# An Analysis of the Accuracy of an Initial Value Representation Surface Hopping Wave Function in the Interaction and Asymptotic Regions

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## Abstract

The behavior of an initial value representation surface hopping wave function is examined. Since this method is an initial value representation for the semiclassical solution of the time independent Schrodinger equation for nonadiabatic problems, it has computational advantages over the primitive surface hopping wave function. The primitive wave function has been shown to provide transition probabilities that accurately compare with quantum results for model problems. The analysis presented in the work shows that the multi-state initial value representation surface hopping wave function should approach the primitive result in asymptotic regions and provide transition probabilities with the same level of accuracy for scattering problems as the primitive method.

## I. Introduction

The accurate description of atomic and molecular collision events poses a challenging computational problem. Classical trajectory calculations can sometimes offer insight into the collision dynamics, but these miss important interference effects and are generally inadequate for problems in which the collision event is reactive or results in a change in the quantum states of the collision partners. On the other hand, quantum calculations are only feasible for systems with a small number of degrees of freedom. Semiclassical methods often provide a useful middle ground, providing approximate quantum wave functions, transition probabilities, etc., by utilizing information obtained by running classical trajectories.

Initial value representation (IVR) semiclassical methods[1-8] have been particularly useful semiclassical approaches. These methods may avoid the singularities at classical turning points and caustics that are present in primitive semiclassical methods.[1,9,10] They also avoid the difficult search for trajectories satisfying double ended boundary conditions that is required by primitive semiclassical calculations. Semiclassical methods have proven especially useful for processes that involve only one electronic quantum state of the collision partners. The situation is less advanced for problems involving changes in the electronic quantum state of the system. Several different semiclassical approaches[11-52] have been purposed for this type of problem.

A specific semiclassical surface hopping method for time independent scattering problems is considered in this work.[44-49] Numerical studies on model problems have shown that this method is capable of providing highly accurate results, even in cases involving significant phase cancellation between different surface hopping trajectories.[44-49] As is the case for single electronic state problems, the multi-state semiclassical surface hopping formalism can be cast as a primitive

semiclassical method[44-48] or as an initial value representation.[49] In this work, the IVR multi-state wave function is examined in more detail. This method is a surface hopping generalization of the single state globally uniform method of Kay and coworkers.[7,8] The wave function is expressed in terms of frozen Gaussian functions traveling along classical trajectories that obey appropriate initial conditions. The method has been found to provide accurate transition probabilities for model problems.[49]

It has been shown[44,45] that the primitive surface hopping method reduces to the WKB approximation in the one state case, and that it satisfies the time independent Schrodinger equation (TISE) to all orders in the nonadiabatic coupling and to first order in $\hbar$, which is the order in $\hbar$ to which the WBK approximation satisfies the TISE.[53] The globally uniform wave function also satisfies the TISE to first order in $\hbar$ in the single state case.[7,8] It is shown in this work that the IVR surface hopping (IVRSH) wave function for multi-state problems satisfies the TISE to first order in $\hbar$ in asymptotic regions. The analysis presented demonstrates that the method should provide accurate wave functions in the asymptotic regions for scattering problems. It is the wave function in these regions that determines the transition probability. It is also shown that the IVRSH wave function can have errors in the interaction region, that these errors do not affect that transition probabilities, and that the errors diminish as the width of the Gaussian functions employed in the method is reduced.

## II. Theory

### A. The IVR Surface Hopping Wave Function

It is common in a quantum mechanical treatment of atomic and molecular systems to split

the degrees of freedom into a set of fast variables, **r**, and a set of comparatively slow variables, **R**. In most cases, the electronic coordinates are chosen as the fast degrees of freedom and the positions of the nuclei are the slow degrees of freedom. In the adiabatic, or Born-Oppenheimer, approximation,[54] the quantum states of the fast degrees of freedom are obtained for fixed values of the slow coordinates by solving the fast coordinate Schrodinger equation

$$\mathbf{H}_f \varphi_j(\mathbf{r};\mathbf{R}) = E_j^{(f)}(\mathbf{R})\,\varphi_j(\mathbf{r};\mathbf{R}) \qquad (1)$$

where $\mathbf{H}_f = \mathbf{T}_f + V(\mathbf{r}, \mathbf{R})$, $\mathbf{T}_f$ is the kinetic energy operator for the fast degrees of freedom, $V(\mathbf{r}, \mathbf{R})$ is the potential energy of the system, and the $\varphi_j(\mathbf{r}; \mathbf{R})$ are the adiabatic quantum states for the fast subsystem. Within the adiabatic approximation, $E_j^{(f)}(\mathbf{R})$ serves as the potential energy $W_j(\mathbf{R})$ for the slow degrees of freedom when the fast subsystem is in quantum state j.

