Chapter N

The Initial Value Representation of Semiclassical Theory: A Practical Way for Adding Quantum Effects to Classical Molecular Dynamics Simulations of Complex Molecular Systems

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It has been known since the 1970's how one can *in principle* use classical molecular dynamics (i.e., numerically computed classical trajectories) as input to a semiclassical (SC) theory that provides a good description of all quantum mechanical effects in the dynamics of molecular systems. Over the last decade, various initial value representations of SC theory have been shown to provide a *practical* way for implementing these SC approaches for large molecular systems, those of interest for applications in bio-molecular and molecular-materials areas.

1. Introduction

With so many exciting things happening nowadays in the bio-molecular and molecular-materials areas, there is a clear need for theoretical calculations to model these large, complex molecular systems, to aid in the interpretation of these phenomena and to carry out exploratory

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calculations to suggest new directions for experimental studies. The only generally available approach heretofore for treating the dynamics of such large systems is classical molecular dynamics (MD), i.e., classical trajectory simulations, but this of course precludes the possibility of describing any of the quantum mechanical aspects of the molecular dynamics. Though for many purposes quantum effects will be unimportant, there is no doubt that they will be significant in some situations, most obviously when the dynamics of hydrogen atom motion is a significant part of the process of interest. Furthermore, unless ones theoretical treatment is able to incorporate quantum effects, even approximately, one will not know whether they are important or not.

It has been known since the earliest days of quantum mechanics that semiclassical approximations, such as the WKB approximation,[1,2] describe quantum effects in molecules quite well, but the WKB approach relies on an analytic solution of the corresponding classical problem, which is in general available only for systems of one degree of freedom (e.g., a diatomic molecule). In the late 1960's and early 1970's, however, it was shown[3-5] how such approaches could be generalized to use *numerically computed* classical trajectories of multidimensional systems as input to a general semiclassical (SC) description of molecular dynamics. Applications[5] of this 'classical S-matrix' theory to treat inelastic and reactive scattering of small molecular systems, e.g., A + BC → AB + C, demonstrated that in fact *all* quantum effects—interference/coherence, tunneling (and all other types of 'classically forbidden' processes), symmetry based selection rules, etc. — are correctly described by this type of semiclassical theory, at least qualitatively, and typically quite quantitatively. In the late 1970's it was furthermore shown[6,7] how electronically non-adiabatic processes can be incorporated within this framework.

So it has been known for some time how one can *in principle* use numerically computed classical trajectories as input to a SC theory for general molecular systems, and that such a treatment provides a good description of essentially all quantum effects in molecular dynamics to a very useful level of accuracy. The way that numerically computed trajectories are used in SC theory, however, is more complicated than the way they are used in ordinary classical mechanics. Thus what has been lacking is a practical way for implementing SC theory for large

molecular systems, and it is in this regard that various initial value representations (IVRs) of SC theory[3b] have emerged[8-14] as providing a starting point for these purposes.

I have reviewed SC-IVR approaches[15] for adding quantum effects to classical MD simulations several times in recent years, so my survey below will be brief. There are several features of SC-IVR calculations that make them more difficult than the corresponding classical MD calculation, but these difficulties have now been largely overcome, as will be discussed below. The main point I would like to make is that SC-IVR calculations are now not extraordinarily more difficult than the corresponding classical MD calculation. My 'goal' is to convince the classical MD simulation community of this, so that they can bring to bear on SC-IVR calculations all of the computational expertise that has been accumulated in MD and Monte Carlo methodology over several decades.

2. SC-IVR Calculation of Time Correlation Functions

Since most quantities of interest in the dynamics of complex systems can be expressed in terms of time correlation functions[16] of the form

$$C_{AB}(t) = tr[\, e^{-\beta\hat{H}/2}\hat{A}\, e^{-\beta\hat{H}/2}\, e^{i\hat{H}t/\hbar}\, \hat{B}\, e^{-i\hat{H}t/\hbar}\,] \ , \qquad (1)$$

I will focus the discussion on such quantities. Here $\hat{H}$ is the (time-independent) Hamiltonian of the complete molecular system, and $\hat{A}$ and $\hat{B}$ are operators relevant to the specific property of interest. [The Boltzmann operator need not be factored as it is in Eq. (1), but it is convenient in many cases to do so.] For example, if $\hat{A} = \hat{B}$ is the dipole moment operator, then the Fourier transform of the correlation function is the absorption spectrum; if it is the velocity operator of a tagged particle, or the flux operator related to a chemical reaction, then its time integral gives the diffusion coefficient and the chemical reaction rate, respectively.

