Applying Bogomolny's quantization method to generic classical systems

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The quantization method of Bogomolny [Nonlinearity **5**, 805 (1992)] can potentially provide semiclassical estimates for energy levels of all bound states of arbitrary systems. This approach requires the formation of the *transfer matrix* $\mathbf{T}_E$ as a function of energy E . Existing practical methods for calculating this matrix require a recalculation of many classical trajectories for each energy. This has hampered the application of Bogomolny's method to generic systems that do not possess special classical scaling properties. Generalizing earlier work [H. Barak and K. G. Kay, Phys. Rev. E **88**, 062926 (2013)], we develop initial value representation formulas for $\mathbf{T}_E$ that overcome this problem. These expressions are obtained from a generalized Herman-Kluk formula for the propagator that allows one to easily derive a family of semiclassical integral approximations for the Green's function that are, in turn, used to form the transfer matrix. Calculations for two-dimensional systems show that Bogomolny's method with the present expressions for $\mathbf{T}_E$ produces accurate semiclassical energy levels from small transfer matrices. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4983748>]

I. INTRODUCTION

The transfer matrix approach of Bogomolny^{1,2} is one of the few semiclassical methods that can, in principle, estimate energy levels for all bound states of an arbitrary multidimensional system, regardless of the chaotic or nonchaotic nature of its classical motion. The purpose of this paper is to develop techniques that allow the practical application of Bogomolny's theory to molecular systems.

In part, interest in this subject is prompted by difficulties in the application of initial value representation (IVR) methods,^{3–5} which are the most computationally convenient existing semiclassical (SC) techniques for multidimensional systems. These methods express quantities such as the time-dependent propagator^{6–8} or the energy-dependent Green's function^{9,10} as phase space integrals over initial conditions for trajectories. Such methods avoid the cumbersome search for periodic orbits or other special classical trajectories obeying the double-ended boundary conditions that are required by the most familiar SC techniques. Unfortunately, severe numerical difficulties in performing the required integrations diminish the usefulness of these methods for calculations requiring evolution for a long period of time. This restriction to short times limits the resolution of energy levels computed by IVR methods. Consequently, it may not be possible to calculate all desired energies by these methods when the level density becomes high, e.g., for large systems or even small systems at high energies.

The source of these problems is the rapid variation of the IVR integrand's phase with an initial integration point and the accompanying large values attained by the integrand's amplitude. These issues become especially serious for systems with many degrees of freedom or with sufficiently strong classical chaos.

A number of approaches have been found useful for extending the applicability of the IVR techniques,^{11–15} but they do not completely solve the problems. For example, even with these techniques, it appears doubtful that existing IVR methods can determine energy eigenvalues for all “bound” states of the standard two-dimensional Hénon-Heiles system.^{11,16–22}

One possibility for side-stepping these problems is to obtain the SC energy levels from Bogomolny's transfer matrix (or T -matrix) $\mathbf{T}_E$ which is constructed solely from short classical trajectories that originate on a Poincaré surface of section (PSS) and return to it for the first time in the initial normal direction. It was shown^{1,2} that the quantization condition for bound systems can be expressed semiclassically as the vanishing of the Fredholm determinant, $\zeta_E \equiv \det(\mathbf{1} - \mathbf{T}_E)$, at energy E . Thus, it should be possible to estimate energy eigenvalues of the quantum system as values of E that make finite approximations to this determinant small.

A problem with the practical application of this method is that Bogomolny's formula for elements $T_E(\mathbf{y}', \mathbf{y})$ of the T -matrix requires a search for special trajectories that leave the PSS at specific positions $\mathbf{y}$ and return to that surface at specific positions $\mathbf{y}'$. Haggerty²³ was apparently the first to suggest that this problem could be solved by replacing Bogomolny's formula with an IVR expression. Calculations based on this expression were not affected by the usual IVR long-trajectory problem because only short classical trajectories that return to a PSS in a single cycle of motion were required. Recently,²⁴ another IVR formula was presented which also requires only short trajectories but, in line with more modern IVR treatments,^{5,6} contains certain Gaussian factors in the integrand. Unlike Haggerty's formula, which was constructed to be exactly equivalent to Bogomolny's expression, the newer IVR approximation becomes equivalent to Bogomolny's formula only in the classical limit. Calculations demonstrated that this approximation allowed the estimation of all energy

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levels of a very highly chaotic system, including levels that could not be obtained by existing IVR approximations for the propagator or Green's function. The calculations showed that the newer approximation was capable of higher numerical efficiency than Haggerty's method and produced energy levels that were more accurate than those obtained from the Bogomolny approximation for this system.

A remaining problem that inhibits the application of this method to more general systems is that, like the Bogomolny expression, the IVR formula for T_E in Ref. 24 requires the calculation of classical trajectories having the precise energy E . However, the search for values of E that satisfy the condition $\zeta_E \approx 0$ requires a repeated calculation of T_E and ζ_E at several E , so that the classical trajectories must be recomputed several times for each quantized level. Of course, this entire procedure must be repeated for every energy level desired. In Ref. 24, this difficulty was avoided by treating scalable systems having a property that allowed trajectories at any energy to be simply determined by scaling the position, momentum, and time variables for trajectories obtained at a single reference energy. Unfortunately, most systems, including those describing the anharmonic vibrations of molecules, do not possess this very special property. The need for repeated trajectory calculations is an important factor that has discouraged the application of Bogomolny's quantization method to the computation of energy spectra for such non-scalable systems. The main goal of this work is to overcome this difficulty by deriving more general IVR formulas for T_E that enable the calculation of a large number of energy levels in an efficient way from a single batch of trajectories with a broadened distribution of energies.

The approach we adopt here to obtain the desired IVR expressions is based on the observation that Bogomolny's expression for $T_E(\mathbf{y}', \mathbf{y})$ is essentially a modified semiclassical formula for the energy-dependent Green's function G_E . An implication is that, once an IVR formula is known for G_E , it can be converted to an IVR expression for T_E very simply. Therefore our method for deriving an IVR formula for T_E is based on the identification of an appropriate IVR formula for G_E .

This approach was also used in Ref. 24 to obtain the IVR expression for T_E which involves trajectories having the energy E and the attendant practical problems described above. In fact, these problems are due to its derivation from an expression for G_E ^{9,10} which also involves classical trajectories having the particular energy E . To avoid these difficulties, we seek SC-IVR approximations for G_E that employ trajectories with a range of energies that includes, but is not limited to, E .

An obvious IVR formula of this kind¹³ can be obtained by expressing G_E as the energy-time Laplace transform of the celebrated Herman-Kluk⁶ (HK) IVR propagator. However, this formula may not be ideal for the present application. We recall that the HK approximation is usually applied to propagate coherent state wave packets $\Phi(\mathbf{r})$ that are localized in the phase space and energy. Integration over $\mathbf{r}$ results in Gaussian factors that effectively restrict the energies of the classical trajectories that need to be calculated to the finite range spanned by the wave packet. However, for the present purposes, the

propagator is not applied to wave packets, and neither the propagator nor the Green's function obtained from it contains explicit factors that damp out trajectories with arbitrary energies that arise from the phase space integrations.

This sharply contrasts to the IVR formula of Ref. 9 and the Gutzwiller SC approximation^{25,26} which determine G_E from trajectories with energies exactly equal to E . In the classical limit, all these approximations become equivalent so that the contributions from energies other than E in a HK calculation of G_E must all cancel due to rapid phase oscillations in the IVR integrals. This means that, in practice, it must be possible to restrict energies in such a calculation to a range near E , but the boundaries of this range generally need to be determined by numerical experimentation. In addition, the rapid phase oscillations involved in the cancellation mechanism are likely to cause slow convergence in a typical Monte Carlo treatment of the phase space integrations. Therefore Laplace transforming the HK propagator expression does not appear to be a very numerically efficient way to calculate the Green's function for the present purposes.

Actually, experience with other IVR cases leads one to suspect that the formula for G_E obtained from the HK propagator and from Ref. 9 represents extreme cases of a more general formula involving trajectory energies in a specified and controllable range about E . One further suspects that the optimal choices for accuracy and numerical efficiency require finite, nonzero values for the energy range. Such an approximation should yield similar advantages for the corresponding IVR formulas for T_E .

In this work, we derive the desired formulas for G_E and T_E from an IVR expression for the propagator which is a generalization of the HK formula. The most general Green's function formula that is obtained is, in itself, interesting. As anticipated, it contains as special, limiting cases, the previous IVR formula⁹ and the expression obtained from Laplace transforming the HK propagator. Additionally, it corrects a formal deficiency that prevents the approximations for G_E of Ref. 9 and of Gutzwiller from being exact for the harmonic oscillator, linear potential, and free particle.

In Sec. II, we briefly review the basics of Bogomolny's T -matrix quantization theory. In Sec. III, we present and discuss the generalized IVR form for the propagator used in our derivations and apply it to obtain IVR expressions for the Green's function and the T -matrix. In Sec. IV, we describe details of numerical computations for energy levels of two-dimensional systems that apply these IVR expressions. In Sec. V, we present the results of these calculations, and finally, in Sec. VI, we summarize our work and make concluding remarks.

II. BOGOMOLNY'S T -MATRIX THEORY

We consider a bound classical system with f degrees of freedom and define a Poincaré surface in the phase space at an energy E through which all trajectories must pass. Although generalizations are possible, for simplicity, we define this surface to correspond to a fixed value x_0 of a particular position coordinate x . A point on the PSS is identified by $f - 1$ position variables along the PSS, forming the vector $\mathbf{y}$, and

an equal number of conjugate momentum variables, constituting the vector $\mathbf{p}_y$. Together with the values of x_0 and E , these vectors uniquely determine the point on the PSS in the full-dimensional phase space once the sign of the velocity normal to the PSS at this point, $\dot{x}_0$, is specified. We refer to this sign as the sense of motion.

The Poincaré map which plays a central role in classical dynamical theory²⁷ refers to the mapping between points $(\mathbf{y}, \mathbf{p}_y)$ and $(\mathbf{y}', \mathbf{p}'_y)$ on a PSS for successive crossings of a trajectory in the same sense. Thus, the motion from the PSS to its first recrossing in the same sense is said to define a single iteration of the map.

The Bogomolny transfer matrix $\mathbf{T}_E$ provides a semiclassical analog of the classical Poincaré map. An element $T_E(\mathbf{y}', \mathbf{y})$ of this matrix can be physically interpreted as the probability amplitude for a transition between positions $\mathbf{y}$ and $\mathbf{y}'$ on the PSS for a single iteration of the map. Although a proper quantum mechanical definition of $\mathbf{T}_E$ can be provided in certain cases,^{28–31} it must generally be defined semiclassically via a formula. Bogomolny's expression for the elements of this matrix is^{1,2}

$$T_E(\mathbf{y}', \mathbf{y}) = \frac{1}{(2\pi i\hbar)^{(f-1)/2}} \sum_{\text{classical traj}} \left| \det \left[\frac{\partial^2 W_E}{\partial \mathbf{y}' \partial \mathbf{y}} \right] \right|^{\frac{1}{2}} e^{iW_E/\hbar - i\mu\pi/2}. \quad (1)$$

The summation is over all classical trajectories that begin at position coordinate $\mathbf{y}$ on the PSS and return to the PSS at position $\mathbf{y}'$ after one iteration of the Poincaré map. W_E , the reduced action along the trajectory, is defined by

$$W_E(\mathbf{r}', \mathbf{r}) = \int_{\mathbf{r}}^{\mathbf{r}'} \mathbf{p}(\mathbf{q}, E) d\mathbf{q}, \quad (2)$$

where $\mathbf{r} = (x_0, \mathbf{y})$ and $\mathbf{r}' = (x_0, \mathbf{y}')$ denote the initial and final positions on the PSS in the full-dimensional configuration space. $\mathbf{p}$ is the momentum along the trajectory and μ is the Maslov index.

