

Semiclassical initial value representation for electronically nonadiabatic molecular dynamics

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The semiclassical initial value representation (SC-IVR), which has recently seen a great deal of interest for treating nuclear dynamics on a single potential energy surface, is generalized to be able to describe electronically nonadiabatic (i.e., multisurface) processes. The essential idea is a quantization of the classical electron-nuclear Hamiltonian of Meyer and Miller [J. Chem. Phys. **70**, 3214 (1979)] within the SC-IVR methodology. Application of the approach to a series of test problems suggested by Tully shows it to provide a good description of electronically nonadiabatic dynamics for a variety of situations. © 1997 American Institute of Physics.
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I. INTRODUCTION

Although the Born–Oppenheimer approximation, i.e., the motion of atomic nuclei on one potential energy surface, is the theoretical basis of much of chemical/molecular dynamics, there are many situations that involve coupling and transitions between different potential energy surfaces (adiabatic electronic states). The purpose of this paper is to present and test a new theoretical model for carrying out calculations for such nonadiabatic processes.

For the collisions of two atoms, or equivalently, nuclear motion in a diatomic molecule, it is usually possible to treat the coupled electronic-nuclear Schrödinger equations without significant approximation. Semiclassical approximation for the atom–atom motion, such as the Landau–Zener–Stueckelberg¹ approximation and its refinements,² are well known and useful for the insight they provide, but they are actually not necessary as a computation/simulation tool.

The situation is quite different for molecular dynamics involving more than two atoms, where the number of nuclear degrees of freedom, and the many vibrational/rotational states associated with them, typically precludes an exact quantum mechanical treatment of the combined electronic-nuclear dynamics. Indeed, the rigorous quantum treatment of the nuclear dynamics for more than three atoms on only *one* potential surface is itself a challenging task,³ so that even in this simpler one surface case, classical mechanics (i.e., classical trajectory simulations) is often used to describe the nuclear dynamics.⁴ It is thus natural to try to treat electronically nonadiabatic processes by using classical mechanics to describe the nuclear dynamics while still retaining a quantum description of the electronic degrees of freedom (i.e., the several adiabatic electronic states involved in the process).

There are several ways this mixed “classical nuclear-quantum electronic” idea has been implemented. The surface hopping model introduced by Tully and Preston⁵ may be thought of as a polyatomic generalization of the Landau–Zener approximation (though Tully’s latest version of the model is able to treat more than simple curve crossing problems⁶). In this model the nuclei move on one adiabatic

potential surface at a time with localized (instantaneous) transitions from one potential surface to another. The probability of such “hops” is determined by an electronic transition probability obtained by integrating the time-dependent electronic Schrödinger equation simultaneously with the nuclear trajectory. (Miller and George⁷ upgraded this model by using a classical *S*-matrix description of the nuclear degrees of freedom, but this has not seen much application because of practical difficulties in applying it.)

Another popular mixed quantum-classical approach is the Ehrenfest model,⁸ in which the classical equations of motion for the nuclear coordinates are also integrated simultaneously with the time-dependent Schrödinger equation, but the nuclear potential energy function which determines the trajectory in this case is the expectation value of the electronic-nuclear potential energy with respect to the electronic wave function,

$$V(\mathbf{R}, t) = \int d\mathbf{x} \Psi_{\text{el}}^*(\mathbf{x}, t) V(\mathbf{x}, \mathbf{R}) \Psi_{\text{el}}(\mathbf{x}, t), \quad (1.1)$$

where \mathbf{x} and \mathbf{R} denote electronic and nuclear coordinates, respectively, and Ψ_{el} the electronic wave function. (The Ehrenfest model maybe thought of as a semiclassical version of the time-dependent self consistent field (TDSCF) approximation.⁹) Since Ψ_{el} is a linear combination of the various adiabatic electronic wave functions involved in the dynamics, the nuclear potential energy surface in Eq. (1.1) is a combination of all the adiabatic potential surfaces, so that this approach is quite a different situation from the surface hopping model described above.

A more rigorous mixed quantum-classical model is that put forth by Pechukas,¹⁰ whereby the nuclear trajectory is determined by a semiclassical evaluation of the electronic-nuclear path integral representation of the time evolution operator. The effective nuclear potential energy surface in this case turns out to be nonlocal in time, and because of the practical difficulties associated with this it has not seen much

application (but see Webster *et al.*¹¹). The Pechukas model is discussed in more detail at the end of Sec. II B in its relation to the present model developed below.

A very different approach to the problem of nonadiabatic dynamics was taken by Miller and co-workers.¹² Here the several electronic states (and the coupling between them) are replaced by classical degrees of freedom, yielding a classical Hamiltonian in terms of the nuclear coordinates and momenta, and coordinates and momenta for the (collective) electronic degrees of freedom. Classical trajectories for the combined electronic and nuclear degrees of freedom are then computed with the standard “quasiclassical” treatment of initial and final conditions.⁴ In the “classical electron analog” model of Meyer and Miller,^{12(c)} the equations of motion for the electronic-nuclear system are the same as in the Ehrenfest/TDSCF model, but the way the boundary condition are interpreted and applied makes the models quite different.

These various models all have their advantages as well as their shortcomings, a detailed analysis of which would be lengthy. In brief, the Ehrenfest/TDSCF approach is best when there is weak (and diffuse) coupling between many electronic states for which the nuclear forces are similar, and the surface hopping model is better when the coupling between the different adiabatic states is localized (though possibly strong). The “classical electron” model was constructed to provide a more even-handed description of the nuclear and electronic degrees of freedom, but it achieves this by reducing the rigor in the description of both sets of degrees of freedom to that of the quasiclassical model. There are also a variety of semiclassical treatments¹³ based on a perturbative (i.e., “golden rule”) approximation for the nonadiabatic coupling that are often very useful, but we are concerned in this paper with approaches that are, in principle at least, not restricted to the perturbative regime.