The SC-IVR approximates the time evolution operator, exp $(-i\hat{H}t/\hbar)$ — which determines all quantum dynamics—as a phase space average over the initial conditions of classical trajectories,

$$e^{-i\hat{H}t/\hbar} = \int d\mathbf{p}_0 \int d\mathbf{q}_0 \sqrt{M_{qp}/(2\pi i\hbar)^F}\; e^{iS_t(\mathbf{p}_0,\mathbf{q}_0)/\hbar} \,|\, \mathbf{q}_t >< \mathbf{q}_0 \,| \;, \qquad (2a)$$

where F is the number of degrees of freedom, $(\mathbf{p}_0,\mathbf{q}_0)$ are the initial coordinates and momenta for a classical trajectory, $\mathbf{q}_t = \mathbf{q}_t\,(\mathbf{p}_0,\mathbf{q}_0)$ is the coordinate (in the F-dimensional space) at time t which evolves from this trajectory, $S_t(\mathbf{p}_0,\mathbf{q}_0)$ is the classical action (the time integral of the Lagrangian) along the trajectory, and M_{qp} is the determinant of the Jacobian (or monodromy) matrix relating the final position and initial momentum,

$$M_{qp} = \det[\partial \mathbf{q}_t(\mathbf{p}_0,\mathbf{q}_0)/\partial \mathbf{p}_0] \;. \qquad (2b)$$

[Eq. (2) is the original coordinate space,[8] or Van Vleck IVR; a popular alternative is the coherent state, or Herman-Kluk IVR,[9] whereby the initial and final states are coherent states, and the pre-exponential Jacobian factor is also modified.] For the correlation function one needs to insert two such representations of the propagator into Eq. (1), yielding the following double phase space average for the correlation function,

$$C_{AB}(t) = (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \int d\mathbf{p}_0' \int d\mathbf{q}_0' (M_{qp}M_{qp}')^{1/2} < \mathbf{q}_0 \,|\, \hat{A}_\beta \,|\, \mathbf{q}_0' >$$
$$e^{iS_t(\mathbf{p}_0,\mathbf{q}_0)/\hbar}\, e^{-iS_t(\mathbf{p}_0',\mathbf{q}_0')/\hbar} < \mathbf{q}_t' \,|\, \hat{B} \,|\, \mathbf{q}_t > \;. \qquad (3a)$$

where

$$\hat{A}_\beta \;=\; e^{-\beta\hat{H}/2}\,\hat{A}\,e^{-\beta\hat{H}/2} \;. \qquad (3b)$$

For comparison, the correlation function is given in classical mechanics by the following single phase space average over initial conditions

$$C_{AB}(t) = (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0\; A_\beta(\mathbf{p}_0,\mathbf{q}_0)\;\; B(\mathbf{p}_t,\mathbf{q}_t) \;, \qquad (4)$$

where $A_\beta(\mathbf{p},\mathbf{q})$ and $B(\mathbf{p},\mathbf{q})$ are the classical functions corresponding to operators $\hat{A}_\beta$ and $\hat{B}$.

Here one sees the two essential 'extra difficulties' which must be dealt with in carrying out SC-IVR calculations compared to a standard classical approach:

1) Eq. 3 requires a double phase space average rather than the single one in Eq. 4, but more serious than that is the phase factor of the integrand in Eq. 3 which results from the difference in the action integrals from the two trajectory beginning at $(\mathbf{p}_0,\mathbf{q}_0)$ and at $(\mathbf{p}_0', \mathbf{q}_0')$. This introduces an oscillatory character to the integrand that makes Monte Carlo evaluation of these phase space averages very inefficient.
2) Eq. 3 also requires the monodromy matrix of Eq. 2b, the calculation of which requires the Hessian of the potential surface (the matrix of second derivatives),

$$\frac{\partial^2 V(\mathbf{q}_t)}{\partial \mathbf{q}_t \partial \mathbf{q}_t} \equiv \mathbf{K}(\mathbf{q}_t) \tag{5}$$

along the trajectory $\mathbf{q}_t$. The classical expression, Eq. 4, requires only the gradient of the potential surface (the vector of first derivatives), $\partial V(\mathbf{q}_t)/\partial \mathbf{q}_t$, in order to compute the trajectory, so requiring the Hessian is a major escalation of effort necessary to implement the SC-IVR approach. Below I will sketch the ways we have developed for overcoming both of these bottlenecks.