The function T_E is closely related to the SC approximation for the energy-dependent Green's function G_E of Gutzwiller.²⁵ If the initial and final positions are both on a PSS, this function can be expressed as³²

$$G_E(\mathbf{r}', \mathbf{r}) = \frac{1}{i\hbar(2\pi i\hbar)^{(f-1)/2}} \times \sum_{\text{classical traj}} \left| \frac{1}{\dot{x}'\dot{x}} \det \left[\frac{\partial^2 W_E}{\partial \mathbf{y}' \partial \mathbf{y}} \right] \right|^{\frac{1}{2}} e^{iW_E/\hbar - i\mu\pi/2}. \quad (3)$$

Here, the sum is over all trajectories from $\mathbf{r}$ to $\mathbf{r}'$ at energy E regardless of the sense of motion and number of PSS crossings, and $\dot{x}$ and $\dot{x}'$ are the velocity components normal to the PSS at the initial and final crossings.

The differences in the prefactors in (1) and (3) bring the equation for the transfer function into close similarity with Van Vleck's semiclassical expression for the time-dependent propagator, $K_t(\mathbf{r}', \mathbf{r}) = \langle \mathbf{r}' | \exp(-i\hat{H}t/\hbar) | \mathbf{r} \rangle$, which, for general

points $\mathbf{r}$ and $\mathbf{r}'$, is given by

$$K_t(\mathbf{r}', \mathbf{r}) = \frac{1}{(2\pi i\hbar)^f} \sum_{\text{classical traj}} \left| \det \left[\frac{\partial^2 S_t}{\partial \mathbf{r}' \partial \mathbf{r}} \right] \right|^{\frac{1}{2}} e^{iS_t/\hbar - i\nu\pi/2}. \quad (4)$$

The sum is now over all trajectories that move from $\mathbf{r}$ to $\mathbf{r}'$ in time t , S_t is the action integral,

$$S_t(\mathbf{r}', \mathbf{r}) = \int_0^t [\mathbf{p}_\tau \dot{\mathbf{q}}_\tau - H(\mathbf{q}_\tau, \mathbf{p}_\tau)] d\tau, \quad (5)$$

where $H(\mathbf{q}_\tau, \mathbf{p}_\tau)$ is the classical Hamiltonian function (henceforth assumed to be time-independent), $(\mathbf{q}_\tau, \mathbf{p}_\tau)$ are the position and momentum variables along the trajectory at time τ , the overdot denotes the time differentiation, and ν is the Morse index.

The similarity between (1) and (4) can be shown to imply that the T -matrix and the propagator share some important properties that are not obeyed by the Green's function. These allow one to think of $T_E(\mathbf{y}', \mathbf{y})$ as a propagator that evolves points on the PSS for a single iteration of the Poincaré map. Shared properties include the following:

1. Unitarity: Like the SC time-dependent propagator, $\mathbf{T}_E$ is unitary in the classical limit, i.e., $\mathbf{T}_E \mathbf{T}_E^\dagger = \mathbf{1}$ or

$$\int d\mathbf{y}'' T_E(\mathbf{y}', \mathbf{y}'') T_E^*(\mathbf{y}, \mathbf{y}'') = \delta(\mathbf{y}' - \mathbf{y}). \quad (6)$$

2. Composition: In a manner analogous to K_t , the T -matrix obeys a composition property, implying that

$$\int d\mathbf{y}_1 d\mathbf{y}_2 \dots d\mathbf{y}_{n-1} T_E(\mathbf{y}', \mathbf{y}_{n-1}) \dots T_E(\mathbf{y}_2, \mathbf{y}_1) T_E(\mathbf{y}_1, \mathbf{y}) = T_E^n(\mathbf{y}', \mathbf{y}) \quad (7)$$

is given by the same equation [i.e., (1)] as $T_E(\mathbf{y}', \mathbf{y})$ in the classical limit, except that the trajectories return to the PSS after n iterations of the Poincaré map. Thus, $(\mathbf{T}_E)^n$ propagates points on the PSS for n iterations of the Poincaré map.

3. Invariance of eigenstates to propagation: We recall that the time evolution changes only the phase of an energy eigenfunction $\Psi_E(\mathbf{r})$ so that the modified propagator $L_t = K_t e^{iEt/\hbar}$ leaves such a function invariant, i.e., $\int d\mathbf{r} L_t(\mathbf{r}', \mathbf{r}) \Psi_E(\mathbf{r}) = \Psi_E(\mathbf{r}')$. Similarly, in the classical limit, propagation by $T_E(\mathbf{y}', \mathbf{y})$ leaves a certain function $\psi_E(\mathbf{y})$ on the PSS invariant, i.e.,

$$\int d\mathbf{y} T_E(\mathbf{y}', \mathbf{y}) \psi_E(\mathbf{y}) = \psi_E(\mathbf{y}'), \quad (8)$$

when E is an energy eigenvalue. $\psi_E(\mathbf{y})$ is closely related to $\Psi_E(\mathbf{r})$ on the PSS [i.e., at $\mathbf{r} = (x_0, \mathbf{y})$] and can be used to form $\Psi_E(\mathbf{r})$ at arbitrary $\mathbf{r}$.¹

The last property can be expressed in a matrix notation as the eigenvalue equation $\mathbf{T}_E \boldsymbol{\psi}_E = \boldsymbol{\psi}_E$. This implies that quantized energy levels E of the system can be obtained by solving the secular equation,

$$\zeta_E \equiv \det(\mathbf{1} - \mathbf{T}_E) = 0. \quad (9)$$

This is Bogomolny's quantization condition. The notation ζ_E has been chosen because this determinant is equivalent¹ to the

Selberg zeta function which is better known in its form as an expansion in periodic orbits.^{33–35}

In practical calculations, it is necessary to replace ζ_E with a determinant of finite dimensions. One way to accomplish this is by discretizing the continuous variables $\mathbf{y}$ and $\mathbf{y}'$. This is done by dividing the range of $\mathbf{y}$ in the classically allowed portion of the PSS into cells of area Δ_j about discrete points $\mathbf{y}_j$. Consequently, $\mathbf{T}_E$ in the quantization formula is replaced by a finite-dimensional matrix with elements

$$(\mathbf{T}_E)_{ij} = (\Delta_i)^{1/2} T_E(\mathbf{y}_i, \mathbf{y}_j) (\Delta_j)^{1/2}. \quad (10)$$

Bogomolny showed that the minimum dimension of this matrix for calculations of levels at energy E can be estimated as

$$\tilde{N}_E = \frac{A_E}{(2\pi\hbar)^{f-1}}, \quad (11)$$

where A_E is the area of the allowed portion of the PSS. $\tilde{N}_E$ is simply the number of Planck cells in the classically allowed region of the PSS. In practice, it is necessary to choose the actual dimension of $\mathbf{T}_E$ to be larger than $\tilde{N}_E$. When this is done and $\hbar$ is suitably small, approximately $\tilde{N}_E$ eigenvalues of $\mathbf{T}_E$ lie near the unit circle in the complex plane, as expected for an approximately unitary matrix, while the remaining eigenvalues are small and lie near the origin.

III. THE PROPAGATOR, GREEN'S FUNCTION, AND T-MATRIX

In this section, we introduce a SC-IVR propagator that generalizes the HK approximation and use it to obtain IVR expressions for the energy-dependent Green's function and the transfer matrix.

A. Propagator

We obtain an IVR approximation for the propagator by applying a method that has been used to derive such formulas on previous occasions.^{7,9,41} We begin by proposing an ansatz for the propagator, $K_t(\mathbf{r}', \mathbf{r}) = \langle \mathbf{r}' | e^{-i\hat{H}t/\hbar} | \mathbf{r} \rangle$, involving phase space integrals over initial conditions for classical trajectories. We then verify this form and determine certain unknown quantities appearing in the expression by requiring that the application of the stationary phase approximation (SPA) to the integrals produces the SC Van Vleck formula (4). Since both the Van Vleck approximation and the SPA become exact in the classical limit, the final formula for the propagator also becomes exact in that limit, verifying that it is a semiclassical approximation.

The assumed form of the propagator in this work is

$$K_t(\mathbf{r}', \mathbf{r}) = \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \int_{-\infty}^{\infty} ds \int d\mathbf{q}_0 \int d\mathbf{p}_0 B e^{i\phi/\hbar}, \quad (12)$$

where

$$\begin{aligned} \phi = & i(\mathbf{r}' - \mathbf{q}_s)^T \mathbf{\Gamma}(\mathbf{r}' - \mathbf{q}_s) + \mathbf{p}_s^T(\mathbf{r}' - \mathbf{q}_s) + S_s(\mathbf{q}_s, \mathbf{q}_0) \\ & + i(\mathbf{r} - \mathbf{q}_0)^T \mathbf{\Gamma}(\mathbf{r} - \mathbf{q}_0) - \mathbf{p}_0^T(\mathbf{r} - \mathbf{q}_0) \\ & + i\beta(t-s)^2 - H(\mathbf{q}_s, \mathbf{p}_s)(t-s), \end{aligned} \quad (13)$$

where $\mathbf{q}_s$ and $\mathbf{p}_s$ are the f -dimensional vectors containing the position and momentum variables for a trajectory at time s

initiated with values $\mathbf{q}_0$ and $\mathbf{p}_0$ at time 0, S_s is the action integral defined in (5), H is again the classical Hamiltonian function, $\mathbf{\Gamma}$ is an arbitrary real symmetric f -dimensional square matrix, β is an arbitrary complex number with a positive real part, and B is a certain function of $(s, \mathbf{q}_0, \mathbf{p}_0)$ that is unspecified at this stage. As in Ref. 7, the above formulas and accompanying definitions can be further generalized in several ways but, for simplicity, we refrain from doing so in this work.

Equation (12) differs from an ansatz for the HK propagator by the presence of an integral over the time-like variable s and the last two terms in (13). However, it reduces to the HK ansatz if the parameter β is allowed to become infinite. Therefore, the IVR expression to be derived will be a generalization of the HK formula.

Despite some resemblance, the IVR propagator that results from this treatment will not be equivalent to the time-averaged HK propagators^{37–40} that have been proposed in order to reduce the number of trajectories needed in numerical calculations. These previous approximations lack the last two terms in (13) for ϕ and, with unmodified prefactors, are exactly equivalent to the HK approximation. In contrast, the present expression becomes equivalent to the HK treatment only in the classical limit or for $\beta \rightarrow \infty$.

