

Application of the semiclassical initial value representation and its linearized approximation to inelastic scattering

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Received 21 September 1998; in final form 13 November 1998

Abstract

The semiclassical (SC) initial value representation (IVR), and its linearized approximation (LA), have been applied to the well-studied Secrest–Johnson model of colinear $\text{He} + \text{H}_2(v_i) \rightarrow \text{He} + \text{H}_2(v_f)$ vibrationally inelastic scattering. The full SC–IVR treatment describes the quantum interference structure in the vibrational transition probabilities quantitatively, while the LA version does so only very qualitatively. This is consistent with earlier work on time correlation functions which found that the LA was able to describe quantum effects accurately in the short time dynamics, but not quantum coherence effects in the longer time dynamics. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The semiclassical (SC) initial value representation (IVR) [1,2] is undergoing a re-birth of interest as a practical way for including quantum interference and tunneling effects in classical molecular dynamics simulations [3–24]. The primary difference in the recent IVR approaches from the original version is that they are now implemented in the cartesian coordinate (or coherent state) representation rather than in action-angle variables, and this is more general, better behaved numerically, and also typically more accurate. The number of successful applications in recent years gives one confidence that the SC–IVR does indeed provide a good description of quantum

effects for a wide range of molecular phenomena (including electronically non-adiabatic processes [21,24]).

Applications of the SC–IVR approach to date, however, have mostly dealt with molecular systems of a relatively few degrees of freedom because of the oscillatory nature of the integrand in the phase space average over initial conditions of classical trajectories (see Section 2 below). For this reason a *linearization approximation* [20,21] to it has been considered which simplifies this oscillatory structure of the IVR integrand. This linearized SC–IVR has been seen to be capable of describing quantum effects correctly in the *short time* regime (time $\leq \hbar\beta$) of thermal reactive flux correlations functions, but not the longer time behavior.

The purpose of this Letter is to provide another test of the SC–IVR approach, and especially the

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linearized approximation, on a problem which has well-understood quantum interference features. This is the well-studied [1,2,25–27] model of inelastic scattering for which Secrest and Johnson [25] carried out coupled channel quantum calculations many years ago, the colinear $\text{He} + \text{H}_2(v_i) \rightarrow \text{He} + \text{H}_2(v_f)$ problem. This was the first example to which ‘classical S-matrix’ theory was applied [1] in 1970, showing prominent interference features in the distribution of final vibrational states due to interference between two classical trajectories that typically contribute to each transition probability. Here we wish first to verify that the full SC–IVR treatment is able to describe this well (as it does), and primarily to see how much error is introduced by its linearized approximation.

As noted before [23], the LA results in classical propagation and overlap of Wigner distribution functions, a result given by a variety of other formulations and approximations [28–30]. In the present application it is very close, though not completely identical, to a model Lee and Scully [31] put forth some years ago and tested on this very same example. Comparison to the Lee and Scully version of the approximation will thus also be presented.

2. SC–IVR for the S-matrix

We consider a multichannel scattering problem characterized by a Hamiltonian of the form,

$$H(P, R, \mathbf{p}, \mathbf{r}) = \frac{P^2}{2\mu} + h(\mathbf{p}, \mathbf{r}) + V(R, \mathbf{r}) \quad (2.1)$$

where (P, R) are the momentum and coordinate for the relative translation of the two collision partners, and (\mathbf{p}, \mathbf{r}) are the momenta and coordinates of the internal degrees of freedom. A rigorous quantum expression for the S-matrix in terms of the time evolution operator (propagator) is [32]

$$S_{2,1}(E) = \frac{-\hbar\sqrt{k_1 k_2}}{\mu} e^{-i(k_1 R_1 + k_2 R_2)} \int_0^\infty dt e^{itE/\hbar} \langle R_2 \phi_2 | e^{-it\hat{H}/\hbar} | R_1 \phi_1 \rangle \quad (2.2)$$

where E is the total energy, $\hbar k_n, n = 1, 2$ are the initial and final translational momenta,

$$k_n = \sqrt{2\mu(E - \mathcal{E}_n)/\hbar^2} \quad (2.3)$$

and \mathcal{E}_n and $\phi_n(\mathbf{r}), n = 1, 2$ are the eigenvalues and eigenfunctions of the internal Hamiltonian $h(\mathbf{p}, \mathbf{r})$; the limit $R_1, R_2 \rightarrow \infty$ is implied in Eq. (2.2), but these values only have to be so large that the interaction potential $V(R, \mathbf{r})$ is negligible.