A. The Linearization Approximation

In the beginning of our efforts to make SC-IVR approaches practical for large molecular systems, we introduced a very primitive approximation in order to get started:[17] namely, we assumed that the dominant contribution to the double phase space average in Eq. 3 comes from phase points $(\mathbf{p}_0,\mathbf{q}_0)$ and $(\mathbf{p}_0',\mathbf{q}_0')$ — and thus the two trajectories emanating from them — that are close to one another. To effect this approximation one changes to the sum and difference variables

$$\bar{\mathbf{p}}_0 = \frac{1}{2}(\mathbf{p}_0 + \mathbf{p}_0'),\ \bar{\mathbf{q}}_0 = \frac{1}{2}(\mathbf{q}_0 + \mathbf{q}_0'),\ \Delta\mathbf{p}_0 = \mathbf{p}_0 - \mathbf{p}_0',\ \Delta\mathbf{q}_0 = \mathbf{q}_0 - \mathbf{q}_0' \tag{6}$$

and then all quantities in the integrand of Eq. (3) are expanded to first order in $\Delta\mathbf{p}_0$ and $\Delta\mathbf{q}_0$; the integrals over $\Delta\mathbf{p}_0$ and $\Delta\mathbf{q}_0$ thus become Fourier integrals (since the phase of the integrand is linear in them), giving the *linearized* SC-IVR (LSC-IVR), or *classical Wigner model* for the correlation function,

$$C_{AB}(t) = (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \ \ A_w^{\ \beta}(\mathbf{p}_0, \mathbf{q}_0)\, B_w(\mathbf{p}_t, \mathbf{q}_t) \ . \tag{7}$$

Here $(\mathbf{p}_0,\mathbf{q}_0)$ are the average values (i.e., the 'bars' have been removed), and A_w and B_w are the Wigner functions corresponding to these operators,

$$O_w(\mathbf{p},\mathbf{q}) \equiv \int d\Delta\mathbf{q} \ \ e^{i\mathbf{p}\cdot\Delta\mathbf{q}/\hbar} \ \ < \mathbf{q} - \Delta\mathbf{q}/2 \,|\, \hat{O} \,|\, \mathbf{q} + \Delta\mathbf{q}/2 > \ , \tag{8}$$

for any operator $\hat{O}$.

The double phase space average of Eq. 3 has thus now become the singe phase space average of Eq. 7, and in the process the monodromy matrices in Eq. 3 have completely disappeared (they have not been neglected, but rather explicitly cancel out in the course of carrying through the linearized approximation). Thus both of the two 'extra difficulties' noted above (after Eqs. 4) are eliminated by the linearized approximation. Eq. 7 is in fact seen to have *precisely the same form as the classical correlation function*, Eq. 4, the only difference being that the Wigner functions for operators $\hat{A}_\beta$ and $\hat{B}$ replace the corresponding classical functions.

The classical Wigner model has been obtained many times before, by a variety of formulations. One such early paper is ref. 18, but it surely goes back further than this. Heller[19] discussed the approximation many years ago (including an illuminating discussion of its limitations), and it was used by Lee and Scully[20] to describe quantum effects in a collinear model of inelastic scattering. More recently it has been obtained from a different approach by Pollak,[21] and also by Rossky *et al.*[22] directly from a

path integral representation of the two time evolution operators in Eq. (1) (again by linearizing in the difference between the two paths).

The importance of the above derivation is thus not the result itself, for as noted, the classical Wigner approximation has been around a long time, having been obtained from a variety of approaches. The important point is realizing that the classical Wigner model is *contained within* the SC-IVR description, resulting from a very well defined approximation to it. This also makes it clear that if the SC-IVR can be implemented with less drastic approximations, it will be even more accurate than the classical Wigner model.