For simplicity, this work considers scattering wave functions for which the incoming wave function is a plane wave. The results can be generalized for problems in which the collision partners have internal and rotational degrees of freedom, if these degrees of freedom can be described using action-angle variables. If only a single adiabatic state is important for a specific problem, the globally uniform IVR semiclassical wave function is given by[7,8]

$$\psi_E(\mathbf{R}) = N \int d\mathbf{s}\, C(\mathbf{s})\, e^{F(\mathbf{s})/i\hbar} \qquad (2)$$

where **R** is a d-dimensional vector. The **s** integration is over d variables. The first integration variable, $s_1$, is the time along the trajectory having $\mathbf{R}_0$ and $\mathbf{P}_0$ as its position and momentum at t = 0. The remaining d-1 integration variables, $s_2$, $s_3$, ... , $s_d$, specify $\mathbf{R}_0$ on a surface $\boldsymbol{\Sigma}$ in the incoming asymptotic region. The magnitude of $\mathbf{P}_0$ is determined by the energy E, its direction is the same for each $\mathbf{R}_0$, and $\boldsymbol{\Sigma}$ is the plane perpendicular to $\mathbf{P}_0$. If, for example, d = 3 and $\mathbf{P}_0$ is in the z

direction, then $\mathbf{\Sigma}$ is the x,y plane corresponding to z equal to a value $z_0$ in the incoming region, and $\mathbf{R}_0 = (s_2, s_3, z_0)$. The mass is taken to be the same for all coordinates. In more general problems, mass weighted coordinates can be used. The N in Eq.(2) is a constant that determines the overall magnitude of the wave function. The prefactor is given by $C(\mathbf{s}) = [\det \mathbf{B}]^{1/2}$, where the elements of $\mathbf{B}$ are given by

$$\mathbf{B}_{jk} = \frac{\partial \mathbf{P}_{sk}}{\partial \mathbf{s}_j} - 2i\gamma \frac{\partial \mathbf{R}_{sk}}{\partial \mathbf{s}_j}, \tag{3}$$

and the exponential function in Eq. (2) is given by $F = -\gamma(\mathbf{R} - \mathbf{R}_s)^2 + i\,\mathbf{P}_s \cdot (\mathbf{R} - \mathbf{R}_s) + i\,w(\mathbf{s})$. In these expressions, $\gamma$ is a constant that determines the width of the Gaussian wave packet $\exp(F/\hbar)$, and $(\mathbf{R}_s, \mathbf{P}_s)$ is the phase space point at time t ( $= s_1$) for the trajectory that starts at the point $\mathbf{R}_0$ with momentum $\mathbf{P}_0$. The results can be easily generalized to allow for different values of $\gamma$ for each coordinate. The function $w(\mathbf{s})$ is given by

$$w = \int_{\mathbf{R}_0}^{\mathbf{R}_s} \mathbf{P} \cdot d\mathbf{R} \tag{4}$$

where the integration is performed along the trajectory.

It has been shown that a specific form of the primitive surface hopping wave function satisfies the TISE to first order in $\hbar$ for each orders of the nonadiabatic coupling, and that it provides very accurate transition probabilities.[44-48] The IVR wave function, Eq. (2), can be generalized for nonadiabatic problems[49] using a surface hopping form analogous to the primitive surface hopping wave function. The component of the IVRSH wave function corresponding to

adiabatic state $\varphi_j$ can be expressed as

$$\psi_{j,E}(\mathbf{R}) = \delta_{i,j}\int ds\, C(s)\, e^{F(\mathbf{R},s)/\hbar} + \sum_{n=1}^{\infty} \psi_{j,E}^{(n)}(\mathbf{R}) \qquad (5)$$

where the incoming particle is in adiabatic state $\varphi_i$ and $\delta_{ij}$ is the Kronecker delta. The wavefunction is given by the sum of $N\varphi_j(\mathbf{r},\mathbf{R})\psi_{j,E}(\mathbf{R})$ over all j. The dependence of the prefactor C and exponential function F on i and E has been suppressed to simplify the notation. The first order contribution to the wave function has the form[44,45] $\psi_{j,E}^{(1)} = \psi_{jT}^{(1)} + \psi_{jR}^{(1)}$. The transition or T-type term has the form

$$\psi_{jT}^{(1)}(\mathbf{R}) = \int ds \int_{-\infty}^{t} dt_1\, \tau_{ij}(s,t_1)\, C_j(s,t_1)\, e^{F_j(\mathbf{R},s,t_1)/\hbar} \qquad (6)$$

This term is the contribution from trajectories that start at $\mathbf{R}_0$ on adiabatic surface $W_i$, hop to adiabatic surface $W_j$ at time $t_1$, and then continue on this surface up to time t. The momentum changes so as to conserve energy at the hop. Only the component of the momentum parallel to $\boldsymbol{\eta}_{ij}$ is altered in the transition, and $\mathbf{P}\cdot\boldsymbol{\eta}_{ij}$ has the same sign before and after the hop,[45] where $\boldsymbol{\eta}_{ij}(\mathbf{R}) = \int \varphi_j^* \, \partial\varphi_i/\partial\mathbf{R}\, d\mathbf{r}$ is the nonadiabatic coupling vector. The transition amplitude $\tau_{ij}$ is discussed below. $C_j(\mathbf{s}, t_1)$ and $F_j(\mathbf{R}, \mathbf{s}, t_1)$ are defined as above except these quantities are now evaluated for the trajectory that hops to $W_j$ at $t_1$.