The coordinate space (or Van Vleck) IVR approximates the propagator as a phase space average over initial conditions for classical trajectories,

$$e^{-it\hat{H}/\hbar} = \int d\mathbf{p}_0 \int d\mathbf{q}_0 \sqrt{\left| \frac{\partial \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0} \right|} / (2\pi i \hbar)^F \times e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{q}_t\rangle \langle \mathbf{q}_0| \quad (2.4a)$$

where (\mathbf{p}, \mathbf{q}) denote all F degrees of freedom of the complete system (i.e., $\mathbf{q} = (R, \mathbf{r})$, etc.), $\mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$ is the coordinate at time t that evolves along the classical trajectory with initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$, and S_t is the action along it,

$$S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' (\mathbf{p} \cdot \dot{\mathbf{q}} - H). \quad (2.4b)$$

Using the SC–IVR for the propagator, Eq. (2.4a), in Eq. (2.2) for the S-matrix thus gives

$$S_{2,1}(E) = \frac{-\hbar}{\mu} \sqrt{k_1 k_2} e^{-i(k_1 R_1 + k_2 R_2)} \times \int_0^\infty dt \int d\mathbf{p}_0 \int d\mathbf{r}_0 \int dP_0 \int dR_0 \quad (2.5)$$

$$\sqrt{\left| \frac{\partial(\mathbf{r}_t, R_t)}{\partial(\mathbf{p}_0, P_0)} \right|} / (2\pi i \hbar)^F e^{iEt/\hbar} e^{iS_t(\mathbf{p}_0, \mathbf{r}_0, P_0, R_0)/\hbar}$$

$$\times \delta(R_t - R_2) \phi_2(\mathbf{r}_t)^* \phi_1(\mathbf{r}_0) \delta(R_0 - R_1),$$

and the two delta functions in the integrand allow the integrals over R_0 and t to be evaluated, so that the final SC–IVR result for the S-matrix is

$$S_{2,1}(E) = -e^{-i(k_1 R_1 + k_2 R_2)} \int d\mathbf{p}_0 \int d\mathbf{r}_0 \int dP_0 \times \sqrt{\left| \frac{\partial(\mathbf{r}_t, R_t)}{\partial(\mathbf{p}_0, P_0)} \right|} / (2\pi i \hbar)^F \quad (2.6)$$

$$e^{i[Et + S_t(\mathbf{p}_0, \mathbf{r}_0, P_0, R_0)]/\hbar} \phi_2(\mathbf{r}_t)^* \phi_1(\mathbf{r}_0) \hbar\sqrt{k_1 k_2} / P_t.$$