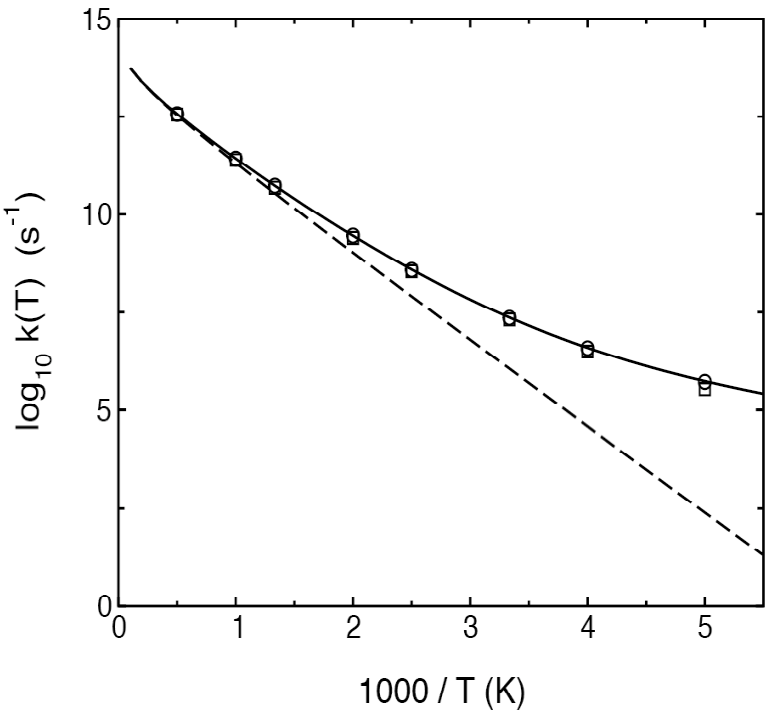
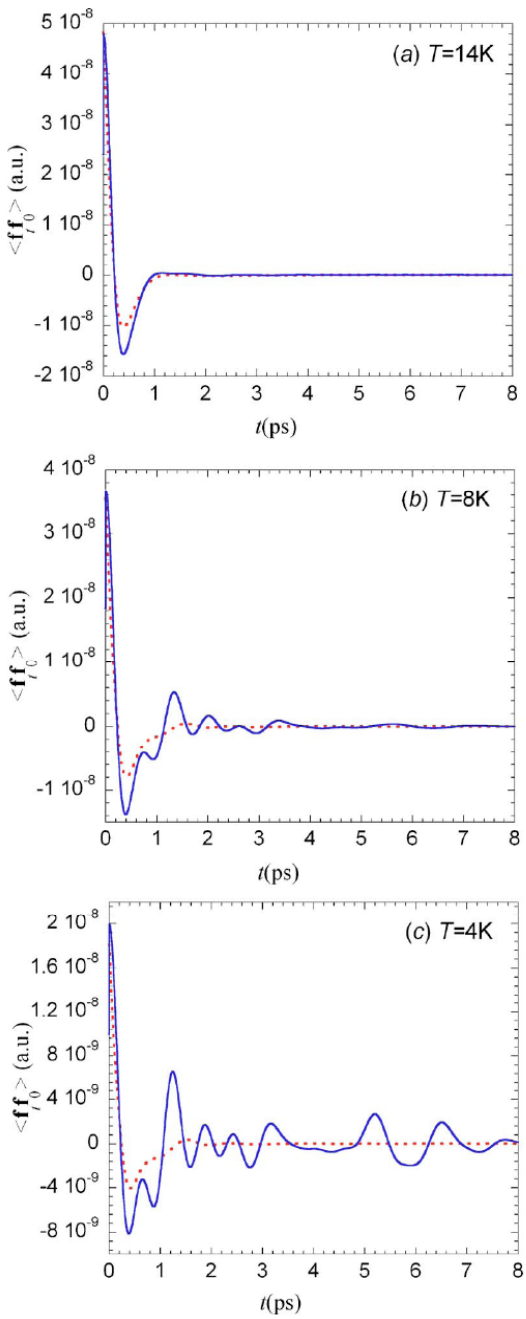


Figure 1. Arrhenius plot of the rate constant for a 1d Eckart barrier (with parameters correspondingly approximately to the H + H_2 reaction). The solid line is the exact quantum value and the dashed line that given by classical mechanics. The circles are values given by the full SC-IVR and the squares its linearized approximation (LSC-IVR).

However, as drastic as the linearization approximation (LSC-IVR) seems, it is surprising that it can in fact describe some quantum effects quite well, even when they are large. The thermal rate constant for a chemical reaction, for example, is given by the long time limit of the flux-side correlation function,[23] i.e., Eq. 1 with operator $\hat{A}$ being the flux operator (with respect to some dividing surface) and operator $\hat{B}$ being a Heaviside function that is 1 (0) on the reactant (product) of the dividing surface. Figure 1[24] shows how it describes tunneling for a standard model of the fundamental hydrogen atom transfer reaction, $H + H_2 \rightarrow H_2 + H$. The Arrhenius plot of the rate shows the expected good agreement with the exact quantum rate at higher temperature, where tunneling corrections are small, but even at lower temperature where tunneling corrections become significant it does reasonably well: at 300K, where the tunneling correction factor is ~20, the rate given by the LSC-IVR is only 10% too small, and at the lowest temperature shown (200K), where the tunneling correction is a factor of ~2000, it is only 35% too small. (The full SC-IVR calculation, on the other hand, is accurate to a few % even down to 200K.)