The first order reflection, or R-type, term $\psi_R^{(1)}$ is defined similarly to the $\psi_T^{(1)}$ term, except that the sign of $\mathbf{P}\cdot\boldsymbol{\eta}_{if}$ changes at the energy conserving hop. Available numerical evidence indicates that the R-type term is generally small compared to the T-type term and the use of only

the T-type term in calculations provides very accurate results.[45-52]

The $n^{th}$ order term is defined analogously for trajectories that have n energy conserving hops. For example, the second order term with two T-type hops is given by

$$\psi^{(2)}_{TT,j}(\mathbf{R}) = \sum_k \int ds \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 \, \tau_{ik}(s,t_1)\tau_{kj}(s,t_1,t_2) C_{kj}(s,t_1,t_2) e^{F_{kj}(\mathbf{R},s,t_1,t_2)/\hbar} \qquad (7)$$

where the first hop is from state i to state k at time $t_1$ and the second hop is from state k to state j at time $t_2$.

**B. The Primitive Wave Function and the Form of the Transition Amplitudes**

The primitive surface hopping wave function is given by $\sum \varphi_j(\mathbf{R})\ \psi^{pr}_{j\,E}(\mathbf{R})$ where the sum is over all adiabatic states and[44,45]

$$\psi^{pr}_{j,E}(\mathbf{R}) = \delta_{ij} A e^{iw/\hbar} + \sum_{n=1}^{\infty} \psi^{(pr,n)}_{j,E}(\mathbf{R}) \qquad (8)$$

The first term on the right hand side is the zero hop term. It has the form of the single surface semiclassical wave function on adiabatic surface $W_i$. For the scattering problems considered in this work, the incoming wave function is a plane wave with momentum $\mathbf{P}_0$ in the incoming asymptotic region. This zeroth order (in the nonadiabatic coupling) term in the wave function is evaluated by running trajectories that end at $\mathbf{R}$ and begin at a point $\mathbf{R}_0$ on $\mathbf{\Sigma}$ with the momentum $\mathbf{P}_0$, where $\mathbf{\Sigma}$ is defined as before. The function w given by Eq. (4) with $\mathbf{R}$ as the upper limit of the integration. The prefactor has the form[2,45]

$$\mathbf{A} = \left[\left|\frac{\partial \boldsymbol{\sigma}_t}{\partial \boldsymbol{\sigma}_0}\right|\left(\frac{P_t}{P_0}\right)\right]^{-1/2} \tag{9}$$

where $P_t$ and $P_0$ are the magnitudes of $\mathbf{P}_0$ and $\mathbf{P}_t$, t is the time at which the trajectory reaches $\mathbf{R}$, and $\partial\boldsymbol{\sigma}_t/\partial\boldsymbol{\sigma}_0$ is the matrix of partial derivatives of the d-1 final coordinates perpendicular to the final momentum $\mathbf{P}_t$ with respect to the d-1 initial coordinates perpendicular to the initial momentum $\mathbf{P}_0$. If there is more than one trajectory starting at a point on $\boldsymbol{\Sigma}$ with the momentum $\mathbf{P}_0$ and ending at $\mathbf{R}$, then the contributions of this form are summed over all such trajectories.

The first order term is given by

$$\psi_{j,E}^{(pr,1)}(\mathbf{R}) = \int dt_1 \tau_{ij}^{(pr)}(t_1) A_{T,j}(\mathbf{R},t_1) e^{iw_{T,j}(\mathbf{R},t_1)/\hbar} + \int dt_1 \rho_{ij}^{(pr)}(t_1) A_{R,j}(\mathbf{R},t_1) e^{iw_{R,j}(\mathbf{R},t_1)/\hbar} \tag{10}$$

This contribution is obtained from trajectories that obey the same initial condition as is the case for the zeroth order term, hop from $W_i$ to $W_j$ at time $t_1$, and end at $\mathbf{R}$. The hop conserves energy, and the change in momentum is in the direction parallel to the nonadiabatic coupling vector, $\boldsymbol{\eta}_{ij}$. The first and second terms on the rhs of Eq. (10) correspond to T-type and R-type hops, and the functions $\tau_{ij}^{(pr)}$ and $\rho_{ij}^{(pr)}$ are the transition amplitudes for the T-type and R-type hops, respectively. The second and higher order terms are defined analogously.

It can be shown[45] that, in order for $\psi_{j,E}^{pr}(\mathbf{R})$ to satisfy the TISE to first order in $\hbar$ for all orders in the nonadiabatic coupling, the hopping amplitudes must satisfy the condition

$$2\mathbf{P}_i\cdot\boldsymbol{\eta}_{ij} A_0 P_{i\eta}/m + (P_{i\eta} + P_{j,\eta})\tau_{ij}^{(pr)} A_{T,j} + (P_{i\eta} - P_{j\eta})\rho_{ij}^{(pr)} A_{R,j} = 0 \tag{11}$$

where the subscripts 0, T, R refer to the zero hop, the T-type single hop, and the R-type single hop terms, $\mathbf{P}_i$ is the value of the momentum on the initial surface at the time of the hop, and where

