{4}(\mathbf{p}_i-\mathbf{p}_0)^2\right].&\end{aligned} \tag{4}$$

This is easily calculated for each trajectory using Monte Carlo integration with the following sampling function:

$$|\langle g_{\mathbf{p}_i,\mathbf{q}_i}|\Psi|=\exp(-\tfrac{1}{4}(\mathbf{q}_i-\mathbf{q}_0)^2-\tfrac{1}{4}(\mathbf{p}_i-\mathbf{p}_0)^2). \tag{5}$$

All the terms are easily propagated over time. Unfortunately, over time the HK method develops two problems. Depending on the system being studied, each trajectory can become chaotic, leading to a large magnitude of the differentials in $R_{\mathbf{p}_i,\mathbf{q}_i,t}$. Additionally, the action can become large. So the signal (the correlation function) degrades over time.

B. Filinov transformation

Currently, these shortcomings with the HK propagator are frequently treated with some form of the Filinov transform:

$$1=\frac{\sqrt{\eta^N}}{(2\pi)^N}\int d^N\overline{\mathbf{y}}\,e^{-1/2(\mathbf{y}-\overline{\mathbf{y}})^2\eta/2}, \tag{6}$$

where $\overline{\mathbf{y}}=(\overline{\mathbf{q}},\overline{\mathbf{p}})$. In these methods η is usually a single number (or has a different fixed value in each dimension, which amounts to a coordinate scaling) that effectively averages in phase space the surrounding trajectories. Essentially, instead of an individual trajectory being propagated, a ''cell'' of trajectories is propagated. By taking the Filinov average, the chaotic parts will hopefully be damped out. Anticipating the development in the next paragraph, we rewrite η as a general matrix, though usually it is treated as a scalar or a diagonal matrix:

$$1=\frac{\sqrt{\det\,\eta}}{(2\pi)^N}\int d^N\overline{\mathbf{y}}\,e^{-1/2(\mathbf{y}-\overline{\mathbf{y}})\eta(\mathbf{y}-\overline{\mathbf{y}})}. \tag{7}$$

The general derivation of the correlation function is then as follows: We write the correlation function as

$$C(t)=\left(\frac{1}{2\pi}\right)^N \int\int d^N\overline{\mathbf{p}}\, d^N\overline{\mathbf{q}}\, F(\overline{\mathbf{p}},\overline{\mathbf{q}},t), \tag{8}$$

where we have defined

$$\begin{aligned} F(\overline{\mathbf{p}},\overline{\mathbf{q}},t)=&\frac{\sqrt{\det\,\eta}}{(2\pi)^N}\int\int d^N\mathbf{p}_i d^N\mathbf{q}_i R_{\mathbf{p}_i,\mathbf{q}_i,t} e^{iS_{\mathbf{p}_i,\mathbf{q}_i,t}} \\ &\times\exp\left[-\frac{1}{4}(\mathbf{q}_t-\mathbf{q}_0)^2-\frac{i}{2}(\mathbf{p}_t+\mathbf{p}_0)(\mathbf{q}_t-\mathbf{q}_0)\right. \\ &\left.-\frac{1}{4}(\mathbf{p}_t-\mathbf{p}_0)\right]\exp\left[-\frac{1}{4}(\mathbf{q}_i-\mathbf{q}_0)^2\right. \\ &\left.-\frac{i}{2}(\mathbf{p}_i+\mathbf{p}_0)(\mathbf{q}_i-\mathbf{q}_0)-\frac{1}{4}(\mathbf{p}_i-\mathbf{q}_0)\right] \\ &\times\exp\left[-\frac{1}{2}(\overline{\mathbf{y}}-\mathbf{y})\,\eta(\overline{\mathbf{y}}-\mathbf{y})\right]. \end{aligned} \tag{9}$$