The only non-trivial task required to implement the LSC-IVR for calculating thermal correlation functions of complex molecular systems — i.e., beyond what is required for an ordinary classical MD calculation — is evaluation of the Wigner function for operator $\hat{A}_\beta$. We have recently found the thermal Gaussian approximation (TGA) that Mandelshtam and Frantsuzov[25] developed for approximating the Boltzmann operator to be a very effective for this purpose. Use of the TGA allows the Fourier transform in Eq. 12 to be evaluated analytically, so that calculation of thermal time correlation functions becomes almost as simple as a standard classical MD calculation. Figure 2 shows recent results[26] for the force-force correlation function of the Ne_{13} cluster at three low temperatures. As the temperature is lowered one sees that the classical correlation function (solid lines) shows the onset of freezing (i.e., structured behavior), while the SC result (dashed lines) shows only the faintest hint of structure. This is clearly a zero point energy effect; i.e., the classical cluster is beginning to freeze at the lower temperatures, while the quantum zero point energy prevents this. We note that in molecular liquids, such as water, one may very well see zero point energy effects even at room temperature because of the high frequency



of H atom motion. Similar calculations have been carried out for the velocity-velocity correlation function of liquid *para*-hydrogen to obtain its diffusion coefficient, and also the correlation functions related to neutron scattering. Thus the linearized approximation to the SC-IVR approach is an 'operational' methodology that can be applied to essentially any problem for which classical MD simulations are feasible, and it should describe tunneling and zero point energy effects in them to a good approximation.

Figure 2. The Kubo-transformed force autocorrelation function per article for the Ne_{13} LJ cluster system. Solid line: the classical result. Dotted line: the TGA-LSC-IVR result. Temperature in three panels are, respectively, (a) T = 14 K; (b) T = 8 K; and (c) T = 4 K.

It should be noted that there are several other approaches that have been developed for

calculating the Wigner function for operator $\hat{A}_\beta$, and thus applying the LSC-IVR. Geva *et al.*[27] have developed a local harmonic approximation that also makes it possible to evaluate the multi-dimensional Fourier transform analytically, and have carried out some impressive applications for vibrational relaxation in liquids (where the relevant quantity is a force-force correlation function). Rossky *et al.*[22] (using a variational harmonic approximation to obtain the Wigner function involving the Boltzmann operator) have treated a 1-dimensional chain of helium atoms, and also liquid oxygen (32 O_2 molecules in a box) at low temperature (70K), and Coker *et al.*[28] have extended the linearized approximation to able to describe electronically non-adiabatic dynamics.

It should also be noted that there are several other approaches that are very similar in character to the LSC-IVR/classical Wigner model, though not identical to it. E.g., the 'forward-backward' approximation to the SC-IVR correlation function used very effectively by Makri *et al.*[29] is closely related to it. The centroid molecular dynamics approach developed by Voth *et al.*[30] and the ring polymer molecular dynamics (RPMD) method of Manolopoulos *et al.*[31] also have very similar behavior to the LSC-IVR in that all of these approaches share the ability to describe *some* of the quantum mechanical aspects of molecular dynamics. They are not, however, able to describe quantum coherence effects. Coherence effects arise (in a semiclassical picture) from the interference between *different* trajectories; and since the LSC-IVR only considers trajectories in the double phase space average [Eq. (3)] that are infinitesimally close to one another, such coherence effects are explicitly excluded within this approximation.

B. A Forward-Backward SC-IVR

To go beyond the linearized approximation, and be able to describe true quantum coherence effects in the dynamics via the SC-IVR approach, requires that one deal more accurately with the 'two difficulties' noted above (following Eq. 4), namely that of the oscillatory integrand and the need for the Hessian of the potential along the trajectory. The 'oscillatory integrand' problem is very effectively dealt with by the 'forward-backward' (FB) approach,[32-34] an idea that was suggested by some earlier work of Makri *et al.*[35] for different purposes.

The motivation of the FB idea is as follows: suppose for the moment that operator $\hat{B}$ in Eq. 1 involved only one degree of freedom, e.g., were a function of coordinate q_1, and furthermore that this degree of freedom was separable from the remaining (many) F-1 degrees of freedom. The Hamiltonian H would thus be separable, $\hat{H} = \hat{H}_1 + \hat{H}_{F-1}$, and the propagators factorable,

$$e^{\pm i\hat{H}t/\hbar} = e^{\pm i\hat{H}_1 t/\hbar} e^{\pm i\hat{H}_{F-1} t/\hbar} \tag{9}$$

The propagator from 0 to t of the F-1 degrees of freedom, $\exp(-i\hat{H}_{F-1}t/\hbar)$, and that from t back to 0, $\exp(+i\hat{H}_{F-1}t/\hbar)$, would then exactly cancel each other [since they commute with $B(q_1)$], and the only time dependence would be that from degree of freedom 1. Similarly, in the IVR expression Eq. 3, the action integrals from the F-1 degrees of freedom would exactly cancel, and the double phase space average would collapse to a single phase space average for all degrees of freedom except the one involving operator $\hat{B}$.

