Semiclassical approximations to quantum dynamical time correlation functions

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Semiclassical approximations for quantum time correlation functions are presented for both electronically adiabatic and nonadiabatic dynamics along with discussions of the operator ordering and the classical limit. With the combined use of the initial-value representation of the semiclassical propagator, a discrete algorithm to evaluate the Jacobi matrices, semiclassical operator ordering rules, and the stationary-phase filter technique, a practical algorithm is developed to calculate quantum time correlation functions. This approach holds considerable promise for simulating the quantum dynamics of realistic many-body systems. Some simple illustrative examples are used to demonstrate the feasibility and accuracy of the algorithm. © *1996 American Institute of Physics.* [S0021-9606(96)02401-5]

I. INTRODUCTION

It is well-known from linear response theory that the response of a system to a weak external force can be formulated in terms of a time correlation function for the relevant dynamical variable of the system (see, e.g., Refs. 1–3). Therefore, time correlation functions play a central role in the study of dynamical processes, such as chemical reactions, light scattering spectra, spectroscopic line shapes, transport properties, etc. Classically, the evolution of the system obeys the Newtonian equation of motion, which serves as the basis for molecular dynamics (MD) simulations. Quantum mechanically, the probabilistic wave function propagates according to the Schrödinger equation, which in principle cannot be solved by means of deterministic trajectory dynamics. Due to the importance of time correlation functions, much effort has been devoted to the development of methods to calculate them quantum mechanically; unfortunately, few methods have been successful in applications to realistic many-body quantum systems. In fact, it turns out that real-time quantum propagation is a truly formidable numerical problem because large sign fluctuations in the real-time propagator can overwhelm the contribution from the physical quantities of interest (see, e.g., Refs. 4–10). Thus, to this day the real-time propagation of many-body quantum systems remains a daunting challenge.

There have been several attempts to calculate quantum time correlation functions exactly using the Feynman path integral formulation.[4,6,11] For example, by virtue of the numerical matrix multiplication method (NMM),[12] Thirumalai and Berne were able to calculate the symmetrized dipole–dipole time correlation function for a proton moving in a one-dimensional bistable potential.[13] While the NMM approach becomes prohibitive for many-dimensional systems, it is also fruitless to directly apply Monte Carlo methods to evaluate time correlation functions in such systems due to large phase cancellations. To treat the generic problem of performing many-dimensional averages of highly oscillatory integrands—which are the origin of the difficulty in direct Monte Carlo calculations of such functions—several stationary phase Monte Carlo (SPMC) methods have been developed.[14–20] The implementation of these and other techniques makes it possible in some cases to simulate the dynamics of simplified many-dimensional quantum systems. For example, there have been a series of studies on electron transfer dynamics as represented by the spin–boson model and its multistate generalization.[20–23] For system-bath-type Hamiltonians having harmonic baths, quasiadiabatic propagator path integral methods (QUAPI) have also been developed which propagate adiabatically a one-dimensional system in which the harmonic bath has been incorporated through an analytic influence functional.[24–28] By virtue of this algorithm and discrete variable representation (DVR) quadrature, a detailed study of quantum rates for a double well coupled to a harmonic bath was recently presented[26] along with a comparison to approximate theories. Unfortunately, all of the methods described above are either not directly applicable to "real" nonlinear many-body potentials or become numerically intractable for anything but the short time dynamics of such systems.[29]

One "exact" alternative to the direct real time quantum dynamics approach is based on the fact that real-time correlation functions can be formally related to their imaginary-time counterparts through analytic continuation ($1/k_B T = \beta \rightarrow it/\hbar$).[30,31] Thus, in principle, one can simulate a quantum system with an equilibrium path integral Monte Carlo method at several values of imaginary time and infer the real-time quantities through the analytic continuation (see, e.g., Refs. 31–34). In practice, however, the analytic continuation is rather sensitive to statistical fluctuations in imaginary time data so this approach has suffered from numerical instabilities. Gubernatis and co-workers have recently introduced the maximum entropy method (MEM) which appears to improve the stability of the analytic continuation.[7,35,36] The MEM has proven to be reliable and efficient in similar ill-posed inversion problems, so its application in path integral simulations seems novel and promising. Using this technique, Gallicchio and Berne[37] have, for example, calculated the dipole absorption spectrum of an

electron in fluid helium and found good agreement with some previous analytic results. The implementation of this and other versions of the MEM allows one to evaluate the lower frequency portion of the absorption spectra with good accuracy, but it probably requires further effort to determine the high-frequency portion which is essential in describing short-to-intermediate time quantum dynamics, e.g., photodissociation processes, optical control experiments, quantum tunneling, and charge transfer.

As an alternative to the numerical evaluation of the exact quantum time propagation in many-body systems, one can develop *approximate* methods for quantum dynamics on which stable and feasible numerical algorithms can be based to compute time correlation functions. One such approach[38–41] has been developed by the present authors and is based on the dynamical properties of the centroid variable in Feynman path integration.[4,11] In this approach, called ''centroid molecular dynamics'' (CMD), a quasiclassical dynamics algorithm is employed to compute an approximation to the Kubo-transformed quantum dynamical time correlation function. There are now several encouraging results from applications of CMD to a variety of nontrivial systems.[41–45] The simplicity and stability of this method makes CMD a promising candidate for quantum dynamical simulations in the condensed phase where other methods become impractical.

In the present paper, however, a different and promising approach for the calculation of approximate quantum dynamical time correlation functions will be developed based on semiclassical arguments, some of which originate from the earliest formulations of the ''old'' quantum theory. Indeed, since those early days many attempts have been made to elucidate and utilize the relationship between classical dynamics and its quantum counterpart. In time-independent quantum mechanics, this is commonly known as the WKB (Wentzel–Kramers–Brillouin) approximation for one-dimensional problems, and it can be generalized to many-dimensional problems as in classical S-matrix theory[46–48] (Miller–Marcus theory) and EBK (Einstein–Brillouin–Keller) quantization theory (see, e.g., Refs. 3 and 49). On the other hand, *time-dependent* semiclassical mechanics were first studied by Van Vleck[50] and later extended by many others.[46–48,51–55]

Although semiclassical approaches have found wide use in various analytical theories, the development of semiclassical quantum dynamics as a numerical algorithm has been hindered by two major drawbacks: the root search problem and the caustics problem. These two difficulties can be avoided in some cases, e.g., in the context of Miller's S-matrix theory,[46,48] with the help of an initial-value representation in which an integration in phase space bypasses the root search. Moreover, Campolieti and Brumer have extended the initial-value analysis to real-time propagation and have thus suggested a semiclassical approach in which the classical trajectories evolve according to the initial phase space representation.[56] Earlier, Miller and Heller proposed an initial-value propagation of wave functions which introduces integrations over initial and final positions and thus allows

for a change of variables to the initial phase space variables.[57–59]

In the present paper, we show how the initial-value semiclassical approach for computing the quantum propagator can be used to calculate time correlation functions. To be more specific, we have rederived the initial-value semiclassical propagator from a discrete perspective and found an alternative for evaluating the Jacobi matrices in the discretized formalism. Importantly, these new developments allow us to formulate the theory and a tractable numerical algorithm for both adiabatic and *nonadiabatic* semiclassical time propagation of the nuclei in quantum systems. This, along with an initial-value expression for the evaluation of quantum operators, makes it possible to implement semiclassical dynamics in the calculation of quantum dynamical time correlation functions. The emphasis in the present paper is on a formulation amenable to realistic many-body simulations.

The sections of this paper are organized as follows: In Sec. II, the semiclassical approximation for quantum time correlation functions is described and rederived in the adiabatic dynamics limit from both the boundary-value and initial-value perspectives, the latter being shown to be superior for our purposes. This derivation is next generalized in Sec. III to the nonadiabatic limit. Then, in Sec. IV a stationary-phase filter method is introduced to aid in the actual implementation of the initial-value semiclassical methodology and some numerical examples are studied in Sec. V to demonstrate the feasibility of the algorithm. Concluding remarks are given in Sec. VI, while the Appendices contain important supporting material.

II. SEMICLASSICAL THEORY: ADIABATIC DYNAMICS

A. Boundary-value formulation

1. Van Vleck formula for the propagator

It is well-known that semiclassical mechanics can be largely understood as an asymptotic analysis of functional integrals in terms of $\hbar^{-1}$, which to second order is equivalent to the stationary phase approximation.[48] In this subsection, the boundary-value Van Vleck formulation of time-dependent semiclassical theory will be reviewed for completeness and as background material for subsequent developments. To start, the real-time propagator can be expressed according to Feynman's prescription of path integrals as[4,11]

$$G(\mathbf{q}_1, \mathbf{q}_t; t) = \langle \mathbf{q}_t | e^{-i\hat{H}t/\hbar} | \mathbf{q}_1 \rangle$$

$$= \int \mathscr{D}\mathbf{q}(t') \exp\{iS[\mathbf{q}(t')]/\hbar\}, \qquad (2.1)$$

where the action $S[\mathbf{q}(t')]$, given by

$$S[\mathbf{q}(t')] = \int_0^t dt' L[\dot{\mathbf{q}}(t'), \mathbf{q}(t')]$$

$$= \int_0^t dt' \{\tfrac{1}{2}\dot{\mathbf{q}}(t') \cdot \mathbf{m} \cdot \dot{\mathbf{q}}(t') - V[\mathbf{q}(t')]\}, \qquad (2.2)$$

is evaluated with the Lagrangian $L[\dot{\mathbf{q}}(t'), \mathbf{q}(t')]$ along the path $\mathbf{q}(t)$ subject to the boundary conditions