We will define B as the exponential part of the integration, excluding the term with η:

$$\begin{aligned} B=&iS_{\mathbf{p},\mathbf{q},t}-\frac{1}{4}(\mathbf{q}_t-\mathbf{q}_0)^2-\frac{i}{2}(\mathbf{p}_t+\mathbf{p}_0)(\mathbf{q}_t-\mathbf{q}_0) \\ &-\frac{1}{4}(\mathbf{p}_t-\mathbf{p}_0)^2-\frac{1}{4}(\mathbf{q}_i-\mathbf{q}_0)^2-\frac{i}{2}(\mathbf{p}_i+\mathbf{p}_0)(\mathbf{q}_i-\mathbf{q}_0) \\ &-\frac{1}{4}(\mathbf{p}_i-\mathbf{p}_0)^2. \end{aligned} \tag{10}$$

B is then expanded to the second order, so that rewriting F,

$$\begin{aligned} F(\overline{\mathbf{p}},\overline{\mathbf{q}},t)=&\frac{\sqrt{\det}\eta}{(2\pi)^N}\int\int d^N\mathbf{p}_i d^N\mathbf{q}_i \\ &\times R_{\mathbf{q},\mathbf{q},t} e^{B(\overline{\mathbf{y}})+B'_y(\mathbf{y}_i-\overline{\mathbf{y}})+1/2(\mathbf{y}_i-\overline{\mathbf{y}})^T(B''_{\mathbf{y}}-\eta)(\mathbf{y}_i-\overline{\mathbf{y}})}. \end{aligned} \tag{11}$$

As mentioned previously, η is usually treated as a constant scalar. Two problems that are related arise then with this method.

First, choosing η is not straightforward. If the surrounding trajectories are spread out (chaotic), a large η is needed to average them. The longer a propagation is run, the larger the η needs to be to keep the trajectories "in check."

The second problem arises from the fact that in this method a second-order expansion of B is employed, as shown above. It is easy to see that at times the second-order term can in fact acquire a large positive real part. The exponential then formally diverges. Of course, this is because of only taking the second-order expansion. We found that for the naphtalene–helium system any trajectory would eventually became chaotic, and at least one of the eigenvalues of B acquires a large positive part that continued to increase and became infinitely large. Specifically, in the formulation shown,[2] $\mathbf{p}_i,\mathbf{q}_i$ are only expanded to first order. Some trajectories become unstable and have an infinite contribution to the correlation function, regardless of the choice of the cellurization parameters (in this case, one for the position and another for the momentum). In this formulation, once a trajectory becomes chaotic, it remains so.[2] Even if unstable trajectories are thrown out, eventually (longer-time propagation) all trajectories can become chaotic. So far, no method has been developed that explicitly restricts this from occurring. Of course, a quick solution to this would be to restrict the entire cellularization term for each trajectory from becoming infinite by placing a cap on its value or removing the trajectory completely. But then information is lost because the chaotic nature of the trajectory is usually coming from only one dimension, while the other dimensions are well behaved. Also, in the case of completely removing a trajectory, future useful information is being removed from that path.

C. TDCFG method

The idea behind the TDCFG method is to allow η to become dependent on the trajectory. Then the real part of the exponential is always prevented from becoming positive and large, by choosing η appropriately. This is an approximation since rigorously the Filinov transformation requires that η be constant. Nevertheless, this approximation is controllable. We find that the results are insensitive to this approximation.

The details are as follows: We do the following transformation to determine what η should be. Set $B''_{\mathbf{y}}=A\lambda A^T$ (λ is diagonal and $AA^T=1$). Then we choose η to have the same eigenvectors as B'', with the eigenvalues denoted by ϕ:

$$\eta=A\phi A^T.$$

We also define

$$\mathbf{g}\equiv A^T B'$$

and

$$\zeta\equiv A^T(\mathbf{y}-\overline{\mathbf{y}}).$$

The constraints on the diagonal matrix ϕ will be derived in the following way. First, the exponential part of $F(\overline{\mathbf{p}},\overline{\mathbf{q}},t)$ will be rewritten in our new coordinates:

$$\begin{aligned} B(\mathbf{y})=&B(\overline{\mathbf{y}})+B'_{\overline{\mathbf{y}}}AA^T(\mathbf{y}-\overline{\mathbf{y}}) \\ &-\tfrac{1}{2}(\mathbf{y}-\overline{\mathbf{y}})^T A^T A(\eta-B'_{\overline{\mathbf{y}}})AA^T(\mathbf{y}-\overline{\mathbf{y}}) \\ =&B(\overline{\mathbf{y}})+\mathbf{g}^T\zeta-\tfrac{1}{2}\zeta^T(\phi-\lambda)\zeta. \end{aligned} \tag{12}$$