To implement this idea — but without making any approximations about separability of degrees of freedom — suppose that operator $\hat{B}$ in the correlation function involves only a few (perhaps collective) degrees of freedom, as is often the case. For example, if $B(\mathbf{q})$ is a function of one collective variable $s(\mathbf{q})$ (e.g., a collective reaction coordinate),

$$B(\mathbf{q}) = B\big(s(\mathbf{q})\big) \ , \tag{10}$$

then the FB-IVR result for the correlation function is given by[32]

$$\begin{aligned} C_{AB}(t) = & \int_{-\infty}^{\infty} dp_s \, \tilde{B}(p_s) \, (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \, C(\mathbf{p}_0, \mathbf{q}_0; p_s) \\ & < \mathbf{p}_0, \mathbf{q}_0 \,|\, \hat{A}(\beta) \,|\, \mathbf{p}_0', \mathbf{q}_0' > e^{iS(\mathbf{p}_0, \mathbf{q}_0; p_s)/\hbar} \ , \end{aligned} \tag{11}$$

where here the coherent state (Herman-Kluk) IVR has been used. $(\mathbf{p}_0, \mathbf{q}_0)$ in Eq. (11) are the initial conditions for a trajectory that is evolved to time t in the usual way, but here the momentum vector undergoes the following *momentum jump,*

$$\mathbf{p}_t \rightarrow \mathbf{p}_t + \frac{\partial s(\mathbf{q}_t)}{\partial \mathbf{q}_t} p_s \ , \tag{12}$$

and the trajectory is then propagated back to time 0; ($\mathbf{p}_0'$,$\mathbf{q}_0'$) is the final phase point of this forward-backward trajectory, S the classical action along it, and C the Herman-Kluk pre-exponential factor; $B(p_s)$ is the (1-dimensional) Fourier transform of B(s).

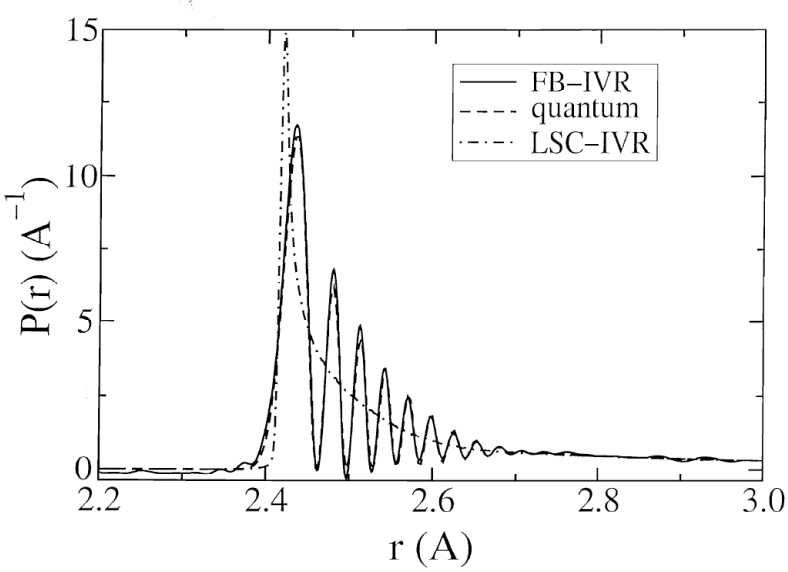


Figure 3. Probability distribution of the vibrational coordinate of I_2 (modeled as a 1d Morse oscillator) at time t = 192 fsec (~vibrational periods after excitation). The dashed line and solid line (almost indistinguishable) are the exact quantum and forward-backward SC-IVR (FB-IVR) results, respectively, and the dash-dot line the results of linearized approximation to the SC-IVR (LSC-IVR).

This FB-IVR result thus involves only a 1d integral (over the 'jump parameter' p_s) in addition to a *single* phase space average over initial conditions (which one recalls is also required for the standard classical calculation), and is perhaps the simplest result of all that is capable of describing quantum coherence. The contribution to the FB action integral S (the phase of the integrand of Eq. 11) from all the degrees of freedom that are coupled only weakly to the motion of the collective

variable s(**q**) will largely cancel, so that the integrand of Eq. 11 is much less oscillatory than the double phase space average of the full SC-IVR expression; i.e., much of the oscillatory structure of the double phase space average that would have cancelled numerically has been eliminated analytically by this FB approach, by combing the forward and backward time evolution operators into one effective forward-backward propagator.