$$\mathbf{q}(0) = \mathbf{q}_1, \quad \mathbf{q}(t) = \mathbf{q}_t. \tag{2.3}$$

Following common notation, fonts with hats denote operators and bold fonts denote vectors or matrices; in particular, the vectors $\mathbf{q} = \{q_1, q_2, \ldots, q_N\}$ and $\mathbf{p} = \{p_1, p_2, \ldots, p_N\}$ represent, respectively, N-dimensional coordinates and their conjugate momenta in an N-degree-of-freedom system, whereas $\mathbf{m}$ is the diagonal mass matrix. An application of the stationary-phase approximation to Eq. (2.1) gives[6]

$$G_{\mathrm{sc}}(\mathbf{q}_1, \mathbf{q}_t; t) = \sum_{\mathrm{st}} \left(\frac{1}{2\pi i\hbar} \right)^{N/2} \sqrt{\det\left(-\frac{\partial^2 S_{\mathrm{st}}}{\partial \mathbf{q}_1 \partial \mathbf{q}_t} \right)}$$
$$\times \exp(iS_{\mathrm{st}}/\hbar), \tag{2.4}$$

where the summation is carried out over all possible stationary paths, and $S_{\mathrm{st}} = S_{\mathrm{st}}(\mathbf{q}_1, \mathbf{q}_t; t)$ is the classical action associated with a given stationary path. The stationary phase condition $[\delta S/\delta q(t')]_{\mathrm{st}} = 0$ determines the classical trajectory, thus leading to the Euler–Lagrange equations

$$\frac{d}{dt'}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}} \right) - \frac{\partial L}{\partial \mathbf{q}} = \mathbf{m} \cdot \ddot{\mathbf{q}} + \frac{\partial V}{\partial \mathbf{q}} = 0 \tag{2.5}$$

with the boundary conditions in Eq. (2.3).

In the short time limit, the determinant in Eq. (2.4) is positive and this semiclassical expression is exactly the original Van Vleck short-time propagator.[50] In general, the determinant, termed the *Van Vleck determinant*, can be written in a more useful form as

$$\sqrt{\det\left(-\frac{\partial^2 S_{\mathrm{st}}}{\partial \mathbf{q}_1 \partial \mathbf{q}_t} \right)} = |\det \mathbf{J}_q(t)|^{-1/2} \exp[-i\pi\nu(t)/2], \tag{2.6}$$

where $\nu(t)$, known as the Maslov index,[51] is the number of sign changes of the determinant as the trajectory evolves in time from 0 to t. The Jacobi matrices, defined as $\mathbf{J}_q(t') = \partial \mathbf{q}(t')/\partial \mathbf{p}_1$ and $\mathbf{J}_p(t') = \partial \mathbf{p}(t')/\partial \mathbf{p}_1$, are the solutions of the coupled Jacobi equations,[6,60] given by

$$\dot{\mathbf{J}}_q(t') = \mathbf{m}^{-1} \cdot \mathbf{J}_p(t'),$$
$$\dot{\mathbf{J}}_p(t') = -\mathbf{K}(t')\mathbf{J}_q(t'), \tag{2.7}$$

with the initial conditions

$$\mathbf{J}_q(0) = 0,$$
$$\mathbf{J}_p(0) = \mathbf{I}, \tag{2.8}$$

where $\mathbf{I}$ is the N-dimensional identity matrix and $\mathbf{K}(\mathbf{t}')$ is the time-dependent force constant matrix, $\mathbf{K}(t') = \partial^2 V(t')/\partial \mathbf{q}\partial \mathbf{q}$, evaluated along the stationary path $V(t') = V[\mathbf{q}_{\mathrm{st}}(t')]$. Clearly, the Jacobi equation in Eq. (2.7) is the same as the classical equation of motion describing an oscillator with a time-dependent force constant determined by the stationary trajectory.

The nonuniform semiclassical formula in Eq. (2.4) is valid as long as the prefactor in Eq. (2.6) remains finite. It happens at certain times that two or more paths may coalesce at a focal point, or *caustic*, where

$$\det \mathbf{J}_q(t_c) = \det \partial \mathbf{q}(t_c)/\partial \mathbf{p}_1 = 0, \tag{2.9}$$

resulting in the divergence of the nonuniform expression Eq. (2.4). In that case, one can resort to more accurate uniform asymptotic approximations[61] which, of course, assume a more complicated form. Also, at a caustic t_c, the number of negative eigenvalues of the matrix $\mathbf{J}_q(t_c)$, denoted by $\mathrm{sign}[\mathbf{J}_q(t_c)]$, will change depending on the order of the caustic. By keeping track of the time evolution of $\mathrm{sign}[\mathbf{J}_q(t)]$, one can express the Maslov index explicitly as

$$\nu(t) = \sum_k \left\{ \mathrm{sign}[\mathbf{J}_q(t_k^+)] - \mathrm{sign}[\mathbf{J}_q(t_k^-)] \right\}, \tag{2.10}$$

where t_k denotes the kth caustic time as the stationary path evolves in time from 0 to t. In fact, it can be seen from Eq. (2.6) that the Maslov index is simply the number of negative eigenvalues of the second-order derivative matrix, which will be discussed later in the context of the initial-value representation.

Apart from the difficulties associated with caustics, the root search problem poses a formidable task in the numerical implementation of Eq. (2.4). Unlike an initial-value problem where the trajectory follows a unique path in phase space, the boundary-value problem requires one to search for a solution to Eq. (2.5) which satisfies both the initial and final conditions in Eq. (2.3), thus giving rise to the possibility of multiple solutions. For many-body potentials there can exist a very large number of such paths for longer time dynamics. One also might obtain imaginary paths in the case of quantum tunneling. The numerical difficulty associated with the search for these solutions increases drastically with the dimensionality of the system.

2. Time correlation functions

As stated earlier, many physical quantities of interest can be related to time correlation functions. In their most general form, these functions can be expressed as

$$\langle \hat{A}(t)\hat{B}(0) \rangle = Z^{-1} \mathrm{Tr}[e^{-\beta\hat{H}} e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} \hat{B}]$$
$$= Z^{-1} \int d\mathbf{q}_1 \int d\mathbf{q}_2 \int d\mathbf{q}_t \int d\mathbf{q}_1' \int d\mathbf{q}_t'$$
$$\times \rho(\mathbf{q}_1, \mathbf{q}_2; \beta)$$
$$\times \langle \mathbf{q}_t | e^{-i\hat{H}t/\hbar} | \mathbf{q}_2 \rangle^* \langle \mathbf{q}_t' | e^{-i\hat{H}t/\hbar} | \mathbf{q}_1' \rangle$$
$$\times \langle \mathbf{q}_t | \hat{A} | \mathbf{q}_t' \rangle \langle \mathbf{q}_1' | \hat{B} | \mathbf{q}_1 \rangle, \tag{2.11}$$

where Z is the partition function, $Z = \mathrm{Tr}\exp(-\beta\hat{H})$, and ρ is the canonical density matrix at temperature $\beta = 1/k_B T$, i.e., $\rho(\mathbf{q}_1, \mathbf{q}_2; \beta) = \langle \mathbf{q}_1 | e^{-\beta\hat{H}} | \mathbf{q}_2 \rangle$. While Eq. (2.11) is a general expression, for the present discussion we will specialize it to the case in which the operators $\hat{A}$ and $\hat{B}$ are dependent on position only, giving

$$\langle \hat{A}(t)\hat{B}(0)\rangle = Z^{-1}\int d\mathbf{q}_1 \int d\mathbf{q}_2 \int d\mathbf{q}_t \rho(\mathbf{q}_1,\mathbf{q}_2;\beta)$$

$$\times \langle \mathbf{q}_t|e^{-i\hat{H}t/\hbar}|\mathbf{q}_2\rangle^*\langle \mathbf{q}_t|e^{-i\hat{H}t/\hbar}|\mathbf{q}_1\rangle A(\mathbf{q}_t)B(\mathbf{q}_1).$$

$$(2.12)$$

The case of general operators depending on both position and momenta will be discussed in Sec. II B within the context of the initial-value formulation. By substituting the semiclassical formula in Eq. (2.4) for the propagators into the above expression, one obtains

$$\langle \hat{A}(t)\hat{B}(0)\rangle_{\mathrm{sc}}$$

$$= Z^{-1}\int d\mathbf{q}_1 \int d\mathbf{q}_2 \int d\mathbf{q}_t A(\mathbf{q}_t)B(\mathbf{q}_1)\rho(\mathbf{q}_2,\mathbf{q}_1;\beta)$$

$$\times \frac{1}{h^N}\sum_{\mathrm{st}} \left(\det \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_1}\det \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_2}\right)^{-1/2}\exp(i\Delta S_{\mathrm{st}}/\hbar),$$

$$(2.13)$$

where the subscript "st" denotes a summation over both the forward and backward stationary paths and $\Delta S_{\mathrm{st}}=S_{\mathrm{st}}(\mathbf{q}_1,\mathbf{q}_t;t)-S_{\mathrm{st}}(\mathbf{q}_2,\mathbf{q}_t;t)$. In principle, time correlation functions can be evaluated based on Eq. (2.13), but such a calculation would be fully vulnerable to the caustic and root search problems described previously. Therefore, the above expression is primarily of formal interest. (It is useful, for example, when one considers the classical limit, cf. Appendix A.) A much more useful approach is based on the initial-value formulation of semiclassical dynamics and this will now be discussed.