Using

$$\sqrt{\det(\eta)}=\sqrt{\det(\phi)}, \tag{13}$$

F is rewritten as

$$F(\overline{\mathbf{p}},\overline{\mathbf{q}},t)=\int d^{2N}\zeta_i\left(\frac{\det\,\phi}{\pi}\right)^{N/2} R_{\mathbf{p}_i,\mathbf{q}_i,t} e^{B(\overline{\mathbf{y}})+J(\zeta,\phi,\lambda,\mathbf{g})}, \tag{14}$$

where

$$J(\zeta,\phi,\lambda,\mathbf{g})=\mathbf{g}^T\zeta-\tfrac{1}{2}\zeta^T(\phi-\lambda)\zeta. \tag{15}$$

TABLE I. Parameters, including Lennard-Jones values, used in all the simulations (see also Table II for individual run parameters). Note that cm^{-1} refers here to an energy unit, wave numbers.

Time step (dt)	10.618 fs$\left(=\frac{0.002}{cm^{-1}}\right)$
He mass (M)	0.12 $(cm^{-1}\ Å^2)^{-1}$
σ_{HeC}	3.099 Å
ϵ_{HeC}	13.92 cm^{-1}
σ_{HeH}	2.903 Å
ϵ_{HeH}	5.761 cm^{-1}
Minimum potential	−122.70 cm^{-1}
Location of minimum potential	(0.794, 0.000, 3.132) Å
	(−0.794, 0.000, 3.132) Å
Position of first C (in naphtalene)	(0.0, 0.7, 0.0) Å
Position of first H (in naphtalene)	(1.212, 2.480, 0.000) Å

$R_{\mathbf{p}_i,\mathbf{q}_{i,t}}$ is only calculated to zeroth order, so that it is essentially the same and therefore can be removed from the integration over $\mathbf{y}_i$.

We want to ensure that at long times J is negative, or a small positive definite number, for all values of ζ. The first constraint is therefore immediately clear: the coefficient of the second-order term in ζ, $\phi-\lambda$, must be positive.

To develop all the constraints systematically, we complete the square:

$$J=-\frac{1}{2}\left(\zeta^T(\phi-\lambda)^{1/2}-\frac{\mathbf{g}}{(\phi-\lambda)^{1/2}}\right)^2+\frac{\mathbf{g}^2}{2(\phi-\lambda)}. \quad (16)$$

The first part of J, by identity, is guaranteed to become a constant upon integration of the exponential. The second term $\mathbf{g}^2/2(\phi-\lambda)$ needs to be constrained from having a large positive real part. We have done this by placing three constraints on ϕ.

First, ϕ must at least have some minimum value of $\phi_{\min}$. If not, we found that the initial results degraded immediately. In effect, we do not want the cellurization turned on immediately because initially all the trajectories are well behaved. Second, the real part of $(\phi_i-\lambda_i)$ (where i represents the ith diagonal element in the matrix) is always prevented from reaching zero. We use the parameter β to denote the minimum allowed difference between ϕ and λ. These two constraints can be expressed as

$$\phi>\max(\phi_{\min},\mathrm{Re}\ \lambda+\beta). \quad (17)$$

Finally, the entire term must be kept from increasing, so we impose

$$\mathrm{Re}\frac{g_i^2}{(\phi_i-\lambda_i)}<\alpha_i, \quad (18)$$

where α is a small positive definite number. We are going to choose ϕ_i to be real as this simplifies the calculation. From these constraints on ϕ and therefore η, we determine η. It should be noted that the relation between α and the eventual "cell" that is averaged is not linear. If $\alpha=\infty$ and $\beta=0$, the factor will give the more traditional constant cellurization dynamics.

