Time averaging the semiclassical initial value representation for the calculation of vibrational energy levels

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An application of the initial value representation (IVR) of semiclassical (SC) theory to approximate the quantum mechanical time evolution operator, $\exp[-i\hat{H}t/\hbar]$, requires an integral over the phase space of initial conditions of classical trajectories. The integrand of this integral is complex, i.e., has a phase, from which quantum coherence (in fact, all quantum) effects arise, but which also makes SC-IVR calculations more difficult than ordinary classical molecular dynamics simulations (the semiclassical version of the “sign problem”). A number of approaches have been devised to ameliorate the sign problem, and here we show how a time averaging procedure—the integrand of the phase space integral is time-averaged over the classical trajectory originating from each initial condition—can be profitably used in this regard, particularly so for the calculation of spectral densities (from which vibrational energy levels can be identified). This time averaging procedure is shown to greatly reduce the number of initial conditions (i.e., the number of classical trajectories) that are needed to converge IVR phase space averages. In some cases useful results can be obtained with only one classical trajectory. Calculations are carried out for vibrational energy levels of $\ce{H2}$ and $\ce{H2O}$ to illustrate the overall procedure. © 2003 American Institute of Physics.

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I. INTRODUCTION

The initial value representation (IVR) of semiclassical (SC) theory provides a general prescription for approximating the quantum mechanical time evolution operator (or propagator), $\exp[-i\hat{H}t/\hbar]$, where $\hat{H}$ is the Hamiltonian of the molecular system. In terms of the propagator, one can of course express any quantum mechanical quantity of interest; see, for example, several reviews for recent applications of SC-IVR approaches to a variety of dynamical problems.1–4

The present paper is concerned with the determination of vibrational energy levels of a bound molecular system, which can be conveniently identified as peaks in the spectral density, $I(E)$,

$$I(E) = \langle |\chi| \delta(E - \hat{H}) |\chi \rangle$$

(1.1a)

$$= \sum_i |\langle \chi | \Psi_i \rangle|^2 \delta(E - E_i),$$

(1.1b)

where $|\chi\rangle$ is some reference state,5 and {$|\Psi_i\rangle$} and {E_i} are the exact eigenstates and eigenvalues of $\hat{H}$. This is expressed in terms of the propagator by using the Fourier representation of the delta function (operator) in Eq. (1.1a),

$$I(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{iE/t/\hbar} \langle \chi | e^{-i\hat{H}t/\hbar} |\chi \rangle$$

(1.2a)

$$= \Re \frac{1}{\pi\hbar} \int_{0}^{\infty} dt e^{iE/t/\hbar} \langle \chi | e^{-i\hat{H}t/\hbar} |\chi \rangle.$$  

(1.2b)

The Herman–Kluk (or coherent state) IVR gives the matrix element of the propagator in Eq. (1.2a) as

$$\langle \chi | e^{-i\hat{H}t/\hbar} |\chi \rangle = (2\pi\hbar)^{-E} \int dp_0 \int dq_0 \langle \chi | p_0 , q_0 \rangle \langle p_0 , q_0 | \chi \rangle$$

$$\times e^{iS_0(p_0, q_0)/\hbar} C_0(p_0, q_0),$$

(1.3a)

where $(p_0, q_0)$ are the initial values of the momenta and coordinates for a classical trajectory, $p_0 = p_0(p_0, q_0)$ and $q_0 = q_0(p_0, q_0)$ are the values of the momenta and coordinates at time $t$ that evolve from these initial conditions, $S_0(p_0, q_0)$ is the classical action integral along this trajectory,

$$S_0(p_0, q_0) = \int_0^t dt \left( \frac{p_0^2}{2m} - V(q) \right)$$

(1.3b)

[where a Cartesian Hamiltonian, $H(p, q) = p^{2}/2m + V(q)$, has been assumed], and $C_0(p_0, q_0)$ is a pre-exponential factor (vide infra); $|p_0, q_0\rangle$ is a coherent state,7,8 whose coordinate space wavefunction is given by

$$\langle q | p_0, q_0 \rangle = \left( \frac{\gamma}{\pi} \right)^{F/2} \exp \left[ -\frac{\gamma}{2} (q - q_0)^2 + \frac{i}{\hbar} p_0 \cdot (q - q_0) \right],$$

(1.3c)

where $F$ is the number of degrees of freedom of the system, and the $\gamma$’s are the coherent state widths. In this work, the $\gamma$’s are chosen to be the harmonic oscillator wave function widths at the global minimum on the potential.

The essential task in a spectral density calculation, therefore, is to carry out the phase space average over initial conditions in Eq. (1.3a)—which requires one to compute a classical trajectory for each set of initial condition $(p_0, q_0)$ and
then to perform the Fourier transform over $t$, Eq. (1.2b), to obtain the spectral density. For systems with many degrees of freedom, the phase space average will be an integral of high dimensionality, so that some kind of Monte Carlo method is the only feasible way to evaluate it. There have been a number of calculations along these lines, most of which have given quite good results for the vibrational energy levels (or other spectral densities relevant to a photo-absorption cross section, a photo-electron spectrum, etc.).\textsuperscript{9-15} Of concern, however, has been the number of trajectories that must be computed, i.e., the number of initial phase points that must be sampled in Eq. (1.3a), in order to obtain converged results. The more one can do to reduce the number of trajectories that are needed, the more practical the overall approach will be for an application to large molecular systems of interest.