The new model we present here for treating nonadiabatic dynamics is based on the semiclassical initial value representation¹⁴ (SC-IVR) applied to the Meyer–Miller version of the classical electron model. In essence, it is a classical model of nuclear and electronic degrees of freedom that is quantized semiclassically via the IVR prescription. The SC-IVR approach has seen considerable interest recently¹⁵ for treating nuclear dynamics on a single potential surface where it has been shown to provide a good description of quantum interference and, to some extent, tunneling effects. The present work may be viewed as a generalization of the SC-IVR methodology to multi-electronic state problems. It will also be seen to have an interesting relation to some of the other models mentioned above.

Section II first reviews the Meyer–Miller version of the classical electron model and then quantizes it via the SC-IVR methodology. The relation of it to other models for treating nonadiabatic dynamics is also discussed. Section III then describes the results of application of the approach to the three test problems suggested by Tully which cover a variety of nonadiabatic coupling situations. The SC-IVR model is seen to provide a reasonably good description of the electronically nonadiabatic dynamics for all of these examples. Section IV

then concludes with a discussion of practical aspects of the model for interesting applications.

II. THEORETICAL DEVELOPMENT

A. Review of the classical electron analog model

Meyer and Miller^{12(c)} (MM) began by considering a $N \times N$ time-dependent electronic Hamiltonian matrix $\{H_{k,k'}(t)\}$, $k, k' = 1, \dots, N$, with the time-dependent electronic wave function expanded in the (diabatic) electronic basis,

$$|\Psi_{\text{el}}(t)\rangle = \sum_{k=1}^N c_k(t)|k\rangle. \quad (2.1)$$

They noted that if the complex amplitudes $c_k(t)$ are written in terms of the real variables $\{n_k(t), q_k(t)\}$,

$$c_k(t) = \sqrt{n_k(t)} e^{-iq_k(t)}, \quad (2.2)$$

and the classical electron analog Hamiltonian defined as (\hbar being 1 throughout this paper),

$$\begin{aligned} H_{\text{el}}(\mathbf{n}, \mathbf{q}; t) &= \langle \Psi_{\text{el}} | \hat{H}_{\text{el}} | \Psi_{\text{el}} \rangle \\ &= \sum_{k,k'=1}^N c_k^* H_{k,k'}(t) c_{k'} \\ &= \sum_{k,k'=1}^N \sqrt{n_k n_{k'}} \cos(q_k - q_{k'}) H_{k,k'}(t), \end{aligned} \quad (2.3)$$

then the classical equations of motion generated by this Hamiltonian,

$$\dot{q}_k(t) = \frac{\partial H_{\text{el}}(\mathbf{n}, \mathbf{q}; t)}{\partial n_k}, \quad (2.4a)$$

$$\dot{n}_k(t) = -\frac{\partial H_{\text{el}}(\mathbf{n}, \mathbf{q}; t)}{\partial q_k}, \quad (2.4b)$$

are equivalent of the time-dependent Schrödinger equation for the complex amplitudes,

$$i\dot{c}_k(t) = \sum_{k'=1}^N H_{k,k'} c_{k'}(t). \quad (2.5)$$

This correspondence has been noted before.¹⁶

In molecular systems, however, the electronic matrix is actually a function of nuclear coordinate \mathbf{R} , $\{H_{k,k'}(\mathbf{R})\}$. [It becomes a time-dependent electronic matrix if \mathbf{R} is assumed to follow a given trajectory $\mathbf{R}(t)$.] With this realization, Eq. (2.3) defines the classical electronic Hamiltonian as a function of nuclear coordinates,

$$H_{\text{el}}(\mathbf{n}, \mathbf{q}; \mathbf{R}) = \sum_{k,k'=1}^N \sqrt{n_k n_{k'}} \cos(q_k - q_{k'}) H_{k,k'}(\mathbf{R}), \quad (2.6)$$

and the classical Hamiltonian for the complete electronic plus nuclear system is obtained by simply adding the nuclear kinetic energy to it,

$$H(\mathbf{n}, \mathbf{q}, \mathbf{P}, \mathbf{R}) = \frac{\mathbf{P}^2}{2m} + H_{\text{el}}(\mathbf{n}, \mathbf{q}; \mathbf{R}). \quad (2.7)$$

Here, we have assumed for simplicity that the nuclear coordinates \mathbf{R} are Cartesian-like, scaled to have a common mass.

Looking ahead to the initial value representation of Sec. II B, it is useful to make a canonical transformation from the electronic action-angle variables (n_k, q_k) to the corresponding Cartesian-like electronic variables (x_k, p_k) which are defined in the standard way,¹⁷

$$x_k = \sqrt{2n_k} \cos q_k, \quad (2.8a)$$

$$p_k = -\sqrt{2n_k} \sin q_k. \quad (2.8b)$$

In terms of these variables, the classical electronic Hamiltonian of Eq. (2.6) becomes,

$$\begin{aligned} H_{\text{el}}(\mathbf{x}, \mathbf{p}; \mathbf{R}) &= \sum_{k, k'=1}^N \frac{1}{2} (p_k p_{k'} + x_k x_{k'}) H_{k, k'}(\mathbf{R}) \\ &= \sum_{k=1}^N \frac{1}{2} (p_k^2 + x_k^2) H_{k, k}(\mathbf{R}) \\ &\quad + \sum_{k < k'=1}^N (p_k p_{k'} + x_k x_{k'}) H_{k, k'}(\mathbf{R}), \quad (2.9) \end{aligned}$$

where it has been assumed in the last line that the diabatic electronic Hamiltonian matrix is real and symmetric. The reason the Cartesian electronic representation is useful is readily apparent: For fixed nuclear coordinates \mathbf{R} , the Hamiltonian of Eq. (2.9) is that of N harmonic oscillators for which the semiclassical IVR is exact! The SC-IVR treatment is also exact for the time-dependent harmonic Hamiltonian that results if \mathbf{R} is a given nuclear trajectory $\mathbf{R}(t)$. The full electronic-nuclear Hamiltonian is of course not harmonic in the full coordinate space (\mathbf{x}, \mathbf{R}) , but the fact that part of the problem is harmonic is expected to help the accuracy of the SC-IVR approach of the next section.

