



Analysis of a surface hopping expansion that includes hops in classically forbidden regions



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ABSTRACT

A surface hopping expansion of the nonadiabatic wave function is generalized to account for hops from the forbidden region on one adiabatic energy surface to a different adiabatic surface in multidimensional problems. This analysis is motivated by previous surface hopping calculations on one dimensional models that provide very accurate transition probabilities, even at low energies, if classically forbidden hops are included in the calculations. It is shown that hops from the classically forbidden region in the previous form of the surface hopping expansion cannot, in general, lead to classically allowed final state trajectories in multidimensional problems. The surface hopping wave function is generalized to allow for two or more hops at each point along the trajectory. These hops correspond to different directions for the energy conserving momentum change, which gives different post-hop trajectories. This generalization allows for the final state trajectory to be classically allowed if the post-hop adiabatic energy surface has sufficiently low energy.

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1. Introduction

Transitions between the electronic states of atoms and molecules are an essential component of many processes in chemical physics. A number of different semiclassical methods have been devised in order to model these nonadiabatic processes [1–38]. These include Ehrenfest methods [3–7], which run trajectories on a potential that has been averaged over the multistate electronic wave function; methods using trajectories in the complex plane [8]; the mapping method [9–12], which replaces the multistate electronic Hamiltonian with a set of harmonic oscillator Hamiltonians that can be included in the semiclassical calculation; and surface hopping approaches [13–38], which include abrupt hops between different adiabatic electronic states.

A specific form of the surface hopping wave function has been developed to formally satisfy the Schrodinger equation [33,34] in the sense that every term in $(\hat{H} - E)\psi$ can be shown to be cancelled by some other term. The lowest order term in this surface hopping wave function is just the primitive semiclassical single surface wave function. The higher order terms include energy conserving hops between adiabatic electronic surfaces and single surface primitive semiclassical propagation between hops. The component of the momentum in the direction of the nonadiabatic coupling is

altered during the hop so as to satisfy energy conservation. There are additional correction terms in the expansion that involve momentum changes without hops along the trajectories. These terms correct for the semiclassical nature of the single surface propagation [39]. Since these non-hopping correction terms are typically neglected in numerical calculations, the resulting method is a semiclassical surface hopping expansion. It has also been shown that the initial value representation version of the semiclassical surface hopping expansion satisfies the Schrodinger equation to order \hbar , which is the order expected for semiclassical methods [32].

Calculations on one dimensional model problems have demonstrated that numerical procedures based on this surface hopping expansion provide very accurate results [38]. They also show that the inclusion of hops in the classically forbidden region can significantly improve the accuracy of the calculated transition probabilities at low energies [35–38]. In many dimensional problems, the momentum vector has perpendicular real and imaginary components in the classically forbidden region, $\mathbf{p} = \mathbf{p}_R + i\mathbf{p}_I$ [44–47]. This is problematic for the semiclassical surface hopping expansion as presented previously [33,34], since the momentum change accompanying a hop between Born Oppenheimer (BO) electronic states φ_i and φ_j occurs in the direction of the nonadiabatic coupling vector, $\boldsymbol{\eta}_{ij}$. In general, both \mathbf{p}_R and \mathbf{p}_I have components in the direction of $\boldsymbol{\eta}_{ij}$ and perpendicular to it. Since the perpendicular components are unchanged in the hop, the post-hop momentum will have a nonzero \mathbf{p}_I . As a result, the post-hop portion of the trajectory

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corresponds to a classically forbidden trajectory on the final surface, even if the hop is from a high energy surface to a lower energy surface.

It is shown in this paper that this problem can be removed by expressing the nonadiabatic coupling vector as a sum of (at least) two perpendicular components, $\boldsymbol{\eta}_{if} = \boldsymbol{\eta}_{ifa} + \boldsymbol{\eta}_{ifb}$, and choosing one of these to be parallel to the imaginary component of the momentum in the forbidden region. A hop at point \mathbf{r}_h from state φ_i to state φ_f with its momentum change, $\Delta\mathbf{p}$, in the $\boldsymbol{\eta}_{if}$ direction in the previous surface hopping expansion is replaced with a hop between these states at \mathbf{r}_h with its $\Delta\mathbf{p}$ in the $\boldsymbol{\eta}_{ifa}$ direction and a hop between these states with its $\Delta\mathbf{p}$ in the $\boldsymbol{\eta}_{ifb}$ direction in this generalized version. Since $\Delta\mathbf{p}$ is different for these two hops, the post-hop trajectories will be different. The hop in the direction parallel to \mathbf{p}_i results in a final momentum with $\mathbf{p}_f = 0$ as long as the energy of the final surface is sufficiently low. On the other hand, the final \mathbf{p}_f is nonzero for the second $\Delta\mathbf{p}$ direction, and the trajectory is classically forbidden after the hop. As such it is expected to provide a significantly less important contribution to $\psi(\mathbf{r})$.