B. Initial-value formulation

1. Propagator

The initial-value representation of the semiclassical propagator is a recasting of the semiclassical boundary-value problem in terms of the initial position and an integral over the initial momentum. Since this approach is formally equivalent to the Van Vleck form, their evaluation is formally equal. However, the initial-value representation is numerically superior since the stationary phase trajectories in the initial-value approach are determined from initial momenta and coordinates. The troublesome boundary-value problem thus becomes an initial-value problem. Moreover, the Van Vleck determinant, which vanishes at the caustics, appears in the numerator, instead of the denominator, of the semiclassical expression. The initial-value representation is a global-time asymptotic semiclassical approximation which is reducible to the Van Vleck formula by a stationary phase integration.

Recently, Campolieti and Brumer[56] presented an in-depth study of the initial-value formalism, with an emphasis on a derivation of the Maslov indices and canonical transformations among alternative phase-space representations. Their analysis follows a simple procedure of concatenating short-time propagators by sequential stationary-phase integrations. In Sec. II B 2, we rederive the initial-value propagator from a discretized perspective which leads to an efficient and transparent alternative for evaluating the Jacobi matrices. These new developments allow us to formulate an initial-value semiclassical algorithm for the quantum propagator in both the adiabatic and nonadiabatic limits. The central result of these efforts in both cases is an initial-value expression for the coordinate representation of the propagator, i.e.,[56]

$$G_{\mathrm{isc}}(\mathbf{q}_1,\mathbf{q}_t;t)=\frac{1}{h^N}\int d\mathbf{p}_1 |\det \mathbf{J}_p(t)|^{1/2}$$

$$\times \exp[i\alpha(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)/\hbar-i\pi\mu(t)/2],$$

$$(2.14)$$

where the phase is a canonical transformation of the classical action S, i.e.,

$$\alpha(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)=S_{\mathrm{st}}[\mathbf{q}_1,\mathbf{q}(t);t]+\mathbf{p}(t)\cdot[\mathbf{q}_t-\mathbf{q}(t)],$$

$$(2.15)$$

and the index $\mu(t)$ is related to the Maslov index by

$$\mu(t)=\nu(t)+\mathrm{sign}[\mathbf{J}_p^T(t)\mathbf{J}_q(t)]. \qquad (2.16)$$

Here, the Jacobi matrices $\mathbf{J}_p(t)$ and $\mathbf{J}_q(t)$ are solved from Eq. (2.7) or by the discrete approach derived in Sec. II B 2. The stationary-phase condition determines the classical trajectory from the usual initial conditions $(\mathbf{q}_1,\mathbf{p}_1)$, namely,

$$\mathbf{q}(t)=\mathbf{q}(\mathbf{q}_1,\mathbf{p}_1;t),$$

$$\mathbf{p}(t)=\mathbf{p}(\mathbf{q}_1,\mathbf{p}_1;t), \qquad (2.17)$$

which is an initial-value problem rather than a boundary-value problem as in Eq. (2.3). Also one sees from Eq. (2.14) that a vanishing determinant, $\det \mathbf{J}_p(t)$, does not lead to a divergent prefactor at the caustics.

Before proceeding to Sec. II B 2, we note that some care is in order when evaluating the initial-value propagator explicitly. Unlike the nonuniform asymptotic expression in Eq. (2.4), the initial-value expression Eq. (2.14) is nonsymmetric with respect to the exchange of the coordinates $\mathbf{q}_1$ and $\mathbf{q}_t$, thus contradicting the symmetry of the Green's function for a real time-independent Hamiltonian. To remedy this, one can construct a symmetrized propagator by inserting a complete coordinate basis set at the half-time, i.e.,

$$G(\mathbf{q}_1,\mathbf{q}_t;t)=\int d\mathbf{q}_3\langle \mathbf{q}_t|e^{-i\hat{H}t/2\hbar}|\mathbf{q}_3\rangle\langle \mathbf{q}_3|e^{-i\hat{H}t/2\hbar}|\mathbf{q}_1\rangle$$

$$=\int d\mathbf{q}_3 G(\mathbf{q}_t,\mathbf{q}_3;t/2)G(\mathbf{q}_1,\mathbf{q}_3;t/2), \quad (2.18)$$

where the symmetry property of the Green's function for time-independent Hamiltonians has been used. In the evaluation of time correlation functions, this symmetrization is not necessary.

2. A new derivation of the propagator

The approach reviewed in Sec. II B 1 involved solving the Jacobi matrices from the Jacobi equation which, in the case of nonadiabatic dynamics described in Sec. III below,

becomes a complex integro-differential equation. To avoid this difficulty, we set out to find an alternative to evaluate the Jacobi matrices and have thereby found it necessary to derive the initial-value expression from a new perspective. Straightforward and self-contained, this derivation leads to a discretized expression for the Jacobi matrices and a simple interpretation of the Maslov-like index. These general expressions are applicable to both adiabatic and nonadiabatic dynamics, and are therefore in some sense more general than the original expressions.

To start, the real-time propagator is rewritten as

$$G(\mathbf{q}_0,\mathbf{q}_t;t)=\langle\mathbf{q}_t|e^{-i\hat{H}t/\hbar}|\mathbf{q}_0\rangle$$

$$=\int d\mathbf{p}_t\langle\mathbf{q}_t|\mathbf{p}_t\rangle\langle\mathbf{p}_t|e^{-i\hat{H}t/\hbar}|\mathbf{q}_0\rangle, \quad (2.19)$$

where a complete set of momentum states has been inserted. It is then essential to evaluate the position–momentum propagator from the initial coordinate $\mathbf{q}_0$ to the final momentum $\mathbf{p}_t$, which differs from the usual position–position propagator $G(\mathbf{q}_0,\mathbf{q}_t;t)$ only in the terminal state. The position–momentum propagator in the discretized path integral form is given as

$$\langle\mathbf{p}_t|e^{-i\hat{H}t/\hbar}|\mathbf{q}_0\rangle=\frac{1}{h^{N/2}}\prod_{i=1}^{P}\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{N/2}\int d\mathbf{q}_i\,\exp(i\phi_P/\hbar), \quad (2.20)$$

where ϕ_P is a discretized canonical transformation of the action, given by

$$\phi_P=\sum_{i=1}^{P}\left[\frac{1}{2\epsilon}(\mathbf{q}_i-\mathbf{q}_{i-1})\cdot\mathbf{m}\cdot(\mathbf{q}_i-\mathbf{q}_{i-1})\right.$$

$$\left.-\epsilon\left(\frac{V(\mathbf{q}_i)+V(\mathbf{q}_{i-1})}{2}\right)\right]-\mathbf{p}_t\cdot\mathbf{q}_P. \quad (2.21)$$

Here, P is the discretization number, ϵ is the discrete time increment $\epsilon=t/P$, and $\mathbf{m}$ is, as before, the diagonal particle mass matrix.

The semiclassical approximation is the functional application of the stationary-phase approximation. The stationary-phase condition $[\partial\phi/\partial\mathbf{q}_i]_{\mathrm{st}}=0$ in the present case determines the *discretized* stationary path for $i\neq P$ as

$$\mathbf{m}\cdot\frac{(\mathbf{q}_{i+1}+\mathbf{q}_{i-1}-2\mathbf{q}_i)}{\epsilon^2}+\nabla V_i=0 \quad (2.22)$$

and, for $i=P$, as

$$\mathbf{p}=\frac{\mathbf{m}}{\epsilon}\cdot(\mathbf{q}_P-\mathbf{q}_{P-1})-\frac{\epsilon}{2}\nabla V_P. \quad (2.23)$$

It is easy to recognize that in the continuous limit Eq. (2.22) is equivalent to the classical equation of motion, that is

$$\mathbf{m}\cdot\ddot{\mathbf{q}}(t')+\nabla V[\mathbf{q}(t')]=0 \quad (2.24)$$

and Eq. (2.23) imposes the terminal boundary condition

$$\mathbf{p}_t=\mathbf{p}(t)=\mathbf{p}(\mathbf{q}_0,\mathbf{p}_0,t). \quad (2.25)$$

Next, the quantum fluctuations are evaluated by a second-order functional derivative, giving

$$\frac{\partial^2\phi_{\mathrm{st}}}{\partial\mathbf{q}_i\partial\mathbf{q}_j}=\frac{\mathbf{m}}{\epsilon}(2\delta_{i,j}-\delta_{i,j+1}-\delta_{i,j-1})-\delta_{i,j}\epsilon\mathbf{K}_{i,j}, \quad (2.26)$$

except for $i=j=P$, which is given by

$$\frac{\partial^2\phi_{\mathrm{st}}}{\partial\mathbf{q}_P\partial\mathbf{q}_P}=\frac{\mathbf{m}}{\epsilon}-\frac{\epsilon}{2}\mathbf{K}_{P,P}, \quad (2.27)$$

where $\mathbf{K}$ is the time-dependent force constant matrix $\mathbf{K}_{i,j}=\partial^2 V/\partial\mathbf{q}_i\partial\mathbf{q}_j$ evaluated along the stationary path.