Still following MM's arguments,^{12(c)} there is one final modification to the classical electron Hamiltonian of Eq. (2.9), namely to subtract from it the term,

$$\frac{1}{2} \sum_{k=1}^N H_{k, k} = \frac{1}{2} \text{tr}(\mathbf{H}_{\text{el}}). \quad (2.10)$$

The classical electron Hamiltonian then becomes,

$$\begin{aligned} H_{\text{el}}(\mathbf{x}, \mathbf{p}; \mathbf{R}) &= \sum_{k=1}^N \frac{1}{2} (p_k^2 + x_k^2 - 1) H_{k, k}(\mathbf{R}) \\ &\quad + \sum_{k < k'=1}^N (p_k p_{k'} + x_k x_{k'}) H_{k, k'}(\mathbf{R}). \quad (2.11) \end{aligned}$$

MM argued for this modification based on a "Langer modification", but it is perhaps more convincingly justified by Stock and Thoss'¹⁸ version of the development whereby Eq. (2.11) is viewed as a quantum Hamiltonian operator for N oscillators,

$$\begin{aligned} \hat{H}_{\text{el}}(\mathbf{R}) &= \sum_{k=1}^N \frac{1}{2} (\hat{p}_k^2 + \hat{x}_k^2 - 1) H_{k, k}(\mathbf{R}) \\ &\quad + \sum_{k < k'=1}^N (\hat{p}_k \hat{p}_{k'} + \hat{x}_k \hat{x}_{k'}) H_{k, k'}(\mathbf{R}). \quad (2.12) \end{aligned}$$

Since the N electronic states correspond to the N oscillator states that each have one quantum of excitation in one mode and zero quanta in all the other modes—i.e., the wavefunctions of the N oscillator states are,

$$\Phi_k(\mathbf{x}) = \phi_1(x_k) \prod_{\substack{k'=1 \\ k' \neq k}}^N \phi_0(x_{k'}), \quad (2.13)$$

where $\{\phi_n(x)\}$ are the standard 1- d harmonic oscillator wave functions—it is easy to show using standard harmonic oscillator matrix elements that,

$$\langle \Phi_k | \hat{H}_{\text{el}} | \Phi_{k'} \rangle = H_{k, k'}. \quad (2.14)$$

Thus, it is necessary to subtract the term in Eq. (2.10) (which is the zero-point energy of the N oscillators) so that the matrix of the oscillator Hamiltonian of Eq. (2.12), with the N oscillator states of Eq. (2.13), reproduces the given diabatic electronic Hamiltonian matrix.

The final form of the electronic-nuclear Hamiltonian is then obtained by adding the nuclear kinetic energy to the electronic Hamiltonian of Eq. (2.11),

$$\begin{aligned} H(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}) &= \frac{\mathbf{P}^2}{2m} + \sum_{k=1}^N \frac{1}{2} (p_k^2 + x_k^2 - 1) H_{k, k}(\mathbf{R}) \\ &\quad + \sum_{k < k'=1}^N (p_k p_{k'} + x_k x_{k'}) H_{k, k'}(\mathbf{R}). \quad (2.15) \end{aligned}$$

We also note that one can express the classical electronic-nuclear Hamiltonian of Eq. (2.15) in the *adiabatic* representation. Following MM, if $(\bar{\mathbf{x}}, \bar{\mathbf{p}})$ are the adiabatic (Cartesian-like) electronic variables, then in terms of them the classical electronic-nuclear Hamiltonian is,

$$\begin{aligned} H(\bar{\mathbf{x}}, \bar{\mathbf{p}}, \mathbf{R}, \mathbf{P}) &= \frac{|\mathbf{P} + \mathbf{F}(\bar{\mathbf{x}}, \bar{\mathbf{p}}, \mathbf{R})|^2}{2m} \\ &= \sum_{k=1}^N \frac{1}{2} (\bar{p}_k^2 + \bar{x}_k^2 - 1) E_k(\mathbf{R}), \quad (2.16) \end{aligned}$$

where $E_k(\mathbf{R})$ are the adiabatic potential energy surfaces [i.e. the eigenvalues of the matrix $H_{k, k'}(\mathbf{R})$], and \mathbf{F} is a vector potential,

$$\mathbf{F}(\bar{\mathbf{x}}, \bar{\mathbf{p}}, \mathbf{R}) = \sum_{k < k'=1}^N (\bar{x}_k \bar{p}_{k'} - \bar{x}_{k'} \bar{p}_k) \mathbf{T}_{k, k'}(\mathbf{R}), \quad (2.17)$$

where $\mathbf{T}_{k, k'}(\mathbf{R})$ is the skew-symmetric nonadiabatic coupling matrix,

$$\mathbf{T}_{k, k'}(\mathbf{R}) = \left\langle \bar{\Phi}_k \left| \frac{\partial \bar{\Phi}_{k'}}{\partial \mathbf{R}} \right. \right\rangle, \quad (2.18)$$

$|\bar{\Phi}_k\rangle$ being the adiabatic electronic eigenfunctions.