To this end, we apply in this paper a time-averaging procedure to reduce the number of trajectories that are required in Eq. (1.3a). (Time averaging has also been used by Elran and Kay to look at time-dependent wave functions for some 1- and 2-dimensional problems.\textsuperscript{16,17} Thus, with the spectral density of Eq. (1.3a), or any phase space average of the form

$$I = \int dp_0 \int dq_0 A(p_0, q_0),$$  \hspace{1cm} (1.4)

we define the time averaged (TA) version as follows:

$$I_{TA} = \frac{1}{T} \int_0^T dt \int dp_0 \int dq_0 A(p(t), q(t));$$  \hspace{1cm} (1.5)

i.e., for each set of initial conditions $(p_0, q_0)$ one time averages the integrand along the trajectory determined by these initial conditions. One can quite easily prove that this leaves the value of the phase space average unchanged, i.e., that $I_{TA}$ of Eq. (1.5) is identical to $I$ of Eq. (1.4), for any value of $T$ (the length of the time average): to prove this, one first interchanges the order of the phase space and time integrals in Eq. (1.5),

$$I_{TA} = \frac{1}{T} \int_0^T dt \int dp_0 \int dq_0 A(p(t), q(t)),$$  \hspace{1cm} (1.6a)

and then uses Liouville’s theorem to change the integration over $(p_0, q_0)$ to one over $(p, q)$ (the Jacobian for which is unity),

$$I_{TA} = \frac{1}{T} \int_0^T dt \int dp \int dq A(p, q).$$  \hspace{1cm} (1.6b)

The phase space average is now simply the original integral $I$ of Eq. (1.4),

$$\int dp \int dq A(p, q) = I,$$  \hspace{1cm} (1.6c)

so that Eq. (1.6b) becomes

$$I_{TA} = \frac{1}{T} \int_0^T dt = I,$$  \hspace{1cm} (1.6d)

thus establishing the equality of $I_{TA}$ [Eq. (1.5)] and $I$ [Eq. (1.4)].

Equation (1.5) is thus equivalent to Eq. (1.4), but one may question why do it, for it seems to require extra work; that is, Eq. (1.5) involves a time average inside of a phase space average, whereas Eq. (1.4) requires only a phase space average. The reason is that the integrand of Eq. (1.5) will typically be a much smoother function of $(p_0, q_0)$ after time averaging it than is the original integrand of Eq. (1.4), so that many fewer values of $(p_0, q_0)$ will be needed for the (Monte Carlo) phase space average. (And the time average is only a one dimensional integral that can be computed by quadrature along with the evaluation of the classical trajectory, thus often requiring little additional computational effort.) For example, if the dynamics of the system were ergodic and the time $T$ large enough, the time average of the integrand would depend on $(p_0, q_0)$ only through the energy of this phase point, i.e.,

$$\frac{1}{T} \int_0^T dt A(p(t), q(t)) = A(E),$$  \hspace{1cm} (1.7a)

with $E = H(p_0, q_0)$, where $A(E)$ is the microcanonical average of $A(p, q)$,

$$A(E) = \int dp \int dq \delta(E - H(p, q)) A(p, q)$$

$$= \int dp \int dq \delta(E - H(p, q)),$$  \hspace{1cm} (1.7b)

which in general is a much smoother function of $(p_0, q_0)$ than $A(p_0, q_0)$ itself. This is especially important if the original integrand has any oscillatory character [as it does for the spectral density, Eq. (1.3a)].

To conclude this Introduction, we therefore note the form taken by the spectral density, Eq. (1.3a), when the above TA procedure is applied to it. Also invoking a separability approximation (see Sec. II below) for the pre-factor, the TA spectral density is given by

$$I(E) = \frac{(2\pi\hbar)^2}{2\pi\hbar T} \int dp_0 \int dq_0$$

$$\times \left| \int_0^T dt |\phi(t)|^2 e^{i(Et + S_f(p_0, q_0) + \phi_f(p_0, q_0))/\hbar} \right|^2,$$  \hspace{1cm} (1.8)

where $\phi_f(p_0, q_0)$ is the phase of the pre-factor $C_f(p_0, q_0)$. Here one sees the enormous simplification that is possible with time averaging: the integrand of the Monte Carlo phase space average is now positive definite [in contrast to that of the original phase space average in Eq. (1.3a)], and in practice one obtains converged results with orders of magnitude fewer trajectories than are required for the original phase space average in Eq. (1.3a) (in some cases obtaining useful results with only one trajectory). In the next section we discuss the application of the TA procedure to the spectral density in more detail, and in Sec. III we present applications to several test problems to illustrate its behavior in practice.

II. THE TIME AVERAGED SPECTRAL DENSITY

Applying the time averaging procedure, Eq. (1.5), to the IVR spectral density [Eqs. (1.2b) with (1.3a)] gives the following [where we drop the designation “TA” from $I(E)$],

$$I(E) = \frac{(2\pi\hbar)^2}{2\pi\hbar T} \int dp_0 \int dq_0$$

$$\times \left| \int_0^T dt |\phi(t)|^2 e^{i(Et + S_f(p_0, q_0) + \phi_f(p_0, q_0))/\hbar} \right|^2,$$  \hspace{1cm} (1.8)
\[ I(E) = (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \frac{1}{T} \int_0^T \frac{\text{Re}}{\pi\hbar} \int_0^\infty dt e^{iEt/\hbar} \times e^{iS_{1+t}(\mathbf{p}_1, \mathbf{q}_1)/\hbar} \langle \chi| \mathbf{p}_1, \mathbf{q}_1, \mathbf{q}_1(\mathbf{p}_1, \mathbf{q}_1) \rangle \times \langle \mathbf{q}_1, \mathbf{p}_1 | \chi \rangle C_{1+t}(\mathbf{p}_1, \mathbf{q}_1) \] \]

