Semiclassical description of vibrational quantum coherence in a three dimensional I₂Arₙ (n ≤ 6) cluster: A forward-backward initial value representation implementation

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The semiclassical (SC) initial value representation (IVR) has been applied to describe true quantum coherence effects in a complex molecular system in full three dimensional space. The specific quantity considered is the time-dependent probability distribution of the I₂ vibrational coordinate following photoexcitation of I₂ in a rare gas cluster. The “forward-backward” version of the IVR method is shown to be capable of capturing detailed quantum coherence in this quantity, coherence that cannot be described by a classical Wigner model (which is equivalent to a linearized approximation to the more general SC-IVR). Solvent effects on this vibrational quantum coherence have also been investigated for a I₂Arₙ (n = 1, 6) cluster. A solvent cage consisting of six argon atoms reduces the fraction of iodine molecules that dissociate (an example of the “cage effect”) and also diminishes, but does not entirely eliminate, quantum coherence in the vibrational motion of the molecules that remain undissociated. © 2009 American Institute of Physics.

I. INTRODUCTION

Quantum effects in chemical molecular dynamics can sometimes be crucial to understanding chemical, or more complicated biological processes at the molecular level.\(^\text{1,2}\) Widely used molecular dynamics simulations, although a powerful tool, are purely classical and can thus not provide information about quantum effects that may exist in the dynamics. Even though, in many cases, quantum effects may be negligible and a classical treatment quite sufficient, one can never be sure of this without at least some approximate treatment of the quantum effects. (It is clear that a complete treatment of the quantum mechanics of complex molecular systems is in general not feasible.) Various mixed quantum-classical treatments\(^\text{3}\) are one class of such approximate approaches, whereby a small number of degrees of freedom are treated quantum mechanically and all others purely classically, with some approximation used to couple the quantum and classical degrees of freedom. Mixed quantum-classical approaches have been widely applied to many problems and provided useful insight, though the inconsistency of treating different degrees of freedom differently can sometimes cause unphysical behavior. Another strategy, which we and others have been pursuing, is to treat all degrees of freedom semiclassically\(^\text{4–6}\) and thus on the same footing. There is ample evidence that this provides an excellent description of the quantum effects in essentially all aspects of molecular dynamics, the only problem being that heretofore it has been more difficult to apply these semiclassical (SC) approaches than most mixed quantum-classical ones. The purpose of this paper is to demonstrate the progress that has been made in implementing SC theory, and how it describes quantum behavior that is present in the dynamics of real molecular systems.

The starting point for applying SC theory to molecular systems with many degrees of freedom is some type of “initial value representation” (IVR), which converts the nonlinear boundary value problem of traditional SC theory into an integral over the phase space of initial conditions of classical trajectories. (IVRs were initially used\(^\text{7}\) in the early 1970s to treat “classically forbidden” processes.) Monte Carlo sampling methods are used to carry out these phase space averages, so that an SC calculation can be cast in a form very similar to a classical MD simulation. Various SC-IVR methods have been formalized and applied to a number of interesting problems.\(^\text{8–21}\) So far, the most powerful version of SC-IVR methods that is capable of describing true quantum coherence phenomena in molecular systems with many degrees of freedom is the forward-backward (FB) version of the IVR.\(^\text{22}\) This is an approximate way\(^\text{23}\) of combining the forward and backward time propagators in the Heisenberg time evolution that appears in a typical time correlation function (see below) so that extraneous oscillatory parts of the phase space averages that are involved are eliminated analytically, and only the relevant coherence features retained in the numerical simulation. Recent applications of the FB-IVR have demonstrated that this method is indeed capable of providing a good description of true quantum coherence/interference effects in molecular dynamics.\(^\text{17,22,24–27}\)

The FB-IVR methodology has previously been shown to accurately describe the coherence structure (and its quenching) of a 1d vibrational coordinate bilinearly coupled with up
to 40 harmonic bath modes. Real molecular dynamics, of course, occurs in 3d space, and the solute-solvent interactions in liquids are highly nonlinear. Furthermore, the successful implementation of semiclassical IVR techniques for multidimensional systems is challenged by the complications in the accuracy and convergence caused by chaotic trajectories. In this work, we show the FB-IVR method to be robust in a realistic application to a realistic three dimensional system consisting of up to 24 degrees of freedom, without any special treatment for chaotic trajectories. Specifically, we use the FB-IVR method to study quantum coherence effects in the time-dependent probability distribution of a diatomic molecule—i.e., real time molecular structure—and the extent of decoherence due to its coupling with a solvent cluster. An overview of the FB-IVR approach is first presented in Sec. II, and Sec. III describes the details of the model system that we treat. The results are presented in Sec. IV, and Sec. V concludes.