The Appendix applies the SPA to the integrals in (12). It is shown there that the result can be made identical to the Van Vleck formula for the propagator by choosing the prefactor B to have the form

$$B = \left[-i \left(\frac{1}{2\pi i \hbar} \right)^f \det \begin{pmatrix} 4i(\partial \mathbf{z}_s / \partial \mathbf{z}_0) \mathbf{\Gamma} & \dot{\mathbf{z}}_s \\ \dot{\mathbf{z}}_0^T & 2i\beta \end{pmatrix} \right]^{1/2}. \quad (14)$$

This expression involves the f -dimensional vectors

$$\mathbf{z}_s = \mathbf{p}_s - 2i\mathbf{\Gamma} \mathbf{q}_s,$$

$$\mathbf{z}_0 = \mathbf{p}_0 - 2i\mathbf{\Gamma} \mathbf{q}_0,$$

and

$$\bar{\mathbf{z}}_0 = \mathbf{p}_0 + 2i\mathbf{\Gamma} \mathbf{q}_0. \quad (15)$$

The partial derivative in this formula adopts the notation $(\partial \mathbf{a} / \partial \mathbf{b})_{ij} = \partial a_i / \partial b_j$ and considers $\mathbf{z}_s$ to be a function of $\mathbf{z}_0$ and $\bar{\mathbf{z}}_0$. Thus,

$$\frac{\partial \mathbf{z}_s}{\partial \mathbf{z}_0} \mathbf{\Gamma} = \frac{1}{2} \frac{\partial \mathbf{z}_s}{\partial \mathbf{p}_0} \mathbf{\Gamma} + \frac{i}{4} \frac{\partial \mathbf{z}_s}{\partial \mathbf{q}_0}. \quad (16)$$

This matrix is f -dimensional, making the determinant in (14) $(f+1)$ -dimensional.

The expected limiting behavior of the IVR propagator as $\beta \rightarrow \infty$ is now easy to verify. We note that, in this limit, the prefactor B tends to $(2\beta)^{1/2} C_{HK}$, where

$$C_{HK} = \left[\det \left(\frac{2}{\pi \hbar} \frac{\partial \mathbf{z}_s}{\partial \mathbf{z}_0} \right) \mathbf{\Gamma} \right]^{1/2} \quad (17)$$

can be recognized as the HK prefactor. Also, since

$$\lim_{\beta \rightarrow \infty} (2\beta)^{1/2} e^{-\beta(t-s)^2/\hbar} = (2\pi\hbar)^{1/2} \delta(s-t), \quad (18)$$

the factor involving β in $\exp(i\phi/\hbar)$ removes the integral over s and replaces this variable in the IVR formula with the propagation time t . This makes the resulting expression for the propagator identical to the HK formula.

We do not suggest replacing the highly successful HK formula with the present expression for the routine propagation of wave packets. First, the evaluation of the integral over s in (12) requires extra computational labor if the propagator is to be calculated for only a few times t . Second, the present propagator has formal disadvantages compared to the HK approximation for the treatment of the harmonic oscillator, free particle, and linear potential. In such cases, the HK propagator expression can be shown to be exact for all choices of the Gaussian width matrix $\mathbf{\Gamma}$. This is no longer true for the generalized propagator of (12) with finite β . On the other hand, the apparent numerical disadvantages associated with the extra time integral may not be important if one needs to calculate the propagator for many values of t as, e.g., in the calculation of energy spectra. Also, despite the above comments about potentials with degree ≤ 2 , a treatment similar to that of Refs. 8 and 36 shows that the present approximation does become exact for such systems, to within an overall normalization factor, for the special values of $\mathbf{\Gamma}$ obeying $4\mathbf{\Gamma}\mathbf{M}\mathbf{\Gamma} = \mathbf{V}''$, where $\mathbf{V}''$ is the Hessian matrix $\partial^2 V / \partial q_i \partial q_j$ and $\mathbf{M}$ is the f -dimensional diagonal matrix of reciprocal particle masses. These limitations are similar to those that apply to IVR formulas for time-independent wave functions.^{36,41} Also, numerical tests of wave packet propagation for more general, anharmonic, one-dimensional systems indicate that the present approximation is very similar in accuracy to the HK formula, even when β is chosen to be small. Still, the principal advantages of the present formula appear in the IVR expressions of the Green's function that are derived from it, as discussed next.

B. General IVR formula for the Green's function

We wish to obtain a SC-IVR formula for the retarded Green's function, defined by

$$G_E(\mathbf{r}', \mathbf{r}) = \langle \mathbf{r}' | (E^+ - \hat{H})^{-1} | \mathbf{r} \rangle, \quad (19)$$

where E^+ means the limit of $E + i\epsilon$ as $\epsilon \rightarrow 0^+$. For notational simplicity, the plus superscript is generally omitted in the following.

The Green's function is related to the propagator by

$$G_E(\mathbf{r}', \mathbf{r}) = \frac{1}{i\hbar} \int_0^\infty dt e^{iEt/\hbar} K_t(\mathbf{r}', \mathbf{r}). \quad (20)$$

To obtain a semiclassical approximation to G_E , we substitute our IVR expression (12) for K_t in (20). The usefulness of this form for the propagator now becomes apparent. The time integral in (20) can be evaluated analytically using the relation

$$\int_0^\infty e^{-\beta(t-s)^2/\hbar} e^{i(E-H)t/\hbar} dt = \left(\frac{\pi\hbar}{\beta} \right)^{1/2} e^{-(E-H)^2/(4\hbar\beta)} e^{i(E-H)s/\hbar} g(s), \quad (21)$$

where

$$g(s) = \frac{1}{2} \left\{ 1 + \operatorname{erf} \left[\left(\frac{\beta}{\hbar} \right)^{1/2} s + i \frac{E-H}{(4\hbar\beta)^{1/2}} \right] \right\} \quad (22)$$

and erf denotes the error function. This yields

$$G_E(\mathbf{r}', \mathbf{r}) = \frac{1}{i\hbar} \left(\frac{\pi\hbar}{\beta} \right)^{1/2} \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \times \int_{-\infty}^\infty ds \int d\mathbf{q}_0 \int d\mathbf{p}_0 B e^{i\phi_1/\hbar} g(s), \quad (23)$$

where

$$\begin{aligned} \phi_1 = & i(\mathbf{r}' - \mathbf{q}_s)^T \mathbf{\Gamma}(\mathbf{r}' - \mathbf{q}_s) + \mathbf{p}_s^T(\mathbf{r}' - \mathbf{q}_s) + W_H(\mathbf{q}_s, \mathbf{q}_0) \\ & + i(\mathbf{r} - \mathbf{q}_0)^T \mathbf{\Gamma}(\mathbf{r} - \mathbf{q}_0) - \mathbf{p}_0^T(\mathbf{r} - \mathbf{q}_0) \\ & + i(E - H)^2/(4\beta) + (E - H)s, \end{aligned} \quad (24)$$

and we have used

$$W_H(\mathbf{q}_s, \mathbf{q}_0) = S_s(\mathbf{q}_s, \mathbf{q}_0) + Hs, \quad (25)$$

to relate the time-dependent action S_s to the energy-dependent action W_H .

An immediate observation is that the exponential $\exp(i\phi_1/\hbar)$ in (23) contains the factor $\exp[(E - H)^2/(4\beta\hbar)]$, which has the attractive property of damping out contributions to the Green's function from trajectories with energy H that differs from E by more than approximately $(4\beta\hbar)^{1/2}$. This may accelerate the numerical convergence of the phase space integrals.

C. Limiting values of β

We now examine two limiting cases for parameter β in the Green's function IVR formula.

1. $\beta \rightarrow \infty$

In this case, the factor $\exp[(E - H)^2/(4\beta\hbar)]$ in the integrand becomes unity and $g \rightarrow \Theta(s)$, where $\Theta(s)$ is the step function that vanishes for $s < 0$ and is unity for $s > 0$. The expression for G_E then becomes identical to that obtained by directly substituting the HK propagator in (20).

2. $\beta \rightarrow 0$

This limit requires some care because the argument of the error function becomes singular. It is simplest to return to (21) which immediately shows that

$$\begin{aligned} \lim_{\beta \rightarrow 0} \frac{1}{i\hbar} \left(\frac{\pi\hbar}{\beta} \right)^{1/2} e^{-(E-H)^2/(4\beta\hbar)} e^{i(E-H)s/\hbar} g(s) \\ = \frac{1}{E^+ - H} \\ = -i\pi\delta(E - H) + \mathcal{P} \frac{1}{E - H}, \end{aligned} \quad (26)$$

where $\mathcal{P}$ denotes the principal value. Applying this to (23), we find

$$G_E(\mathbf{r}', \mathbf{r}) = \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \int_{-\infty}^\infty ds \int d\mathbf{q}_0 \int d\mathbf{p}_0 \times B e^{i\phi_0/\hbar} \frac{1}{E^+ - H}, \quad (27)$$

where

$$\begin{aligned} \phi_0 = & i(\mathbf{r}' - \mathbf{q}_s)^T \mathbf{\Gamma}(\mathbf{r}' - \mathbf{q}_s) + \mathbf{p}_s^T(\mathbf{r}' - \mathbf{q}_s) + W_H(\mathbf{q}_s, \mathbf{q}_0) \\ & + i(\mathbf{r} - \mathbf{q}_0)^T \mathbf{\Gamma}(\mathbf{r} - \mathbf{q}_0) - \mathbf{p}_0^T(\mathbf{r} - \mathbf{q}_0), \end{aligned} \quad (28)$$

and the variable β in B is set to zero. Interestingly, the SC formula for the Green's function now contains the naive classical approximation $(E^+ - H)^{-1}$ to the quantum resolvent operator $(E^+ - \hat{H})^{-1}$.

The integral over s can be broken up into an integral from $-\infty$ to 0 and an integral 0 to ∞ . However, these two integrals are equal. This is so because reversing the sign of the propagation time s in the first integral simply reverses the sign of the momenta $\mathbf{p}_0$ but, since the momentum integrals are over limits $-\infty$ to ∞ , the variables $-\mathbf{p}_0$ can be changed back to $\mathbf{p}_0$ without affecting the integrals. As a result, (27) can be written as

$$G_E(\mathbf{r}', \mathbf{r}) = 2 \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \int_0^\infty ds \int d\mathbf{q}_0 \int d\mathbf{p}_0 \times B e^{i\phi_0/\hbar} \frac{1}{E^+ - H} \quad (29)$$

or

$$G_E(\mathbf{r}', \mathbf{r}) = -2\pi i \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \int_0^\infty ds \int d\mathbf{q}_0 \int d\mathbf{p}_0 \times B e^{i\phi_0/\hbar} \delta(E - H) + 2 \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \int_0^\infty ds \int d\mathbf{q}_0 \int d\mathbf{p}_0 \times B e^{i\phi_0/\hbar} \mathcal{P} \frac{1}{E - H}. \quad (30)$$

The delta function in the first term of (30) restricts the phase space integration to the energy surface $H(\mathbf{q}_0, \mathbf{p}_0) = E$. This term is equivalent to the IVR expression for the Green's function obtained in Ref. 9 by a different route. Although the formulas for the prefactor look different, this is due to the differently defined monodromy elements in the two expressions. Their equivalence can be verified by applying Eqs. (45)–(48) of Ref. 10.

As demonstrated in Ref. 9, the first term of (30) yields Gutzwiller's formula in the classical limit. The imaginary part of G_E obtained with just this term yields good approximations to quantum energies and wave functions for bound levels. For this reason, the term containing the principal value will be neglected in much of the work presented below. However, at the very least, this term is formally important. Like the Gutzwiller approximation, the first term in (30) is incapable of reproducing the exact Green's function for the harmonic oscillator, free particle, and linear potential for arbitrary f even with special choices for Γ . In contrast, since no approximations were introduced in the derivation of (30) from the propagator (12), the full expression in (30) can reproduce the exact results in these cases (to within an overall normalization) provided that Γ is chosen to obey $4\Gamma\mathbf{M}\Gamma = \mathbf{V}''$, as discussed in Sec. III A. The second term in (30), involving the principle value, provides the correction needed to accomplish this.