B. Semiclassical initial value representation

Various dynamical quantities of interest are given quantum mechanically as matrix elements of the time evolution operator,

$$\begin{aligned} & \langle \chi_2 \Phi_{k_2} | e^{-i\hat{H}t} | \Phi_{k_1} \chi_1 \rangle \\ & \equiv S_{2,1}(t) = \int d\mathbf{x}_1 d\mathbf{R}_1 \int d\mathbf{x}_2 d\mathbf{R}_2 \chi_2^*(\mathbf{R}_2) \Phi_{k_2}^*(\mathbf{x}_2) \\ & \times \langle \mathbf{x}_2, \mathbf{R}_2 | e^{-i\hat{H}t} | \mathbf{x}_1, \mathbf{R}_1 \rangle \Phi_{k_1}(\mathbf{x}_1) \chi_1(\mathbf{R}_1), \end{aligned} \quad (2.19)$$

where $\chi_1(\chi_2)$ is the initial (final) nuclear wave function, $\Phi_k(\mathbf{x})$ are the ‘‘electronic’’ oscillator wave functions of Eq. (2.13), and H is the electronic-nuclear Hamiltonian of Eq. (2.15). As has been described in detail several times recently,¹⁵ the semiclassical initial value representation (SC-IVR) of Eq. (2.19) is obtained by making the semiclassical (Van Vleck) approximation for the coordinate matrix of the propagator and then using the IVR trick of changing the integration variables from the initial and final coordinates to the initial coordinates and momenta. This gives the SC-IVR for the amplitude in Eq. (2.19) as,

$$\begin{aligned} S_{2,1}(t) &= \int d\mathbf{x}_1 d\mathbf{R}_1 \int d\mathbf{p}_1 d\mathbf{P}_1 \\ & \times \sqrt{\frac{\partial(\mathbf{x}_t, \mathbf{R}_t)}{\partial(\mathbf{p}_1, \mathbf{P}_1)}} / (2\pi i)^{F+N} \chi_2^*(\mathbf{R}_t) \Phi_{k_2}^*(\mathbf{x}_t) \\ & \times \Phi_{k_1}(\mathbf{x}_1) \chi_1(\mathbf{R}_1) e^{iS_t(\mathbf{x}_1, \mathbf{p}_1, \mathbf{R}_1, \mathbf{P}_1) - i\pi\nu_t/2}, \end{aligned} \quad (2.20)$$

where $\mathbf{x}_t(\mathbf{x}_1, \mathbf{p}_1, \mathbf{R}_1, \mathbf{P}_1)$ and $\mathbf{R}_t(\mathbf{x}_1, \mathbf{p}_1, \mathbf{R}_1, \mathbf{P}_1)$ are the coordinates at time t that evolve along classical trajectory with the indicated initial conditions, S_t is the corresponding action integral, and ν_t is the number of zeros experienced by the Jacobian determinant in the interval $(0, t)$. The classical trajectories here are for the full set of N electronic and F nuclear degrees of freedom (in the MM spirit) obtained from the classical Hamiltonian of Eq. (2.15). It is also possible to calculate explicitly the nuclear wave functions on the various electronic surfaces by projecting out the electronic wave functions,

$$\begin{aligned} & \chi_{k_2-k_1}(\mathbf{R}, t) \\ & = \langle \mathbf{R}, \Phi_{k_2} | e^{-i\hat{H}t} | \Phi_{k_1} \chi_1 \rangle \\ & = \int d\mathbf{x}_1 d\mathbf{R}_1 \int d\mathbf{p}_1 d\mathbf{P}_1 \sqrt{\frac{\partial(\mathbf{x}_t, \mathbf{R}_t)}{\partial(\mathbf{p}_1, \mathbf{P}_1)}} / (2\pi i)^{F+N} \\ & \times \delta(\mathbf{R} - \mathbf{R}_t) \Phi_{k_2}^*(\mathbf{x}_t) \Phi_{k_1}(\mathbf{x}_1) \chi_1(\mathbf{R}_1) \\ & \times e^{iS_t(\mathbf{x}_1, \mathbf{p}_1, \mathbf{R}_1, \mathbf{P}_1) - i\pi\nu_t/2}. \end{aligned} \quad (2.21)$$

It is of course not possible to obtain this quantity via the usual mixed quantum-classical surface hopping methods.

It is interesting to note the relation of the present SC-IVR model, Eq. (2.20), to that of the Pechukas approach. In the latter one writes a Feynman path integral expression for the time evolution operator in Eq. (2.19),

$$\langle \mathbf{x}_2, \mathbf{R}_2 | e^{-i\hat{H}t} | \mathbf{x}_1, \mathbf{R}_1 \rangle = \int_{\mathbf{R}_1}^{\mathbf{R}_2} \mathcal{D}[\mathbf{R}] \int_{\mathbf{x}_1}^{\mathbf{x}_2} \mathcal{D}[\mathbf{x}] e^{iS[\mathbf{x}(t), \mathbf{R}(t)]}, \quad (2.22)$$

and imagines first evaluating (exactly) the path integral over the electronic degrees of freedom, whereby Eq. (2.19) becomes

$$\begin{aligned} S_{2,1}(t) &= \int d\mathbf{R}_2 \int d\mathbf{R}_1 \chi_2^*(\mathbf{R}_2) \chi_1(\mathbf{R}_1) \\ & \times \int_{\mathbf{R}_1}^{\mathbf{R}_2} \mathcal{D}[\mathbf{R}] e^{i\int_0^t dt' \frac{1}{2m} \dot{\mathbf{R}}(t')^2} K_{2,1}[\mathbf{R}(t)], \end{aligned} \quad (2.23)$$