II. SUMMARY OF THEORY

Most dynamical quantities of interest in complex molecular systems can be expressed in terms of a time correlation function of the general form

\[
C_i(p_0, q_0) = \sqrt{\det \left[ \frac{1}{2} \left( \gamma^{1/2} \frac{\partial q_i}{\partial q_0} \gamma^{-1/2} + \gamma^{-1/2} \frac{\partial p_i}{\partial p_0} \gamma^{1/2} - i \hbar \gamma^{1/2} \frac{\partial q_i}{\partial p_0} \gamma^{-1/2} + \frac{\partial q_i}{\partial q_0} \gamma^{-1/2} \right) \right]}.
\]

The wave function for the \(N\)-dimensional coherent state \((p, q)\) is a product of \(N\) one-dimensional minimum uncertainty (frozen Gaussian) wave packets

\[
\langle x | pq \rangle = \prod_{i=1}^{N} \left( \frac{\gamma_i}{\pi} \right)^{1/4} e^{-\left( \gamma_i/2 \right) (x_i - \xi_i)^2 + i (\hat{H} \xi_i)}.
\]

where \(\gamma_i\) is a parameter chosen for convenience which characterizes the localization of the coherent state in either momentum or coordinate space.

Using the SC-IVR, Eq. (2.2), for the two propagators that appear in Eq. (2.1) thus gives the time correlation function as a phase space average over two sets of initial conditions of classical trajectories,

\[
C_{AB}(t) = (2 \pi \hbar)^{-N} \int dq_0 dp_0 \int dq'_0 dp'_0 C_i(p_0, q_0) C_i(p'_0, q'_0)^* \times e^{i [S(p, q) - S(p', q')] / \hbar} \langle p_0, q_0 | \hat{A} | p'_0, q'_0 \rangle \langle p'_0, q'_0 | \hat{B} | p, q \rangle.
\]

Because of the high dimensionality for systems with many degrees of freedom, it is necessary to use Monte Carlo methods to evaluate this double phase space integral, but the phase of the integrand (the difference of the action integrals for the two trajectories) makes this extremely inefficient. The most drastic approximation for dealing with this “phase problem” is to assume that the only significant contribution to the integral is from phase space points \((p_0, q_0)\) and \((p'_0, q'_0)\) (and thus trajectories) that are infinitesimally close to one another, so that one can linearize all relevant quantities in the integrand to first order in the difference variables \((p_0 - p'_0)\) and \((q_0 - q'_0)\). This linearized approximation to the SC-IVR, or LSC-IVR, yields a classical-like expression of the correlation function,

\[
C_{AB}(t) = (2 \pi \hbar)^{-N} \int dq_0 dp_0 A_w(p_0, q_0) B_w(p, q),
\]

where \(A_w\) and \(B_w\) are the Wigner functions of the corresponding operators. The Wigner function for any operator \(\hat{O}\) is defined by

\[
C_{AB}(t) = \text{tr} \left[ \hat{A} e^{i \hat{H} t / \hbar} \hat{B} e^{-i \hat{H} t / \hbar} \right]
\]
The LSC-IVR has been applied to a number of interesting problems and is able to describe some quantum effects quite successfully.\textsuperscript{31-33} However, it cannot describe true quantum coherence effects since these typically arise from two trajectories in Eq. (2.5) that are not infinitesimally close to one another.

A more accurate semiclassical method is thus necessary when coherence effects are important, and the FB IVR (Ref. 22) has emerged as the simplest version of the IVR that is able to capture true coherent effects, while being much more efficient than the full SC-IVR treatment. The idea\textsuperscript{23} is to combine the forward and backward operators, $e^{-i\hbar/\hbar}$ and $e^{i\hbar/\hbar}$, into one overall semiclassical propagator—from time 0 to $t$, and from $t$ back to 0—by making a SC approximation also at time $t$.\textsuperscript{34} In so doing, much of the extraneous oscillatory character in the double phase space average, Eq. (2.5), is eliminated analytically, rather than it having to be canceled out numerically. The FB-IVR result is most easily illustrated for the case that operator $\hat{B}$ is a local function of a single collective variable $s(q)$, which as indicated may be a function of all the coordinates $q$ (typically Cartesian) of the system. Writing operator $\hat{B}$ as a (1d) Fourier integral,

$$\hat{B} = B[s(q)] = \int_{-\infty}^{\infty} dp \tilde{B}(p)e^{ip\cdot s(q)/\hbar},$$  \hspace{1cm} (2.8a)