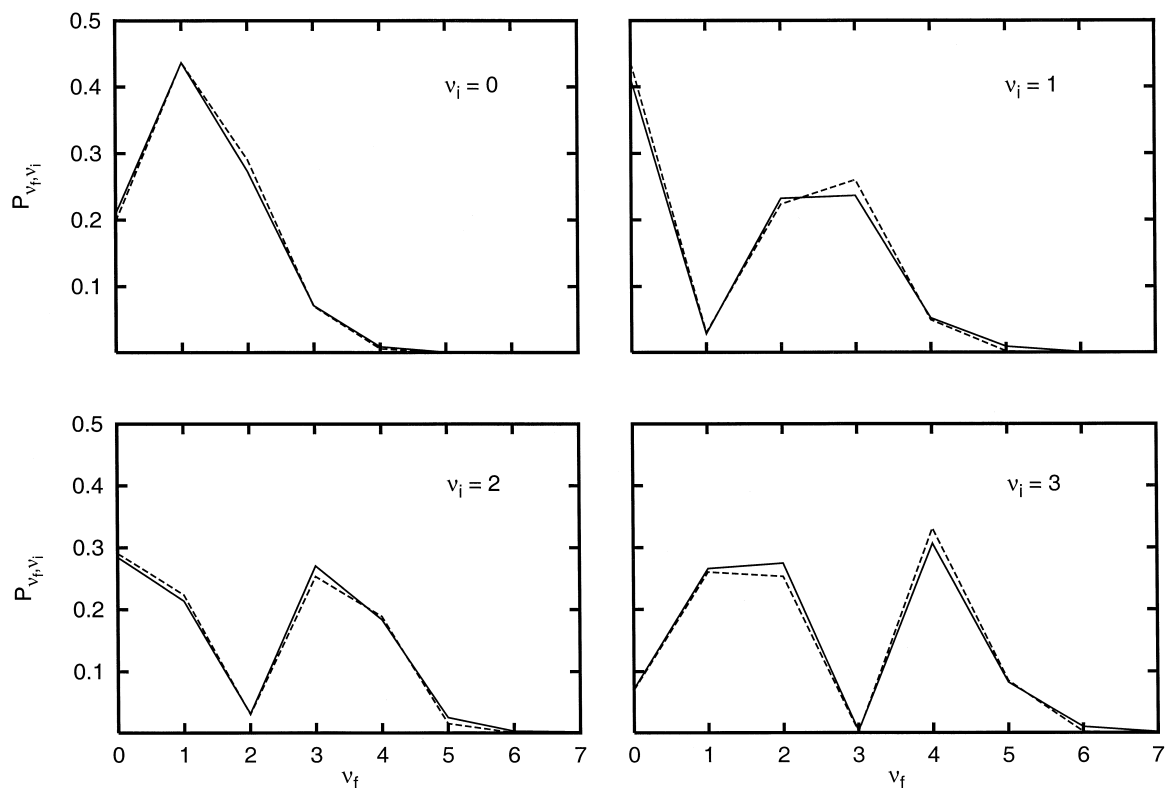


Fig. 1. Vibrational transition probabilities as a function of final vibrational quantum number v_f , for several initial vibrational states v_i , and total energy $E = 8$. The solid lines connect the exact quantum values, and the dashed lines are those given by the SC-IVR (Eq. (2.6)).

(The factor of $1/P_i$ arises from $\int dt \delta(R_i - R_2) = 1/R_i$.) The trajectories in Eq. (2.6) begin with initial conditions $\mathbf{r}_0, \mathbf{p}_0, P_0$, and $R_0 = R_1$ (an arbitrary fixed, large value), and terminate when $R_i = R_2$ (an arbitrary fixed, large value), this latter relation being what determines the value of t in the integrand of Eq. (2.6).

Eq. (2.6) is what we have used to compute the SC-IVR transition probabilities,

$$P_{2,1}(E) = |S_{2,1}(E)|^2 \quad (2.7)$$

discussed below in Section 3. We also carried out calculations using the Herman–Kluk coherent state version [8,9] of the IVR and obtained essentially identical results.

The *linearized approximation* (LA) is obtained by explicitly squaring the SC-IVR S-matrix of Eq. (2.6)

to obtain the transition probability via Eq. (2.7), giving an expression of the form,

$$P_{2,1}(E) = \int d\mathbf{r}_0 \int d\mathbf{p}_0 \int dP_0 \int d\mathbf{r}'_0 \int d\mathbf{p}'_0 \int dP'_0 \{ \dots \} \quad (2.8)$$

$$e^{i[Et + S_i(\mathbf{p}_0, \mathbf{q}_0, P_0, R_0) - Et' - S_f(\mathbf{p}'_0, \mathbf{q}'_0, P'_0, R'_0)]/\hbar}$$