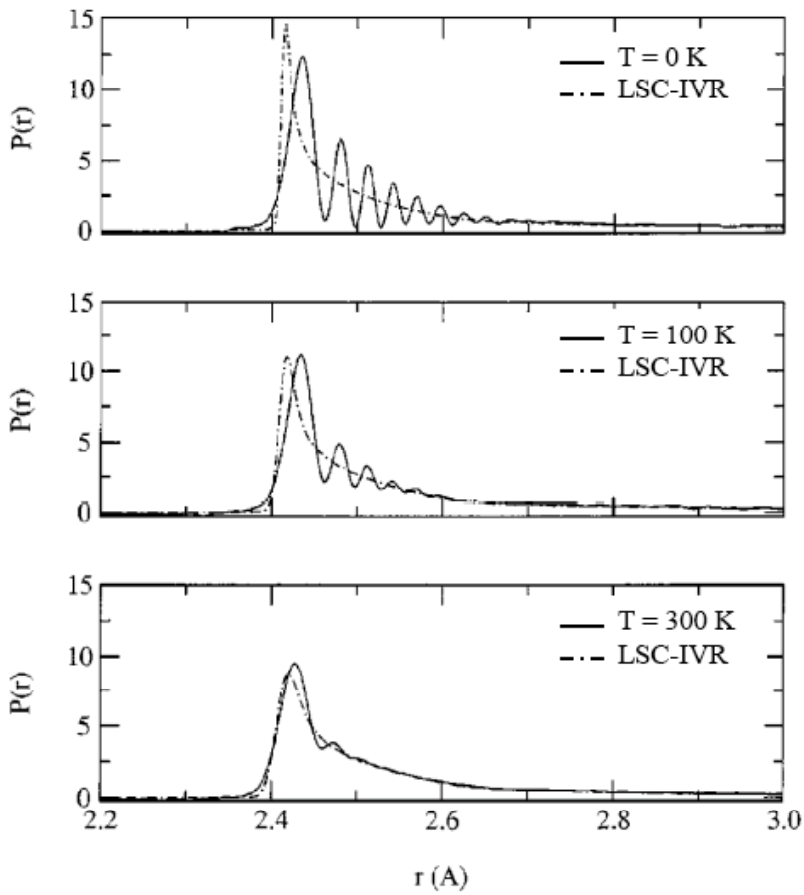


Figure 4. Same quantity as Fig. 3, but with the addition of a harmonic bath that is coupled to the Morse oscillator (I_2); T is the temperature of the harmonic bath. The solid line is the result of the FB-IVR, and the dash-dot line that of the LSC-IVR.

Figures 3 and 4 show the results[36] of a calculation which illustrates this FB-IVR approach, namely a model of real time molecular structure (i.e., a time-dependent radial distribution function). The specific model is a Morse potential (with parameters corresponding to the B-state of I_2) coupled to a harmonic bath (modeling the environmental degrees of freedom, e.g. a cluster, a liquid, etc.). $|\phi>$ is the ground vibrational state of the diatomic in the ground electronic state, which becomes (upon Franck-Condon excitation) the initial vibrational wavefunction in the B-state. The time-dependent radial distribution function — i.e., the probability distribution of the diatomic coordinate at time t — is given by the correlation function of Eq. (1), where operators $\hat{A}(\beta)$ and $\hat{B}$ are

$$\hat{A}(\beta) = |\phi><\phi| \; e^{-\beta \hat{H}_b} \tag{13a}$$

$$\hat{B}(r) = \delta(r - \hat{r}) \tag{13b}$$

where $\hat{H}_b$ is the Boltzmann operator for the harmonic bath. The correlation $C_{AB}(t)$ is then $P_t(r)$, the probability distribution of the diatomic coordinate at time t, i.e., the radial distribution function of I_2. Fig. 3 shows this for a time of 192 fsec (about $1\frac{1}{4}$ vibrational periods of I_2) for the isolated diatomic (i.e., no coupling to the bath), and one sees very pronounced coherence structure (due to the fact that the initial state is a coherent superposition of many different vibrational eigenstates of the B-state); the FB-IVR result is essentially indistinguishable from that of the exact quantum calculation (which is easy for the isolated diatom case). Also shown is the result of the LSC-IVR/classical Wigner calculation, which shows none of the coherence structure. Fig. 4 then shows $P_t(r)$ with coupling to the bath, for several values of the bath temperature T. For T = 0, the result is essentially the same as the isolated molecule result of Fig. 3, i.e., the bath is 'frozen out'. But as T is increased, the coherence structure is progressively quenched (or 'de-coherred') by coupling to the bath, and by the time it has increased to 300K the coherence features have mostly disappeared (for the assumed coupling strength), and in this case one sees that the LSC-IVR does an excellent job in describing $P_t(r)$. So just as one would expect, when

quantum coherence features are averaged out, classical mechanics (which is effectively what the LSC-IVR gives) works well. This is not a surprising result. The point of this example is to show that semiclassical theory is able to simulate these coherence effects (and the extent to which they are quenched) in systems with many degrees of freedom. This model system is of course a simple one, but the nature of the calculation for a realistic model of a large molecular system would be essentially the same (though the computational time for each trajectory would of course be greater for a more complicated potential energy surface).