The determinant of the matrix $[\partial^2\phi/\partial\mathbf{q}_i\partial\mathbf{q}_j]$ in the large P limit can now be defined as

$$\det\mathbf{D}_p(t)=\lim_{P\to\infty}\det{}_P\epsilon\,\mathbf{m}^{-1}\frac{\partial^2\phi_{\mathrm{st}}}{\partial\mathbf{q}_i\partial\mathbf{q}_j}, \quad (2.28)$$

where $\det_P$ refers to the discretization of time into P slices but not to the system dimensionality N. This determinant is the product of the eigenvalues and hence the phase $\mu(t)$ of $\mathbf{D}_p(t)$ is determined by the number of negative eigenvalues of the matrix, i.e.,

$$\det\mathbf{D}_p(t)=|\det\mathbf{D}_p(t)|\exp[i\pi\mu(t)]. \quad (2.29)$$

Thereby, the semiclassical limit of the propagator in Eq. (2.20) can be explicitly written as

$$\langle\mathbf{p}_t|e^{-i\hat{H}t/\hbar}|\mathbf{q}_0\rangle_{\mathrm{sc}}=\frac{1}{h^N\sqrt{|\det\mathbf{D}_p(t)|}}$$

$$\times\exp[i\phi_{\mathrm{st}}(t)/\hbar-i\pi\mu(t)/2], \quad (2.30)$$

where $\phi_{\mathrm{st}}(t)=S_{\mathrm{st}}[\mathbf{q}_1,\mathbf{q}(t);t]-\mathbf{p}(t)\cdot\mathbf{q}(t)$. Thus, the propagator in Eq. (2.19) can be rewritten as

$$G_{\mathrm{isc}}(\mathbf{q}_0,\mathbf{q}_t;t)=\frac{1}{h^N}\int d\mathbf{p}_0|\det\mathbf{J}_p(t)|\frac{1}{\sqrt{|\det\mathbf{D}_p(t)|}}$$

$$\times\exp\{i[\phi_{\mathrm{st}}(t)+\mathbf{p}(t)\cdot\mathbf{q}_t]/\hbar-i\pi\mu(t)/2\}, \quad (2.31)$$

where a change of variables from the final to the initial momenta has been carried out which introduces the Jacobi factor $\mathbf{J}_p(t)$. It is proven in Appendix B that $\mathbf{D}_p(t)$ is equal to the Jacobi matrix, i.e.,

$$\mathbf{D}_p(t)=\mathbf{J}_p(t). \quad (2.32)$$

This result allows us to reach the final expression of the initial-value representation given by Eq. (2.14) with $\mathbf{p}_1$ in that expression replaced by $\mathbf{p}_0$.

3. Time correlation functions

By substituting Eq. (2.14) into Eq. (2.11), it is straightforward to obtain an initial-value semiclassical expression for general time correlation functions, i.e.,

$$\langle \hat{A}(t)\hat{B}(0)\rangle_{\mathrm{isc}} = \frac{1}{Z}\frac{1}{h^{2N}}\int d\mathbf{q}_1 \int d\mathbf{q}_2 \int d\mathbf{q}_t \int d\mathbf{q}_1' \int d\mathbf{q}_t'$$

$$\times \int d\mathbf{p}_1 \int d\mathbf{p}_2 \rho(\mathbf{q}_1,\mathbf{q}_2;\beta)$$

$$\times g(\mathbf{q}_1',\mathbf{p}_1,\mathbf{q}_t';t)g^*(\mathbf{q}_2,\mathbf{p}_2,\mathbf{q}_t;t)$$

$$\times \langle \mathbf{q}_t|\hat{A}|\mathbf{q}_t'\rangle\langle \mathbf{q}_1'|\hat{B}|\mathbf{q}_1\rangle, \qquad (2.33)$$

where g is the integrand in the initial-value propagator in Eq. (2.14), i.e.,

$$g(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t) = |\det \mathbf{J}_p(t)|^{1/2}$$

$$\times \exp[i\alpha(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)/\hbar - i\pi\mu(t)/2].$$

$$(2.34)$$

In this case, $\hat{A}$ and $\hat{B}$ are general operators which can depend on both position and momentum. If one knows the position matrix elements of these operators, and if they are "simple" products of position and momentum, then one can readily express the above correlation function in a more explicit form. For example, if $\hat{A}$ and $\hat{B}$ depend only on the position operator, then Eq. (2.33) simplifies to read

$$\langle \hat{A}(t)\hat{B}(0)\rangle_{\mathrm{isc}} = \frac{1}{Z}\frac{1}{h^{2N}}\int d\mathbf{q}_1 \int d\mathbf{q}_2 \int d\mathbf{q}_t \int d\mathbf{p}_1 \int d\mathbf{p}_2$$

$$\times \rho(\mathbf{q}_1,\mathbf{q}_2;\beta)g(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)$$

$$\times g^*(\mathbf{q}_2,\mathbf{p}_2,\mathbf{q}_t;t)A(\mathbf{q}_t)B(\mathbf{q}_1). \qquad (2.35)$$

In many cases of interest, however, the operators $\hat{A}$ and $\hat{B}$ are complicated functions of positions and momenta. In such cases, it is better to concentrate one's efforts on the time correlation function written in the form

$$\langle \hat{A}(t)\hat{B}(0)\rangle = \frac{1}{Z}\int d\mathbf{q}_0 \int d\mathbf{q}_1 \int d\mathbf{q}_2 \rho(\mathbf{q}_0,\mathbf{q}_2;\beta)$$

$$\times \langle \mathbf{q}_2|\hat{A}(t)|\mathbf{q}_1\rangle\langle \mathbf{q}_1|\hat{B}(0)|\mathbf{q}_0\rangle, \qquad (2.36)$$

where $\hat{A}(t)$ and $\hat{B}(0)$ are Heisenberg operators. The focus therefore shifts to deriving a semiclassical initial-value expression for the matrix element $\langle \mathbf{q}_2|\hat{A}(t)|\mathbf{q}_1\rangle$. Through the Weyl correspondence, an operator can be expressed as[62,63]

$$\langle \mathbf{q}_2'|\hat{A}(\hat{q},\hat{p})|\mathbf{q}_1'\rangle = \frac{1}{h^N}\int d\mathbf{p}' A_W[(\mathbf{q}_1'+\mathbf{q}_2')/2,\mathbf{p}']$$

$$\times e^{i\mathbf{p}'\cdot(\mathbf{q}_1'-\mathbf{q}_2')/\hbar}, \qquad (2.37)$$

where $A_W(\mathbf{q},\mathbf{p})$ is the classical symbol corresponding to the quantum operator $\hat{A}(\hat{\mathbf{q}},\hat{\mathbf{p}})$. By combining Eq. (2.37) and the initial-value expression in Eq. (2.14), one obtains

$$\langle \mathbf{q}_2|e^{i\hat{H}t/\hbar}\hat{A}(\hat{\mathbf{q}},\hat{\mathbf{p}})e^{-i\hat{H}t/\hbar}|\mathbf{q}_1\rangle_{\mathrm{isc}}$$

$$= \frac{1}{h^N}\int d\mathbf{q}_1' \int d\mathbf{q}_2' \int d\mathbf{p}' A_W[(\mathbf{q}_1'+\mathbf{q}_2')/2,\mathbf{p}']$$

$$\times e^{i\mathbf{p}'\cdot(\mathbf{q}_1'-\mathbf{q}_2')/\hbar}\langle \mathbf{q}_1'|e^{-i\hat{H}t/\hbar}|\mathbf{q}_1\rangle_{\mathrm{isc}}\langle \mathbf{q}_2'|e^{-i\hat{H}t/\hbar}|\mathbf{q}_2\rangle_{\mathrm{isc}}^*.$$

$$(2.38)$$

We then make a change of variables to $\tilde{\mathbf{q}} = (\mathbf{q}_1' - \mathbf{q}_2')$ and $\mathbf{q}_t = (\mathbf{q}_1' + \mathbf{q}_2')/2$, integrate over the first variable resulting in a delta function of momentum which is also integrated over, and finally arrive at the initial-value semiclassical representation of the Heisenberg operator, i.e.,

$$\langle \mathbf{q}_2|e^{i\hat{H}t/\hbar}\hat{A}(\hat{\mathbf{q}},\hat{\mathbf{p}})e^{-i\hat{H}t/\hbar}|\mathbf{q}_1\rangle_{\mathrm{isc}}$$

$$= \frac{1}{h^{2N}}\int d\mathbf{q}_t \int d\mathbf{p}_1 \int d\mathbf{p}_2 A_W(\mathbf{q}_t,[\mathbf{p}_1(t)+\mathbf{p}_2(t)]/2)$$

$$\times g(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)g(\mathbf{q}_2,\mathbf{p}_2,\mathbf{q}_t;t)^*, \qquad (2.39)$$

where the classical momentum in the symbol $A_W(\mathbf{q},\mathbf{p})$ takes the average value at the end of the trajectories which are used in the computation of $g(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)$ and $g(\mathbf{q}_2,\mathbf{p}_2,\mathbf{q}_t;t)^*$. Thus, momentum symbols in the Weyl ordering of Heisenberg operators are essentially the symmetrized final momentum variables from the initial-value semiclassical representation. It can be shown that Eq. (2.37) is recovered from the $t\to 0^+$ of Eq. (2.39). With this formulation of semiclassical Heisenberg operators in hand, the time correlation function in Eq. (2.36) can be written in the initial-value representation as

$$\langle \hat{A}(t)\hat{B}(0)\rangle_{\mathrm{isc}}$$

$$= \frac{1}{Z}\frac{1}{h^{2N}}\int d\mathbf{q}_0 \int d\mathbf{q}_1 \int d\mathbf{q}_2 \int d\mathbf{q}_t \int d\mathbf{p}_1$$

$$\times \int d\mathbf{p}_2 \rho(\mathbf{q}_0,\mathbf{q}_2;\beta)A_W(\mathbf{q}_t,[\mathbf{p}_1(t)+\mathbf{p}_2(t)]/2)$$

$$\times \langle \mathbf{q}_1|\hat{B}(0)|\mathbf{q}_0\rangle g(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)g^*(\mathbf{q}_2,\mathbf{p}_2,\mathbf{q}_t;t), \qquad (2.40)$$

where the zero-time matrix element $\langle \mathbf{q}_1|\hat{B}(0)|\mathbf{q}_0\rangle$ has been left in a general form.