The LA corresponds to expanding the difference of the action integrals in the integrand of Eq. (2.8) to linear order in $(\mathbf{r}_0 - \mathbf{r}'_0)$, etc., with the corresponding approximation for the pre-exponential Jacobian factors. The details of this calculation have been given before [23], and one obtains the following

$$P_{2,1}^{\text{LA}}(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}_0 \int d\mathbf{r}_0 \frac{\hbar^2 k_1 k_2}{|P_0 P_i|} \times \rho_2(\mathbf{r}_i, \mathbf{p}_i)^* \rho_1(\mathbf{r}_0, \mathbf{p}_0), \quad (2.9a)$$

where again $R_0 = R_1$ and $R_t = R_2$ determines t , and the initial translational momentum is given by,

$$P_0 = -\sqrt{2\mu(E - h(p_0, r_0))}. \quad (2.9b)$$

$\{\rho_n\}, n = 1, 2$ in Eq. (2.9a) are the Wigner distribution functions for the initial and final internal states

$$\rho_n(\mathbf{r}, \mathbf{p}) = \int d\mathbf{r}' e^{-i\mathbf{p} \cdot \mathbf{r}' / \hbar} \phi_n\left(\mathbf{r} + \frac{1}{2}\mathbf{r}'\right) \phi_n^*\left(\mathbf{r} - \frac{1}{2}\mathbf{r}'\right) \quad (2.9c)$$

Finally, as noted before [23], the LA expression in Eqs. (2.9a), (2.9b) and (2.9c) is very similar to one put forth many years ago by Lee and Scully [31] (LS) and tested on the same system we treat presently, the only difference being that LS take the initial momentum to be the quantum value,

$$P_0 = -\hbar k_1 = -\sqrt{2\mu(E - \mathcal{E}_1)} \quad (2.10)$$

rather than the value in Eq. (2.9b) that is determined by total energy conservation and the initial condi-

tions of the internal degrees of freedom. The transition probability given by the LA procedure is microscopically reversible, i.e.,

$$P_{2,1}^{\text{LA}} = P_{1,2}^{\text{LA}} \quad (2.11)$$

while that given in the LS prescription is not. Nevertheless, it will be seen that even though the LA result, Eq. (2.9b), is on sounder theoretical ground, the LS version, i.e., with Eq. (2.10) replacing Eq. (2.9b), gives better numerical results for the present example (though neither the LS or LA versions are nearly as accurate as the full SC-IVR results based on Eq. (2.6)).

3. Results and discussion

The Secrest–Johnson [25] model of colinear $A + BC(v_i) \rightarrow A + BC(v_f)$ vibrationally inelastic scattering corresponds to the Hamiltonian of Eq. (2.1) for