$P_{i\eta}$ and $P_{j\eta}$ are the components of the momentum in the direction of $\boldsymbol{\eta}_{ij}$ immediately before and after the hop, respectively. One solution of Eq.(11) is

$$\tau_{ij}^{(pr)} = -\frac{(P_{i\eta}+P_{j\eta})}{2P_{j\eta}}\frac{P_{i\eta}}{m}\frac{A_0}{A_{T,j}}\eta_{ij} \tag{12}$$

$$\rho_{ij}^{(pr)} = -\frac{(P_{j\eta}-P_{i\eta})}{2P_{j\eta}}\frac{P_{i\eta}}{m}\frac{A_0}{A_{R,j}}\eta_{ij} \tag{13}$$

where $\eta_{ij} = |\boldsymbol{\eta}_{ij}|$. This solution is suggested by a formally exact surface-hopping expansion for the multi-state wave function in one dimension.[44] The exact wave function contains all terms in the expansion described here in exactly the same form, plus additional reflection terms involving momentum reversal without a change in adiabatic state. These additional single surface reflection terms correct for the semiclassical nature of the wave function on each surface in the one dimensional case.[55]

There is a condition of the form of Eq. (11) for every set of transition amplitudes $\tau_{ij}^{(pr)}$ and $\rho_{ij}^{(pr)}$ for multi-hop trajectories. If the transition amplitudes are for the $n^{th}$ hop in a trajectory, then the zeroth hop term in Eq. (11) is replaced with the appropriate (n-1)-hop term, and the first order T and R type first order terms in Eq. (11) are replaced with the n-hop terms with a T or R type hop occurring end of the (n-1)-hop trajectory in the (n-1)-hop term. If the transition amplitudes given by Eqs. (12) and (13) are used in all hopping terms, the conditions of the form of Eq. (11) are satisfied and the primitive wave function satisfies the TISE to first order in $\hbar$ for all orders in the nonadiabatic coupling.

The situation is somewhat more complicated for the IVRSH wave function. The

condition for the IVRSH wave function that is similar to Eq.(11) is[49]

$$\int d\boldsymbol{\sigma}_0 \left( \mathbf{P}_{it} \cdot \boldsymbol{\eta}_{ij} C_0 e^{F_0/\hbar} \mathbf{P}_{i\eta}/m + \tau_{ij} C_{T,j} e^{F_{T,j}/\hbar} + \rho_{ij} C_{R,j} e^{F_{R,j}/\hbar} \right) = 0 \qquad (14)$$

where the subscripts 0, T, and R have the same meaning as above, and all quantities are evaluated for t equal to the time of the hop, $t_h$. Therefore, $F_0 = -\gamma(\mathbf{R} - \mathbf{R}_h)^2 + i\,\mathbf{P}_i \cdot (\mathbf{R} - \mathbf{R}_h) + iw_0$, where $\mathbf{P}_i$ is the pre-hop momentum at the hopping point $\mathbf{R}_h$ and $w_0$ is given by Eq.(4) with the integration taken up to the $\mathbf{R}_h$. Likewise, $F_{T,j} = -\gamma(\mathbf{R} - \mathbf{R}_h)^2 + i\,\mathbf{P}_j \cdot (\mathbf{R} - \mathbf{R}_h) + iw_T$ and $F_{R,j} = -\gamma(\mathbf{R} - \mathbf{R}_h)^2 - i\,\mathbf{P}_j \cdot (\mathbf{R} - \mathbf{R}_h) + iw_R$, where $\mathbf{P}_j$ is the momentum on the final surface at the hopping point for the T-type trajectory. Since $w_T$ and $w_R$ are evaluated up to the point of the hop, they are both equal to $w_0$. It is the different value of $\mathbf{P}$ in the $i\mathbf{P} \cdot (\mathbf{R} - \mathbf{R}_h)$ terms in $F_0$, $F_{T,j}$, and $F_{R,j}$ that is the problem. Due to this difference, it is not possible to solve for $\tau_{ij}$ and $\rho_{ij}$ such that they satisfy Eq. (14) and do not depend on $\mathbf{R}$, the position at which the wave function is being evaluated. If the transition amplitude depends on $\mathbf{R}$, then the wave function no longer has the form of a set of Gaussian functions in $\mathbf{R}$, and a different transition amplitude must be used at each $\mathbf{R}$. The fact that the order $\hbar$ condition, Eq. (14), is not satisfied for the IVRSH wave function was not appreciated in previous work.[49] Nonetheless, excellent results for transition probabilities were obtained for a one dimensional curve crossing problem in that work using the primitive transition amplitude in the IVR method.

This raises the question of why the IVRSH expansion can obtain excellent results for transition probabilities if transition amplitudes do not satisfy Eq. (14). The transition probability is determined by the flux on the final surface in the final asymptotic region where $W_j(\mathbf{R})$ is constant. Ignoring R-type hops, the $n^{th}$ order term of the component of the IVRSH wave function

corresponding to adiabatic state $\varphi_j$ has the form[49]

$$\psi_j^{(n)}(\mathbf{R}) = \sum_{\mathbf{k}} \int d\mathbf{s} \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_{n-1} \cdots \int_{-\infty}^{t_2} dt_1 \tau_1 \tau_2 \cdots \tau_n C_{\mathbf{k}}(\mathbf{s}, t_1, \cdots, t_n) e^{F_{\mathbf{k},j}(\mathbf{R}, \mathbf{s}, t_1, \cdots, t_n)/\hbar} \tag{15}$$