where $K_{2,1}[\mathbf{R}(t)]$ is the electronic transition amplitude as a functional of the nuclear path $\mathbf{R}(t)$. Up to this point the formulation is exact, but one now evaluates the nuclear path integral semiclassically via the functional version of the stationary phase approximation. This determines the nuclear classical trajectory. (The Miller–George⁷ approach corresponds to the further approximation that the electronic transition amplitude functional $K_{2,1}[\mathbf{R}(t)]$ is also obtained semiclassically via the generalized Stuckelberg (complex crossing time) procedure.) As noted in Sec. II A, however, the SC-IVR treatment of the time-dependent electronic problem is *exact* for a given nuclear path. The SC-IVR model thus gives $K_{2,1}[\mathbf{R}(t)]$ of the Pechukas approach exactly. It also effectively makes a semiclassical approximation to the nuclear path integral but evaluates the integral over \mathbf{R}_1 and \mathbf{R}_2 exactly rather than via stationary phase. The present SC-IVR treatment of the MM classical electronic-nuclear Hamiltonian may thus be viewed as a practical way to implement the Pechukas model, with the further advantage that it treats the nuclear degrees of freedom within the SC-IVR framework.

The present approach is also seen to be of the same spirit as the original MM model in that it treats the electronic and nuclear degrees of freedom on the same dynamical footing, except here the treatment is via the SC-IVR description rather than the more primitive quasiclassical procedure. (We note that MM and others¹⁹ did carry out semiclassical treatments of the classical electron model within the classical S-matrix formulation, and that the results were in fact excellent. Applications to more general situations, however, were difficult.)

III. APPLICATIONS TO TEST SYSTEMS

To gain some indication of how well the present SC-IVR quantization of the classical electronic-nuclear model works in practice we have carried out applications to the ‘‘Tully canon,’’ i.e., the three model problems suggested by Tully⁶ for testing a variety of situations in nonadiabatic dynamics. These scattering problems involve one nuclear degree of freedom (e.g., an atom–atom collision system) and two ‘‘electronic states,’’ so the classical Hamiltonian of Eq. (2.15) takes the specific form,

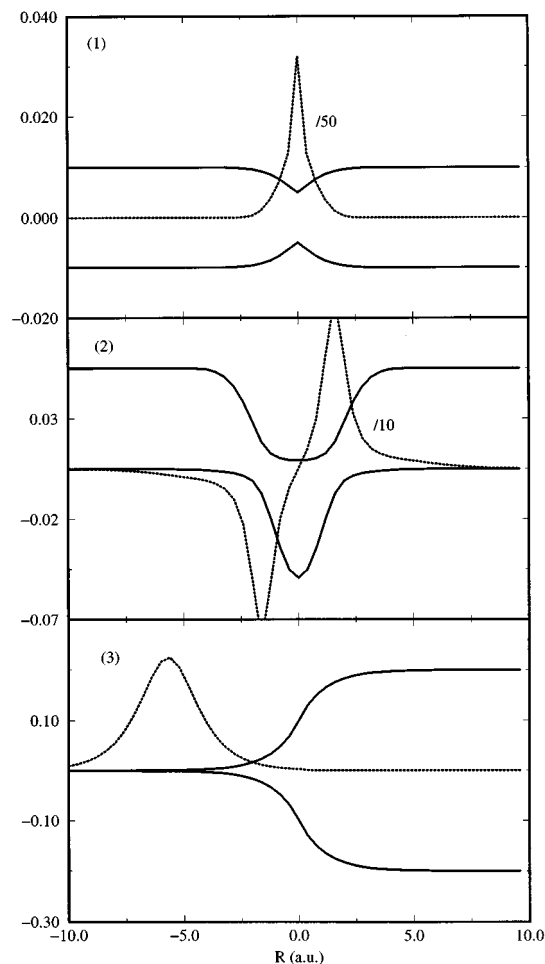


FIG. 1. The adiabatic potential curves (solid) and the nonadiabatic coupling (dash) for the three systems considered. (1) Single avoided crossing. (2) Dual crossing. (3) Extended coupling.

$$\begin{aligned}
 H(x_1, p_1, x_2, p_2, R, P) = & \frac{P^2}{2m} + \frac{1}{2} (p_1^2 + x_1^2 - 1) H_{11}(R) \\
 & + \frac{1}{2} (p_2^2 + x_2^2 - 1) H_{22}(R) \\
 & + (p_1 p_2 + x_1 x_2) H_{12}(R) \quad (3.1)
 \end{aligned}$$

for various forms of the 2×2 diabatic electronic matrix $\{H_{k,k'}(R)\}$. The two “electronic” wave functions of Eq. (2.13) are,

$$\Phi_1(x_1, x_2) = \sqrt{\frac{2}{\pi}} x_1 e^{-1/2(x_1^2 + x_2^2)}, \quad (3.2a)$$

$$\Phi_2(x_1, x_2) = \sqrt{\frac{2}{\pi}} x_2 e^{-1/2(x_1^2 + x_2^2)}. \quad (3.2b)$$