C. Calculating the Hessian along a trajectory

Though the FB-IVR approach described above largely solves the problem of the oscillatory integrand, it still requires the monodromy matrices and thus the Hessian of the potential [Eq. 5] along the trajectory. Having to explicitly calculate $\mathbf{K}(\mathbf{q})$ along the trajectory $\mathbf{q}_t$ would be a major increase in computational complexity for a large molecular system with a very complicated potential energy function. Very recently, though, we have found a way to generate the Hessian along the trajectory without explicitly calculating the matrix of second derivatives of the potential.[37]

We avoid explicit calculation of **K** by differentiating one of Hamilton's equations

$$\dot{\mathbf{p}}_t = -\frac{\partial V(\mathbf{q}_t)}{\partial \mathbf{q}_t} \tag{14}$$

with respect to time, which (for a Cartesian Hamiltonian) gives

$$\ddot{\mathbf{p}}_t = -\frac{\partial^2 V}{\partial \mathbf{q}_t, \partial \mathbf{q}_t} \cdot \dot{\mathbf{q}}_t = -\mathbf{K}(\mathbf{q}_t) \cdot \mathbf{p}_t / m \ . \tag{15}$$

Along a trajectory it is quite easy to obtain $\ddot{\mathbf{p}}_i = \ddot{\mathbf{p}}(t_i)$at time grid point i by finite difference,

$$\ddot{\mathbf{p}}(t_i) \;\cong\; \left[\mathbf{p}(t_{i+1}) + \mathbf{p}(t_{i-1}) - 2\mathbf{p}(t_i)\right]/\Delta t^2 \;, \tag{16}$$

so knowing $\ddot{\mathbf{p}}(t_i)$ and $\mathbf{p}(t_i)$at times $\{t_i\}$, one can use Eq. 15 to determine **K** (assuming it to be approximately constant for a short time interval). To see how this works, it is useful to write Eq. 15 in component notation

$$m\ddot{p}_{k,i} \;=\; -\sum_{k'} K_{k,k'}\;\; p_{k',i} \;, \tag{17}$$

where k and k′ = 1, …, F (the number of degrees of degrees of freedom), and the matrix $p_{k,i} = p_k(t_i)$, etc. If one uses F time points $\{t_i\}$, then $\{\ddot{p}_{k,i}\}$ and $\{p_{k,i}\}$ are square matrices, so that one can solve the matrix equation, Eq. 17, to obtain

$$K_{k,k'} \;=\; -\; m \sum_i \ddot{p}_{k,i}(\mathbf{p}^{-1})_{i,k'} \;, \tag{18}$$

where $\mathbf{p}^{-1}$ is the inverse matrix of $\{p_{k,i}\}$.

As described above, one needs F time points $\{t_i\}$, a large number for a large molecular system, and this would largely invalidate our assumption that **K** is approximately constant for a short time interval. But this is not the case. Thus consider Eq. 17: for *fixed* k, the LHS is a vector (index i), $K_{k,k'}$ is a vector (index k′), and $p_{k',i}$ is a matrix. For *fixed* k, the index k′ takes on only a small number of values, because the force constant matrix is highly banded (along its diagonal), i.e., it is only non-zero for a small number of k′ values (for *fixed* k). Thus only a small number of time values $\{t_i\}$ are necessary to make $\{p_{k',i}\}$ a square matrix (and thus invertible). The matrix $\mathbf{p}^{-1}$ in Eq. 18 is the inverse of this 'small square' matrix. Since one needs only a small number of time steps for each inversion, the approximation of a constant **K** matrix should be reasonable for that time interval. This calculation does have to be carried out for every value of k, which takes on F values, meaning that the overall procedure is linear in the number of degrees of freedom, i.e., the same order as the trajectory calculation itself.

3. Concluding Remarks

Ways of handling the additional complications of a semiclassical dynamics calculation, compared to the corresponding classical treatment, are now in hand, and a number of examples of increasing complexity have been carried out which demonstrate these capabilities. The simplest, most approximate version of semiclassical initial value methods — its linearized approximation, which leads to the classical Wigner model — is able to provide a good description of tunneling effects in chemical reactions and zero point energy effects in dynamical processes. The forward-backward IVR goes further and is able also to describe true quantum coherence effects in the dynamics, thus showing when these effects are present or when they are averaged out (quenched, or 'de-cohered'). Both of these approaches are more difficult to apply than a standard classical MD simulation, but not extraordinarily so.

There are many cases, of course, for which quantum mechanical aspects of the dynamics will not be significant, but one may not always know this *a priori*; and if one is only able to perform classical MD simulations there is no way to know whether such effects are present or not. In other situations, e.g., dynamical processes which involve H atom motion, one can be fairly certain that quantum effects will indeed be important. In these cases the ability to still use classical MD methodology, but as input to a semiclassical treatment, should provide a useful enhancement of theoretical capabilities.

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