(2.1)

here \( t \) is the Fourier transform time variable [as in Eq. (1.2b)], and \( t_1 \) is the “time averaging” time variable, with \( (\mathbf{p}_1, \mathbf{q}_1) = (\mathbf{p}_1(\mathbf{p}_0, \mathbf{q}_0), \mathbf{q}_1(\mathbf{p}_0, \mathbf{q}_0)) \) being the momenta and coordinates at time \( t_1 \) that evolve from initial conditions \((\mathbf{p}_0, \mathbf{q}_0)\), and \( \mathbf{p}_1(\mathbf{p}_0, \mathbf{q}_0) \) and \( \mathbf{q}_1(\mathbf{p}_0, \mathbf{q}_0) \) the variables that begin with values \((\mathbf{p}_1, \mathbf{q}_1)\) and evolve for a time \( t \). It is thus clear that

\[ \mathbf{p}_1(\mathbf{p}_0, \mathbf{q}_0) = \mathbf{p}_1(\mathbf{p}_0, \mathbf{q}_0), \]
\[ \mathbf{q}_1(\mathbf{p}_0, \mathbf{q}_0) = \mathbf{q}_1(\mathbf{p}_0, \mathbf{q}_0), \]

(2.2)

i.e., \( \mathbf{p}_1(\mathbf{p}_1, \mathbf{q}_1) \) and \( \mathbf{q}_1(\mathbf{p}_1, \mathbf{q}_1) \) are the variables that begin at \((\mathbf{p}_0, \mathbf{q}_0)\) and evolve for a time \( t_1 + t \). Changing from integration variable \( t \) to \( t_2 \) in Eq. (2.1), where \( t_2 = t_1 + t \), or \( t = t_2 - t_1 \), and using the fact that

\[ S_{1+t}(\mathbf{p}_1, \mathbf{q}_1) = S_{t_1}(\mathbf{p}_1, \mathbf{q}_1) = \int_{t_1}^{t_2} dt' \mathcal{L}(t'), \]

(3.2a)

where \( \mathcal{L} \) is the Lagrangian, \( \mathbf{p}^2/2m - V(\mathbf{q}) \), and that

\[ \int_{t_1}^{t_2} dt' \mathcal{L}(t') = \int_0^{t_1} dt' \mathcal{L}(t') - \int_0^{t_1} dt' \mathcal{L}(t') \]

(3.2b)

the spectral density becomes

\[ I(E) = (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \frac{1}{T} \int_0^T \frac{\text{Re}}{\pi\hbar} \int_0^\infty dt_2 \langle \chi| \mathbf{p}_2, \mathbf{q}_2 \rangle \times e^{i(S_{t_2} - S_{t_1})/\hbar} \times \langle \chi| \mathbf{p}_1, \mathbf{q}_1 \rangle C_{t_2}(\mathbf{p}_1, \mathbf{q}_1) \]

(2.4)

here \((\mathbf{p}_2, \mathbf{q}_2)\) and \((\mathbf{p}_1, \mathbf{q}_1)\) are the variables that evolve from initial conditions \((\mathbf{p}_0, \mathbf{q}_0)\) to times \( t_2 \) and \( t_1 \), respectively.

The standard Herman–Kluk prefactor in Eq. (1.3a) is the square root of a determinant of a linear combinations of various blocks of the \( 2F \times 2F \) monodromy matrix \( \mathbf{M}(t) = \partial(\mathbf{p}, \mathbf{q})/\partial(\mathbf{p}_0, \mathbf{q}_0) \),

\[ C_p(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\frac{1}{2} \frac{\partial \mathbf{q}_1}{\partial \mathbf{q}_0} + \frac{\partial \mathbf{p}_1}{\partial \mathbf{p}_0} - i\hbar \gamma \frac{\partial \mathbf{q}_1}{\partial \mathbf{p}_0} + \frac{i}{\gamma \hbar} \frac{\partial \mathbf{p}_1}{\partial \mathbf{q}_0}} \]

(2.5a)

The pre-factor in the time averaged expression [Eq. (2.4)] is therefore given by

\[ C_{t_2}(\mathbf{p}_1, \mathbf{q}_1) = \sqrt{\frac{1}{2} \frac{\partial \mathbf{q}_2}{\partial \mathbf{q}_1} + \frac{\partial \mathbf{p}_2}{\partial \mathbf{p}_1} - i\hbar \gamma \frac{\partial \mathbf{q}_2}{\partial \mathbf{p}_1} + \frac{i}{\gamma \hbar} \frac{\partial \mathbf{p}_2}{\partial \mathbf{q}_1}} \]

(2.5b)

where the latter notation emphasizes that both \((\mathbf{p}_2, \mathbf{q}_2)\) and \((\mathbf{p}_1, \mathbf{q}_1)\) evolve from the same initial conditions, \((\mathbf{p}_0, \mathbf{q}_0)\). only for different lengths of time. The partial derivatives in Eq. (2.5b) can all be referenced to the initial phase space variables \((\mathbf{p}_0, \mathbf{q}_0)\) by using the chain rule

\[ \frac{\partial(\mathbf{p}_2, \mathbf{q}_2)}{\partial(\mathbf{p}_1, \mathbf{q}_1)} = \left( \frac{\partial(\mathbf{p}_2, \mathbf{q}_1)}{\partial(\mathbf{p}_0, \mathbf{q}_0)} \right)^{-1} \]