Section 2 demonstrates that the surface hopping wave function formally satisfies $(\hat{\mathbf{H}} - E)\psi(\mathbf{r}) = 0$. The surface hopping wave function is expressed as $\psi = \psi_0 + \psi_1 + \psi_2 + \dots$ where the zeroth order term, ψ_0 , is the primitive semiclassical wave function for the system in the initial BO electronic state and the n^{th} order term includes the contributions from all trajectories with n hops between surfaces and non-hopping momentum changes. In Section 2.1 the action of $\hat{\mathbf{H}} - E$ on ψ_0 is evaluated, showing the types of terms that are produced, demonstrating the cancellation of some of the terms which results due to the semiclassical form of ψ_0 , and identifying the types of terms that must be canceled by the action of $\hat{\mathbf{H}} - E$ on the higher order terms in ψ . Each term in the first order wave function, ψ_1 , has a single hop or non-hopping momentum change and an integration over the curve of points at which this hop or momentum change can occur for a given value of the trajectory end point, \mathbf{r} . Section 2.2 considers the cancellation of terms in $(\hat{\mathbf{H}} - E)\psi$ that have a single hop and a single integration over the curve of points for the hop. This cancellation is explicitly shown for single integration terms that are of order \hbar^0 or \hbar^1 arising from the action of $(\hat{\mathbf{H}} - E)$ on the single hop term in ψ . The details of the cancellation of all other terms having a single hop and a single integration are provided in the [supplementary data](#). This cancellation is first demonstrated for this type of term because it is the simplest case in which all complications due to the multidimensional nature of the problem are present. It is shown that the amplitudes for the hops for this generalized expansion are simple generalizations of those used in previous work [33,34]. However, the amplitude for the non-hopping momentum changes differs somewhat from that used previously, correcting for a feature neglected in that work [33,34]. It is then discussed in Section 2.3 how the results obtained in Section 2.2 can be applied to all terms in $(\hat{\mathbf{H}} - E)\psi = 0$ by simply changing the number and sequence of hops and momentum changes and the corresponding number of integrations over points at which these hops and momentum changes occur.

Model surface hopping calculations for a 2-d, two state scattering problem are presented in Section 3 and compared with exact quantum results. The calculations are evaluated in the small interaction (i.e., single hop) limit, so that they can be performed without the use of a Monte Carlo (MC) procedure. Since there is no sampling error, this allows for a more accurate comparison between the surface hopping and quantum results. The differential cross section, $d\sigma/d\theta$, is evaluated as a function of the outgoing direction of the hopping trajectories, θ . While the accurate calculation of $d\sigma/d\theta$ would be very difficult in a MC calculation, the evaluation of $d\sigma/d\theta$ provides for a more demanding comparison of the

quantum and surface hopping results than would be provided by the calculation of the integrated final state cross section, σ , which could be evaluated in a MC calculation. Since the full surface hopping wave function formally satisfies the Schrodinger equation, it is reasonable to assume that the level of accuracy found in the calculations presented here would be preserved in more realistic calculations.

The implications of the formal analysis and the results for the model calculations are discussed in Section 4.

2. Theory

The surface hopping expansion of the wave function is based on the single surface semiclassical wave function. The semiclassical amplitudes and phases for the wave function are integrated along trajectories for the motion of the nuclei. These trajectories obey the classical equations of motion on each BO electronic energy surface, and they have energy conserving hops between the different energy surfaces. They also have changes in the direction of the momentum without a change in electronic state. These hops and momentum changes are referred to as non-classical events (NCEs) in this work. The wave function is expressed as an expansion with the n^{th} order term including the contribution from trajectories with n NCEs. The NCEs can occur at any point along the trajectory, and each term in the wave function includes integrations over the points at which the NCEs occur. It is shown that the wave function constructed from the NCE containing trajectories formally satisfies the TISE by demonstrating that all terms in $(\hat{\mathbf{H}} - E)\psi$ sum to zero. It has been previously shown by a different method that this wave function expansion satisfies the Schrodinger equation in one dimension [31]. Therefore, the types of NCEs required and the form of each term is known for 1-d case, and the form of the wave function in this work is the generalization of the one dimensional wave function to many dimensions. The form of the terms that arise from the action of $\hat{\mathbf{H}} - E$ on the zeroth order term in ψ is first considered. Then it is explicitly demonstrated that all terms with a single integration in $(\hat{\mathbf{H}} - E)\psi$ sum to zero. The cancellation of the single integration terms is considered in detail since this is the simplest case that involves all complications arising from the many dimensional nature of the problem. This same analysis can then be applied to all terms in $(\hat{\mathbf{H}} - E)\psi$ by simply changing the number and type of NCEs, the number of integrations over the positions of the NCEs, and the number of summations over the components $\boldsymbol{\eta}$.

2.1. Zero integral terms in $(\hat{\mathbf{H}} - E)\psi$

Let $\varphi_j(\mathbf{r})$ be the j^{th} Born–Oppenheimer electronic state. The Hamiltonian for the system is $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{\mathbf{V}} = \hat{\mathbf{K}} + \hat{\mathbf{V}}$. The potential energy operator is defined such that $\hat{\mathbf{V}}\varphi_j = V_j(\mathbf{r})\varphi_j$, where $V_j(\mathbf{r})$ is the BO energy for state φ_j . The wave function is expressed as $\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \psi_1(\mathbf{r}) + \psi_2(\mathbf{r}) + \dots$, where $\psi_n(\mathbf{r})$ is the contribution from trajectories containing n NCEs and ending at \mathbf{r} . It is assumed in this work that the incoming d -dimensional wave function corresponds to the system in a specific adiabatic electronic state, φ_i , that the incoming wave function is known everywhere on a $d-1$ dimensional surface in the asymptotic region, and that this surface is chosen such that the phase of the initial wave function is constant on it. This surface, S_i , and the value of the semiclassical wave function at each point on it define the wave function $\psi(\mathbf{r})$ at energy E . The $\psi_0(\mathbf{r})$ term is given by the initial surface primitive semiclassical wave function [40,41]

$$\psi_0(\mathbf{r}) = \sum \varphi_i A_i e^{iW_i/\hbar} \quad (1)$$

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