where $\tau_m$ is the $m^{th}$ transition amplitude and the summation is over all possible sequences of the n-1 intermediate adiabatic states [e.g., see Eq. (7) for the n = 2 case]. For **R** in the asymptotic region, the upper limit on the $t_n$ integration can be extended to infinity without significantly altering the value of the integrals over hopping points, since only values of $t = s_1$ corresponding to $\mathbf{R}_s$ in the asymptotic region contribute significantly to the wave function due to the $\exp(F/\hbar)$ factor, and because $\tau_n \approx 0$ in this region. Performing the **s** integration by stationary phase gives

$$\psi_j^{(n)}(\mathbf{R}) = \sum_{\mathbf{k}} \int dt_n \int dt_{n-1} \cdots \int dt_1 \tau_1 \cdots \tau_n (2\pi\hbar)^{d/2} \left| \frac{\partial^2 F_{sp}}{\partial \mathbf{s} \partial \mathbf{s}} \right|^{-1/2} C_{sp} e^{F_{sp}/\hbar} \tag{16}$$

where the subscript sp indicates that the function is evaluated at a stationary phase value of **s**. The stationary phase condition $\partial F/\partial \mathbf{s} = 0$ gives the condition

$$(\mathbf{R} - \mathbf{R}_s) \cdot [2\gamma(\partial \mathbf{R}_s/\partial \mathbf{s}) + i\partial \mathbf{P}_s/\partial \mathbf{s}] = 0 \tag{17}$$

which has real solutions when $\mathbf{R}_s = \mathbf{R}$. Thus, the stationary phase condition selects trajectories that start somewhere on the initial defining surface with initial momentum $\mathbf{P}_0$ and reach **R** at some time t. If there is more than one such trajectory then the contribution from the different trajectories are summed. At the stationary phase point, the second derivative matrix for F is given by

$$\frac{\partial^2 F}{\partial \mathbf{s}\partial \mathbf{s}} = -i\frac{\partial \mathbf{R}_s}{\partial \mathbf{s}}\cdot\left[\frac{\partial \mathbf{P}_s}{\partial \mathbf{s}} - 2i\gamma\frac{\partial \mathbf{R}_s}{\partial \mathbf{s}}\right] \tag{18}$$

The $|\,\partial\mathbf{P}_s/\partial\mathbf{s} - 2i\gamma\,\partial\mathbf{R}_s/\partial\mathbf{s}\,|^{-1/2}$ factor from $|\partial^2 F/\,\partial\mathbf{s}\partial\mathbf{s}|^{-1/2}$ cancels the prefactor $C_{sp}$. Since $s_1$ is the time along the trajectory, the first column of $\partial\mathbf{R}_s/\partial\mathbf{s}$ is given by $\mathbf{P}_s/m$. If the coordinate system at $\mathbf{R}_s$ is chosen so that the first coordinate is in the $\mathbf{P}_s$ direction and the other coordinates are in the d-1 directions perpendicular to $\mathbf{P}_s$, then the first column of $\partial\mathbf{R}_s/\partial\mathbf{s}$ has $P_s/m$ for its first component and zeros for the remaining components, where $P_s = |\mathbf{P}_s|$ is the magnitude of the momentum at time t. The determinant of $\partial\mathbf{R}_s/\partial\mathbf{s}$ is then given as $P_s/m$ multiplied by the determinant of the d-1 by d-1 matrix obtained by eliminating the first row and column of $\partial\mathbf{R}_s/\partial\mathbf{s}$

$$\left|\frac{\partial \mathbf{R}_s}{\partial \mathbf{s}}\right| = \left|\frac{\partial \boldsymbol{\sigma}_t}{\partial \boldsymbol{\sigma}_0}\right|\frac{\mathbf{P}_s}{m} \tag{19}$$

as long as $\boldsymbol{\Sigma}$ is perpendicular to $\mathbf{P}_0$ for each $\mathbf{R}_0$. Thus, $|\partial^2 F/\,\partial\mathbf{s}\,\partial\mathbf{s}|^{-1/2}\,C_{sp}$ is proportional to the prefactor for the primitive wave function, and the IVRSH wave function reduces to the primitive surface hopping wave function in the asymptotic region in the stationary phase approximation for the **s** integration, if the same transition amplitudes are used in both cases. Furthermore, since $\eta_{ij}$ and the transition amplitudes $\tau_{ij}$ and $\rho_{ij}$ vanish in the asymptotic regions, every term in the IVRSH wave function satisfies the TISE to first order in $\hbar$ in the asymptotic regions. The proof is similar to the proof for the globally uniform single surface wave function.[7,8]

The stationary phase approximation for the **s** integration becomes a better approximation at large **R** for the case considered in this work. The final momentum, $\mathbf{P}_f$, can be taken to be