where

$$\tilde{B}(p) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} ds e^{-ip\cdot s(q)/\hbar} B(s),$$ \hspace{1cm} (2.8b)

the correlation function of Eq. (2.1) becomes

$$C_{AB}(t) = \int_{-\infty}^{\infty} dp \tilde{B}(p)tr[\hat{A}\hat{U}(t)],$$ \hspace{1cm} (2.9a)

where

$$C_{AB}(p_0, q_0, p_0', q_0') = \sqrt{\det\left[\begin{array}{cc} \gamma_0' & \gamma_0'' \\ \gamma'_{00} & \gamma''_{00} \end{array}\right]}. \hspace{1cm} (2.10d)$$

The FB-IVR result for the correlation function thus involves a single phase space average over initial conditions—the same as for a classical MD simulation—although over these more complicated FB trajectories, plus a one parameter integral over the Fourier transform variable $p$, which is related to the momentum “jump” at time $t$. This seems to be the most modest step up the “ladder of rigor” of SC-IVR methodology that is able to describe true quantum coherence phenomena.

III. DETAILS IN THE CALCULATION

We apply the FB-IVR method to investigate quantum coherence and decoherence in a three dimensional system.
consisting of an iodine molecule in an argon cluster. The initial
state of the iodine is assumed to be prepared by photo-
excitation from its ground state to an electronic excited
state, and we calculate the probability distribution of the I2
coordinate (i.e., the diatomic radius \( r \)) at various times \( t \) later,
\( P_r(r) \). In this case operator \( \hat{A} \) in Eq. (2.10a) is a projection
operator for the initial state, and operator \( \hat{B} \) is a local
function, i.e., \( B(s(q)) = \alpha(r - s(q)) \), so the FB-IVR expression for
\( P_r(r) \) becomes

\[
P_r(r) = \frac{1}{2\pi\hbar} \int \int \int d\mathbf{p}_0 d\mathbf{p}_0 \left| \right\rangle \langle \mathbf{p}_0 | \hat{C} \left( \mathbf{p}_0, q_0 ; p_r \right) \left\rangle \langle \mathbf{p}_0 \right| \left. \int d\mathbf{q}_0 d\mathbf{q}_0 \left| \right\rangle \langle \mathbf{q}_0 | \hat{C} \left( \mathbf{p}_0, q_0 ; p_r \right) \left\rangle \langle \mathbf{q}_0 \right| \right. \times e^{i\delta(s_0)\hat{P}_0\hat{q}_0} \langle \Psi_0 (q_0, \Phi_0) | \Psi_0 (q_0, \Phi_0) \hat{p}_r \hat{g}_0 \rangle,
\]

(3.1)

where \( \Phi_0 \) and \( \Psi_0 \) are the initial states of the diatomic
solute and of the bath cluster, respectively. The projection of
the initial state onto the \( N \)-dimensional coherent state is
straightforward:

\[
\langle p_0, q_0 | \Psi, \Phi_0 \rangle \langle \Psi, \Phi_0 | p_r, q_r \rangle = \left\langle p_0, q_0 | \Phi_0 \right\rangle \left\langle \Phi_0 | p_r, q_r \right\rangle \prod_{j=1}^{N_B} \left\langle P_j Q_j | \Psi_0 \right\rangle \left\langle \Psi_0 | P_j Q_j \right\rangle.
\]

(3.2)

Since the initial states \( \Phi_0 \) and \( \Psi_0 \) are chosen also to be
cohesent states, the overlap integrals in Eq. (3.2) are elemen-
tary: for the solvent Ar atoms, they are simple Gaussians in
the Cartesian variables

\[
\langle p_j Q_j | \Psi_0 \rangle = e^{-0.5\gamma_j/\gamma_j (Q_j - R_j)^2} e^{-0.5\gamma_j/\gamma_j (P_j - R_j)^2} \hbar^2,
\]

(3.3)

where \( R_j \) and \( P_j \) are the initial position and momentum of the
\( j \)th argon solvent, respectively, and \( \gamma_j \) and \( \gamma_j \) are corre-
sponding coherent state parameters. For the I2 molecule, the
ground state vibrational wave function is a Gaussian (and thus a coherent state)

\[
\langle r | \Phi_0 \rangle = \left( \frac{\gamma_0}{\pi} \right)^{1/4} \frac{1}{r} e^{-\gamma_0/2(r - R_0)^2},
\]

(3.4a)

where \( R_0 = 2.6663 \) Å is the equilibrium bond length of I2 in
the ground state. Equation (3.4a) is normalized in three di-

(3.4b)

mensional space, i.e.,

\[
\int_0^\infty r^2 dr |\Phi_0 (r)|^2 = 1.
\]

For the translational degrees of freedom of iodine molecule,
coherent states are chosen as the same form as that in Eq.
(3.3).