We can now return to the original derivation. We use the analytical formula[18]

$$\int d^{2N}z\ \exp[-\mathbf{z}^T\mathbf{D}\mathbf{z}-\mathbf{m}^T\mathbf{z}]=\frac{\pi^N}{\det\ \mathbf{D}^{1/2}}\exp\left(\frac{1}{4}\mathbf{m}^T\mathbf{D}^{-1}m\right), \quad (19)$$

where $\mathbf{z}=\mathbf{y}_i-\overline{\mathbf{y}}$, so $d^{2N}\mathbf{y}_i$ is replaced by $d^{2N}\mathbf{z}$. Given that

$$C(t)=\left(\frac{1}{2\pi}\right)^N\int\int d^{2N}\overline{\mathbf{y}}\,R_{\overline{\mathbf{y}}_t}e^{B(\overline{\mathbf{y}})}\frac{\sqrt{\det\ \eta}}{(2\pi)^N}\times\int d^{2N}\mathbf{z}\exp\left[B_{\overline{y}}'^T\mathbf{z}+\frac{1}{2}\mathbf{z}^T(B_{\overline{y}}''-\eta)\mathbf{z}\right]. \quad (20)$$

We define

$$\mathbf{D}=\frac{\eta-B_{\overline{y}}''}{2} \quad (21)$$

and

$$\mathbf{m}=-B_{\overline{y}}'. \quad (22)$$

The end equation that is to be integrated becomes

$$C(t)=\left(\frac{1}{2\pi}\right)^N\int\int d^N\overline{\mathbf{p}}\,d^N\overline{\mathbf{q}}R_{\overline{\mathbf{p}}_i,\overline{\mathbf{q}}_i,t}e^{B(\overline{\mathbf{y}})}\times\frac{\sqrt{\det\ \eta}}{\sqrt{\det(\eta-B_{\overline{\mathbf{y}}}'')}}\exp\left[\frac{1}{2}B_{\overline{y}}'(\eta-B_{\overline{\mathbf{y}}}'')^{-1}B_{\overline{\mathbf{y}}}'\right], \quad (23)$$

where, as mentioned previously, the one approximate aspect of this expression is that we do not take into account the position dependence of η in doing the integral.

The challenging aspect of this method is that while all the terms in the usual HK method can easily be calculated at each time step through simple Hamiltonian-type equations, the calculations of $B_{\overline{\mathbf{y}}}'$ is more complicated. At this time, they are obtained by explicitly calculating the derivatives. This is done by a three-point formula. The middle point is the actual trajectory, and then B is calculated at $\pm\delta$ away from each trajectory in each dimension $(2N)$. This leads to an additional $4N\times4N$ matrix around each trajectory. This is obviously the most time-consuming part of the calculation.

III. RESULTS

The system we used for our trial is naphtalene with a single helium atom, i.e., a three-dimensional (3D) system. We used the Lennard-Jones potential energy surface where the carbons and hydrogens are idealized, with infinite mass and equidistant apart. The origin is the center of the naphtalene ring, which is defined to lie in the $x-y$ plane. The parameters we used are given in Table I. Unlike the helium–benzene system we studied in an earlier work,[14] the x and y components are not symmetrical here. The placement of the initial wave function and conditions are given in Table II. Unless otherwise noted, the runs were for 5000 trajectories.

TABLE II. Parameters for the runs shown.

Case	A	B	C	D
Num. of traj.	5000	1000	2000	5000
α	5.0	5.0	5.0	5.0
β	10.0	10.0	10.0	10.0
$\phi_{\min}$	100	100	100	100
$\mathbf{q}_i$	(1.2,0.0,3.1)	(1.2,0.0,3.1)	(1.2,0.0,3.1)	(0.8,0.5,3.1)

Very high energy trajectories that had an initial energy over 100 cm^{-1} were thrown out. This does not affect the final results.