(2.6a)

Furthermore, the symplectic property of the monodromy matrix,

\[ \mathbf{M}(t)^{-1} = -\mathbf{J} \cdot \mathbf{M}(t) \cdot \mathbf{J} \]

(2.6b)

where the blocks of \( \mathbf{J} \) are

\[ J_{11} = J_{22} = 0, \quad J_{12} = -J_{21} = -1, \]

(2.6c)

gives the following useful expression:

\[ \frac{\partial(\mathbf{p}_2, \mathbf{q}_2)}{\partial(\mathbf{p}_1, \mathbf{q}_1)} = -\mathbf{M}(t_2) \cdot \mathbf{J} \cdot \mathbf{M}(t_1) \cdot \mathbf{J} \]

(2.6d)

See Appendix C for additional details. The following properties of the two-time pre-factor of Eq. (2.5b)—which we now denote as \( C(t_2, t_1) \)—its dependence on \((\mathbf{p}_0, \mathbf{q}_0)\) being implied—are apparent from its definition:

\[ C(t_2, t_1) = C(t_1, t_2)^*, \]

(2.7a)

\[ C(t, t) = 1, \quad \forall t, \]

(2.7b)

\[ C(t, 0) = C_{\text{HK}}(t), \]

(2.7c)

the latter quantity being the standard (i.e., “one-time”) HK pre-factor of Eq. (2.5a).

In summary, Eq. (2.4) gives the time averaged version of the spectral density, which we emphasize is completely equivalent to the original IVR expression [Eq. (1.2b) with Eq. (1.3a)]; for each initial phase point \((\mathbf{p}_0, \mathbf{q}_0)\) one must evaluate each classical trajectory and perform the two-time integrals as indicated. For comparison, the original (non-TA) expression involves only one time integral, but typically requires many more values of \((\mathbf{p}_0, \mathbf{q}_0)\) (i.e., trajectories) in order to converge the phase space average over these initial conditions.

A. The separable approximation

Equation (2.4) for the time averaged spectral density would be especially simple if the two-time pre-factor of Eqs. (2.5b) and (2.7a)–(2.7c) were separable, i.e., if

\[ C(t_2, t_1) = f(t_2)g(t_1). \]

(2.8a)

If so, then Eq. (2.7a) demands that

\[ g(t) \propto f(t)^*, \]

(2.8b)

and then Eq. (2.7b) requires that

\[ |f(t)|^2 = 1, \]

(2.8c)

so that the two-time pre-factor is of the form

\[ C(t_2, t_1) = e^{i\phi(t_2)/\hbar} e^{-i\phi(t_1)/\hbar} \]

(2.8d)

where \( \phi(t) = \phi_0(\mathbf{p}_0, \mathbf{q}_0) \) is real. It is not possible also to satisfy Eq. (2.7c) with this separable approximation, but one.
can come as close as possible by choosing the phase \( \phi_s(p_0, q_0) \) to be that of the standard HK pre-factor,
\[
\phi_s(p_0, q_0) = \text{phase}[C_s(p_0, q_0)].
\]  
(2.8e)

We note that if the system were harmonic, and the coherent state parameter \( \gamma \) chosen to be \( \gamma_k = m \omega_k \hbar \) for each mode \( k \), then the separable approximation, Eq. (2.8d), would in fact be exact, with \( \phi(t) = -\sum_{k=1}^{F} \hbar \omega_k t/2 \). With the separable approximation [Eq. (2.8d)] for the two-time pre-factor, and choosing the upper limit of the \( t_i \) integral to be \( T \), it is then easy to show that the expression for the time averaged spectral density [Eq. (2.4)] becomes that previewed in the Introduction, Eq. (1.8), with all the desirable features discussed here. The applications presented in Sec. III utilize this approximation.

**B. Eigenvector expansion of the two-time pre-factor**

One can improve the above separable approximation for the two-time pre-factor by thinking of it as a matrix, e.g., on an equally spaced time grid \( \{t_n\} \),
\[
C_{n,n'} = C(t_n, t_{n'}).
\]  
(2.9)

The property in Eq. (2.7a) shows it to be a Hermitian matrix [and Eq. (2.7b) shows that all its diagonal elements are unity], so that it can be expanded in terms of its eigenvectors (or eigenfunctions) \( \{f_j(t)\} \) and eigenvalues \( \{a_k\} \) as
\[
C(t, t') = \sum_{k=1}^{N} a_k f_k(t_2) f_k(t_1) \delta(t_2, t_1).
\]  
(2.10)

One now recognizes that the above separable approximation [Eq. (2.8d)] corresponds to retaining only one term in this sum, i.e., to assuming that only one eigenvalue is nonzero (i.e., that the matrix is of rank 1). The eigenfunctions are of course orthogonal and can be normalized,
\[
\sum_{n=1}^{N} \int f_k(t_n) f_k(t_1) \delta(t_2, t_1) \, dt = \delta_{k,k'},
\]  
(2.11)

and from Eq. (2.7b) one sees that the trace of the matrix is \( N \), which is equal to the sum of its eigenvalues,
\[
\text{tr}[C_{n,n'}] = \sum_{n=1}^{N} C(t_n, t_n) = \sum_{k=1}^{N} a_k = N.
\]  
(2.12a)

[One could equally well normalize the eigenvectors as follows:
\[
\sum_{n=1}^{N} \int f_k(t_n)^2 \, dt = N,
\]  
(2.12b)

and the eigenvalue sum would be unity,
\[
\sum_{n=1}^{N} a_k = 1;
\]  
(2.12c)

this normalization makes the connection to the separable approximation even more transparent.]