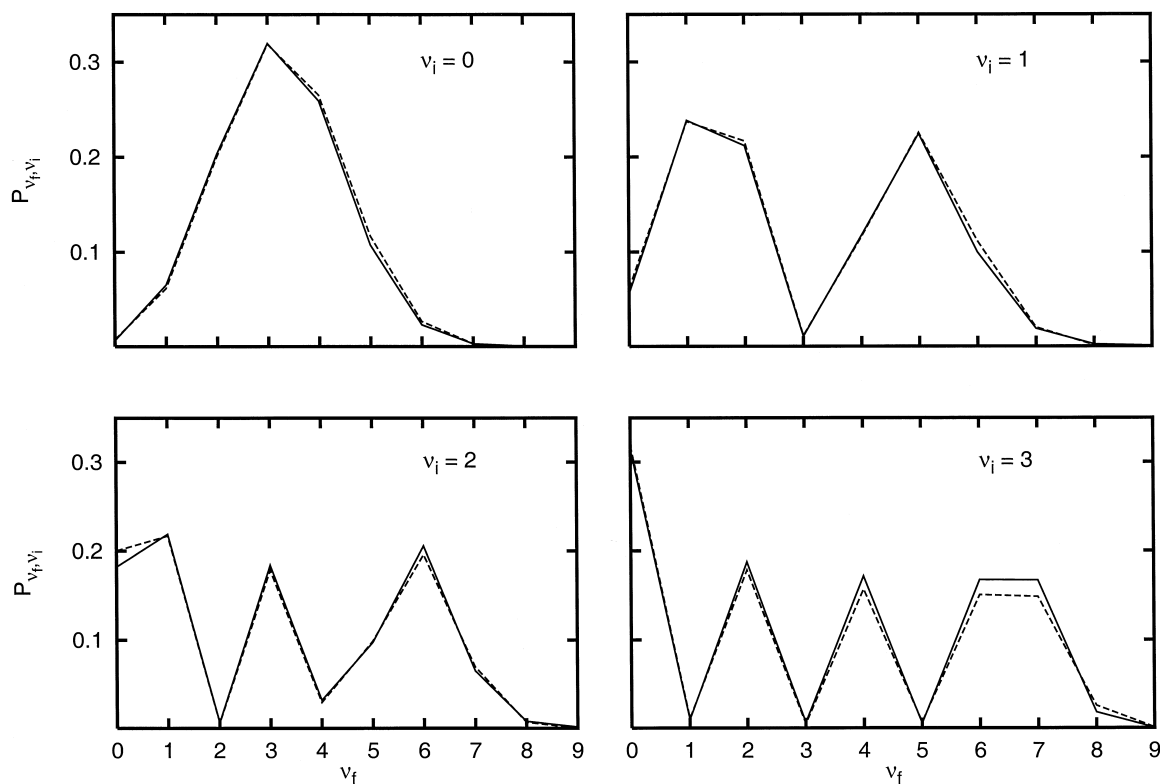


Fig. 2. Same as Fig. 1, except for total energy $E = 12$.

one internal degree of freedom, a harmonic oscillator, for which

$$H(P, R, p, r) = \frac{p^2}{2\mu} + h(p, r) + V(R, r) \quad (3.1a)$$

and with the following internal Hamiltonian and interaction potential,

$$h(p, r) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2 \quad (3.1b)$$

$$V(R, r) = e^{\alpha(r-R)}. \quad (3.1c)$$

In the reduced units used by Secrest and Johnson, $m = 1$, $\omega = 1$, $\alpha = 0.3$, and $\mu = 2/3$ for the He + H₂ system.

Figs. 1 and 2 show the comparison of the exact quantum results for the vibrational transition probabilities $P_{v_f, v_i}(E)$ and the SC-IVR results given by Eq. (2.6), for two different total energies. One sees that the SC-IVR results agree extremely well with

the correct QM values in all cases. The interference structure in P_{v_f, v_i} versus v_f – i.e., the product state distribution – is well understood from the earlier classical S-matrix treatment [1] of this system as arising from the interference of two classical trajectories that emerge from the stationary phase approximation to the IVR integral over initial conditions.

For the present application the SCI-IVR expression (Eq. (2.6)) involves only a three-dimensional integration, which was evaluated by a quasi-random space filling method [33]. Since the integration points are independent of the initial and final states (and the energy), one can evaluate the entire matrix of transition probabilities for all energies with one batch of classical trajectories. It required $\approx 10^4$ – 10^5 classical trajectories to obtain convergence in the transition probabilities. For higher dimensional problems one will typically wish to use Monte Carlo methods to perform the integration over initial conditions, with