The form of Eq. (2.40) also suggests a series of approximations in which[64]

$$A_W(\mathbf{q},\mathbf{p}) = A_0(\mathbf{q},\mathbf{p}) + \sum_{n=1}^{\infty} \frac{(i\hbar)^n}{n!} A_n(\mathbf{q},\mathbf{p}), \qquad (2.41)$$

where $A_0(\mathbf{q},\mathbf{p}) = A_{\mathrm{cl}}(\mathbf{q},\mathbf{p})$ is the classical function of the dynamical variables $\mathbf{q}$ and $\mathbf{p}$. In particular, if $A_W(\mathbf{q},\mathbf{p})$ is a polynomial such a truncation will be exact for sufficiently large, but finite, values of n. In general, such a truncation is not strictly equivalent to the semiclassical approximation because the error is in the preexponential part. Nonetheless, the truncation is tantamount to that used by Wigner[65] in his formulation of the leading quantum correction to the classical partition function.

III. SEMICLASSICAL THEORY: NONADIABATIC DYNAMICS

Many advances have taken place in the field of nonadiabatic dynamics simulation.[66-71] The theoretical basis for several algorithms is the Pechukas theory of nonadiabatic collisions based on the stationary phase approximation to Feynman path integrals.[53,54] As far as the nuclear motion is concerned, classical dynamics has been assumed in most of

the nonadiabatic dynamics algorithms based on the Pechukas formulation. Clearly, neglect of the quantum nature of the nuclear dynamics is inadequate for treating light nuclei such as protons. Therefore, the combination of the initial-value semiclassical approximation and nonadiabatic dynamics will represent a more accurate description of such systems and this is the focus of the present section.

Consider the dynamics of nuclei on a potential resulting from multiple electronic diabatic surfaces. One then needs to extend adiabatic dynamics to nonadiabatic dynamics to allow for the possibility of transitions between the different surfaces. To put the formalism in the most general context, we consider the Hamiltonian of a many-body, multilevel system written as

$$H = H_0(\dot{\mathbf{q}}) + H_d(\mathbf{q}), \tag{3.1}$$

where $\mathbf{q}$, as before, is the collection of N nuclear degrees of freedom of the system of interest, and $H_0 = \dot{\mathbf{q}}(t') \cdot \mathbf{m} \cdot \dot{\mathbf{q}}(t')/2$ is the kinetic energy term for the nuclei. The Hamiltonian H_d can be explicitly expressed in terms of the elements h_{ii} (for the ith diabatic surface) and h_{ij} (for the coupling between the ith and jth diabatic surfaces), i.e.,

$$H_d(\mathbf{q}) = \sum_i h_{ii} + \sum_i \sum_{j>i} h_{ij}. \tag{3.2}$$

Here, the elements are defined as

$$h_{ii} = |i\rangle V_{ii}(\mathbf{q})\langle i|, \tag{3.3}$$

and

$$h_{ij} = |i\rangle V_{ij}(\mathbf{q})\langle j| + |j\rangle V_{ij}^{\dagger}(\mathbf{q})\langle i|, \tag{3.4}$$

where the off-diagonal coupling elements satisfy the Hermitian relation $V_{ij} = V_{ji}^*$. The potential energy terms V_{ii} in the elements h_{ii} describe the diabatic surfaces, so the above formulation of the problem is completely general.

For the Hamiltonian in Eq. (3.1), the matrix element of the nuclear time propagator in the diabatic basis reads

$$G_{\mu\nu}(\mathbf{q}_0, \mathbf{q}_t; t) = \int \mathscr{D}\mathbf{q}(t') \exp\{iS_0[\mathbf{q}(t')]/\hbar\} T_{\mu\nu}[\mathbf{q}(t')], \tag{3.5}$$

where $S_0[\mathbf{q}(t')]$ is the action functional associated with the kinetic energy term H_0 and $T_{\mu\nu}$ is the overlap between the initial and final diabatic states. Explicitly, the time evolution operator for the diabatic Hamiltonian evolves according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial u(t')}{\partial t'} = H_d[\mathbf{q}(t')]u(t') \tag{3.6}$$

with the initial condition $u(0) = 1$. The transition amplitudes are thus given by

$$T_{\mu\nu}[\mathbf{q}(t')] = \langle \mu | u(t') | \nu \rangle \tag{3.7}$$

which is a functional of the nuclear path $\mathbf{q}(t')$.

To facilitate the subsequent analysis, the quantum average over the diabatic basis is introduced as

$$\langle \hat{f}(t') \rangle_d = \frac{\langle \mu | u(t,t') \hat{f}(t') u(t',0) | \nu \rangle}{\langle \mu | u(t,t') u(t',0) | \nu \rangle}, \tag{3.8}$$

where the denominator is independent of the variable t', and $\hat{f}(t')$ is in general an operator. This quantum average is carried out by assuming a particular nuclear path $\mathbf{q}(t')$ and is thus a functional of the nuclear paths. Equations (3.1)–(3.8) represent the exact formulation of the nonadiabatic quantum dynamics for a given nuclear path $\mathbf{q}(\mathbf{t}')$.

Following the Pechukas analysis, we apply the stationary phase approximation to Eq. (3.5) and thus obtain the equation of motion for the nuclear coordinates[53,54]

$$\mathbf{m} \cdot \ddot{\mathbf{q}}(t') = -\left\langle \frac{\partial H_d[\mathbf{q}(t')]}{\partial \mathbf{q}(t')} \right\rangle_d, \tag{3.9}$$

which is to be solved together with Eqs. (3.6)–(3.8) to obtain the nonadiabatic stationary solution(s). Clearly, the coupling between the diabatic state propagation and the stationary trajectory imposes the self-consistency condition for the solution of the nonadiabatic trajectories.

With the stationary solutions in hand, the semiclassical expression for the propagation is given as

$$\langle \mu, \mathbf{q}_t | e^{-i\hat{H}t/\hbar} | \nu, \mathbf{q}_1 \rangle_{\text{isc}} = \frac{1}{h^N} \int d\mathbf{p}_1 |\det \mathbf{J}_p(t)|^{1/2}$$
$$\times \exp[i\alpha(t)/\hbar - i\pi\mu(t)/2] \tag{3.10}$$

which is the same as the adiabatic semiclassical expression in Eq. (2.14) except that the S_{st} is now defined as

$$S_{\mu\nu,\text{st}}(\mathbf{q}_1, \mathbf{q}_t; t) = S_{0,\text{st}}(\mathbf{q}_1, \mathbf{q}_t; t) - i\hbar \ln T_{\mu\nu}[\mathbf{q}_{\text{st}}(t)], \tag{3.11}$$

so that $\phi_{\text{st}}(t) = S_{\mu\nu,\text{st}} - \mathbf{p}(t) \cdot \mathbf{q}(t)$ and $\alpha(t) = S_{\mu\nu,\text{st}} + \mathbf{p}(t) \cdot [\mathbf{q}_t - \mathbf{q}(t)]$. The prefactor $\mathbf{J}_p(t)$ obeys the Jacobi equation which can be obtained from taking the partial derivative of Eq. (3.9) with respect to the initial values $\mathbf{p}_0$ or $\mathbf{q}_0$, giving the Jacobi matrix equation

$$\mathbf{m} \cdot \ddot{\mathbf{J}}_q(t') + \langle \nabla' \cdot \nabla' H_d \rangle_d \mathbf{J}_q(t')$$
$$- \frac{i}{\hbar} \int_0^t dt'' [\langle (\nabla' H_d) u(t',t'')(\nabla'' H_d) \rangle_d - \langle \nabla' H_d \rangle_d$$
$$\cdot \langle \nabla'' H_d \rangle_d] \mathbf{J}_q(t'') = 0, \tag{3.12}$$

where $\nabla' \equiv \partial/\partial \mathbf{q}(t')$, $\nabla'' \equiv \partial/\partial \mathbf{q}(t'')$, and $\mathbf{m} \cdot \dot{\mathbf{J}}_q = \mathbf{J}_p$. The latter equations are the nonadiabatic analog to the adiabatic Jacobi equations of Eqs. (B6) and (B7) (cf. Appendix B).