Using this eigenvector expansion for the two-time pre-factor in Eq. (2.4) thus gives the time averaged spectral density as
\[
I(E) = \langle \frac{2\pi \hbar}{2\pi \hbar} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \sum_{k=1}^{N} a_k \int_{0}^{T} dt (\chi(t) | \mathbf{p}, \mathbf{q}_0 \rangle f_k(t) e^{(i/\hbar)(E + S_i(p_0, q_0))} \rangle^2.
\]  
(2.13)

While this result is exact, it is more computationally demanding than the separable approximation (1.8) due to the diagonalization and summation that must be performed for every value of \( (p_0, q_0) \) (i.e., every trajectory) required in the Monte Carlo phase space average. In the following examples we show, however, that the summation over eigenvalues \( \{a_k\} \) can be dramatically reduced without significant loss of accuracy in the final result.

**III. NUMERICAL TESTS**

To see how well the time averaging procedure works, and in particular how well the separable approximation of Sec. II A performs, we apply it first to a one dimensional example, the nonrotating \( \text{H}_2 \) molecule (modeled as a Morse potential), and then to a polyatomic molecule, \( \text{H}_2\text{O} \). Atomic units \( (\hbar = 1) \) are assumed throughout the rest of the paper unless specified otherwise.

**A. \( \text{H}_2 \)**

A Morse potential form was used in the calculations for \( \text{H}_2 \), where the harmonic frequency was taken as \( \omega = 4401 \text{ cm}^{-1} \) and the bond energy as \( D_s = 38293 \text{ cm}^{-1} \). The reference state \( \chi \) was chosen to be a coherent state [cf. Eq. (1.3a)],
\[
\langle \chi | = | \bar{q} \rangle,
\]  
(3.1)

with \( \bar{q} = q_e \) being the equilibrium position, and \( \bar{p} = \sqrt{\alpha} \). The various coherent state overlaps in Eqs. (1.8), (2.4), or (2.13) are then given analytically,
\[
\langle \bar{p} \bar{q} | p q \rangle = e^{-\gamma/2} e^{-1/4(\gamma)(p-\bar{p})^2} e^{-1/2(p+\bar{p})(q-\bar{q})},
\]  
(3.2)

and here we use the harmonic choice for \( \gamma, \gamma = \omega \) (with mass-scaled coordinates). The Husimi distribution function,\(^{18}\)
\[
| \langle \chi | \rho_0 q_0 \rangle |^2 = | \langle \bar{p} \bar{q} | p_0 q_0 \rangle |^2 = e^{-\omega(2)(q_0-\bar{q})^2} e^{-1/2\omega}(p_0-\bar{p})^2,
\]  
(3.3)

was used for the Monte Carlo sampling function for the phase space average over \( (p_0, q_0) \). The trajectories were propagated for 244 fs \( (10^3 \text{ steps}, \Delta t = 10 \text{ a.u.}) \), and the time integrals are evaluated by quadrature on this Fourier grid.

Figure 1 shows the results for the time averaged spectral density with only 10 trajectories: panel (a) is from the exact time averaging expression, 2.4; panel (b) utilizes the eigenstate expansion of the two-time pre-factor, Eq. (2.13), but retaining only the one term with the largest eigenvalue, and panel (c) uses the separable approximation for the two-time pre-factor, formula (1.8). The three calculations yield essentially identical results for the peak positions, i.e., for the
energy levels \{E_i\}, differing only in the size of the spurious peaks (which diminish as the number of trajectories is increased).

Figure 2 provides a different perspective on the effect of time averaging: the results shown there are from the exact time-averaging spectral density expression, Eq. (2.4) (with the same 10 trajectories as in Fig. 1) for various values of \(T\), the length of the time average. Panel (a), with \(T\to 0\), corresponds to a standard HK-IVR calculation, i.e., no time averaging, and one sees the significant spurious oscillations typical of unconverged IVR calculations. The successive panels show the results obtained for progressively larger values of \(T\), i.e., more time averaging, showing how the spurious behavior is (partially) quenched even with only 10 trajectories.

Figure 3 shows the eigenvalues \(\{a_k/N\}\) of the two-time pre-factor matrix of Eq. (2.9) on the time grid \(\{t_n\}\), \(n = 1, \ldots, 1000\). One sees that only \(-3\) eigenvalues are effectively nonzero, meaning that one can obtain essentially exact TA results with only a few terms in Eq. (2.13). Figure 4 plots the eigenvector \(f_k(t_n)\) for the largest eigenvalue \(a_k\), showing that it is distributed along a unit circle in the complex plane, qualitatively similar to that suggested by the separable approximation [Eq. (2.8d)].

Finally, Fig. 5 shows the result given by the separable approximation (which was seen above to be a little different from the full TA results) that is converged with respect to the Monte Carlo average over \((p_0,q_0)\), i.e., the number of trajectories; 8000 trajectories were used. For comparison, the result is also shown with only one trajectory, the one with the initial condition \((p_0,q_0)\) having the most probable value of the Husimi distribution function [Eq. (3.3)], i.e., \(q_0 = \bar{q}\) and

FIG. 1. The spectral density for \(H_2\) calculated using ten trajectories for the phase space average, (a) exactly [Eq. (2.4)], (b) with the largest eigenvalue expansion [Eq. (2.13)], (c) with the separable approximation [Eq. (1.8)].