constant at large values of $\mathbf{R}_t$ along a trajectory and the exponential function has the asymptotic form $F = -\gamma(\mathbf{R} - \mathbf{R}_t)^2 + i\,\mathbf{P}_f \cdot (\mathbf{R} - \mathbf{R}_f) + iw_f$, where $\mathbf{R}_f$ is the point along the trajectory at which $|\mathbf{R}_f| = |\mathbf{R}| \equiv R_f$, and where $w_f$ is given by Eq. (4) with $\mathbf{R}_f$ as the upper limit. In addition, the upper limit of the integration over the last hopping time can be extended to infinity. Since $\mathbf{R}_t = \mathbf{R}_f + \mathbf{P}_f t/m$, the exponential function F is a quadratic function in t. The prefactor C changes little over the range of t for which $\exp(F/\hbar)$ is significant for large enough $|\mathbf{R}_t|$. Thus, C(t) can be approximated as a constant and the $s_1$ integration can be performed exactly. Since initially nearby trajectories diverge after passing through the interaction region, $\partial\mathbf{R}_t/\partial s_j$ becomes large for j = 2, 3, ..., d when $|\mathbf{R}_t|$ is large, and the integrations over $s_2$, $s_3$, ..., $s_d$ become sharply peaked about the stationary phase point [see Eq. (18)]. Consequently, the integrand approaches a delta function in $s_2$, $s_3$, ..., $s_d$, and the IVRSH result approaches the primitive result.

For the more general case in which the collision partners have internal and/or rotational degrees of freedom, the components of $\mathbf{P}_t$ corresponding to these additional degrees of freedom are not constant in the asymptotic region. The integrations over $s_2$, $s_3$, ..., $s_d$ still approach delta function integrations, as in the simpler case. For this reason, one would expect the differences between the IVRSH and primitive wave functions to be smaller in the asymptotic regions. However, F does not become a quadratic function in t, so the $s_1$ integration may still introduce some differences between the IVRSH and primitive wave functions. This difference is also present when comparing globally uniform and primitive wave functions for single surface problems. It is not the result of the surface hopping aspects of the problem.

The IVRSH wave function also approaches the primitive wave function for all $\mathbf{R}$ in the large $\gamma$ limit, since the $\exp(F/\hbar)$ factor is proportional to a delta function in this limit due to the -

$\gamma(\mathbf{R} - \mathbf{R}_s)^2$ term in F. As a result, only values of **s** for which $\mathbf{R}_s$ is very close to **R** contribute to the integral, and the IVRSH wave function reduces to the primitive wave function without the need for the stationary phase approximation.

## III. Numerical Results

In this section, the accuracy and behavior of the IVRSH wave function in both the interaction and asymptotic regions are explored through numerical calculations on a pair of one dimensional model problems, each with two quantum states. The adiabatic quantum states

$$\varphi_1 = \varphi_1^{(d)}\cos(\theta) + \varphi_2^{(d)}\sin(\theta) \tag{20a}$$

$$\varphi_2 = -\varphi_1^{(d)}\sin(\theta) + \varphi_2^{(d)}\cos(\theta) \tag{20b}$$

are defined in terms of the diabatic states,[12,13] $\varphi_1^{(d)}$ and $\varphi_2^{(d)}$, and the corresponding diabatic potential matrix elements $V_{ij}(R)$. The angle $\theta$ is obtained by diagonalizing the matrix $\mathbf{V}(R)$ yielding $\theta(R) = \frac{1}{2}\tan^{-1}\{2V_{12}(R)/[V_{11}(R) - V_{22}(R)]\}$. The adiabatic state energies, $W_1(R)$ and $W_2(R)$, are given by $W_j(R) = \frac{1}{2}(V_{11} + V_{22}) \pm \frac{1}{2}[(V_{11} - V_{22})^2 + 4V_{12}^2]^{1/2}$, where the minus (plus) sign corresponds to j = 1 (j = 2). The quantum wave functions are calculated by numerically integrating the TISE in the diabatic representation from a point $R_0 << 0$ to a point $R_f >> 0$ for three sets of initial conditions at $R_0$. These three initial conditions correspond to an incoming wave function on the upper surface and $\psi_2 = 0$, an outgoing wave function on the upper surface and $\psi_2 = 0$, and an outgoing wave function on the lower surface and $\psi_1 = 0$. The linear combination of these three independent solutions to the TISE is evaluated such that there is no incoming flux on either surface for $R >> 0$ and an incoming flux of unit magnitude on the upper

surface for R << 0. This wave function can have no incoming flux on the lower surface for R << 0, since all three initial conditions correspond to zero incoming flux on the lower surface. The transition probability is given by the outgoing flux on the lower surface at $R_f$. The quantum wave functions are converted to the adiabatic representation when comparing with the semiclassical wave functions. The procedure used in the semiclassical calculations is described in the appendix.

The first system has a single curve crossing in the diabatic representation. The diabatic potential matrix elements are $V_{11}(R) = \tanh(R)$, $V_{22}(R) = -\tanh(R)$, and $V_{12}(R) = V_{21}(R) = 0.1 \exp(-R^2/20)$. The curve crossing occurs at R = 0, where $V_{11} = V_{22}$. Atomic units are employed and the mass is taken to be the proton mass, m = 1836.2. A comparison of the IVRSH transition probabilities with the quantum results are given in fig. 1 for a range of energies. The agreement is excellent. The quantum wave functions for the two states are compared with the corresponding primitive semiclassical surface hopping wave functions and the IVRSH wave functions for E = 1.3 in fig. 2. The IVRSH results are given for different values of the width parameter $\gamma$. The primitive wave functions are in excellent agreement with the quantum wave functions for all R. The IVRSH wave functions differ from the quantum wave functions in the interaction region (i.e., near R = 0) and approaches the quantum wave functions at large R. The differences between the IVRSH and quantum wave functions diminish as $\gamma$ is increased, as expected from the analysis in the previous section.