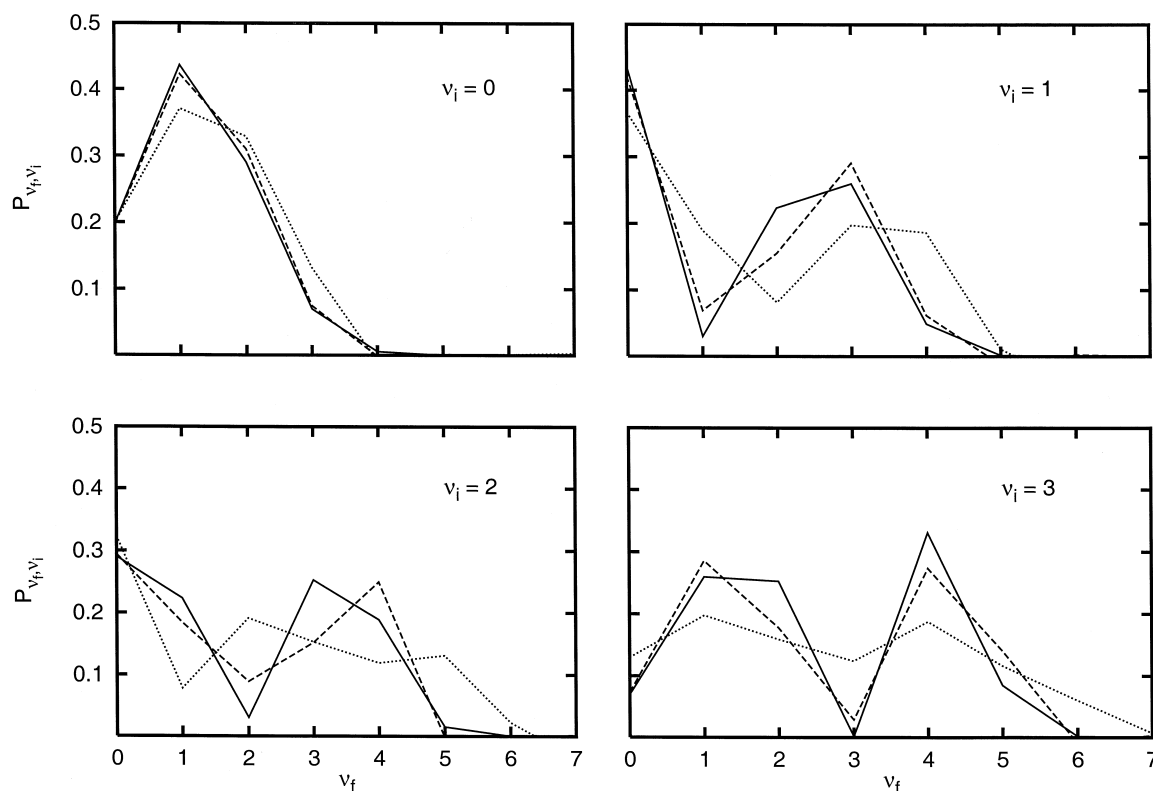


Fig. 3. Same as Fig. 1, except the dotted lines connect the values given by the linearized approximation (LA) to the SC-IVR (Eqs. (2.9a), (2.9b) and (2.9c)), and the dashed lines those of the Lee-Scully (LS) version of the LA (Eq. (2.10)).