The specific forms of the 2×2 diabatic electronic matrix $\{H_{k,k'}(R)\}$ correspond to a single avoided crossing, a double avoided crossing, and an extended coupling problem. The adiabatic potentials for the three cases are shown in Fig. 1. The nuclear mass is $m = 2000$ a.u., about the mass of an H atom. As with Tully’s calculations, the initial nuclear wave

function is a Gaussian wave packet (coherent state) located in the reactant asymptotic region (to the far left in Fig. 1),

$$\chi_1(R) = \left(\frac{f}{\pi}\right)^{1/4} e^{-(f/2)(R-R_0)^2 + iP_0 R}, \quad (3.3)$$

where R_0 is far from the interaction region, and P_0 is the initial momentum. f is taken to be 1. The total wave function at $t = 0$ is therefore,

$$\Psi_1(R, x_1, x_2, 0) = \chi_1(R) \Phi_1(x_1, x_2). \quad (3.4)$$

This wave function is then propagated in time to the product asymptotic region ($R \rightarrow \infty$) using the SC-IVR formalism described in the previous section. The nuclear wave functions on each surface are found by projecting out the electronic part as described before. The quantities Tully calculated are the various transmission and reflection probabilities on either surface. We obtain these by integrating the final nuclear probability density in the asymptotic regions,

$$P_k^{\text{trans}} = \lim_{t \rightarrow \infty} \int_0^{\infty} dR |\chi_k(R, t)|^2, \quad (3.5a)$$

$$P_k^{\text{refl}} = \lim_{t \rightarrow \infty} \int_{-\infty}^0 dR |\chi_k(R, t)|^2. \quad (3.5b)$$

Because the initial wave function is narrow in momentum, the final transmission and reflection probabilities are approximately the scattering probabilities as a function of initial translational energy $P_0^2/2m$.

The specific IVR we used for the calculation is the Herman–Kluk IVR,^{14(f)} the generic form of which is,

$$\begin{aligned}
 \langle \Psi_2 | e^{-i\hat{H}t} | \Psi_1 \rangle = & \int \frac{d\mathbf{q}_1 d\mathbf{p}_1}{(2\pi)^F} C_{\mathbf{q}\mathbf{p}t} \Psi_1^g(\mathbf{q}_1, \mathbf{p}_1) \\
 & \times \Psi_2^{g*}(\mathbf{q}_t, \mathbf{p}_t) e^{iS_t(\mathbf{q}_1, \mathbf{p}_1)}, \quad (3.6)
 \end{aligned}$$

where $\{\Psi_n^g\}$ are the coherent state transforms of the two wave functions,

$$\begin{aligned}
 \Psi^g(\mathbf{q}, \mathbf{p}) = & \langle g | \Psi \rangle \\
 = & \int d\mathbf{q}' \Psi(\mathbf{q}') \left(\frac{\gamma}{\pi}\right)^{F/4} e^{-\gamma/2(\mathbf{q}-\mathbf{q}')^2 + i\mathbf{p}\cdot(\mathbf{q}-\mathbf{q}')}, \quad (3.7)
 \end{aligned}$$

the Jacobian factor $C_{\mathbf{q}\mathbf{p}t}$ is

$$C_{\mathbf{q}\mathbf{p}t} = \sqrt{\det\left(\frac{1}{2} \begin{pmatrix} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_1} + \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_1} - i\gamma \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_1} + \frac{i}{\gamma} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_1} \end{pmatrix}\right)}, \quad (3.8)$$

and γ is an adjustable parameter. When applied to the current specific problem, the time-dependent nuclear wave function on surface k is,

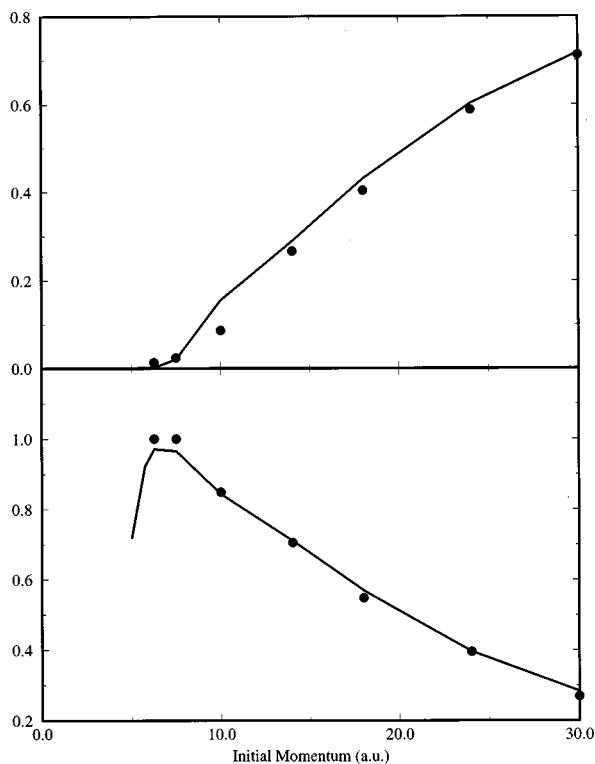


FIG. 2. Case 1, single avoided crossing. Upper panel, transmission probabilities on the first diabatic state (upper adiabatic state). Lower panel: Transmission probabilities on the second diabatic state (lower adiabatic state). Solid lines are the quantum mechanical results. Filled circles are the SC-IVR model.

$$\begin{aligned} \chi_{k \leftarrow 1}(R, t) = & \int dR dP dx_1 dp_1 dx_2 dp_2 C_{\text{xp}} \chi_1^g(R, P) \\ & \times \Phi_1^g(x_1, p_1, x_2, p_2) g(R_t, P_t; R) \\ & \times \Phi_k^{g*}(x_{1t}, p_{1t}, x_{2t}, p_{2t}) \\ & \times e^{iS_t(R, P, x_1, p_1, x_2, p_2) - i\pi\nu/2}, \end{aligned} \quad (3.9)$$

where

$$g(R_t, P_t; R) = \langle R | g \rangle = \left(\frac{\gamma}{\pi} \right)^{1/4} e^{-\gamma/2(R-R_t)^2 + iP_t(R-R_t)}. \quad (3.10)$$

The integration over the initial conditions is done with weighted Monte Carlo sampling. A typical number of trajectories required for convergence is 4×10^4 . From the wave functions, transmission probabilities, and reflection probabilities are calculated for both electronic states. Quantum mechanical calculations are also performed for comparison purposes with the standard split operator technique.