Even with the restrictions, at times an individual correlation contribution can become large (but *not* infinite) for a short period of time. At a later time, they again become well behaved. By not removing the trajectory permanently, the information is retained. For our runs we did induce a cap on the total contribution to the correlation function. Because the trajectories did not have infinite values, even without a cap, the phase information can be retained. The specific value of the cap does not appear to affect the eventual outcome of the calculated eigenvalues.

The correlation function proved to be stable and meaningful for a longer-time propagation than without the TDCFG method. An example is shown in Fig. 1, depicting the real part of the correlation function. In the Herman–Kluk method, the correlation function becomes larger than one at about 3 ps, while the TDCFG stays below 1.

A certain amount of high-energy ''jitter'' is introduced in this approach. It originates from two sources. First, at times the damping is turned on rather suddenly because of a rapidly changing λ. In this case there can be almost a discontinuity in a trajectory's contribution to the correlation function. Second, the Filinov approach (including the TDCFG method) is an approximation based on only the second-order expansion of B. Under certain conditions, a very-high-energy oscillation appears in the exponential. We believe it is related to only having the second-order and at times the first- and second-order terms in the exponential, which can cancel each other except for a high-energy oscillation. We have used filter diagonalization for signal processing. This method filters out this high-energy ''jitter'' and does not appear to effect the energies of interest.

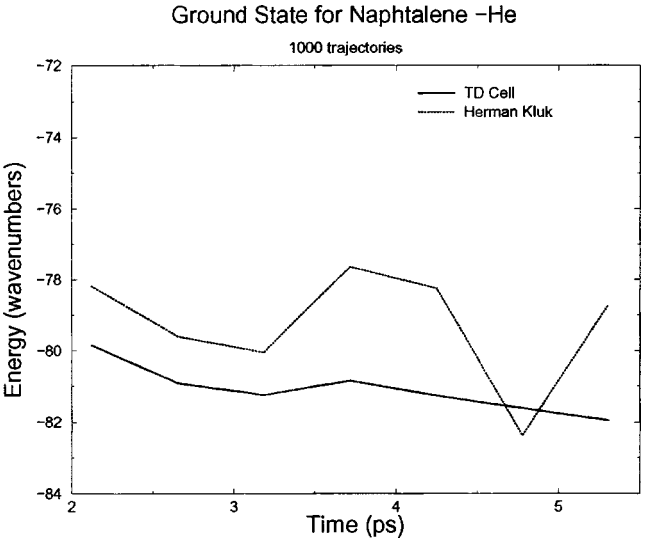

FIG. 2. Comparison of ground-state eigenvalues resolved with respect to signal length used for 1000 trajectories, case B.

Figures 2–4 show the ground and first excited energies derived from both the HK and TDCFG methods. Conditions for each case are listed in Table II. The advantages of the TDCFG can be seen. First, looking at Figs. 2, 3, and 4, the need for fewer trajectories is evident. Semiclassical techniques usually require a large number of trajectories in order to converge the signal. Both Figs. 2 and 3, with 1000 and 2000 trajectories, respectively, show results for exceptionally low numbers of trajectories. Even with as few as 1000 trajectories the TDCFG method converges and becomes stable around -80.6 cm^{-1}. The HK method has values fluctuating