This analysis shows that the previously known IVR formulas for the Green's function, i.e., the expression derived in Ref. 9 and the approximation obtained by Laplace transforming the HK formula, can be identified as special limiting cases of a more general expression for the Green's function (23), which is derived from a single IVR formula for the propagator.

D. Poincaré variables and the Off-PSS formula for the Green's function

As a step towards applying the above results to the T -matrix, we consider the case where a particular Poincaré surface is chosen for all energies and points $\mathbf{r}$ and $\mathbf{r}'$ both lie on this PSS. As in Sec. II, we resolve the position variables $\mathbf{r}$ and $\mathbf{r}'$, respectively, as $(x, \mathbf{y})$ and $(x', \mathbf{y}')$ in terms of variables x and x' that measuring displacements normal to the PSS and $\mathbf{y}$ and $\mathbf{y}'$ that denote the positions along the PSS. Because both $\mathbf{r}$ and $\mathbf{r}'$ are on the PSS, $x = x' = x_0$. Similarly, we resolve variables $(\mathbf{q}_s, \mathbf{p}_s)$, representing the position and momentum along a trajectory at time s , in terms of the same coordinate system as $(\bar{x}_s, \bar{\mathbf{y}}_s, \bar{p}_{xs}, \bar{\mathbf{p}}_{ys})$.

Unlike $\mathbf{r}$ and $\mathbf{r}'$, the initial conditions $(\mathbf{q}_0, \mathbf{p}_0)$ for trajectories in the IVR formulas for G_E do not necessarily lie on the PSS. However, in order to express the IVR integrations in a convenient way, it is useful to describe these variables with reference to trajectories that do begin on the PSS and pass through $(\mathbf{q}_0, \mathbf{p}_0)$ at a time τ . To do this, we carry out the canonical change from variables $(\mathbf{q}_0, \mathbf{p}_0)$ to the set $(\tau, \mathcal{E}, \mathbf{y}_0, \mathbf{p}_{y0})$ described in Ref. 9. We use $(\mathbf{y}_0, \mathbf{p}_{y0})$ to denote the point on the PSS reached in the shortest absolute time by a trajectory that begins at $(\mathbf{q}_0, \mathbf{p}_0)$. τ is the time (which may be positive or negative) along this trajectory in the opposite direction, i.e., from the PSS at the intersection point to $(\mathbf{q}_0, \mathbf{p}_0)$. The variable $\mathcal{E} = H(\mathbf{q}_0, \mathbf{p}_0)$ is the energy of this trajectory. Some of these definitions are illustrated in Fig. 1.

Note that, in this notation, the subscript 0 in $\mathbf{y}_0, \mathbf{p}_{y0}$ no longer refers to the initial point, i.e., the subscript does not denote the time $s = 0$ as it does in $(\mathbf{q}_0, \mathbf{p}_0)$ or $(\bar{x}_0, \bar{\mathbf{y}}_0, \bar{p}_{x0}, \bar{\mathbf{p}}_{y0})$ but specifies the variables at the closest-in-time intersection with the PSS. Thus, reckoned from this PSS intersection, the components of integration variables $(\mathbf{q}_0, \mathbf{p}_0)$ are denoted by $(x_\tau, \mathbf{y}_\tau, p_{x\tau}, \mathbf{p}_{y\tau})$ while the components of $(\mathbf{q}_s, \mathbf{p}_s)$ for the

FIG. 1. The initial point $(\mathbf{q}_0, \mathbf{p}_0)$ for the trajectory and the nearest-in-time intersection point with the PSS $(\mathbf{y}_0, \mathbf{p}_{y0})$. The quantities in brackets are times along the trajectory reckoned from its PSS intersection. $(\mathbf{q}_0, \mathbf{p}_0)$ should lie on the green portion of the trajectory curve marking the time interval (τ_-, τ_+) so that the initial velocity $\dot{x}_\tau$ has the same sign as $\dot{x}_0$, the velocity at the PSS (positive in this example).

trajectory at time s are now written as $(x_{\tau'}, \mathbf{y}_{\tau'}, p_{x\tau'}, \mathbf{p}_{y,\tau'})$, where $\tau' = \tau + s$.

With these changes, (23) can be re-expressed as

$$G_E(\mathbf{r}', \mathbf{r}) = \frac{1}{i\hbar} \left(\frac{\pi\hbar}{\beta} \right)^{1/2} \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \sum_{\sigma=\pm} \int d\mathcal{E} \int_{\tau_-}^{\tau_+} d\tau \int_{-\infty}^{\infty} d\tau' \int d\mathbf{y}_0 \int d\mathbf{p}_{y0} \times B e^{i\phi_1/\hbar} g(\tau' - \tau). \quad (31)$$

The integration variables in this expression, together with the value of x_0 , defining the PSS, determine only the absolute value of the normal velocity component $\dot{x}_0$ at the PSS. The variable σ is the sign of $\dot{x}_0$, and the summation over $\sigma = \pm$ indicates that the contributions from trajectories with both signs must be considered.

The limits τ_- and τ_+ of the τ integration have to be chosen so that τ is uniquely defined at $(\mathbf{q}_0, \mathbf{p}_0)$. To do this, it is convenient to choose these limits so that the normal direction of motion at the initial point $(\mathbf{q}_0, \mathbf{p}_0)$ is the same as that at the PSS intersection. In other words, we choose $\tau_- < 0$ and $\tau_+ > 0$ so that $\dot{x}_\tau$ is zero at these limits and has the sign σ at all intermediate values of τ . This is illustrated in Fig. 1.

E. On-PSS formula for the Green's function

Because the trajectories in (31) do not generally begin or end on the PSS where points $\mathbf{r}$ and $\mathbf{r}'$ lie, we call this IVR expression an Off-PSS formula. A simpler On-PSS formula in which all trajectories begin and end on the PSS can be obtained by choosing the arbitrary width matrix Γ to have the block form

$$\Gamma = \begin{pmatrix} \gamma_1 & \mathbf{0}^T \\ \mathbf{0} & \Gamma_2 \end{pmatrix}, \quad (32)$$

where $\mathbf{0}$ is the $(f-1)$ -dimensional null column vector and Γ_2 is an $(f-1)$ -dimensional square matrix. ϕ_1 then has the form

$$\begin{aligned} \phi_1 = & i\gamma_1(x_0 - x_{\tau'})^2 + p_{x\tau'}(x_0 - x_{\tau'}) \\ & + i(\mathbf{y}' - \mathbf{y}_{\tau'})^T \Gamma_2 (\mathbf{y}' - \mathbf{y}_{\tau'}) + \mathbf{p}_{y\tau'}^T (\mathbf{y}' - \mathbf{y}_{\tau'}) \\ & + W_{\mathcal{E}}(x_{\tau'}, \mathbf{y}_{\tau'}; x_{\tau}, \mathbf{y}_{\tau}) \\ & + i\gamma_1(x_0 - x_{\tau})^2 - p_{x\tau}(x_0 - x_{\tau}) \\ & + i(\mathbf{y} - \mathbf{y}_{\tau})^T \Gamma_2 (\mathbf{y} - \mathbf{y}_{\tau}) - \mathbf{p}_{y\tau}^T (\mathbf{y} - \mathbf{y}_{\tau}) \\ & + i(E - \mathcal{E})^2/(4\beta) + (E - \mathcal{E})(\tau' - \tau). \end{aligned} \quad (33)$$

We now exploit the arbitrariness of γ_1 by allowing it to become infinite. Then we find

$$\lim_{\gamma_1 \rightarrow \infty} \gamma_1 e^{i\phi_1/\hbar} = \pi\hbar \delta(x_0 - x_{\tau'}) \delta(x_0 - x_{\tau}) e^{i\phi_2/\hbar}, \quad (34)$$

where

$$\begin{aligned} \phi_2 = & i(\mathbf{y}' - \mathbf{y}_{\tau'})^T \Gamma_2 (\mathbf{y}' - \mathbf{y}_{\tau'}) + \mathbf{p}_{y\tau'}^T (\mathbf{y}' - \mathbf{y}_{\tau'}) \\ & + W_{\mathcal{E}}(x_0, \mathbf{y}_{\tau'}; x_0, \mathbf{y}_{\tau}) \\ & + i(\mathbf{y} - \mathbf{y}_{\tau})^T \Gamma_2 (\mathbf{y} - \mathbf{y}_{\tau}) - \mathbf{p}_{y\tau}^T (\mathbf{y} - \mathbf{y}_{\tau}) \\ & + i(E - \mathcal{E})^2/(4\beta) + (E - \mathcal{E})(\tau' - \tau). \end{aligned} \quad (35)$$

Since the arguments of the delta functions are functions of τ and τ' , we have

$$\delta(x_0 - x_{\tau}) = \delta(\tau)/|\dot{x}_0| \quad (36)$$

and

$$\delta(x_0 - x_{\tau'}) = \sum_{k=-\infty}^{\infty} \delta(\tau' - \tau'_k)/|\dot{x}_k|, \quad (37)$$

where $\dot{x}_k$ are the values of the normal velocity $\dot{x}_{\tau'}$ at times $\tau' = \tau'_k$ that correspond to the k th crossing of the PSS, when $x_{\tau'} = x_0$. Here, $\dot{x}_k$ may have either sign at crossings for $k \neq 0$, regardless of σ . Negative values of the summation index k correspond to crossings for trajectories at negative times ($s = \tau' - \tau = \tau'_k < 0$), although their contributions are damped by the factor g in the IVR integrand when $\beta \neq 0$.

As a result of these operations, we obtain

$$G_E(\mathbf{r}', \mathbf{r}) = -i\pi \left(\frac{\pi\hbar}{\beta} \right)^{1/2} \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \times \sum_{\sigma=\pm} \sum_{k=-\infty}^{\infty} \int d\mathcal{E} \int d\mathbf{y}_0 \int d\mathbf{p}_{y0} \frac{A e^{i\phi_2/\hbar} g(\tau'_k)}{|\dot{x}_k \dot{x}_0|} \quad (38)$$

with τ' and τ , respectively, replaced by τ'_k and 0 in ϕ_2 . The prefactor A in this equation is defined as

$$A = \left[-i \left(\frac{1}{2\pi i\hbar} \right)^f \det \mathbf{D} \right]^{1/2}, \quad (39)$$

where

$$\mathbf{D} = \begin{pmatrix} 4\partial x_k/\partial p_{x0} & 8(\partial x_k/\partial \zeta_0)\Gamma_2 & -2i\dot{x}_k \\ 2i\partial \zeta_k/\partial p_{x0} & 4i(\partial \zeta_k/\partial \zeta_0)\Gamma_2 & \dot{\zeta}_k \\ 2ix_0 & \dot{\zeta}_0^T & 2i\beta \end{pmatrix}. \quad (40)$$

In this matrix, we have abbreviated subscripts τ'_k as k and defined the $(f-1)$ -dimensional vectors

$$\begin{aligned} \zeta_k &= \mathbf{p}_{yk} - 2i\Gamma_2 \mathbf{y}_k, \\ \zeta_0 &= \mathbf{p}_{y0} - 2i\Gamma_2 \mathbf{y}_0, \\ \bar{\zeta}_0 &= \mathbf{p}_{y0} + 2i\Gamma_2 \mathbf{y}_0, \end{aligned} \quad (41)$$

in analogy to (15) so that, e.g.,

$$\frac{\partial x_k}{\partial \zeta_0} \Gamma_2 = \frac{1}{2} \frac{\partial x_k}{\partial \mathbf{p}_{y0}} \Gamma_2 + \frac{i}{4} \frac{\partial x_k}{\partial \mathbf{y}_0} \quad (42)$$

is an $(f-1)$ -dimensional row vector and

$$\frac{\partial \zeta_k}{\partial \zeta_0} \Gamma_2 = \frac{1}{2} \frac{\partial \zeta_k}{\partial \mathbf{p}_{y0}} \Gamma_2 + \frac{i}{4} \frac{\partial \zeta_k}{\partial \mathbf{y}_0} \quad (43)$$

is an $(f-1)$ -dimensional square matrix.