A. Case 1, avoided crossing

This example of an isolated avoided crossing of adiabatic potential surfaces is the most elementary and most common situation. The diabatic potentials in the case are,

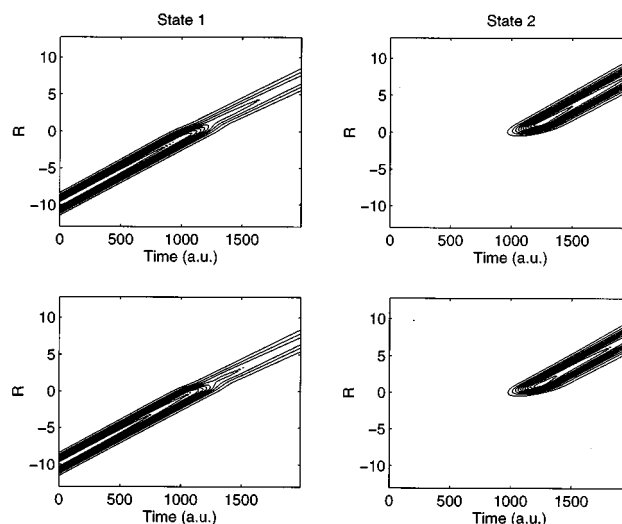


FIG. 3. Case 1, avoided crossing. Contours of the absolute value of the nuclear wave functions squared on each of the diabatic states, quantum (upper two panels) vs. SC-IVR (lower two panels). The initial momentum is $P_0 = 18.0$.

$$H_{11}(R) = \begin{cases} V_0(1 - e^{-\alpha R}) & R > 0, \\ -V_0(1 - e^{\alpha R}) & R < 0, \end{cases} \quad (3.11a)$$

$$H_{22}(R) = -H_{11}(R), \quad (3.11b)$$

$$H_{12}(R) = V_1 e^{-\beta R^2}. \quad (3.11c)$$

The parameters used here are the same as used by Tully, $V_0 = 0.001$, $V_1 = 0.005$, $\alpha = 1.6$, and $\beta = 1.0$, all in atomic units. The transmission probabilities in state 1 and 2 vs the initial momentum are shown in Fig. 2. The quantum results are plotted also. The semiclassical results are essentially quantitative for higher initial energies. For lower energies though, the results are not as well reproduced compared to the quantum answers. The reason we believe is due to the long time problem of the semiclassical IVR formalism. It is well known that the accuracy of the semiclassical IVR approximation to the time-dependent propagator diminishes as time becomes long.^{14(e)} The Herman-Kluk IVR used here is no exception. Since at lower energies, it takes longer for the wave packet to go from one asymptotic region to another, the final probabilities are not very accurate. In fact, for times longer than 5000 atomic units, the system becomes chaotic and the IVR expression gives unstable results. This is one of challenges of SC-IVR calculations where chaotic dynamics of the problem can give unphysical answers.

In addition to the probabilities, with this method, we are able to obtain also the wave functions on each surface. These wave functions and their time evolution are shown as contours in Fig. 3. Compared with the quantum mechanical results, they are in excellent agreement.

B. Case 2, double crossing

This example is more challenging in that there is quantum mechanical interference between the two crossings, giving Stueckelberg oscillations.²⁰ The diabatic potentials in this case are,

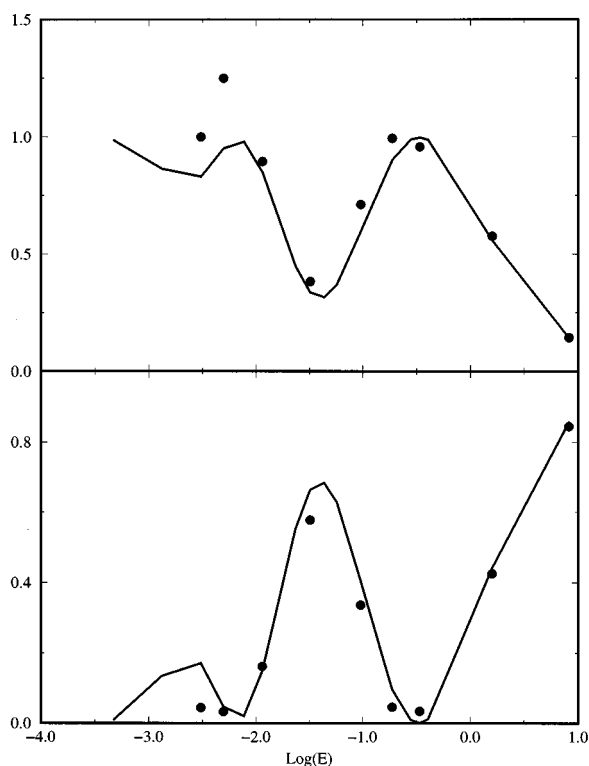


FIG. 4. Case 2, dual avoided crossing. Upper panel, transmission probabilities on the first diabatic state. Lower panel, transmission probabilities on the second diabatic state. Symbols are the same as Fig. 2.

$$H_{11}(R) = 0, \quad (3.12a)$$

$$H_{22}(R) = -V_0 e^{-\alpha R^2} + E_0, \quad (3.12b)$$

$$H_{12}(R) = V_1 e^{-\beta R^2}, \quad (3.12c)$$

with $V_0 = 0.1$, $E_0 = 0.05$, $V_1 = 0.015$, $\alpha = 0.28$, and $\beta = 0.06$. Again, comparisons between quantum and semiclassical results are shown in Fig. 4. The present SC-IVR model reproduces the oscillatory transmission probabilities at higher energies very well. At lower energies, we have the same problem of long time accuracy of the semiclassical propagation.