Solving the integral-differential equation in Eq. (3.12) is a formidable task. In addition, the fact that the Jacobi matrices are generally complex introduces ambiguities in defining the Maslov index $\mu(t)$. To circumvent these difficulties, we resort to a discretized expression for the Jacobi matrix which is equivalent to solving the Jacobi equation. To be more explicit, the Jacobi determinant, $\det \mathbf{J}_p(t)$, can be evaluated in a discretized format as in the previous section, giving in the nonadiabatic case

$$\frac{\partial^2 \phi_{st}}{\partial \mathbf{q}_i \partial \mathbf{q}_j} = \frac{\mathbf{m}}{\epsilon} (2\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1})$$

$$-\epsilon\delta_{i,j}\left\langle\frac{\partial^2 H_d[\mathbf{q}(t')]}{\partial \mathbf{q}_i^2}\right\rangle_d + i\hbar\,\epsilon^2 \mathbf{C}_{i,j}, \qquad (3.13)$$

except for $i = j = P$, which is given by

$$\frac{\partial^2 \phi_{st}}{\partial \mathbf{q}_P \partial \mathbf{q}_P} = \frac{\mathbf{m}}{\epsilon} - \frac{\epsilon}{2}\left\langle\frac{\partial^2 H_d[\mathbf{q}(t')]}{\partial \mathbf{q}_P^2}\right\rangle_d + i\hbar\,\frac{\epsilon^2}{2}\,\mathbf{C}_{P,P}.$$

$$(3.14)$$

The quantum fluctuation correlation matrix $\mathbf{C}_{i,j}$ here is given by

$$\mathbf{C}_{i,j} = \left\langle\frac{\partial H_d[\mathbf{q}(t')]}{\partial \mathbf{q}_i}\,u(t_i',t_j')\,\frac{\partial H_d[\mathbf{q}(t')]}{\partial \mathbf{q}_j}\right\rangle_d$$

$$-\left\langle\frac{\partial H_d[\mathbf{q}(t')]}{\partial \mathbf{q}_i}\right\rangle_d\left\langle\frac{\partial H_d[\mathbf{q}(t')]}{\partial \mathbf{q}_j}\right\rangle_d. \qquad (3.15)$$

The dimensionality implicit in the above equations is such that $\partial^2\phi_{st}/\partial \mathbf{q}_i\partial \mathbf{q}_j$ is a matrix of dimension $N\times P$. After taking the limit $P\to\infty$, we obtain the explicit expression for the prefactor

$$\det \mathbf{J}_p(t) = \lim_{P\to\infty}\,\det_P\,\epsilon\mathbf{m}^{-1}\,\frac{\partial^2\phi_{st}}{\partial \mathbf{q}_i\partial \mathbf{q}_j}. \qquad (3.16)$$

Here, the determinant denotes the product of eigenvalues which are complex and defined counterclockwise in the complex plane. Therefore, the Maslov-like index $\mu(t)$ equals the summation of the phase angles of the complex eigenvalues of the discretized second-order derivative matrix in Eqs. (3.13) and (3.14) in the large P limit. The above derivation represents a different approach for calculating the Jacobi matrices and the Maslov-like index without solving the Jacobi equations. It is applicable in both the adiabatic and nonadiabatic limits.

IV. NUMERICAL ALGORITHMS

Though the initial-value semiclassical expression in Eq. (2.14) represents a significant simplification of the exact path integral, the integrand g of Eq. (2.34) as a function of the initial momenta is oscillatory and thus does not render itself to simple integration schemes. Since the usual Monte Carlo method is not applicable to integrate such complex exponents, one has to introduce a positive definite weight function such that the integration domains which dominate the integral will be sampled preferentially over those which barely contribute because of phase cancellations. Indeed, such an approach, termed *stationary phase Monte Carlo*, has been proposed and applied in some quantum dynamical path integral simulations.[14–16,19] Here, we will describe a simplified version of the stationary phase method as it applies to the present semiclassical formalism.

In general, consider a one-dimensional integral of the form

$$I(\hbar) = \int_{-\infty}^{\infty} dx\; e^{i\phi(x)/\hbar}, \qquad (4.1)$$

which is a generic integral having a complex exponent. If $\hbar$ is small, the integral is dominated by regions where the phase $\phi(x)$ is stationary, i.e., where $\phi'(x) = 0$. In the non-stationary regions, the complex exponential is highly oscillatory, thus effectively canceling the contribution from those regions. Therefore, it is advantageous to introduce a weight function which suppresses the oscillatory integrand and thus acts effectively as a *filter*. A simple example is a Gaussian filter, defined as

$$W_\epsilon(x) = \exp\{-\epsilon[\phi'(x)]^2\}, \qquad (4.2)$$

where ϵ is the filter parameter. Then, the integration in Eq. (4.1) becomes

$$I_\epsilon(\hbar) = \int_{-\infty}^{\infty} dx\; e^{i\phi(x)/\hbar}W_\epsilon(x), \qquad (4.3)$$

and, for example, an expectation value is approximated as

$$\langle A\rangle = \frac{\int_{-\infty}^{\infty} dx\, A(x)e^{i\phi(x)/\hbar}}{\int_{-\infty}^{\infty} dx\; e^{i\phi(x)/\hbar}}$$

$$\simeq \frac{\int_{-\infty}^{\infty} dx\, A(x)W_\epsilon(x)e^{i\phi(x)/\hbar}}{\int_{-\infty}^{\infty} dx\; W_\epsilon(x)e^{i\phi(x)/\hbar}}. \qquad (4.4)$$

A general form of filters and the relationship between the filtered integral in Eq. (4.3) and the exact one in Eq. (4.1) have been analyzed in detail by others.[14–16,19] It should be noted that there is some flexibility in the definition of the preexponential factor of the filter function depending on the final numerical target, but these factors will cancel in the calculation of expectation values or time correlation functions as outlined below.

Although approximations to the exact integrals, Eqs. (4.3) and (4.4) converge much faster than the original integrals. If the parameter ϵ is small, the filtered integral is closer to the exact one but takes much longer to converge; in the case of $\epsilon\to 0$, the exact integral is recovered. If the parameter ϵ is large, the filtered integral is localized near stationary points and thus ignores fluctuations away from those points. A proper choice of the filter parameter is indeed crucial for carrying out an accurate and efficient calculation. Given a required level of convergence, the filtered integral exhibits poor statistics for $\epsilon < \epsilon_{min}$, but it may deviate substantially from the exact value for $\epsilon > \epsilon_{max}$. Thus, the optimal choice of ϵ is located in the intermediate region, $\epsilon_{min} < \epsilon < \epsilon_{max}$, where the filtered integral becomes both stable and accurate.

Following the above discussion of the stationary-phase filter method, it is now specialized to treat the integrations in the initial-value representation of semiclassical time correlation functions explicit in Eq. (2.33). Since the general term $\alpha(\mathbf{q}_1,\mathbf{p}_1,\mathbf{q}_t;t)$ defined by Eq. (2.15) is the phase, the filtered propagator is given by

$$\langle q_2|e^{-i\hat{H}t/\hbar}|q_1\rangle_{isc} = \frac{1}{\hbar}\int dp_1 g(q_1,p_1,q_2;t)W_\epsilon(p_1),$$

$$(4.5)$$

where the filter can be defined as

$$W_{\epsilon,p_1} = \exp[-\epsilon_p(\partial\alpha/\partial p_1)^2]$$

$$= \exp(-\epsilon_p\{J_p(t)[q_t - q(t)]\}^2) \tag{4.6}$$

and a one-dimensional notation has been adopted here for

notational simplicity. It is also straightforward to write down the filtered expression for the semiclassical time correlation function. For example, the case of position-dependent operators is given from Eq. (2.35) by

$$\langle \hat{A}(t)\hat{B}(0)\rangle_{\mathrm{isc}} = \frac{\int dq_1 \int dq_2 \int dq_t \int dp_1 \int dp_2 \rho(q_1,q_2;\beta) K_g(t) W_{\epsilon,p_1} W_{\epsilon,p_2} W_{\epsilon,q_t} A(q_t) B(q_1)}{\int dq_1 \int dq_2 \int dq_t \int dp_1 \int dp_2 \rho(q_1,q_2;\beta) K_g(t) W_{\epsilon,p_1} W_{\epsilon,p_2} W_{\epsilon,q_t}}, \tag{4.7}$$

where $K_g(t) = g(q_1,p_1,q_t;t)^* g(q_2,p_2,q_t;t)$, and a filter is also applied here to the q_t integration, i.e.,

$$W_{\epsilon,q_t} = \exp\{-\epsilon_q[\partial(\alpha_1 - \alpha_2)/\partial q_t]^2\}$$

$$= \exp\{-\epsilon_q[p_1(t) - p_2(t)]^2\}. \tag{4.8}$$

In Eq. (4.7), the quantum density matrix element $\rho(q_1,q_2;\beta)$ also provides a natural "filter" for the integration over the variables q_1 and q_2. The functions $A(q_t)$ and $B(q_1)$ in Eq. (4.7) may also aid in the filtering, depending on their form. Note that the denominator of Eq. (4.7) equals the partition function Z, but it has been written so that the overall equation is amenable to a Monte Carlo algorithm. It should also noted that the trajectories $q(t)$ in Eq. (4.6) which contribute to W_{ϵ,p_1} and W_{ϵ,p_2} in Eq. (4.7) are different (i.e., they have different initial momenta) and therefore must be treated as such.

V. NUMERICAL EXAMPLES

A. Propagator for a solvable potential

To demonstrate the feasibility and accuracy of the initial-value semiclassical approximation and the stationary-phase filter technique, we first present a numerical study of a solvable potential, given by

$$V(q) = \frac{1}{q^2} \tag{5.1}$$

with $m = 1.0$ and $\hbar = 1.0$. The real-time propagator of this potential is given in a closed form by[6]

$$G(q_1,q_t;t) = (m\sqrt{q_1 q_t}/i\hbar t)\exp[im(q_1^2 + q_t^2)/2\hbar t]$$

$$\times I_{3/2}(mq_1 q_t/i\hbar t), \tag{5.2}$$

where I_ν is the modified Bessel function of index $\nu = 3/2$. In Fig. 1 is plotted the unfiltered integrand g of Eq. (2.34), the filtered integrand in Eq. (4.5), and the filter in Eq. (4.6) as a function of the initial momentum for $q_1 = 3$, $q_t = 4$, $t = 3$. The filter parameter in Eq. (4.6) was taken as $\epsilon_p = 0.01$. It can be seen clearly from Fig. 1 that the integrand is highly oscillatory except near the origin. The filter selects two stationary regions, one to the left of the origin, the other to the

right of the origin, which indeed correspond to two possible classical trajectories, the direct path and the indirect path bounced from the repulsive wall.