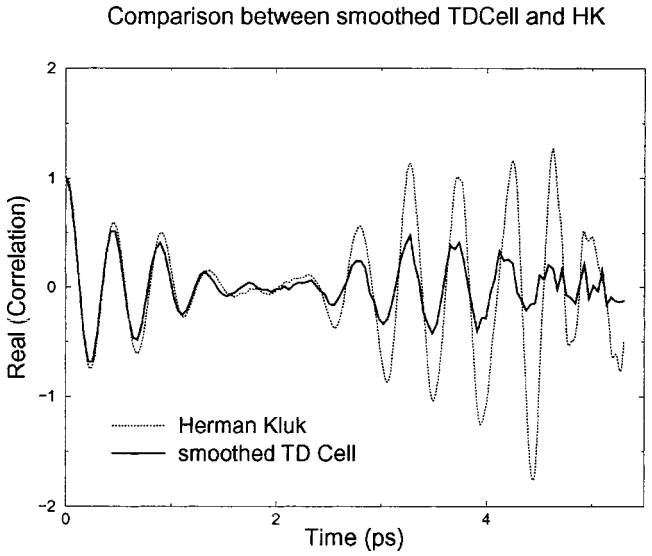

FIG. 1. Comparison of $\mathrm{Re}[C(t)]$ for the TDCFG and standard HK methods, case A.

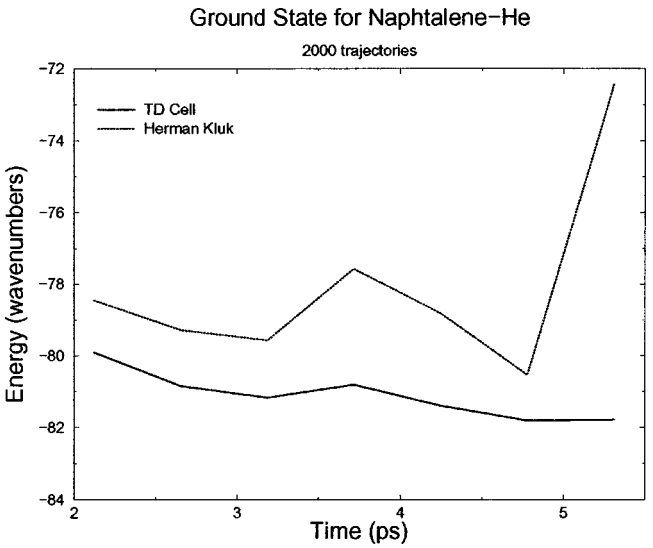

FIG. 3. Comparison of ground-state eigenvalues resolved with respect to signal length used for 2000 trajectories, case C.

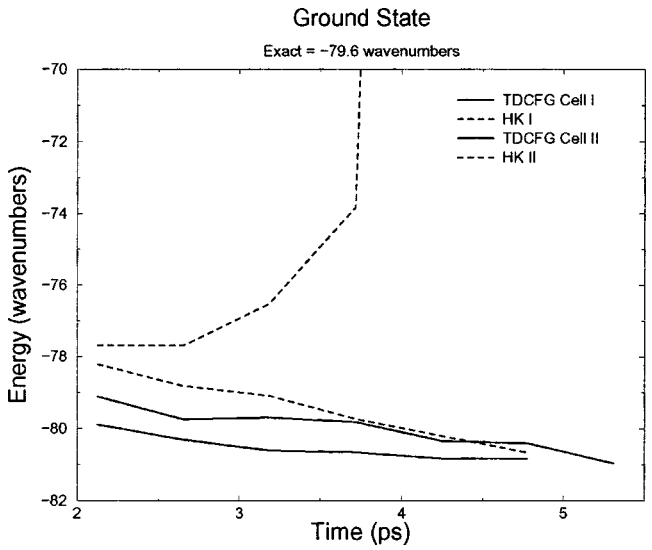

FIG. 4. Comparison of ground-state eigenvalues resolved with respect to signal length used for 5000 trajectories, case D. Two different applications of the signal processing are shown. There is always some deviation, based on parameters used in the filter diagonalization. The more stable the results are with respect to these parameters, the more reliable are the results.