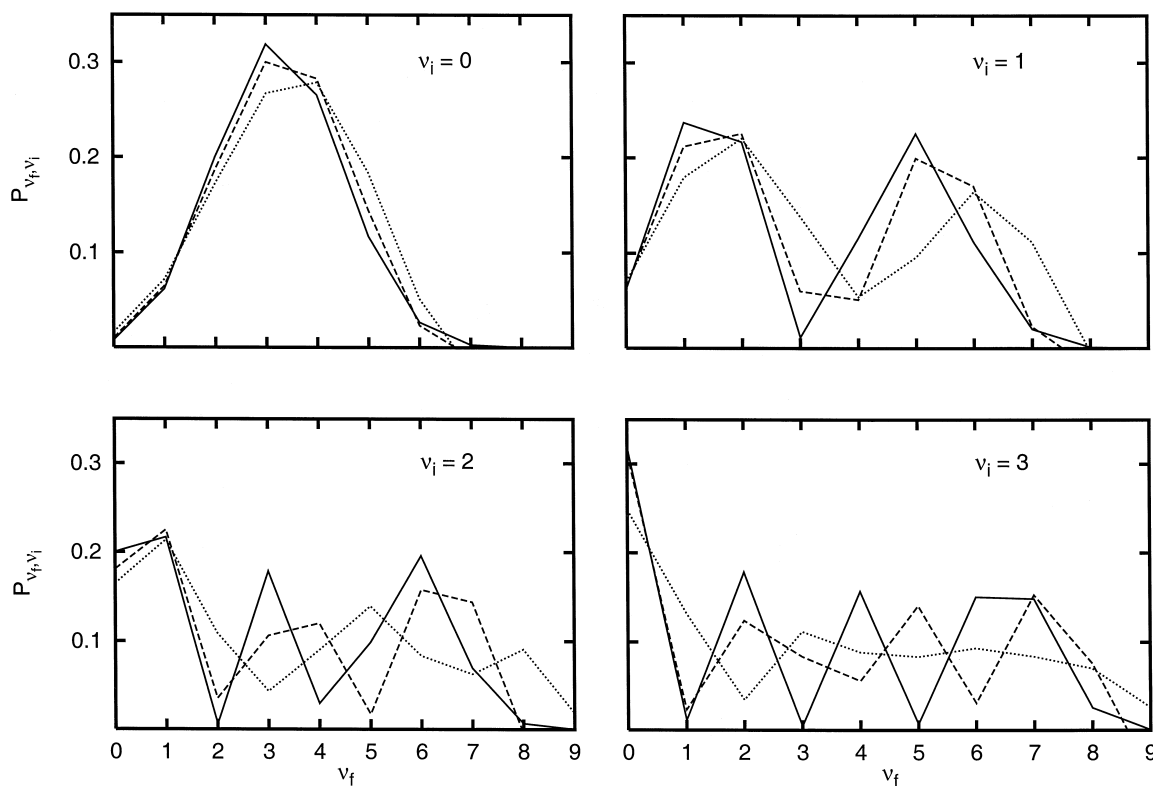


Fig. 4. Same as Fig. 3, except for total energy $E = 12$.

filtering methods to smooth the oscillatory integrand, and importance sampling that may depend on the initial and final states.

Figs. 3 and 4 show the same quantum results but compared here to the *linearized approximation* (LA) of Eqs. (2.9a), (2.9b) and (2.9c)). One sees that the LA results are in reasonable agreement on the average, but they do not describe the quantum interference structure very accurately. The original LS version of this approximation, using Eq. (2.10) rather than Eq. (2.9b), is seen to do somewhat better than the more theoretically justifiable version, a result hard to rationalize.

For state-to-state transitions such as these, the LA actually represents only a minor savings in effort compared to the full SC–IVR approach; i.e. Eq. (2.6) shows that the full IVR calculation requires a $2F - 1$ -dimensional integral and the LA of Eq. (2.9a) reduces this only to a $2F - 2$ -dimensional integral. The LA has the simplifying feature, however, of not

requiring elements of the monodromy matrix (the pre-exponential Jacobian factor in Eq. (2.4a)), though it requires the additional effort of calculating the Wigner transforms of the initial and final states rather than needing only their wavefunctions. At the full state-to-state description there is thus little point in not carrying out the full SC–IVR calculation, especially given the fact that it is more accurate. This conclusion applies only for state-to-state processes, however; the LA leads to a much simpler approach than the full SC–IVR treatment for the calculation of time correlation functions.

4. Concluding remarks

The purpose of this Letter has been two-fold: first to verify that the current version of the semiclassical initial value representation is able to provide a good description of quantum effects in this well-studied

benchmark for inelastic scattering, and second to test the degree of error introduced by using the linearized approximation (LA) to the SC–IVR. The first goal is clearly met, i.e., the SC–IVR describes the quantum structure in the vibrational transition probabilities quite accurately. Secondly, the LA describes the average value of the transition probability fairly well, but the interference features much less so.

This behavior of the LA is consistent with our earlier experiences with it. For the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction, for example, it described [23] the *average* energy dependence of the reaction probability quite well, but not the resonance structure, which arises semiclassically from the interference of different reactive trajectories. Similarly, in using the LA for reactive flux correlation functions [20,23] it was seen to describe quantum effects well in the short time regime, but the longer time dynamics was essentially that given by classical mechanics. A quantitative description of the quantum interference/coherence structure thus requires the full SC–IVR approach. This gives one further incentive to develop methods that will make such calculations more efficient. In this regard, we note that the recently suggested [34,35] ‘forward–backward’ algorithm shows considerable promise, at least for time correlation functions. On the other hand, for applications where interference/coherence features are unimportant (i.e., expected to be averaged out), the LA provides a very useful and much simpler approach.