The weight function used for the Monte Carlo evalua-
tion\(^{35}\) of the phase space integral over initial condi-
tions takes the form

\[
\langle p_0, q_0 | \Psi, \Phi_0 \rangle \left\langle \Psi, \Phi_0 | p_0, q_0 \right\rangle = \left\langle p_0, q_0 | \Phi_0 \right\rangle \left\langle \Phi_0 | p_0, q_0 \right\rangle \prod_{j=1}^{N_B} \left\langle P_j Q_j | \Psi_0 \right\rangle \left\langle \Psi_0 | P_j Q_j \right\rangle.
\]

(3.5)

The projection of the initial state wave function onto the
coherent state \( \langle \Phi_0 | p_0, q_0 \rangle \) is calculated numerically by insert-

\begin{table}
\centering
\caption{Parameters for the Morse potential. \cite{36} [Atomic interactions for ex-
cited state of iodine molecule and for I–Ar, used in Eq. (3.6a) taken from Ref. 36].}
\begin{tabular}{ccc}
\hline
\textbf{D}_{ab} (cm⁻¹) & \textbf{R}_{ab} (Å) & \textbf{α}_{ab} (Å⁻¹) \\
\hline
I–I & 4600.2 & 3.0139 & 1.811 \\
I–Ar & 122 & 4.2000 & 1.323 \\
\hline
\end{tabular}
\end{table}

ing a complete set \( \{ \delta(x) \} \) and by using Eq. (2.4), Eq.
(3.4a) and a necessary transformation between Cartesian co-
ordinate and Spherical coordinate. For a typical calculation of
\( P_r(r) \), 50 000 trial moves are used in the Monte Carlo
evaluation, and the acceptance ratio is in the range of 30%–
50%.

The potential energy function is taken to be a sum of
pairwise interactions between all the atoms: that between the
two I atoms (for an electronically excited state of I2) and
between an I atom and an argon atom, are Morse poten-
tials

\[
V_{a,b} = D_{ab}(e^{-2α_{ab}(r_{ab} - R_{ab})} - 2e^{-α_{ab}(r_{ab} - R_{ab})}),
\]

(3.6a)

where \( a \) and \( b \) are either both I atoms, or one I atom and one
Ar atom. The potential parameters are given in Table I. The interactions
between two solvent argon atoms is a Lennard-
Jones (LJ) potential

\[
V_{LJ} = 4σ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}.
\]

(3.6b)

We use conventional LJ parameters\(^{35}\) for argon, namely,
\( ε/k_B = 119.8 \) K and \( σ = 3.405 \) Å. The classical trajectory is
propagated by an accurate symplectic integrator proposed by
Brewer et al.\(^{15}\)

\section*{IV. RESULTS AND DISCUSSIONS}

To verify the accuracy of the FB-IVR method, we first
reproduce the time-dependent probability distribution of a
one-dimensional Morse oscillator. The parameters and initial
conditions are taken from Ref. 26. Briefly, the initial coher-
ent state with an average position at 2.4 Å and zero average
momentum is prepared on a Morse potential with an equili-
rium position at 2.6663 Å, which corresponds to the ground
state of I2. The harmonic vibrational period of ground state is
about 156 fs. Figure 2 compares the probability distributions
calculated by the FB-IVR method to the exact quantum re-
sult \cite{37,38} at two different times (196 and 640 fs).
The FB-IVR is shown to be able to capture essentially all
detailed coherence structure, even at a relatively long time.

We now consider the time-dependent probability distribu-
tions for a three dimensional version of the I2 system,
calculated by the FB-IVR method. The initial vibrational
state of I2 is the ground state wave function of the ground
electronic state, which is centered at 2.666 Å. At time \( t=0 \)
the molecule undergoes a Franck–Condon excitation which
promotes this wave function to the excited electronic state on
which the dynamics then ensues. (The equilibrium position
of the excited state is 3.014 Å, with a corresponding har-
monic vibrational period of 276 fs.) The probability distribu-

\begin{table}
\centering
\caption{Parameters for the Morse potential. \cite{36} [Atomic interactions for ex-
cited state of iodine molecule and for I–Ar, used in Eq. (3.6a) taken from Ref. 36].}
\begin{tabular}{ccc}
\hline
\textbf{D}_{ab} (cm⁻¹) & \textbf{R}_{ab} (Å) & \textbf{α}_{ab} (Å⁻¹) \\
\hline
I–I & 4600.2 & 3.0139 & 1.811 \\
I–Ar & 122 & 4.2000 & 1.323 \\
\hline
\end{tabular}
\end{table}
The time-dependent probability distribution of the I$_2$ coordinate in the excited electronic state is then calculated from various times $t$ after the excitation.