F. On-PSS formula on the energy surface

Finally, it is interesting to consider the limit of the On-PSS IVR formula in the limit $\beta \rightarrow 0$. To do this, we apply (26) to $g(\tau'_k)$ as it appears in the IVR expression (38). We focus attention on the contribution from the delta function $\delta(E - \mathcal{E})$ and recall that, in the present limit, the contributions from negative- and positive-time trajectories are equal. In this way, we obtain

$$G_E(\mathbf{r}', \mathbf{r}) = -2i\pi^2 \hbar \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \times \sum_{\sigma=\pm} \sum_{k=0}^{\infty} a_k \int d\mathbf{y}_0 \int d\mathbf{p}_{y0} \frac{A e^{i\phi_3/\hbar}}{|\dot{x}_k \dot{x}_0|}, \quad (44)$$

where $a_k = 1/2$ for $k = 0$ and 1 otherwise, and $\beta = 0$ is substituted in (40). We have also defined

$$\phi_3 = i(\mathbf{y}' - \mathbf{y}_k)^T \Gamma_2(\mathbf{y}' - \mathbf{y}_k) + \mathbf{p}_k^T(\mathbf{y}' - \mathbf{y}_k) + W_E(x_0, \mathbf{y}_k; x_0, \mathbf{y}_0) + i(\mathbf{y} - \mathbf{y}_0)^T \Gamma_2(\mathbf{y} - \mathbf{y}_0) - \mathbf{p}_0^T(\mathbf{y} - \mathbf{y}_0) \quad (45)$$

with $\mathbf{y}_k = \mathbf{y}_{\tau'_k}$ and $\mathbf{p}_k = \mathbf{p}_{y\tau'_k}$.

We note that the only integrations here are over points on the PSS at energy E . This IVR formula is equivalent to Eq. (44) of Ref. 9 for the case $x' = x = x_0$. Again, as in the case of (30), apparent differences in the present and former expressions for the prefactor are due to the use of differently defined monodromy elements.

G. Transfer matrix

We recall that the IVR expression (12) for the propagator was derived by requiring it to reduce to the SC Van Vleck formula (4) when the integrals are evaluated by the SPA. Either directly or by recognizing the relationship between the Van Vleck formula and the Gutzwiller formula (3) for the Green's function, it is easy to show that the various IVR formulas for G_E obtained here reduce to the Gutzwiller expression when the SPA is applied to the integrals. We now wish to derive IVR expressions for the transfer function $T_E(\mathbf{y}', \mathbf{y})$ in an analogous way, by requiring that an SPA treatment of the integrals yields the Bogomolny formula (1).

Due to the similarity of the Bogomolny and Gutzwiller formulas, this is easily accomplished by introducing small modifications in the IVR expressions for the Green's function $G_E(\mathbf{r}', \mathbf{r})$ derived above for the case that positions $\mathbf{r}$ and $\mathbf{r}'$ lie on the same PSS. We therefore identify the differences between the Bogomolny and Gutzwiller formulas and describe how our IVR expressions for G_E should be changed in order to convert them into formulas for T_E .

The first difference is that trajectories in Gutzwiller's formula for G_E begin at a PSS with either sign of the normal velocity $\dot{x}$ while those in the transfer function begin only with a particular sign of this velocity. To simplify discussion, we henceforth arbitrarily take this to be positive. It is clear that this difference can be incorporated in IVR formulas (31), (38), and (44) for the Green's function by removing the summation over σ and setting $\sigma = +$.

The second difference is that the trajectories in G_E are of arbitrary length and can cross the PSS any number of times, while those in T_E are terminated when they recross the PSS in the positive sense for the first time. This recrossing occurs at time τ_2 ; the earlier recrossing at time τ_1 is in the negative direction. This restriction of trajectory lengths can be imposed on (31) for G_E by introducing time limits τ'_- and τ'_+ for the integration over "final time" τ' , in analogy to the limits for the integration over τ . Thus τ'_- and τ'_+ bracket time τ_2 . The normal velocity $\dot{x}_{\tau'}$ is positive in this time range and vanishes at the limits τ'_- and τ'_+ . See Fig. 2. In (38) and (44), these modifications also restrict the sum over k to the single term $k = 2$.

The third difference is that the prefactor in the Gutzwiller expression contains the factor $(i\hbar|\dot{x}\dot{x}'|^{1/2})^{-1}$ that is absent from the Bogomolny formula. It is possible to prevent this factor from appearing in the stationary phase approximant

FIG. 2. The initial point at time τ and the final point at time τ' relative to crossing points at times $\tau_0 = 0$ and τ_2 . The initial and final points should lie on the green portions of the trajectory curve marking the time intervals (τ_-, τ_+) and (τ'_-, τ'_+) when the normal velocities $\dot{x}_\tau$ and $\dot{x}_{\tau'}$ have the same sign as that at τ_0 and τ_2 .

to the IVR formulas by multiplying the integrands by the factor $(i\hbar|\dot{x}_0\dot{x}_2|)^{1/2}$. This works because the multiplication of an integrand by a slowly varying factor multiplies the result obtained in the SPA treatment by the same factor evaluated at the critical points, where $\dot{x}_0 = \dot{x}$ and $\dot{x}_2 = \dot{x}'$.

These modifications applied to (31) yield an Off-PSS formula for the transfer function,

$$T_E(\mathbf{y}', \mathbf{y}) = \left(\frac{\pi\hbar}{\beta}\right)^{1/2} \left(\frac{1}{2\pi\hbar}\right)^{f+1/2} \times \int d\mathcal{E} \int_{\tau_-}^{\tau'_+} d\tau \int_{\tau'_-}^{\tau'_+} d\tau' \int d\mathbf{y}_0 \int d\mathbf{p}_{0y} \times B |\dot{x}_2\dot{x}_0|^{1/2} e^{i\phi_1/\hbar} g(\tau' - \tau). \quad (46)$$

Similar steps applied to (38) give an On-PSS IVR for T_E ,

$$T_E(\mathbf{y}', \mathbf{y}) = \pi\hbar \left(\frac{\pi\hbar}{\beta}\right)^{1/2} \left(\frac{1}{2\pi\hbar}\right)^{f+1/2} \times \int d\mathcal{E} \int d\mathbf{y}_0 \int d\mathbf{p}_{y0} \frac{A e^{i\phi_2/\hbar} g(\tau_2)}{|\dot{x}_2\dot{x}_0|^{1/2}}, \quad (47)$$

with τ' and τ , respectively, replaced by τ_2 and 0 in (35) for ϕ_2 , and k replaced by 2 in (39) and (40) for A . Finally, applying these changes to (44) produces an On-PSS expression for G_E

for the case $\beta \rightarrow 0$,

$$T_E(\mathbf{y}', \mathbf{y}) = \left(\frac{\pi\hbar}{2}\right)^{1/2} \left(\frac{1}{2\pi\hbar}\right)^{f-1} \int d\mathbf{y}_0 \int d\mathbf{p}_{y0} \frac{A e^{i\phi_3/\hbar}}{|\dot{x}_2 \dot{x}_0|^{1/2}}, \quad (48)$$

with β replaced by 0 and k replaced by 2 in A [see (39) and (40)] and ϕ_3 [see (45)]. This result involves only integrations over the PSS at energy E . It is equivalent to the IVR formula $T_E(\mathbf{y}', \mathbf{y})$ that was derived and numerically applied in Ref. 24. As discussed in Sec. I, for most systems, this expression has the practical disadvantage of requiring a different set of trajectories for each energy E . In contrast, by disassociating the trajectory energies $\mathcal{E}$ from the target energies E at which T_E is to be determined, (46) and (47) allow the same batch of trajectories to be used for the calculation of the T -matrix at all energies E lying sufficiently within the range of the $\mathcal{E}$ integration.

IV. IMPLEMENTATION DETAILS

In this work, we apply IVR formulas (46) and (47) to calculations of the transfer matrix and SC energy levels for systems with two degrees of freedom. Here we discuss some practical details of these calculations.

All integrals in the IVR formulas, including those over τ and τ' in (46), are evaluated by a simple Monte Carlo method based on the uniform sampling of the integration variables over the integration limits. This effectively converts the integrals to a sum over classical trajectories with specified initial conditions that do not depend on E , making it possible to use the same trajectories for many values of E . Consistent with the development presented in Sec. III, each such trajectory begins from a point on or near the PSS, moving in a specified normal direction, and ends at the first return to the PSS or its vicinity with the same normal direction of motion. Such a trajectory provides a contribution to all elements of T_E weighted by Gaussian factors.

In practice, the calculations are carried out in two stages. In the first, all trajectories needed for the Monte Carlo calculations are run and information for the computation of the T -matrix is stored for each trajectory. In the second stage, this information is used to calculate T_E for desired energies E and to obtain the quantized energy levels.

To form the data for a T -matrix calculation, it is necessary to choose values for the essentially arbitrary parameters β and γ_2 already in the first stage, where the scalar γ_2 is the “matrix” Γ_2 for the case $f = 2$. For an Off-PSS calculation, the value of parameter γ_1 also has to be chosen at this stage. Additionally, it is necessary to choose the limits for integration over $\mathcal{E}$ in the IVR formulas. Guided by the E -dependent Gaussian factor in the integrand, the limits of $\mathcal{E}$ are chosen to exceed the range of the desired energy levels by approximately $(4\beta\hbar)^{1/2}$ on each side. If this would lead to a negative value for the lower limit of $\mathcal{E}$, it is chosen as zero. Test calculations show that for large β (say $\beta > 10$) the upper limit of $\mathcal{E}$ can be chosen smaller than this condition would imply. Numerical experimentation is then required to determine its value.

Trajectory calculations for the On-PSS T -matrix, constituting the first stage, are straightforward. A random value of the trajectory energy $\mathcal{E}$ is chosen within the boundaries described in the previous paragraph, and random values of the position y_0 and momentum p_{y0} are selected within a rectangular box (with dimensions denoted by δy and δp_y) enclosing the classically allowed region of the PSS at energy $\mathcal{E}$. If the point (y_0, p_{y0}) falls outside the classically allowed region, these values are rejected and new random PSS positions and momenta are chosen. The accepted (y_0, p_{y0}) , together with the energy conservation, the value of x_0 defining the PSS, and the sign chosen for $\dot{x}_0$ (positive) uniquely determine initial conditions for a trajectory launched from the PSS. This trajectory is evolved forward in time until it recrosses the PSS in the initial direction at time τ_2 . The linearized equations of motion for monodromy matrix elements are integrated along with Hamilton’s equations, permitting the formation of the prefactor A in (47). As usual for IVR methods, the phase of the complex function A [which involves a square root; see (39)] is monitored during the trajectory and, if necessary, adjusted to ensure its continuity with time. At the end of each trajectory, initial and final values of all variables (x, y, p_x, p_y) , the energy $\mathcal{E}$, the time τ_2 , the full pre-exponential factor in the integrand of (47), the box volume $\delta y \delta p_y$, and the action W_E are stored for use in the second stage of the calculation.