The squared amplitude of the time propagator for the potential in Eq. (5.1) with the same parameters as in Fig. 1 is plotted as a function of time in Fig. 2, where the exact and semiclassical results are represented by a solid and dashed lines, respectively. The initial momentum was integrated on a 200-point grid from -10 to 10 with a filter parameter of $\epsilon_p = 0.01$. Despite the small discrepancies due to the nature of the semiclassical approximation, good agreement with the exact result is achieved.

B. Anharmonic quantum oscillator: Position correlation function

In this subsection, the initial-value semiclassical method is used to compute the position correlation function for an anharmonic potential, defined as

$$V(q) = \tfrac{1}{2}q^2 + \tfrac{1}{4}q^4 \tag{5.3}$$

with $m = 1.0$, $\hbar = 1.0$ and $\beta = 1.0$. The position correlation function was computed with filters on the momentum integrations having a value of $\epsilon_p = 0.1$. The thermal density matrix was calculated by the numerical multiplication method (NMM),[12] and the coordinates and momenta were integrated on grids. The numerically exact correlation function was obtained from a harmonic oscillator basis set calculation. In Fig. 3, the real parts of the exact and semiclassical time correlation functions are plotted as functions of time. The semiclassical approximation is more accurate for time correlation functions than for propagators, probably because correlation functions result from a thermal average of forward and backward real-time propagators and are thereby less sensitive to errors introduced by the semiclassical approximation. In general, the agreement between the exact and semiclassical results is excellent for this system.

C. Double well: Reactive flux

As a final example, the flux–flux correlation function was calculated for a double well potential, defined as

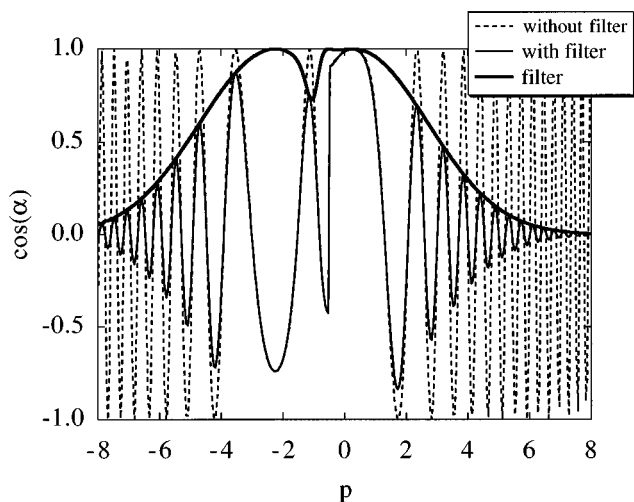$$V(q) = -\tfrac{1}{2}q^2 + \tfrac{1}{4}q^4 \tag{5.4}$$

FIG. 1. The unfiltered integrand g in the initial-value semiclassical approximation (dashed line), the filtered integrand in Eq. (4.5) (solid line), and the filter function (bold line) plotted as functions of the initial momentum for the $1/q^2$ potential with $q_1=3$, $q_2=4$, and $t=3$.

FIG. 3. The real part of the initial-value semiclassical position correlation function (solid diamonds) for the potential in Eq. (5.3) at a temperature $\beta=1.0$. The numerically exact result obtained from a basis set calculation is shown by the solid line.

with $m=1.0$, $\beta=1.0$, and $\hbar=1.0$. The quantum dynamics of a double well exhibits coherence at low temperature, thermal activation at high temperature, and assumes an exponential decay in the presence of dissipation. Miller and co-workers have shown that thermal rate constants can be obtained from the time integration of the flux–flux correlation function, defined as[72]

$$C_{FF}(t) = \text{Tr}(\hat{F}e^{-\beta\hat{H}/2 - i\hat{H}t/\hbar}\hat{F}e^{-\beta\hat{H}/2 + i\hat{H}t/\hbar}), \qquad (5.5)$$

where the flux operator is given by

$$\hat{F} = \frac{1}{2m}\left[\hat{p}\,\delta(q-q_b) + \delta(q-q_b)\hat{p}\right] \qquad (5.6)$$

with q_b defined as the position of the dividing surface. To be more explicit, we define a complex time propagator as

$$\tilde{G}(q_1,q_2;\beta,t) = \langle q_2|e^{-\beta\hat{H}/2 - i\hat{H}t/\hbar}|q_1\rangle \qquad (5.7)$$

such that the flux–flux correlation function can be expressed as[72]

$$C_{FF}(t) = -\lim_{q \to q_b}\frac{1}{2m^2}\left[|\hat{p}\tilde{G}(q_b,q;\beta,t)|^2\right.$$
$$\left. + \text{Re } \hat{p}\hat{p}_b\tilde{G}(q_b,q;\beta,t)\tilde{G}^*(q_b,q;\beta,t)\right], \qquad (5.8)$$

where $\hat{p}_b$ is the momentum operator acting on q_b. Although the flux–flux correlation function depends upon the choice of the dividing surface, the rate constant is a physical quantity independent of q_b. For convenience, we choose $q_b=0$ so that the first term in Eq. (5.8) vanishes for a symmetric barrier. In Fig. 4, the semiclassical value of $C_{FF}(t)$ is plotted for
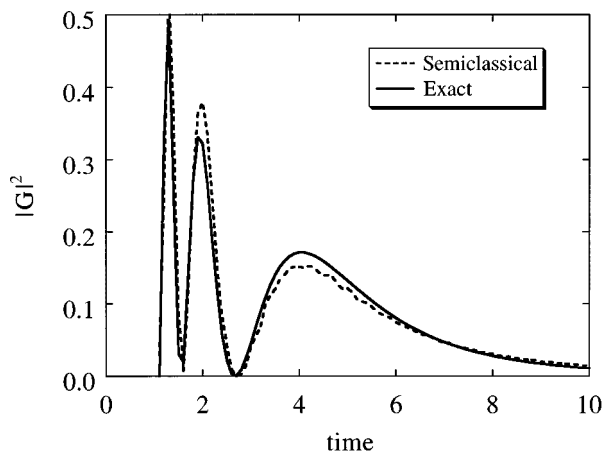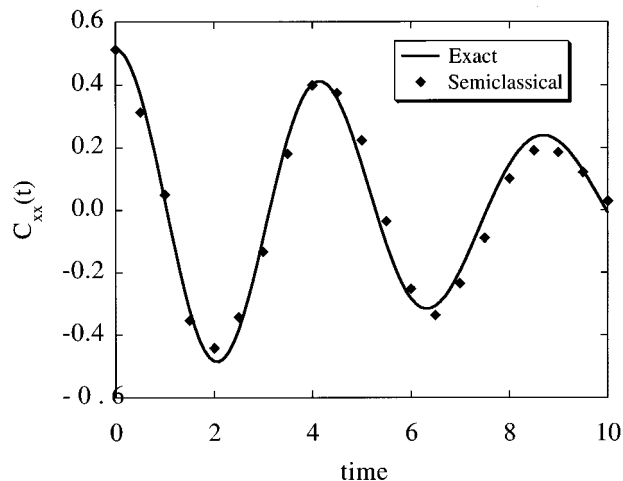
FIG. 2. A plot of $|G_{isc}(3,4;t)|^2$ vs time (dashed line) for the $1/q^2$ potential. The exact result is shown for comparison by the solid line.
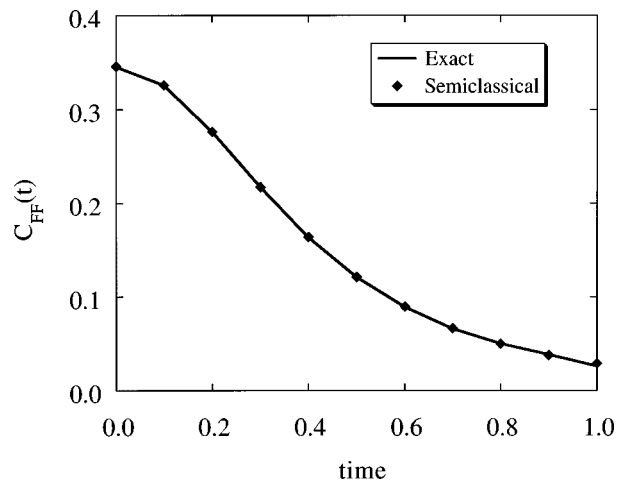
FIG. 4. The initial-value semiclassical flux–flux correlation function (solid diamonds) for the potential in Eq. (5.4) plotted along with the numerically exact result (solid line) obtained from a basis set calculation.

the double well and compared with the exact result obtained from a basis set calculation. Again, excellent agreement is obtained.

VI. CONCLUDING REMARKS

In this paper, we have discussed the semiclassical formulation of quantum dynamical time correlation functions and have also investigated the numerical feasibility of the semiclassical approximation for calculating such functions. We demonstrated the reduction from the exact quantum time correlation function to a nonuniform boundary-value semiclassical expression, then to a global-time initial-value semiclassical representation, and finally to the limit of electronically nonadiabatic quantum nuclear dynamics. Much of this formulation was accomplished with the help of a discrete approach. The resulting discrete initial-value representation of the semiclassical approximation proves to be advantageous for the implementation of semiclassical dynamics since the global-time formula avoids the problems associated with caustics and root searches.

The studies presented in this paper are not only instructive and revealing, but they also serve as the formal basis for numerical algorithms. To achieve numerical efficiency in such algorithms, a stationary-phase filter technique was introduced into the method to effectively suppress the oscillatory region of the integrations. Several examples were tested with the semiclassical method and compared with the exact results obtained from basis-set calculations. These studies clearly demonstrate the feasibility and accuracy of the algorithm.