The quantum and IVRSH transition probabilities for a model where the $V_{11}$ and $V_{22}$ cross twice are shown as functions of energy in fig. 3. In this model $V_{11} = -V_{22} = \tanh(R - 2) \tanh(R + 2)$, and $V_{12} = \exp(-R^2/20)$. Atomic units are employed. The quantum and IVRSH wave

functions for E = 10 and m = 1836.2 are compared in fig. 4. The transition probabilities from the IVRSH methods are again in excellent agreement with the quantum results. As is found for the previous model, the IVRSH wave functions differs from the quantum wave functions in the interaction regions, approach the quantum wave functions at large R, and the errors in the IVRSH wave functions decrease as $\gamma$ increases.

**IV. Discussion**

The numerical calculations show that the IVRSH method provides accurate results for transition probabilities. The corresponding wave functions are found to be in very good agreement with the quantum results in the asymptotic regions, but they differ from the quantum wave functions in the interaction region. As demonstrated in section II, the primitive semiclassical wave function is obtained from the IVRSH wave function in the asymptotic regions if the **s** integration is performed by stationary phase and the expression from the primitive wave function, Eq. (14), is employed for the transition amplitude, $\tau_{ij}$. Previous numerical work shows that the primitive surface hopping method provides a very good approximation to the exact quantum transition probabilities. For one dimensional problems, such as those considered here, the **s** integration in the IVRSH method is an integration over the time for which the trajectory is propagated. This integration becomes a simple Gaussian integration in the asymptotic region and can be performed exactly. Therefore, the IVRSH wave function must agree with the primitive wave function in the asymptotic region for one dimensional problems if the primitive $\tau_{jk}$ is used. Consequently, IVRSH method provides the same probability of transition as the primitive method, since this is determined by the wave function in the asymptotic region.

It is also shown in this work that the IVRSH wave function approaches the primitive wave function in the large **R** and large $\gamma$ limits. Since the IVRSH wave function approaches the primitive wave function in the large **R** limit, the IVRSH transition probabilities are expected to provide a similar level of accuracy for these quantities as the primitive surface hopping method, and these probabilities should be insensitive to the value of $\gamma$ employed. On the other hand, if the quantity of interest depends on the wave function in the interaction region, then this quantity will be sensitive to the value of $\gamma$.

The upper limit on the integration over the time of the last hop is t, the time for which the trajectory is run, in both the IVR and primitive wave functions. Only the value of t for which $\mathbf{R}_t = \mathbf{R}$ contributes to the primitive wave function at **R**, and the interaction at points along the trajectory up to **R** contribute to the hopping terms in the wave function. On the other hand, the IVRSH wave function has an integration over all t, and the range of t for which $\exp(F/\hbar)$ is significant contribute to the wave function at **R**. This results in the interaction along the trajectory up to the point $\mathbf{R}_t$ (rather than **R**) contributing to the hopping terms in the IVRSH wave function $\psi_E(\mathbf{R})$ for each value of t. This difference in the range of hopping points along a trajectory that contributes the wave function is a significant source of difference between the primitive and IVR wave functions in the interaction region.

To illustrate this point, consider the case of a very sharply peaked nonadiabatic coupling near an avoided crossing point with the incoming particle in adiabatic state $\varphi_1$. There is essentially no amplitude in the component of the wave function corresponding to $\varphi_2$ up to points very close to the crossing point. The amplitude for this component of the wave function rises rapidly as the crossing point is passed, and then it quickly levels off due to the narrow width of $\eta_{if}$.

In the IVR case, the amplitude of this component of the wave function will begin to rise farther from the crossing point and level off farther after the crossing point is passed than in the primitive case, and the width of this rise will depend on the width of the Gaussian factor $\exp(F/\hbar)$. This can result in errors in the wave function near the crossing point unless $\gamma$ is large enough that the width of $\exp(F/\hbar)$ is less than the length scale over which $\eta_{if}$ changes significantly.

The discussion in this work has considered only problems for which the interaction is largely in the classically allowed region. As with most semiclassical methods, the IVRSH method cannot accurately account for transitions induced by nonadiabatic interaction in the classically forbidden regions without the implementation of additional features designed to handle this situation.

The numerical evaluation of semiclassical surface hopping wave functions is relatively easy for one dimensional problems such as those considered in this work. The calculations are much more computationally demanding for case of multidimensional systems. The use of the IVR method removes the need to perform the difficult root search for trajectories obeying the double ended boundary condition required by the primitive wave function calculation. However, the IVR calculation involves integrations over initial conditions, trajectory time, and hopping times. In most cases, the integrations over initial conditions and hopping times must be performed using monte carlo techniques. The accurate monte carlo evaluation of the wave function is made more difficult by the phase interference between the contributions from different trajectories. Recent work has provided techniques that can greatly improve the statistical accuracy of the monte carlo procedures for model systems.[48] The application of these techniques to IVRSH calculations on multidimensional problems is a topic of current interest.