Trajectory calculations for the Off-PSS T -matrix are more involved, and it is important to keep Figs. 1 and 2 in mind during the following description. Random values of $\mathcal{E}$, y_0 , and p_{y0} are chosen as explained above for the On-PSS case, but these do not provide the initial conditions for the IVR trajectories in the present case. Instead we run test trajectories from the accepted point (y_0, p_{y0}) on the PSS for positive and negative times until $\dot{x}$ changes sign or $\gamma_1(x_0 - x)^2/\hbar$ becomes large enough to make $\exp(i\phi_1/\hbar)$ in (46) negligible. These times determine the limits $\tau_{\pm}$ for integration over the variable τ . The value of τ for the Monte Carlo integration is chosen as a random value in the range (τ_-, τ_+) and a trajectory is re-run from the point (y_0, p_{y0}) on the PSS to time τ to obtain the point $(q_0, p_0) = (x_\tau, y_\tau, p_{x\tau}, p_{y\tau})$ that serves as the true initial value for the trajectory that contributes to the IVR formula. Beginning from this point, the IVR trajectory is run forward in time until it crosses the PSS in the positive sense (at time τ_2), having previously crossed the PSS in the negative sense (at time τ_1). To determine limits $\tau'_\pm$ for the τ' integration, the procedure described above for $\tau_\pm$ is repeated: test trajectories are run from the PSS intersection point at time τ_2 for positive and negative times until $\dot{x}$ changes sign or $\gamma_1(x_0 - x)^2/\hbar$ becomes large. The value of τ' for the Monte Carlo integration is chosen as a random value in the range (τ'_-, τ'_+) , and the IVR trajectory is “continued” from the intersection point on the PSS at time τ_2 to time τ' in order to obtain the final point $(x_{\tau'}, y_{\tau'}, p_{x\tau'}, p_{y\tau'})$. The comments concerning the prefactor A in the On-PSS case apply here for the prefactor B .

Certain data for each IVR trajectory are stored to allow the formation of Monte Carlo sums in the next stage. These include values for variables (x, y, p_x, p_y) at the initial time τ and final time τ' , the energy $\mathcal{E}$, the duration $\tau' - \tau$ of the IVR trajectory, the full pre-exponential factor in the integrand, the

action W_E , and the Jacobian factor $\delta y \delta p_y (\tau'_+ - \tau'_-)(\tau_+ - \tau_-)$ that arises when adjusting the integration ranges in (46) for the Monte Carlo treatment.

Calculations of $\mathbf{T}_E$ in the second stage require the specification of the desired energies E and the dimension N_E of $\mathbf{T}_E$ for each energy. N_E is chosen as the greater of 4 and $c\tilde{N}_E$, where c is a constant (to be specified) and $\tilde{N}_E$ is the minimum theoretical dimension defined in (11). The discrete values of y and y' for the calculation of the transfer matrix are chosen to be equally spaced between the limits of the classically allowed region along y on the PSS. This equal spacing makes it possible to determine the y and y' -dependent Gaussian factors in the IVR formulas by a simple recursion method.

The calculation of the quantized levels from $\mathbf{T}_E$ requires some further explanation. Although it might seem straightforward to determine these energies by searching for values of E which make $\zeta_E = \det(\mathbf{1} - \mathbf{T}_E)$ vanish, this method cannot be used in practice because, away from the classical limit, ζ_E is never zero for real E . This problem can be traced to the nonunitarity of the matrix $\mathbf{T}_E$ when $\hbar \neq 0$. Since the eigenvalues of $\mathbf{T}_E$ are never precisely equal to unity at any energy, ζ_E is always complex; its real and imaginary parts do not vanish simultaneously.

The most common way to overcome this problem is to determine energy levels from the minima of the absolute value of ζ_E .^{42–46} Although this method is sometimes useful when the energy levels are far enough apart, it may fail to locate all quantized levels when they are closely spaced.

When this method is unsatisfactory, we apply an alternative technique which we have found always to be reliable in this and previous work.²⁴ Recall that, for finite T -matrices, the complex eigenvalues $r_j \exp(i\theta_j)$ of $\mathbf{T}_E$ are expected to fall into two categories, with approximately $\tilde{N}_E$ having “large” moduli r_j near unity and the remaining eigenvalues having very small moduli. Following the work of Haggerty,²³ we identify E as a quantized energy level if $\theta_j = 0$ for some eigenvalue j of $\mathbf{T}_E$ with r_j greater than a predetermined cut-off. In other words, we require an eigenvalue of $\mathbf{T}_E$ with a sufficiently large modulus to cross the positive real axis in the complex plane.

In practice, we find such energies from zeros of the function²⁴ $Z_E = Z_E^{(1)} Z_E^{(2)}$, where

$$Z_E^{(1)} \equiv \prod_{r_j > a} \sin \frac{\theta_j}{2} \quad (49)$$

and

$$Z_E^{(2)} \equiv \prod_{b \leq r_j \leq a} \left[(1 - v_j)^2 + \left(v_j \sin \frac{\theta_j}{2} \right)^2 \right]^{1/2}, \quad (50)$$

with

$$v_j = \frac{r_j - b}{a - b}, \quad (51)$$

where a is the cut-off (usually somewhere in the range 0.7 to 1.0) defining a minimum value for the “large” moduli r_j and b is an arbitrary parameter smaller than a . After a preliminary graphical survey of Z_E over a grid of energies, approximate roots of Z_E are refined by the Newton-Raphson search.

We also mention an alternative method for determining the quantized energy levels. Although we did not systematically apply this method in the calculations presented here, it has the advantage of obtaining the levels directly from the determinant ζ_E , without requiring the diagonalization of $\mathbf{T}_E$, and was found to be successful in several tests. The method recognizes that, although ζ_E may never exactly vanish for real energies, it does become zero for complex energies E near the real axis. Approximate quantized energies are, thus, identified as the real parts of the complex roots of ζ_E . The formation of the transfer matrix for complex energies does not introduce complications; it only requires the substitution of complex values for the parameter E in the IVR expression. It does not require running complex classical trajectories. The resulting estimates of the quantized energy levels are found to be close to those obtained from the roots of Z_E .

V. NUMERICAL RESULTS

A. Harmonic system

As a preliminary investigation, we apply the IVR formulas to obtain energy eigenvalues for a two-dimensional harmonic oscillator. This serves as a convenient case for testing the various IVR approximations we have described. The Hamiltonian for this system is

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\omega_x^2 x^2 + \omega_y^2 y^2), \quad (52)$$

with $\omega_x = 0.7$ and $\omega_y = 1.0$. The PSS is chosen as the y -axis (i.e., $x = x_0 = 0$) and $\hbar$ is chosen as unity for the quantum system.

For all calculations of the present system, it was found that the dimension N_E of the T -matrix could be chosen as small as $1.6\tilde{N}_E$ where, numerically, $\tilde{N}_E = E/\hbar\omega_y = E$ for our PSS. Choosing larger dimensions did not significantly change the resulting energy levels. For comparison, values of $c = N_E/\tilde{N}_E = 1.3$ – 1.4 were found to be adequate for calculations of the quartic system in Ref. 24 while direct applications of Bogomolny’s formula usually require c on the order of 10.^{42,43,45}

Like the quartic system, the harmonic oscillator has special scaling properties that allow trajectories for all energies to be easily obtained from those calculated at a fixed reference energy. Since this makes it possible to apply the On-PSS IVR expression with $\beta = 0$ (48) in an efficient way, we first present results using that treatment. These are displayed in Fig. 3 which shows a plot of $|\det(\mathbf{1} - \mathbf{T}_E)|$ vs. E . The T -matrix was calculated here using $\gamma_2 = 0.5$. Convergence of the IVR integrals was obtained using only 200 trajectories—a much smaller number than that required in Ref. 24 for the Monte Carlo treatment of the quartic systems using the same IVR expression. The present rapid convergence attests to the especially well-behaved nature of the IVR integrands for harmonic systems.

A similar calculation using the On-PSS IVR formula (47) with the finite but nonzero value $\beta = 0.5$ is also presented in Fig. 3. The results are seen to be qualitatively similar to those

FIG. 3. $|\zeta_E|$ as a function of energy E for the harmonic oscillator system using the On-PSS formula with $\beta = 0$ (blue curve) and $\beta = 0.5$ (red curve). The drop lines indicate the exact energy eigenvalues.

for $\beta = 0$. These calculations were performed with a sample of 500 trajectories having energies randomly distributed over the range $0 < \mathcal{E} < 9$. This number of trajectories is larger than that needed for $\beta = 0$ but is still very small compared to those in previous IVR calculations of the transfer matrix²⁴ and produces estimates for the same levels obtained in the first calculation. It is important to stress that, if the $\beta = 0$ calculation had been performed without using the special scaling properties of the system, it would have been necessary to recalculate the batches of 200 trajectories several times for each of the 40 energy levels in the figure so that many more than 500 trajectories would have been needed. This clearly demonstrates the

great enhancement in efficiency that can be achieved using the expressions with nonzero β for generic, nonscalable, systems.

In this and other calculations using $\beta > 0$ presented in this paper, the factor $g(s)$ was computed numerically. However, we found that almost identical results for the SC levels could be obtained by replacing $g(s)$ with unity. This is consistent with the behavior of the error function in (22) for the reasonably large values of $s = \tau'_k$ or $\tau' - \tau$ in the present applications.

Examination of Fig. 3 shows that $|\zeta_E|$ has minima that lie very close to the exact energy levels of the system for most states. However, for certain energy levels, the minima are replaced by shoulders or are completely missing. Calculations of Z_E with $a = 0.6$ (not shown) also fail to detect these levels. Such levels correspond to states with quantum numbers (v_x, v_y) , such as $(0, 2)$, $(0, 3)$, $(0, 4)$, $\dots$, $(1, 3)$, $(1, 4)$, $(1, 5)$, $\dots$, that are associated with low excitation along the x -direction, normal to the PSS. These results are reminiscent of those obtained by Biechele *et al.*⁴³ in calculations that applied Bogomolny's formula to a similar harmonic system.

To further understand the missing energy levels, Fig. 4(a) plots the path of an eigenvalue of T_E in the complex plane as a function of energy, computed using the Off-PSS formula. The eigenvalue begins near the origin at low energy and spirals out as E is increased. However, the spiraling is rather slow, similar to the behavior observed by Haggerty for another system in the near-integrable regime.²³ We recall that such an eigenvalue is expected to cross the positive real axis with a modulus near unity when E is near a quantized level. It is seen that the eigenvalue plotted in this figure indeed crosses the real axis at $E \approx 2.85$, corresponding to the “missing” state

FIG. 4. Paths of a T -matrix eigenvalue in the complex plane as the energy is varied up to $E \approx 5.1$. (a) The harmonic oscillator system using the On-PSS formula; (b) the harmonic oscillator system using the Off-PSS formula; (c) the Hénon-Heiles system using the On-PSS formula; (d) the Hénon-Heiles system using the Off-PSS formula. The red curve is the unit circle. The blue markers in subfigures (a) and (c) show intersections of the eigenvalue with the real positive axis that correspond to quantum levels. $\beta = 0.5$ in all these calculations.

(0, 2). However, the modulus r at the crossing is only 0.46. This small value is responsible for the problems observed here. The resulting factor $|1 - r|$ in $|\zeta_E|$ is too large to cause the determinant to have a minimum at this energy. Similarly, it prevents the function Z_E from having a root at this energy unless the parameter a in (49) and (50) is chosen to be smaller than 0.46.