FIG. 2. Convergence of the spectral lineshape from Fig. 1(a) with the length of time averaging. \(T\) is 1, 10, 50, 100, 500, 1000 \(\Delta t\), while \(T\) is 1000 \(\Delta t\).

FIG. 3. Eigenvalues of the two-time pre-factor for \(H_2\) (for a single trajectory) on a 1000\(\times\)1000 time grid. One sees a well-defined positive eigenvalue, and a pair of smaller negative ones; the remainder of the eigenvalues are of the order of \(10^{-15}\).

FIG. 4. A plot of the (complex) eigenvector \(f_k\) corresponding to the largest eigenvalue of the two-time pre-factor of Fig. 3. Deviation from the unit circle signifies higher order corrections to anharmonicity embedded in the expression (2.13).
with \( \tilde{q}_j = q_{ej} \) (their equilibrium values) and \( \tilde{p}_j = \sqrt{\omega_j} \), for \( j = 1, 2, 3 \). We also wish, however, for the reference state to be of a specific symmetry of the molecular system: modes 1 and 2—the bending and symmetric stretch vibrations, respectively—are totally symmetric (\( a_1 \)) modes, but mode 3, the asymmetric stretch, is of \( b_2 \) symmetry. The reference state can be made to have + or − symmetry upon \( q_3 \rightarrow -q_3 \) by replacing the coherent state for mode 3 in Eq. (3.5) as follows:

\[
|\tilde{p}_3\tilde{q}_3\rangle \rightarrow \frac{1}{\sqrt{2}} (|\tilde{p}_3\tilde{q}_3\rangle + |\tilde{p}_3\tilde{q}_3\rangle); \tag{3.6}
\]

\( \epsilon = +1 \) or −1 gives a state of \( a_1 \) or \( b_2 \) symmetry, respectively. The final form we choose for the reference state is thus

\[
|\chi^\epsilon\rangle = \frac{1}{\sqrt{2}} (|\tilde{p}_1\tilde{q}_1\rangle|\tilde{p}_2\tilde{q}_2\rangle(|\tilde{p}_3\tilde{q}_3\rangle + |\tilde{p}_3\tilde{q}_3\rangle) \tag{3.7}
\]

As before, the sampling function used for the Monte Carlo average over \( \{p_0, q_0\} \) is the Husimi distribution function,

\[
\langle p_0 q_0 | \chi^\epsilon \rangle = \frac{1}{2} |\langle p_1^{(0)} q_1^{(0)} | \tilde{p}_1\tilde{q}_1 \rangle |^2 |\langle p_2^{(0)} q_2^{(0)} | \tilde{p}_2\tilde{q}_2 \rangle |^2
\]

\[
\times |\langle p_3^{(0)} q_3^{(0)} | \tilde{p}_3\tilde{q}_3 \rangle + \epsilon |\langle p_3^{(0)} q_3^{(0)} | -\tilde{p}_3\tilde{q}_3 \rangle |^2,
\tag{3.8}
\]

where \( q_0 = (q_1^{(0)}, q_2^{(0)}, q_3^{(0)}) \). In practice, however, the cross term that arises when squaring the third factor of Eq. (3.8) is very small and can be neglected, so that the sampling function becomes

\[
\langle p_0 q_0 | \chi^\epsilon \rangle = \frac{1}{2} |\langle p_1^{(0)} q_1^{(0)} | \tilde{p}_1\tilde{q}_1 \rangle |^2 |\langle p_2^{(0)} q_2^{(0)} | \tilde{p}_2\tilde{q}_2 \rangle |^2
\]

\[
\times |\langle p_3^{(0)} q_3^{(0)} | \tilde{p}_3\tilde{q}_3 \rangle |^2 + |\langle p_3^{(0)} q_3^{(0)} | -\tilde{p}_3\tilde{q}_3 \rangle |^2.
\tag{3.9}
\]

which is independent of \( \epsilon \). This means that calculations for both symmetries can be carried out with the same sampling function (and therefore simultaneously).

We use a rejection Monte Carlo algorithm\(^\text{22}\) combined with the Box–Muller method to select trajectories. Figure 6 shows the phase-space distribution along the antisymmetric mode for a converged calculation. The two closely overlapping Gaussians [Eq. (3.8)] can be clearly seen in the plot. The trajectories are propagated for 244 fs (1000 steps, \( \Delta t = 10 \text{ a.u.} \)), and a tight convergence (<1%) is reached with 32 000 trajectories.

Figure 7 shows the spectrum, the structure in which is well resolved up to 15 000 cm\(^{-1}\) as the bending progression is well separated from the stretching modes, and the symmetry allows for an easy distinction of the two stretches. The zero point energy along with the fundamentals are marked on the graph. We also applied the single trajectory approximation, \( \text{SC}^{(0)} \), propagating this trajectory for a much longer time, 2.44 ps (10\(^4\) steps), which gives much sharper lines. As before for the \( \text{H}_2 \) example, the \( \text{SC}^{(0)} \) gives excellent results for the ground state (i.e., zero point energy) and the fundamentals (i.e., the states with only one quantum of excitation

\[ p_0 = \tilde{p}; \] we refer to this “one trajectory approximation” as \( \text{SC}^{(0)} \). One sees in Fig. 5 that the \( \text{SC}^{(0)} \) result is reasonably good for the ground and first excited vibrational states, but the accuracy diminishes for higher overtones.