With the results of the present work in hand, nontrivial applications of the semiclassical theory should be within reach. For example, the combined use of the initial-value semiclassical formalism and the stationary phase Monte Carlo technique should allow us to calculate time correlation functions for realistic many-body systems, particularly for one (or a few) quantum particles in a classical-like environment. It will also be very interesting to apply this algorithm when the semiclassical nuclear dynamics of such systems must be treated nonadiabatically. For more complex quantum systems in the condensed phase, the semiclassical method can also be used to accurately propagate an "important" quantum subsystem (e.g., solute) under the influence of an approximate quantum environmental force calculated by CMD[38–41] or from a quantum Gaussian bath. We have, in fact, developed a simple and flexible scheme[73] to generate the quantum forces in the latter scenario which can readily be incorporated into the semiclassical methodology described in this paper. These and other developments should greatly facilitate our ongoing efforts to numerically simulate a wide range of complex quantum dynamical processes in condensed matter.

APPENDIX A: THE CLASSICAL LIMIT OF QUANTUM TIME CORRELATION FUNCTIONS

To reveal the relationship between classical and quantum time correlation functions, one can introduce into Eq. (2.13) a set of collective coordinates[74]

$$\tilde{\mathbf{q}}(t') = \mathbf{q}_f(t') - \mathbf{q}_b(t'),$$
$$\overline{\mathbf{q}}(t') = [\mathbf{q}_f(t') + \mathbf{q}_b(t')]/2 \tag{A1}$$

with corresponding collective momenta

$$\tilde{\mathbf{p}}(t') = \mathbf{p}_f(t') - \mathbf{p}_b(t'),$$
$$\overline{\mathbf{p}}(t') = [\mathbf{p}_f(t') + \mathbf{p}_b(t')]/2, \tag{A2}$$

where $\mathbf{q}_f(t')$ and $\mathbf{q}_b(t')$ are the forward and backward classical paths, respectively, and $\mathbf{p}_f(t')$ and $\mathbf{p}_b(t')$ are the corresponding momenta. Note that in the context of the time correlation function given by Eq. (2.13) the initial collective coordinates are given by $\overline{\mathbf{q}}(0) = (\mathbf{q}_1 + \mathbf{q}_2)/2$ and $\tilde{\mathbf{q}}(0) = \mathbf{q}_1 - \mathbf{q}_2$ and the final collective coordinates are given by $\overline{\mathbf{q}}(t) = \mathbf{q}_t$ and $\tilde{\mathbf{q}}(t) = 0$. Assuming that the path difference $\tilde{\mathbf{q}}(t')$ is small, one can expand the action difference ΔS_{st} in Eq. (2.13) to linear order in $\tilde{\mathbf{q}}$ such that

$$\Delta S_{st} = S_{st}(\mathbf{q}_1, \mathbf{q}_t; t) - S_{st}(\mathbf{q}_2, \mathbf{q}_t; t) \simeq -\overline{\mathbf{p}}_0 \cdot \tilde{\mathbf{q}}_0, \tag{A3}$$

where $\overline{\mathbf{p}}_0 = \overline{\mathbf{p}}_{st}(0)$ and $\overline{\mathbf{q}}_0 = \overline{\mathbf{q}}_{st}(0)$. Furthermore, the difference of the forward and backward stationary paths can be ignored in the nonexponential factor of Eq. (2.13) and a Jacobian transformation can be performed, giving

$$\int d\mathbf{q}_t |\det \partial \mathbf{q}_t / \partial \overline{\mathbf{p}}_0|^{-1} = \int d\overline{\mathbf{p}}_0 \tag{A4}$$

which changes the semiclassical boundary-value problem to an initial-value problem. Putting all the pieces together and omitting the irrelevant indices, we have

$$\langle \hat{A}(t)\hat{B}(0) \rangle_W = \frac{1}{h^N} \int d\mathbf{q} \int d\mathbf{p} W(\mathbf{q}, \mathbf{p}; \beta)$$
$$\times A[\mathbf{q}_{cl}(t)] B[\mathbf{q}_{cl}(0)], \tag{A5}$$

where $\mathbf{q}_{cl}(t)$ is the classical trajectory and $W(\mathbf{q}, \mathbf{p})$ is the well-known Wigner distribution function, defined as[65]

$$W(\mathbf{q}, \mathbf{p}; \beta) = \frac{1}{Z} \int d\tilde{\mathbf{q}} e^{-i\mathbf{p}\cdot\tilde{\mathbf{q}}/\hbar} \rho(\mathbf{q} + \tilde{\mathbf{q}}/2, \mathbf{q} - \tilde{\mathbf{q}}/2; \beta). \tag{A6}$$

Assuming the high-temperature approximation of the canonical density matrix, i.e.,

$$\rho(\mathbf{q}_1, \mathbf{q}_2; \beta) = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{N/2} \exp\left\{-\frac{1}{2\hbar^2\beta}(\mathbf{q}_1 - \mathbf{q}_2)\cdot\mathbf{m}\right.$$

$$\cdot (\mathbf{q}_1 - \mathbf{q}_2) - \beta V\left(\frac{\mathbf{q}_1 + \mathbf{q}_2}{2}\right)\Bigg\}, \tag{A7}$$

the Wigner distribution function (A6) reduces to the Boltzmann distribution function. The classical time correlation function is then completely recovered, giving

$$\langle A(t)B(0)\rangle_{\text{cl}} = \frac{1}{Z_{\text{cl}}} \frac{1}{h^N} \int d\mathbf{q} \int d\mathbf{p}$$

$$\times \exp[-\beta H_{\text{cl}}(\mathbf{p},\mathbf{q})] A[\mathbf{q}_{\text{cl}}(t)] B[\mathbf{q}_{\text{cl}}(0)] \tag{A8}$$

with $H(\mathbf{p},\mathbf{q})$ and Z_{cl} being the classical Hamiltonian and partition function, respectively. Thus, classical dynamics results from the high temperature approximation of the density matrix and the linear expansion of the action difference of the forward and backward stationary paths in the semiclassical expression for the time correlation function. The reduction to the classical limit starting from the initial-value approximation does not differ from the above derivation. The Weyl ordering of operators simplifies the analysis, though the classical limit does not depend on operator orderings.

Clearly, Eq. (A5) implies that a quasiclassical dynamics can be constructed based on the Wigner distribution function. On the other hand, the fact that the Wigner distribution function is not positive definite complicates the interpretation of the Wigner distribution as a phase-space quantum distribution function. However, one might adopt a coarse-grained Wigner distribution, such as the Husimi distribution function,[75] as a quantum analogy to the classical Boltzmann distribution function.

APPENDIX B: DISCRETE DERIVATION OF THE JACOBI EQUATION

For convenience, the derivation in this Appendix is presented for one degree of freedom as the multidimensional generalization presents no special difficulties. To start, we define the determinant of the following two matrices as

$$D_q(P) = \det\begin{pmatrix} 2 - \epsilon^2 W_1 & -1 & 0 & \cdots \\ -1 & 2 - \epsilon^2 W_2 & -1 & \cdots \\ \vdots & \vdots & \vdots & \vdots \\ \cdots & -1 & 2 - \epsilon^2 W_{P-2} & -1 \\ \cdots & 0 & -1 & 2 - \epsilon^2 W_{P-1} \end{pmatrix} \tag{B1}$$

which appears in the discrete expression for the position–position propagator, and

$$D_p(P) = \det\begin{pmatrix} 2 - \epsilon^2 W_1 & -1 & 0 & \cdots \\ -1 & 2 - \epsilon^2 W_2 & -1 & \cdots \\ \vdots & \vdots & \vdots & \vdots \\ \cdots & -1 & 2 - \epsilon^2 W_{P-1} & -1 \\ \cdots & 0 & -1 & 1 - \frac{1}{2}\epsilon^2 W_P \end{pmatrix} \tag{B2}$$

which appears in the position–momentum propagator. Note that the determinant here is the product of the eigenvalues and thereby does not imply the absolute value. It is then easy to observe the following iterative relations:

$$D_q(P+1) = (2 - \epsilon^2 W_P) D_q(P) - D_q(P-1) \tag{B3}$$

and

$$D_p(P) = [1 - (\epsilon^2/2)W_P] D_q(P) - D_q(P-1). \tag{B4}$$

Combining Eqs. (B3) and (B4), we have

$$D_p(P) = \tfrac{1}{2}[D_q(P+1) - D_q(P-1)]. \tag{B5}$$

To associate the above difference equation to differential equations, we take the limit $\epsilon \to 0$, define the continuous variable $t = \epsilon P$, and introduce continuous variables $J_q(t) = \epsilon D_q(P)/m$ and $J_p(t) = D_p(P)$. With these definitions in hand, we can rewrite Eqs. (B3) and (B5) as

$$\ddot{J}_q + W(t) J_q = 0 \tag{B6}$$

and

$$m \dot{J}_q = J_p \tag{B7}$$

with the boundary conditions specified as $J_q(0) = 0$ and $J_p(0) = 1$. Obviously, Eqs. (B6) and (B7) are identical to the Jacobi equations if $W(t)$ is specified by $m W(t) = d^2 V[q_{\text{st}}(t)]/dq^2$; therefore, J_q and J_p are the usual Jacobi variables, i.e., $J_q(t) = \partial q(t)/\partial p_1$ and $J_p(t) = \partial p(t)/\partial p_1$.

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