C. Case 3, extended coupling

This case is a still more difficult test for the semiclassical method. Here, the coupling between the diabatic states does not go to zero in the asymptotic region. The diabatic potentials are,

$$H_{11}(R) = -V_0, \quad (3.13a)$$

$$H_{22}(R) = V_0, \quad (3.13b)$$

$$H_{12}(R) = \begin{cases} V_1 e^{\beta R} & R < 0, \\ V_1 (2 - e^{-\beta R}) & R > 0, \end{cases} \quad (3.13c)$$

with $V_0 = 6 \times 10^{-4}$, $V_1 = 0.1$, and $\beta = 0.9$. Since the diabatic states are very close in energy, the transmission and reflection probabilities are essentially identical for both states. The

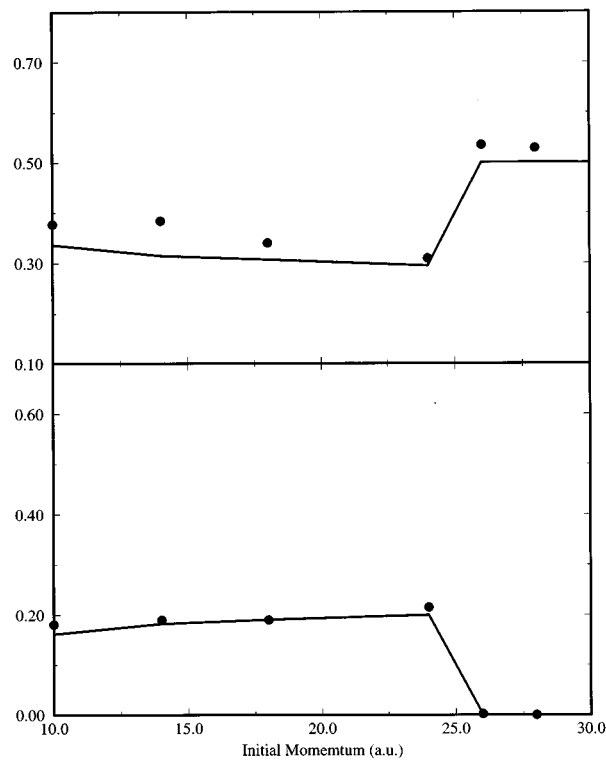


FIG. 5. Case 3, extended coupling. Upper panel, transmission probabilities for both of the diabatic states. Lower panel, reflection probabilities for both of the diabatic states. Symbols are the same as Fig. 2.

adiabatic states show a barrier for the upper state, thus one would expect some reflection for energies below this barrier. These effects are all observed in the quantum and the semiclassical calculations. Their comparison is again very good. Tully in his calculations observed unphysical oscillatory effects with the surface-hopping model. We do not observe this in the transmission and reflection probabilities as shown in Fig. 5. However, the probabilities as a function of time do show some small oscillations around the correct value in Fig. 6. These oscillations are of course due to the extended coupling in the asymptotic region. The extent to which they effect the final answer however is small.

IV. CONCLUDING REMARKS

It has been shown how the semiclassical initial value representation methodology can be generalized to include electronically nonadiabatic dynamics. The basic idea is to quantize the classical electronic-nuclear Hamiltonian of Meyer and Miller within the SC-IVR framework. Electronic and nuclear degrees of freedom are thus treated on the same dynamical footing, in the original spirit of MM, except the treatment is now via the SC-IVR description rather than the more primitive quasiclassical one.

Application of the approach to a variety of test problems shows it to provide a good description of nonadiabatic transitions in essentially all these cases. The only difficulties were seen at low energies, where the SC-IVR approach has had difficulties in the past for treating nuclear dynamics even

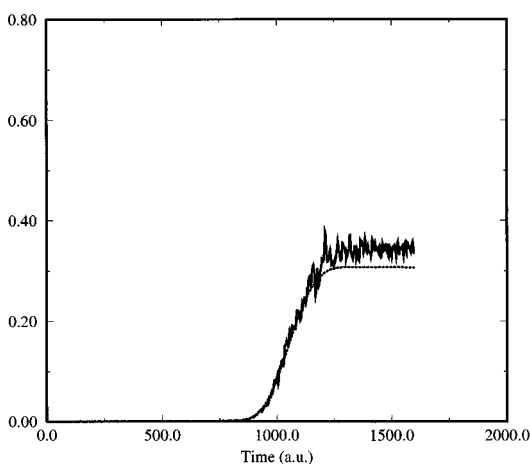


FIG. 6. Transmission probability as function of time for the extended coupling. The initial momentum is $P_0=18.0$. This plot is the same for either diabatic state. Solid line, SC-IVR. Dashed line, quantum mechanical.

on one potential surface. We believe that this model has a great deal of potential for providing a realistic description of electronically nonadiabatic dynamics in a variety of situations, though like any model, there will be cases where it is not accurate.

Perhaps more serious is the question of applicability of the SC-IVR approach. The computational task is to evaluate a rather high dimensional integral (a phase space average over initial conditions) with an oscillatory integrand. The various filtering, or smoothing, procedures provided by the Herman–Kluk approach, or the stationary phase Monte Carlo methods,²¹ help to make the integral approachable by Monte Carlo methods. It is clear, though, that one needs to make further progress in this regard to make the SC-IVR methodology truly practical.

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