Nevertheless, it is interesting that even such crossings appear to occur at or very near the exact energy levels. This is not entirely surprising since Tong and Goodings⁴⁷ showed analytically that the eigenvalues of $\mathbf{T}_E$, as obtained by Bogomolny's formula, cross the positive real axis exactly at the quantum levels for the isotropic harmonic oscillator. However, even if it is somehow possible to extract quantized energy levels from $\mathbf{T}_E$ in such cases, the small moduli for the eigenvalues of the T -matrix are troubling. They indicate that the computed matrix seriously violates the expected unitarity condition. This behavior is incompatible with the basic interpretation of $T_E(\mathbf{y}', \mathbf{y})$ as a kind of propagator and can have serious consequences in applications beyond those in the present work.

It is clear that such numerical results signal a breakdown in the semiclassical approximations inherent in Bogomolny's formula and the IVR expressions of (47) and (48). To understand this, we note that trajectories quantizing the problematic states with low x -excitation have small values of the normal velocity $\dot{x}$. These velocities vanish near the PSS where the T -matrix is calculated. At such points, Gutzwiller's semiclassical formula for the Green's function, from which the expressions for $\mathbf{T}_E$ are derived, has caustic singularities indicating the breakdown of the SC approximation. An analysis of the lowest-order corrections to Bogomolny's formula by Prosen³¹ indeed shows that the semiclassical approximation for $\mathbf{T}_E$ fails when $\dot{x} = 0$ near the PSS, even though factors such as $|\dot{x}'\dot{x}|^{-1/2}$ in G_E no longer appear in Bogomolny's formula (1) for T_E . Similarly, (38) and (44) show that the On-PSS IVR formulas for G_E also have caustic singularities when the normal velocity at the PSS vanishes. It can be verified by an analysis analogous to that of Ref. 8 that these can cause the semiclassical approximation to break down, as for the case of the Gutzwiller formula. The implication is that the semiclassical approximations for the On-PSS IVR formulas (47) and (48) for $\mathbf{T}_E$ will also lose accuracy in such cases. Consistent with other studies showing that IVR approximations become less accurate when some of the Gaussian width parameters are made infinite,^{48,49} the present problems are due to the extreme value $\gamma_1 \rightarrow \infty$ used to derive the On-PSS formulas for G_E and T_E . The Off-PSS IVR expressions with finite γ_1 should be free from such problems.

We verify this claim by applying the Off-PSS IVR formula (46) to the present system. Figure 5 shows the function $|\zeta_E|$ obtained from such a calculation using parameters $\beta = \gamma_1 = \gamma_2 = 0.5$ and 2000 trajectories with energies $0 < \mathcal{E} < 9$. This increase in the number of trajectories over those needed for the On-PSS calculations is the price for the additional integrations over τ and τ' .

Accurate estimates are now obtained for all energy levels in the figure, including those that were missing in the previous calculations. The improved success of these calculations is a reflection that the computed T -matrices are more nearly

FIG. 5. $|\zeta_E|$ as a function of energy E for the harmonic oscillator system using the Off-PSS formula with $\beta = 0.5$ (red curve) and $\beta = 1000$ (blue curve). The drop lines indicate the exact energy eigenvalues.

unitary. This is verified in Fig. 4(b) which shows that eigenvalues in the complex plane now spiral out from the origin much more quickly than before, so that the moduli are nearer to 1 when E is at quantized energies. This behavior is very different from that observed in the On-PSS case and now resembles the behavior reported by Haggerty for a case exhibiting chaotic dynamics.²³

We recall that the Off-PSS formula for the T -matrix is closely related to the HK approximation for the propagator when β is made infinite. To examine the numerical consequences of such a choice for β , we perform calculations using (46) with the large value $\beta = 1000$ and with $\gamma_1 = \gamma_2 = 0.5$. As in the previous case of $\beta = 0.5$, this choice is found to give estimates of all eigenvalues in Fig. 5. However, to achieve this, it is necessary to calculate trajectories for the larger energy range $0 < \mathcal{E} < 15$, which necessitates increasing the number of such trajectories to 5000. This illustrates how moderate values of β can be advantageous, leading to more rapid convergence of the IVR calculations.

B. Hénon-Heiles system

We now apply our IVR expressions to obtain energy levels of the well-studied two-dimensional Hénon-Heiles system.^{11,17–22} This is an interesting case for our purposes because it is more representative of molecular systems: it is anharmonic and nonseparable, lacks scaling properties that make the IVR formula of Ref. 24 practicable, and displays the generic transition from near integrability to predominate chaos as the energy is increased.

The Hamiltonian is

$$H = \frac{1}{2} (p_x^2 + p_y^2) + \frac{1}{2} (x^2 + y^2) + \lambda x \left(y^2 - \frac{1}{3} x^2 \right), \quad (53)$$

with $\lambda = 0.111\,803$. The PSS is again chosen as the y -axis ($x_0 = 0$) and $\hbar$ is set to unity in the quantum calculations.

As a preliminary step, we wish to determine whether the problems encountered for the harmonic system with the On-PSS IVR expression (47) also occur for the present system. To do so, we again apply (47) with $\beta = \gamma_2 = 0.5$ and plot

a resulting eigenvalue of $\mathbf{T}_E$ as a function of E in the complex plane. We focus on low energies where the classical motion is mostly regular. Figure 4(c) shows that, as in the harmonic oscillator case, the eigenvalue spirals out from the origin of the complex plane slowly. The first crossing of the positive real axis that corresponds to a quantum energy level occurs at $E \approx 2.985$ where the modulus of the eigenvalue is only 0.67. Although this is larger than the corresponding value for the harmonic oscillator in Fig. 4(a), it is still rather far from unity and again points to an inaccuracy in the semiclassical approximation. Evidently, this problem is not confined to the harmonic oscillator system.

Figure 4(d) presents the corresponding results obtained by applying the Off-PSS formula (46) with $\beta = \gamma_1 = \gamma_2 = 0.5$. We see that, as for the harmonic oscillator system, the small-eigenvalue problem is largely solved. The eigenvalue curve now spirals out quickly from the origin, and the modulus is near to unity at all quantized energy levels.

It should be emphasized that problems with the On-PSS formula for the Hénon-Heiles system are confined to low energies where the classical motion is mostly regular. At high energies, where the behavior is predominantly chaotic, the eigenvalues of $\mathbf{T}_E$ corresponding to quantized levels have moduli near unity for both the On-PSS and Off-PSS treatments, and these two approximations produce very similar SC energy levels. In such cases, the On-PSS method may be preferred because the required calculations are simpler and the convergence of the Monte Carlo integration is faster. Nevertheless, for the sake of consistency, only the results of the Off-PSS treatment are presented in the remainder of this paper.

The calculations reported here were performed with parameter values $\beta = \gamma_1 = \gamma_2 = 0.5$. As in the harmonic oscillator case, it was found that converged energy levels could be obtained using transfer matrix dimensions N_E that were only 1.6 times the theoretical minimum $\tilde{N}_E$, which is again numerically equal to E for the chosen PSS. For levels in the high-energy chaotic regime, this factor could be reduced to 1.4 so that energies for all 99 “bound” states of the system (i.e., with energies below the saddle point of the potential at $E = 13.33$) could be calculated with matrices of dimensions ranging from 4 to 19.

Due to the high spectral density, not all energy levels of the present system could be obtained from the minima of $|\zeta_E|$ as in the harmonic oscillator case, so estimates for the quantized energies were determined here from zeros of the function Z_E , defined in Sec. IV. It was found that many more trajectories were needed to obtain converged results from the Monte Carlo calculations of $\mathbf{T}_E$ than those in the harmonic oscillator case. Although rough estimates of the energies could already be deduced from much smaller samples, convergence to within the mean accuracy of the SC approximation required about 1×10^5 trajectories for the lowest energies ($E \approx 2$). For moderate energies ($E \approx 6$), this number increased to 4×10^5 , and for high energies ($E > 11$), it further increased to about 1×10^6 . It should be recalled, however, that these trajectories are all very short so that this step did not dominate the total time required for the calculation of levels.

FIG. 6. Portion of the Z_E curve for the Hénon-Heiles system. Blue drop lines indicate the quantum nondegenerate energy levels (A states); green drop lines indicate the doubly degenerate quantum energy levels (E states). Due to the limited resolution in the figure, pairs of closely spaced blue lines at $E \approx 8.8113$, 8.8152 and $E \approx 10.0354$, 10.0356 appear as a single line. Similarly, a green line at $E = 11.152$ practically merges with a blue line at $E = 11.160$. It is useful to note that the “effective degeneracy” of an imperfectly resolved energy in the figure is odd if the Z_E curve appears to continue in the same direction after passing through zero and is even if it reverses the direction at zero.

Figure 6 presents a plot of Z_E for energies in the approximate range $8.5 < E < 11.6$ where classical chaos becomes significant. Close examination shows that Z_E becomes zero near the energy of each quantum state of the system. As in this figure, unambiguous SC estimates of energy levels are also obtained for each quantum state in the entire energy range $0 < E < 13.33$. Figure 7 summarizes these results by displaying the errors in the computed SC energy levels. The accuracy of the present treatment is found to be generally good; the root mean square error in the energies is 5×10^{-3} which corresponds to less than 10% of the mean level spacing. This is substantially smaller than errors in the energies obtained in previous SC treatments of this system based on the Einstein-Brillouin-Keller quantization.^{17,20,21}

There is, however, a feature of the present results that is not entirely satisfactory. Quantum mechanically, energy levels of the system are either nondegenerate (corresponding to states with A symmetry in the C_3 point group classification)

FIG. 7. Difference between the semiclassical and quantum energy levels¹⁹ for the Hénon-Heiles system.

or doubly degenerate (corresponding to states with E symmetry). This degeneracy is, however, not preserved in the present SC calculations which, instead, yield two levels for each E state. The splitting of these energies is typically small in the high-energy, chaotic regime. The same is true in the low-energy, regular regime for precessing states¹⁷ (characterized by large values of the approximate angular momentum quantum number l). However, the splitting can be relatively large in the regular regime for librating states¹⁷ (characterized by low l).

To understand this, we recall that the trajectories that quantize the librating states occur in symmetry-related sets of three: one set is confined to a narrow region about the x -axis and the other two are obtained by rotating the first set by $\pm 120^\circ$.¹⁷ The splitting of E -states occurs because the particular PSS chosen in the present calculations treats the quantization of the trajectories in the first set (which cross the PSS in a nearly perpendicular manner) differently from those in the remaining two (which cross the PSS at angles of approximately $\pm 30^\circ$). The artificial splitting can be effectively avoided by choosing a PSS that has higher symmetry. Test calculations verify that the splitting becomes negligible if the PSS is chosen, as in Ref. 17, to correspond to a circle defined by a constant value of the radial coordinate $r = \sqrt{x^2 + y^2}$.

VI. DISCUSSION AND CONCLUDING REMARKS

The transfer matrix theory developed by Bogomolny is a powerful quantization method that should allow semiclassical estimates for all energy levels of arbitrary systems, even in congested spectral regions and even in the presence of highly chaotic classical motion. This method requires the calculation of the transfer matrix $\mathbf{T}_E$ for a range of energies E near each quantized level. Bogomolny's work, however, presents the transfer matrix in a form that makes such calculations difficult for generic systems that have no energy-scaling properties. Apart from the familiar problem of requiring searches for special trajectories, it requires a repeated numerical computation of trajectories at each energy. This has discouraged the application of Bogomolny's treatment to typical systems of interest in chemical physics. The main goal of this work has been to develop and test new semiclassical IVR expressions for the transfer matrix that allow efficient calculations of this sort.