It is expected that the use of a smaller $\gamma$ will reduce the statistical errors in a monte carlo calculation, since the wider Gaussian wide should result in more averaging over nearby trajectories. On the other, a larger $\gamma$ should result in a more accurate wave function in the interaction region. Since the same set of hopping trajectories are required to construct the IVRSH wave function independent of the choice of $\gamma$, different values of $\gamma$ can be employed at different points, using the IVRSH wave function with the best balance between reducing $\gamma$ dependent errors and statistical errors at each point. The primitive surface hopping wave function is capable of providing highly accurate results, but can be very difficult to implement numerically. Although the IVRSH wave function is less accurate in the interaction region, the errors are controllable, and the method has advantages over the primitive method in the numerical implementation and provides the same level of accuracy for transition probabilities.

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## Appendix

In this appendix, the calculation of the IVRSH wave functions presented in section III is described. First consider the primitive surface hopping wave function for one dimensional two state problems. This wave function can be expressed as[44]

$$\psi_E^{(pr)}(R) = \varphi_1(R)\left[\frac{P_1(R_0)}{P_1(R)}\right]^{1/2}\chi_1(R) + \varphi_2(R)\left[\frac{P_1(R_0)}{P_2(R)}\right]^{1/2}\chi_2(R) \qquad \text{(A1)}$$

where

$$\chi_1(R) = e^{iw_0(R)/\hbar} + \int_{R_0}^{R} dR_2 \int_{R_0}^{R_2} dR_1 \tau'_{12}(R_1)\tau'_{21}(R_2) e^{iw_2(R,R_1,R_2)/\hbar} + \cdots \quad \text{(A2)}$$

and

$$\chi_2(R) = \int_{R_0}^{R} dR_1 \tau'_{12}(R_1) e^{iw_1(R,R_1)/\hbar} + \int_{R_0}^{R} dR_3 \int_{R_0}^{R_3} dR_2 \int_{R_0}^{R_2} dR_1 \tau'_{12}(R_1)\tau'_{21}(R_2)\tau'_{12}(R_3) e^{iw_3(R,R_1,R_2,R_3)/\hbar} + \cdots \quad \text{(A3)}$$

Only T-type hops are included here. In these expressions, the hopping times, $t_1$, $t_2$, ... , have been converted into hopping points, $R_1$, $R_2$, ... and the Jacobian for this change of integration variable is has been absorbed into the transition amplitudes, which are now defined as[44]

$$\tau'_{jk}(R_h) = -\frac{P_j(R_h) + P_k(R_h)}{2[P_j(R_h)P_k(R_h)]^{1/2}} \eta_{jk}(R_h) \quad \text{(A4)}$$

The exponential functions $w_n$ (R, $R_1$,$R_2$, ...,$R_n$) in Eqs.(A2) and (A3) are given by Eq.(4) with the integration performed from $R_0$ to R for the trajectory with hops at $R_1$ , $R_2$ , ..., $R_n$.

Differentiating Eqs. (A2) and (A3) yields

$$\partial\chi_1/\partial R = iP_1(R)\chi_1(R)/\hbar + \tau'_{21}(R)\chi_2(R) \quad \text{(A5)}$$

and

$$\partial\chi_2/\partial R = iP_2(R)\chi_2(R)/\hbar + \tau'_{12}(R)\chi_1(R) \quad \text{(A6)}$$

If the hopping times in the IVRSH wave function are also converted to hopping points and the $s_1$ integration over time is converted to an integration over $R_t$, the IVRSH wave function can be expressed as

$$\psi_E(R) = N\int dR_t C'(R_t)\psi_E^{pr}(R_t)\, e^{[-\gamma(R-R_t)^2 + iP_t(R-R_t)]/\hbar} \quad \text{(A7)}$$

where the Jacobian for the change of integration variable and the factor $[P_t(R_t)/P_0(R)]^{1/2}$ to compensate for the prefactor in primitive wave function, $\psi_E^{(pr)}(R_t)$, have been absorbed into the prefactor

$$C'(R_t) = [(\partial P_t/\partial R_t - 2i\gamma)m/P_0]^{1/2} \quad \text{(A8)}$$

The calculations presented in this work are performed by numerically integrating Eqs. (A5) and (A6), and then computing the integral in Eq. (A7).

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## Figure Captions

Fig. 1. Comparison of IVRSH (⋯) and quantum (——) transition probabilities for the single crossing model problem. A width parameter of $\gamma = 1$ is employed in the IVRSH calculations.

Fig. 2. Comparison of the magnitude of the IVRSH (- - -) and quantum (——) wave functions on the upper and lower adiabatic energy surfaces for E = 1.3 for the single crossing model problem. Figures 2a, 2b, 2c, and 2d correspond to $\gamma = 1$, 10, 100, and 1000, respectively. The primitive wave functions (•••••) are also shown on the plots with the $\gamma = 1$ IVRSH wave functions.

Fig. 3. Comparison of IVRSH (•••••) and quantum (——) transition probabilities for the two crossing model problem. A width parameter of $\gamma = 1$ is employed in the IVR calculations.

Fig. 4. Comparison of the magnitude of the IVRSH (- - -) and quantum (——) wave functions on the upper and lower adiabatic energy surfaces for E = 10 for the two crossing model problem. Figures 2a, 2b, 2c, and 2d correspond to $\gamma = 1$, 10, 100, and 1000, respectively. The primitive wave functions (•••••) are also shown on the plots with the $\gamma = 1$ IVRSH wave functions.