Finally, although the expressions in Section 2 were written explicitly for non-reactive scattering, it should be clear from general semiclassical theory [32] that Eq. (2.6) applies to reactive scattering essentially as written; the only modification is that in the final wavefunction, $\exp(-ik_2 R_2)\phi_2(\mathbf{r}_2)$, the coordinates (R_2, \mathbf{r}_2) are the Jacobi coordinates for the final (product) arrangement of atoms rather than those of the initial (reactant) arrangement.

Acknowledgements

This work has been supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division, of the US

Department of Energy under Contract No. DE-AC03-76SF00098 and also by the National Science Foundation under Grant No. CHE94-22559. D.S. acknowledges a fellowship from the Fannie and John Hertz Foundation.

References

- [1] W.H. Miller, J. Chem. Phys. 53 (1970) 3578.
- [2] W.H. Miller, T.F. George, J. Chem. Phys. 56 (1972) 5668, Appendix D.
- [3] E.J. Heller, J. Chem. Phys. 94 (1991) 2723.
- [4] W.H. Miller, J. Chem. Phys. 95 (1991) 9428.
- [5] E.J. Heller, J. Chem. Phys. 94 (1991) 9431.
- [6] M.A. Sepulveda, S. Tomsovic, E.J. Heller, Phys. Rev. Lett. 69 (1992) 402.
- [7] N.T. Maitra, E.J. Heller, Phys. Rev. Lett. 78 (1997) 3035.
- [8] M.F. Herman, E. Kluk, Chem. Phys. 91 (1984) 27.
- [9] M.F. Herman, Chem. Phys. Lett. 275 (1997) 445.
- [10] D. Provost, P. Brummer, Phys. Rev. Lett. 74 (1995) 250.
- [11] G. Campolieti, P. Brummer, Phys. Rev. A 50 (1994) 997.
- [12] K.G. Kay, J. Chem. Phys. 100 (1994) 4377.
- [13] K.G. Kay, J. Chem. Phys. 107 (1997) 2313.
- [14] A.R. Walton, D.E. Manolopoulos, Mol. Phys. 87 (1996) 961.
- [15] S. Garashchuk, D.J. Tannor, Chem. Phys. Lett. 262 (1996) 477.
- [16] F. Grossman, Chem. Phys. Lett. 262 (1996) 470.
- [17] S. Keshavamurthy, W.H. Miller, Chem. Phys. Lett. 218 (1994) 189.
- [18] B.W. Spath, W.H. Miller, Chem. Phys. Lett. 262 (1996) 486.
- [19] X. Sun, W.H. Miller, J. Chem. Phys. 108 (1998) 8870.
- [20] H. Wang, X. Sun, W.H. Miller, J. Chem. Phys. 108 (1998) 9726.
- [21] X. Sun, H. Wang, W.H. Miller, J. Chem. Phys. 109 (1998) 4190.
- [22] X. Sun, H. Wang, W.H. Miller, J. Chem. Phys. 109 (1998) 7064.
- [23] X. Sun, H. Wang, W.H. Miller, J. Chem. Phys. 106 (1997) 6346.
- [24] G. Stock, M. Thoss, Phys. Rev. Lett. 78 (1997) 578.
- [25] D. Secrest, B.R. Johnson, J. Chem. Phys. 45 (1966) 4556.
- [26] E.J. Heller, J. Chem. Phys. 62 (1975) 1544.
- [27] J.W. Duff, D.G. Truhlar, Chem. Phys. 9 (1975) 243.
- [28] H.W. Lee, M. O. Scully, J. Chem. Phys. 77 (1982) 4604.
- [29] V.S. Filinov, Mol. Phys. 88 (1996) 1529.
- [30] E. Pollak, J.L. Liao, J. Chem. Phys. 108 (1998) 2733.
- [31] H.W. Lee, M.O. Scully, J. Chem. Phys. 73 (1980) 2238.
- [32] W.H. Miller, Adv. Chem. Phys. 25 (1974) 69.
- [33] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical Recipes in C, Cambridge Univ. Press, Cambridge, 1992, Chap. 7.
- [34] N. Makri, K. Thompson, Chem. Phys. Lett. 291 (1998) 101.
- [35] W.H. Miller, Faraday Disc. Chem. Soc. 110 (1998) 1.