To accomplish this, we began by presenting a generalization of the Herman-Kluk IVR approximation for the time-dependent propagator. We showed that this leads to IVR formulas for the energy-dependent Green's function G_E that generalize previous expressions and allow a more efficient recalculation of G_E for different values of E . These formulas were easily modified to obtain a general IVR expression for the transfer matrix that differs from a formula obtained in an earlier work²⁴ in two crucial ways: (1) It contains an additional integration over trajectory energies $\mathcal{E}$ that removes the requirement that all trajectories in the calculation of $\mathbf{T}_E$ have energy $\mathcal{E} = E$. This makes it possible to calculate the transfer matrix for a range of E from the same batch of trajectories. (2) It contains additional time integrals that improve the accuracy of the computed transfer matrix for integrable and near-integrable systems.

Calculations for the Hénon-Heiles system produced semiclassical energy estimates for all levels below the saddle in the potential. In contrast, due to the chaotic nature of the classical high-energy dynamics and the many nearly-degenerate levels, the most successful semiclassical IVR approximation for the propagator, the Herman-Kluk method, does not seem to be capable of determining all energy eigenvalues unambiguously for this system. The convergence problem that limits the ability of the HK and other IVR methods to treat chaotic or large systems is avoided in the present method because it uses only short trajectories. Thus, no filtering or trajectory removal techniques were needed to converge the phase space integrals in the calculations reported here even when the classical behavior was chaotic.

It should be straightforward to apply the methods described in this paper to larger systems. The required trajectories can usually be kept short, even for such systems, by an appropriate choice of the PSS, e.g., by situating this surface so that it intersects a high-frequency vibration. There is, however, a trade-off between trajectory lengths and T -matrix sizes. PSS's with short recrossing times generally have relatively large phase space areas that require larger dimensions of $\mathbf{T}_E$. Conversely, PSS's with long recrossing times (e.g., phase space bottlenecks) generally have small phase space areas that allow the formation of T -matrices with small dimensions. Since one may wish to sacrifice the advantages of short trajectories for the benefits of smaller matrices, future work should investigate whether the filtering^{11,12} or trajectory truncation methods,¹³ which accelerate the convergence of IVR propagators, can produce useful results for the transfer matrix.

The subject of larger systems raises the issue of scaling. It may appear discouraging that, like purely quantum mechanical methods, the present technique for determining energy levels requires matrix manipulations such as determinant formation or diagonalization. Such steps scale as N^3 , where N is the matrix dimension, and will dominate the computational time for large systems. Worse, the present method requires the repetition of these matrix calculations for each desired energy level. Nevertheless, provided that the number of such levels is not too large, the current technique may be significantly advantageous, even for systems with many degrees of freedom, because the value of N here is much smaller than for quantum calculations. The reason is that the T -matrix is formed from states on a PSS with only $f - 1$ degrees of freedom whereas the Hamiltonian matrix in quantum calculations is formed from states of the full system with f degrees of freedom. Apart from this consideration, our results suggest that T -matrix sizes for energy level calculations can be kept surprisingly small. The converged energies in this paper were obtained from matrices that are only 40%-60% larger than the number of PSS Planck cells $\tilde{N}_E$. Similarly, the IVR T -matrix treatment of Ref. 24 produced converged energy levels using matrix sizes that are only 33%-40% larger than $\tilde{N}_E$. Although the discrete variable basis set $|\mathbf{y}_i\rangle$ used to form $\mathbf{T}_E$ in these calculations is localized only in the configuration space, its efficiency compares favorably with that achieved using phase space-localized basis functions in one-dimensional quantum calculations of similar accuracy and comparable energies.⁵⁰⁻⁵² It should be noted that

the T -matrix can also be expressed in such bases if it is deemed useful.

We have focused on the application of the T -matrix for the estimation of energy levels. However, in principle, the transfer matrix can also be used to form SC energy eigenfunctions¹ and to obtain a superior approximation for the Green's function⁵³ having poles near each bound energy level. An interesting possibility is that such a Green's function could be used to construct a time-dependent propagator that is free from the time limitations that affect the existing IVR formulas. To form such a Green's function, one must supplement the T -matrix with additional quantities.⁵³ However, like the T -matrix, these can also be identified as modified SC Green's functions, so they too can be expressed in an IVR form using the results presented in Sec. III and the approach described in this paper. Further investigation of this idea seems worthwhile.

APPENDIX: STATIONARY PHASE TREATMENT OF THE PROPAGATOR

To apply the SPA to the IVR ansatz for the propagator (12) and examine its relationship to the Van Vleck formula, we begin by evaluating the partial derivatives of the complex phase function ϕ , defined in (13), with respect to the integration variables. Applying the identities,

$$\begin{aligned} \left[\frac{\partial S_s(\mathbf{q}_s, \mathbf{q}_0)}{\partial \mathbf{q}_0} \right]_{\mathbf{p}_0, s} &= -\mathbf{p}_0 + \frac{\partial \mathbf{q}_s}{\partial \mathbf{q}_0}^T \mathbf{p}_s, \\ \left[\frac{\partial S_s(\mathbf{q}_s, \mathbf{q}_0)}{\partial \mathbf{p}_0} \right]_{\mathbf{q}_0, s} &= \frac{\partial \mathbf{q}_s}{\partial \mathbf{p}_0}^T \mathbf{p}_s, \\ \left[\frac{\partial S_s(\mathbf{q}_s, \mathbf{q}_0)}{\partial s} \right]_{\mathbf{q}_0, \mathbf{p}_0} &= \mathbf{p}_s^T \dot{\mathbf{q}}_s - H, \end{aligned} \quad (\text{A1})$$

we obtain

$$\begin{aligned} \frac{\partial \phi}{\partial \mathbf{p}_0} &= \frac{\partial \mathbf{z}_s}{\partial \mathbf{p}_0}^T (\mathbf{r}' - \mathbf{q}_s) - (\mathbf{r} - \mathbf{q}_0) - \dot{\mathbf{q}}_0(t - s), \\ \frac{\partial \phi}{\partial \mathbf{q}_0} &= \frac{\partial \mathbf{z}_s}{\partial \mathbf{q}_0}^T (\mathbf{r}' - \mathbf{q}_s) - 2i\Gamma(\mathbf{r} - \mathbf{q}_0) + \dot{\mathbf{p}}_0(t - s), \\ \frac{\partial \phi}{\partial s} &= \dot{\mathbf{z}}_s^T (\mathbf{r}' - \mathbf{q}_s) - 2i\beta(t - s). \end{aligned} \quad (\text{A2})$$

The critical points, where these derivatives vanish, are at $\mathbf{q}_s = \mathbf{r}'$, $\mathbf{q}_0 = \mathbf{r}$, and $s = t$. Trajectories with initial conditions $(\mathbf{q}_0, \mathbf{p}_0)$, that contribute to the propagator in (12) and that correspond to such points, begin at positions $\mathbf{r}$ at time 0 and reach $\mathbf{r}'$ at time t , as in the Van Vleck formula (4). Since $\phi = S_t(\mathbf{r}', \mathbf{r})$ at the critical points, the SPA formula for the propagator can be expressed as

$$K_t(\mathbf{r}', \mathbf{r}) \sim \left(\frac{1}{2\pi\hbar} \right)^{f+1/2} \times \sum_{\text{classical traj}} \left[\frac{(2\pi i \hbar)^{2f+1}}{\det \mathbf{C}} \right]^{1/2} B e^{iS_t(\mathbf{r}', \mathbf{r})/\hbar}, \quad (\text{A3})$$

where

$$\mathbf{C} = \begin{pmatrix} \frac{\partial^2 \phi}{\partial \mathbf{p}_0 \partial \mathbf{p}_0} & \frac{\partial^2 \phi}{\partial \mathbf{p}_0 \partial \mathbf{q}_0} & \frac{\partial^2 \phi}{\partial \mathbf{p}_0 \partial s} \\ \frac{\partial^2 \phi}{\partial \mathbf{q}_0 \partial \mathbf{p}_0} & \frac{\partial^2 \phi}{\partial \mathbf{q}_0 \partial \mathbf{q}_0} & \frac{\partial^2 \phi}{\partial \mathbf{q}_0 \partial s} \\ \frac{\partial^2 \phi}{\partial s \partial \mathbf{p}_0} & \frac{\partial^2 \phi}{\partial s \partial \mathbf{q}_0} & \frac{\partial^2 \phi}{\partial s^2} \end{pmatrix} \quad (\text{A4})$$

is the $(2f + 1)$ -dimensional matrix of second derivatives of ϕ evaluated at the critical points. Differentiating (A2) yields the explicit formula

$$\mathbf{C} = \begin{pmatrix} \frac{\partial \mathbf{z}_s}{\partial \mathbf{p}_0}^T \frac{\partial \mathbf{q}_s}{\partial \mathbf{p}_0} & -\frac{\partial \mathbf{z}_s}{\partial \mathbf{p}_0}^T \frac{\partial \mathbf{q}_s}{\partial \mathbf{q}_0} + 1 & -\frac{\partial \mathbf{z}_s}{\partial \mathbf{p}_0}^T \dot{\mathbf{q}}_s + \dot{\mathbf{q}}_0 \\ -\frac{\partial \mathbf{z}_s}{\partial \mathbf{q}_0}^T \frac{\partial \mathbf{q}_s}{\partial \mathbf{p}_0} & -\frac{\partial \mathbf{z}_s}{\partial \mathbf{q}_0}^T \frac{\partial \mathbf{q}_s}{\partial \mathbf{q}_0} + 2i\Gamma & -\frac{\partial \mathbf{z}_s}{\partial \mathbf{q}_0}^T \dot{\mathbf{q}}_s - \dot{\mathbf{p}}_0 \\ -\dot{\mathbf{z}}_s^T \frac{\partial \mathbf{q}_s}{\partial \mathbf{p}_0} & -\dot{\mathbf{z}}_s^T \frac{\partial \mathbf{q}_s}{\partial \mathbf{q}_0} & -\dot{\mathbf{z}}_s^T \dot{\mathbf{q}}_s + 2i\beta \end{pmatrix}, \quad (\text{A5})$$

in terms of derivatives of the vector $\mathbf{z}_s$ defined in (15). Standard determinant manipulations now allow one to factor $\det \mathbf{C}$ as the product

$$\det \mathbf{C} = - \left(\det \frac{\partial \mathbf{q}_s}{\partial \mathbf{p}_0} \right) \Delta \quad (\text{A6})$$

of the f -dimensional matrix $\det(\partial \mathbf{q}_s / \partial \mathbf{p}_0)$ and the $(f + 1)$ -dimensional matrix

$$\Delta = \det \begin{pmatrix} 4i(\partial \mathbf{z}_s / \partial \mathbf{z}_0) \Gamma & \dot{\mathbf{z}}_s \\ \dot{\mathbf{z}}_0^T & 2i\beta \end{pmatrix}. \quad (\text{A7})$$

Substituting (A6) in (A3) and using the relation

$$\left| \det \left(\frac{\partial^2 S_t(\mathbf{q}_t, \mathbf{q}_0)}{\partial \mathbf{q}_t \partial \mathbf{q}_0} \right) \right| = \left| \det \left(\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \right|^{-1}, \quad (\text{A8})$$

it is seen that the SPA formula can be made identical to Van Vleck's expression for the propagator by choosing

$$B = \left[-i \left(\frac{1}{2\pi i \hbar} \right)^f \Delta \right]^{1/2}. \quad (\text{A9})$$

This result verifies (14) for the prefactor B in the IVR formula (12) for the propagator.

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