Figure 3 first shows results for a free iodine molecule at times 88, 176, 265, and 352 fs after the initial excitation. For short times the probability distribution shows dispersion while keeping a Gaussian shape, with the coherence structure building up after a time corresponding to one vibrational period. The FB-IVR result describes the detailed coherence structure for small $r$, i.e., in the bounded region of the molecule, and also shows the existence of dissociation of the molecule for large $r$. Not surprisingly, a simple linearized SC (LSC) approximation is not capable of providing meaningful information about the quantum coherence structure. Figure 4 shows the comparison between the FB-IVR and LSC-IVR methods for the probability distribution at $t=352$ fs.

An even more complex coherence structure emerges at longer times, as shown in Fig. 5, and again the FB-IVR does an excellent job in describing it, while the LSC-IVR cannot. Interestingly, even for times up to $t \approx 700$ fs in the current system, we encounter no problems with chaotic trajectories, as is sometimes the case in IVR calculations. The lack of any difficulties with chaotic trajectories—and the common practice of having to discard them—may be due to the cancellation between forward and backward trajectories, and this could be another advantage of the FB-IVR approach. Further investigation would be helpful to clarify these issues regarding the treatment of chaotic trajectories.

To investigate solvent effects on quantum coherence in the time-dependent probability distribution, we introduce argon atoms as a rare gas matrix about the I$_2$ molecule. Figure 6 shows the results with one and six argon atoms as the “solvent,” at time $t=352$ fs after excitation. One still sees coherent structure in the I$_2$ probability distribution at small distances, as well as some probability at large distances due to dissociation. With only a single argon atom clustered with I$_2$, the probability distribution function changes little, except for slightly more population in the coherent region and less in the large $r$ region due to dissociation. With 6 argon atoms as solvent, however, the results are quite different from that of a free I$_2$ molecule: the most striking feature in $P(r)$ for the I$_2$Ar$_6$ cluster system is the steep drop in the probability distribution around $r=3.2$ Å, i.e., much less dissociation.
is an indication of a dynamical solvent cage around the iodine molecule. Interestingly, the solvent cage significantly reduces dissociation while still preserving coherence of the vibrational motion of the bound I$_2$; this was unexpected. In comparing the coherence structure in the free and solvated I$_2$, however, we do note a shift in the phase of the coherence oscillations caused by interaction with the solvent cage. A more comprehensive study of these solvent effects on quantum coherence with progressively larger clusters would obviously be quite interesting.

V. CONCLUDING REMARKS

We have applied the FB version of the SC-IVR method to study quantum coherence of vibrational motion of iodine molecule in a small argon cluster. The specific quantity considered is the probability distribution of the I$_2$ distance following a Franck–Condon excitation of the molecule. The FB-IVR is shown to be able to describe detailed coherence structure in this model of a “real” molecular system, here with up to 24 degrees of freedom, i.e., one iodine molecule and six argon atoms, and the methodology can readily be extended to larger systems. Interesting solvent effects on the coherence structure are revealed even for this still small system: a solvent cage of six argon atoms in this study causes a significant decrease in dissociation of the I$_2$ molecule, while still preserving quantum coherence (although with a phase shift) in short range corresponding to the bound molecule.

The difficulty of applying SC-IVR methods for calculating time correlation functions of complex molecular systems due to the oscillatory integrand in the phase space average is thus seen to be largely, if not completely, solved by the FB-IVR approach. This is because the FB approach combines the forward and backward propagators in the correlation function into one overall FB propagator, and the self-cancellation in the forward and backward propagation is accomplished analytically rather than numerically. A further bonus of this FB combination is that it also minimizes the classical chaotic behavior in the pre-exponential factor, which is a function of monodromy matrix elements. The successful application of the FB-IVR method in this work demonstrates that it can be implemented for describing true quantum effects in the dynamics of real molecular systems.

Although much effort is still being expended in trying to reduce the computational cost of applying the FB-IVR approach to more complex molecular systems, even at the present stage it can be applied to investigate interesting dynamical processes in realistic models of complex molecular systems, such as solvation dynamics in a liquid environment, and hydrogen transfer in a molecular complex.

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