Table I summarizes the results for the four lowest vibrational levels of \( \text{H}_2 \). The one trajectory result, \( \text{SC}^{(0)} \), is seen to be better than the harmonic (HO) approximation, but not as accurate as the full semiclassical (SC) results for the higher vibrational states.

### B. \( \text{H}_2\text{O} \)

A polyatomic molecule, \( \text{H}_2\text{O} \), provides a more challenging test of the time averaged SC-IVR approach. We use a well studied potential energy surface for which exact QM results have been reported.\(^\text{10}\) We also use a standard normal mode vibrational Hamiltonian that ignores vibration-rotation coupling.\(^\text{20,21}\) The \( 3N - 6 = 3 \) normal mode coordinates are mass-weighted in the usual way, so the Hamiltonian is of Cartesian form,

\[
H(p, q) = \frac{1}{2} p^2 + \frac{1}{2} q^T D q + \Delta V(q), \tag{3.4}
\]

where \( D \) is the Hessian matrix in the normal modes, and \( \Delta V(q) \) contains the higher order terms of the full Taylor series. For a harmonic system \( \Delta V(q) = 0 \).

As before, we choose the reference state \( \chi \) to be a coherent state,

\[
|\chi\rangle = |pq\rangle = |\tilde{p}_1\tilde{q}_1\rangle|\tilde{p}_2\tilde{q}_2\rangle|\tilde{p}_3\tilde{q}_3\rangle, \tag{3.5}
\]

### Table I. The low vibrational levels of the Morse oscillator \( \text{H}_2 \).

<table>
<thead>
<tr>
<th>State</th>
<th>HO</th>
<th>\text{SC}^{(0)}</th>
<th>SC</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v = 0 )</td>
<td>2201</td>
<td>2168</td>
<td>2177</td>
<td>2169</td>
</tr>
<tr>
<td>( v = 1 )</td>
<td>6602</td>
<td>6441</td>
<td>6348</td>
<td>6317</td>
</tr>
<tr>
<td>( v = 2 )</td>
<td>11003</td>
<td>10714</td>
<td>10252</td>
<td>10212</td>
</tr>
<tr>
<td>( v = 3 )</td>
<td>15404</td>
<td>14985</td>
<td>13876</td>
<td>13854</td>
</tr>
</tbody>
</table>

\[ (0) \]
in one of the modes). And even for the overtones and combination levels it is much better than the harmonic approximation; see Table II which lists the energy levels that we were unambiguously able to assign, comparing the exact quantum results to the harmonic (HO), \(SC^{(0)}\), and Monte Carlo converged (SC) results. The \(SC^{(0)}\) approximation is thus a very inexpensive way of obtaining a rough approximation for excited vibrational levels, and it is a significant improvement over the simple harmonic approximation.

**IV. CONCLUDING REMARKS**

In summary, therefore, the procedure described in Sec. II, of time-averaging the integrand of the IVR phase space average over initial conditions, dramatically reduces the number of initial conditions that must be sampled (and thus the number of trajectories that must be computed) in the Monte Carlo evaluation of the phase space average. This simplification is most apparent if one also makes a separable approximation for the two-time HK pre-factor (as described in Sec. II A), whereby the integrand of the phase space average becomes positive definite [cf. Eq. (1.8)]. Quite useful results for the spectral density, for example, can be obtained with only one classical trajectory, i.e., one set of initial conditions for the phase space average; the one-trajectory results for the ground state and fundamental excitations were seen (in the examples presented in Sec. III) to be quite good, and even for higher excited states the one-trajectory results were significantly better than the simple harmonic energy levels (but not as good as the results obtained if one carries out the phase space average fully).

Another bonus of the separable approximation for the two-time pre-factor is that it avoids problems related to the exponential growth of the magnitude of the HK pre-factor for a long time (since the separable approximation requires only the phase of the pre-factor). And finally, the separable approximation can be systematically improved by using the eigenstate expansion of the two-time pre-factor as described in Sec. II B.

We thus feel that this time averaged version of the SC-IVR goes a long way toward making such calculations practical for molecular systems of an interesting size. Within the one-trajectory approximation it would certainly be possible, for example, to implement an “on the fly” evaluation of the potential energy surface, as has recently become very popular.

**ACKNOWLEDGMENTS**

One of the authors (W.H.M.) would like to thank Professor David Chandler for some very helpful discussions sev-
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APPENDIX A: EQUATIONS OF MOTION

The equations of motion required to propagate the classical trajectory are given below. The coordinates and momenta are mass scaled. The gradient vector is needed to evaluate the positions and momenta,

\[ \dot{p}_i = -\frac{\partial V(q_i)}{\partial q_i}, \]

(A1a)

\[ \dot{q}_i = p_i. \]  

(A1b)

The action is a time integral of the Lagrangian and is readily calculated,

\[ S_i = \int_0^t dt \left( \frac{p_i^2}{2} - V(q_i) \right), \]

(A1c)

\[ \dot{S}_i = \frac{p_i^2}{2} - V(q_i). \]

(A1d)