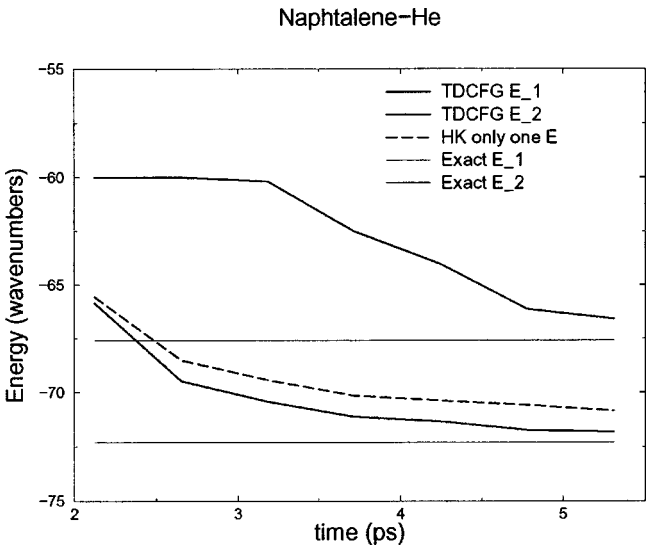

FIG. 5. Comparison of the first two excited eigenvalues resolved with respect to signal length used for 5000 trajectories, case D.

from -77.5 to -82.5 cm^{-1}. This is too varied to pull out an eigenvalue. Though the TDCFG method is about a wave number off from the exact calculation, it gives a relatively good result. By 5000 trajectories (Fig. 4), the usual number we used, then with the signal processing (FDG) the results come close to the exact and are stable. The HK method barely stabilizes around -78.8 cm^{-1} and then drifts.

Finally, Fig. 5 shows one of the more astounding advantages of the TDCFG method. The ground and first excited states are only separated by 4.5 cm^{-1}. Usually, this would require a large number of trajectories and symmetrization of the correlation function to resolve. In this case a single wave packet is able to resolve this splitting remarkably well. The HK method only picks up one state well, and the higher-energy one is not resolved. In this case the TDCFG method is obviously advantageous to the HK method.

IV. CONCLUSIONS

The trajectory-dependent frozen cellularized Gaussian method appears to be a very promising extension to semiclassical dynamics. Usual semiclassical signals degrade rapidly and become chaotic in nature. This method allows us to tune the damping so that it affects only the individual trajectory's specific dimension at the time they become problematic. This method greatly expands the time a signal is still viable. Other ways of calculating the second-order terms need to be investigated in the future in order to increase the speed of this method.

Overall, we believe these results are promising and should be further studied as semiclassical techniques are pushed to longer-time signals and less ideal potentials and, most importantly, higher dimensions.

[1] M. F. Herman and E. Kluk, Chem. Phys. **91**, 27 (1984).
[2] A. R. Walton and D. E. Manolopoulos, Mol. Phys. **87**, 961 (1996).
[3] S. Garashchuk, F. Grossman, and D. Tannor, Faraday Discuss. **93**, 781 (1997).
[4] B. E. Guerin and M. F. Herman, Chem. Phys. Lett. **286**, 361 (1998).
[5] K. G. Kay, J. Chem. Phys. **101**, 2250 (1994).
[6] X. Sun and W. H. Miller, J. Chem. Phys. **108**, 8870 (1998).
[7] V. A. Mandelshtam and M. Ovchinnikov, J. Chem. Phys. **108**, 9206 (1998).
[8] G. Campolieti and P. Brumer, J. Chem. Phys. **109**, 2999 (1998).
[9] K. Thompson and N. Makri, J. Chem. Phys. **110**, 1343 (1999).
[10] W. H. Miller, Adv. Chem. Phys. **25**, 69 (1974).
[11] W. H. Miller, J. Chem. Phys. **95**, 9428 (1991).
[12] E. J. Heller, J. Chem. Phys. **95**, 9431 (1991).
[13] E. J. Heller, J. Chem. Phys. **75**, 2923 (1981).
[14] S. M. Anderson, J. K. Ka, P. Felker, and D. Neuhauser, Chem. Phys. Lett. **328**, 516 (2000).
[15] D. Neuhauser, J. Chem. Phys. **93**, 2611 (1990).
[16] M. R. Wall and D. Neuhauser, J. Chem. Phys. **102**, 8011 (1995).
[17] M. F. Herman, Chem. Phys. Lett. **275**, 445 (1997).
[18] K. G. Kay, J. Chem. Phys. **100**, 4377 (1994).