The elements of the Jacobian matrix [Eq. (2.6a)] are the most difficult to calculate since they require the Hessian matrix at every time step. Differentiating Eqs. (A1a) and (A1b) with respect to \( p_0 \) and \( q_0 \) yields the following set of equations:

\[ \frac{d}{dt} \frac{\partial p_i}{\partial p_0} = -\frac{\partial^2 V(q_i)}{\partial q_i \partial q_0} \frac{\partial q_i}{\partial p_0}, \]  

(A1e)

\[ \frac{d}{dt} \frac{\partial q_i}{\partial q_0} = \frac{\partial p_i}{\partial q_0}, \]  

(A1f)

\[ \frac{d}{dt} \frac{\partial p_i}{\partial q_0} = -\frac{\partial^2 V(q_i)}{\partial q_i \partial q_0} \frac{\partial q_i}{\partial q_0}, \]  

(A1g)

\[ \frac{d}{dt} \frac{\partial q_i}{\partial p_0} = \frac{\partial p_i}{\partial p_0}. \]  

(A1h)

Various integrators can be used for the above equations of motion. We have experimented with both the Runge–Kutta formula and the symplectic algorithm. It may be advantageous to use the latter method due to its natural ability to preserve the symplectic symmetry of the Jacobian.

For the applications discussed in this paper, both the gradient and the Hessian were evaluated numerically, by finite differences. For expensive potentials and in \textit{ab initio} direct dynamics we advise the user to have analytical forms for both the gradient and the Hessian.

APPENDIX B: PREFACTOR

An evaluation of the Herman–Kluk pre-factor, Eq. (2.5b), requires taking the square root of a complex number,

\[ C(t,t') = \sqrt{C(t,t')}^2. \]

(B1)

Care needs to be taken in order to preserve the continuity of the pre-factor in the complex plane. Normally, a very small time step is used to keep track of the branch cuts in the complex plane, but as the dimension of the system grows, the task becomes increasingly difficult. One way to see the problem with keeping track of the phase of the pre-factor is to refer to a system of harmonic oscillators for which the pre-factor is known analytically,

\[ C(t,t') = \exp \left[ -i \sum_j \frac{\omega_j}{2} (t-t') \right], \]

(B2)

where \( \omega_j \) is used for the coherent state width \( \gamma_j \). The phase acquires higher oscillations with each additional bound degree of freedom with real frequency. Wang et al. showed that a simple way to control the rate is to evaluate the square root \textit{after} factoring out the harmonic contribution. We use the following equivalence in calculating the pre-factor:

\[ C(t,t') = \exp \left[ -i \sum_j \frac{\omega_j}{2} (t-t') \right] \times \sqrt{\exp \left[ i \sum_j \omega_j (t-t') C(t,t') \right]^2}. \]

(B3)

The quantity in the square root is now much less oscillatory due to the “removal” of the harmonic contribution, regardless of the size of the system. In fact, the minimal time step required to track the phase can be the same as the propagation step and is independent of the total energy of the system.

APPENDIX C: STABILITY CRITERIA

Each trajectory in the Monte Carlo ensemble is checked for stability at every time step. The stability (or goodness) of a trajectory is purely a numerical property which comes from using a finite time step \( \Delta t \) in the propagation. In MD simulations the stability is simply the conservation of the constants of motion, such as the total energy and the angular momentum and its components. In the semiclassical Herman–Kluk calculations one also needs to maintain the symplectic symmetry of the Jacobian appearing in Eqs. (2.5a), (2.5b), (2.6a), and (2.6d). The stability matrix (monodromy matrix) for a one-time pre-factor is usually defined as follows:

\[ M_{11} = M_{pp} = \langle \partial p_i / \partial p_0 \rangle \]  

\[ M_{12} = M_{pq} = \langle \partial p_i / \partial q_0 \rangle \]  

\[ M_{21} = M_{qp} = \langle \partial q_i / \partial p_0 \rangle \]  

\[ M_{22} = M_{qq} = \langle \partial q_i / \partial q_0 \rangle, \]  

(C1a)

(C1b)

(C1c)

(C1d)

and we remind that the symplectic property [Eq. (2.6b)] is written as

\[ M(t) = -J \cdot M(t) \cdot J. \]  

(C2a)

\[ J_{11} = J_{22} = 0, \quad J_{12} = -J_{21} = -1. \]  

(C2b)

As a corollary, the determinant of \( M \) is unity, for all times \( t \),

\[ |M| = 1, \quad \forall t. \]  

(C3)

The most primitive way to establish whether or not the trajectory is stable is simply to enforce Eq. (C3). A more rigorous procedure was outlined by Wang et al. and involves the construction of the positive definite matrix \( D = M^T M \). It can
be shown that (a) the eigenvalues of $\mathbf{D}$ are non-negative and (b) $\mathbf{D}$ satisfies Eq. (C3). In the calculations of water we enforce both of the above criteria with a very low tolerance, e.g., $10^{-6}$ for part (b). As a result, $\approx 5\%$ of the trajectories were discarded, typically after 100 fs. All the discarded trajectories failed criterion (b) and passed criterion (a).

5. If $|\chi\rangle$ were chosen to be $\mu(q)|\Psi_g\rangle$, where $\mu$ is the dipole moment function of the molecule and $|\Psi_g\rangle$ the ground vibrational state, then $I(E)$ would be the 0 K infrared absorption spectrum, with $E = E_g + h\omega$, $E_g$ being the ground state energy. In this paper, however, we take $|\chi\rangle$ to be an arbitrary reference state and focus only on identifying the peaks in $I(E)$, i.e., the vibrational energy levels $\{E_i\}$.