

Accurate and efficient evaluation of transition probabilities at unavoided crossings in ab initio multiple spawning



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ABSTRACT

Recently we introduced a norm-preserving wavefunction interpolation (NPI) method which allows the accurate and efficient integration of the time-dependent Schrödinger equation in regions of rapidly varying time-derivative coupling (TDC), e.g. near conical intersections (CIs) and effectively $(N-1)$ -dimensional trivial unavaoided crossings (TUCs). Herein we report the implementation of the NPI scheme into the ab initio multiple spawning (AIMS) method and investigate its behavior in two test systems: one which exhibits a CI and another which exhibits a TUC. In the CI case, AIMS–NPI predicts transfer probabilities that agree to within 0.6% of simulations based on the analytical evaluation of the nonadiabatic couplings, without the need for computationally expensive adaptive integration. In the TUC case, AIMS–NPI results in less than 0.08% error in the population transfer probability when a 0.12 fs time step is used, while simulations based on the analytical approach exhibit catastrophic errors for all finite time steps.

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1. Introduction

Molecular dynamics (MD) simulations with electronic state transitions provide valuable insights into the behavior of photoexcited molecules and materials, including ultrafast processes such as non-radiative decay. Leading approaches include classical-trajectory [1–22] methods, an example of which is Tully's fewest switches surface-hopping, and fully quantum mechanical [23–32] schemes, including wavepacket-based approaches such as ab initio multiple spawning (AIMS). Each of these approaches involves integration of the time-dependent Schrödinger equation (TDSE) with a Hamiltonian that includes non-Born–Oppenheimer terms. Ab initio (AI) MD methodologies, which solve for the electronic structure of the system on-the-fly, can be particularly useful in describing such photochemical processes because they do not require assumptions about the potential energy surface (PES) or the character of the electronic states involved, but computational expense limits the system sizes, time scales, and accuracies accessible via such simulations.

The TDSE is most often solved by numerical integration, which requires the discretization of time into finite steps. For the sake of numerical accuracy, it is necessary that the chosen time step is shorter than the timescale on which the Hamiltonian matrix elements vary. However, at each time step computationally

expensive electronic structure calculations are performed, and thus efficiency demands the choice of the longest time step possible. When working in the adiabatic representation, this dilemma can become intractable because the time-derivative coupling (TDC) between two electronic states may vary arbitrarily rapidly. The TDC is defined as

$$\sigma_{KJ} = \langle \phi_K(\mathbf{r}; t) | \partial \phi_J(\mathbf{r}; t) / \partial t \rangle \quad (1)$$

where J and K are electronic state indices. In modern AIMD simulations the TDC is often computed from the nonadiabatic coupling matrix element (NACME) vector,

$$\mathbf{d}_{KJ}(\mathbf{R}) = \langle \phi_K(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} \phi_J(\mathbf{r}; \mathbf{R}) \rangle \quad (2)$$

and the nuclear velocity via the chain rule. NACMEs can now be efficiently calculated at many quantum chemical levels of theory using analytical gradient techniques [33–41].

The TDC exhibits infinitesimally narrow spikes of infinite magnitude at conical intersections (CIs), points of degeneracy between PESs known to facilitate non-radiative decay [42–46], and thus simple numerical integration of the TDSE through a CI requires an infinitesimal time step, which is obviously computationally intractable. In practice, however, CIs are $(N-2)$ -dimensional features of the PES (where N is the total number of nuclear degrees of freedom), so the probability of a particular trajectory hitting one directly (Fig. 1, arrow 1) is exceedingly low. Most trajectories will instead pass around the intersection, leading to a more slowly varying TDC (Fig. 1, arrow 2). More troublesome are trivial

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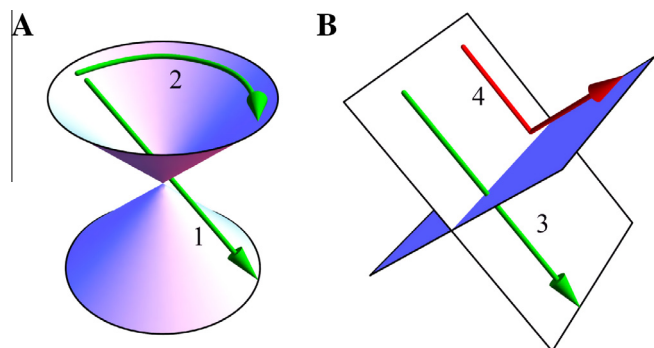


Fig. 1. Illustrations of potential energy surfaces near (A) a CI and (B) a TUC. The three green arrows illustrate possible nuclear motion near each crossing: (1) diabatic passage through a CI, (2) adiabatic passage around a CI, and (3) diabatic passage through a TUC. The red arrow (4) illustrates unphysical adiabatic passage through a TUC, which could manifest itself as e.g. unphysical long range charge transfer in a real simulation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

unavoided crossings (TUCs), effectively ($N-1$)-dimensional intersections which arise in the adiabatic representation when the coupling between two diabatic electronic states is negligible (e.g. when modeling long range charge or energy transfer or intersystem crossing in the limit of weak spin-orbit coupling). In such cases, direct passage of a trajectory through the intersection seam (Fig. 1, arrow 3) is unavoidable, and adiabatic motion through the intersection (Fig. 1, arrow 4) is impossible. Passage through the TUC necessarily involves an infinitesimally narrow spike in the TDC, which a simulation based on finite time steps is unable to resolve, leading to inaccurate predictions of the probabilities of electronic state transitions.

Several strategies can be proposed to circumvent numerical issues associated with the integration of the TDSE through regions where the TDC spikes sharply. Working in the diabatic representation eliminates the spike entirely, but the integration of the relatively small, temporally delocalized coupling between diabatic states can also lead to inaccurate prediction of transition probabilities [9,47]. In the case of CIs, adaptive time step integration effectively circumvents numerical problems in all but the worst cases, but at a significant computational cost [48,49]. In the context of trajectory surface hopping simulations, formulations for the hopping probability have been proposed which accurately predict transition probabilities resulting from sharply spiked TDCs [12,50–53]. However, formulations for the hopping probability are not directly applicable in fully quantum mechanical simulation methods such as AIMS.

An alternative to the above approaches is to eschew the analytical calculation of the NACME at a finite number of time steps altogether. Approaches in which the TDC is computed directly from the overlaps of the adiabatic wavefunctions at the beginning of each time step with those at the end of each step have long been used when analytical NACME calculations are not available [4,54,55]. An often overlooked advantage of these overlap-based approaches is that they guarantee that the full change in the adiabatic wavefunction over each time step is resolved, even if the instantaneous TDC is varying on timescales much shorter than this step. We have recently developed an overlap-based approach derived from a continuous interpolation of the adiabatic electronic wavefunction over the time step, the norm-preserving interpolation (NPI) scheme [55]. NPI has been demonstrated to predict very accurate state transition probabilities when employed in the numerical integration of a simple (adiabaticized Landau-Zener [56,57]) model of a very narrowly avoided crossing. NPI provides an explicit approximation to the TDC, and can therefore be applied in either trajectory- or wavepacket-based simulations of nonadiabatic dynamics.

In the present work we report the implementation of the NPI scheme into the AIMS nonadiabatic molecular dynamics method and assess its performance by application to two different chemical systems: propylene, which exhibits a CI, and a long range charge transfer couple, which exhibits a TUC. In the next section, we present a brief introduction to the NPI scheme, discuss its implementation in the AIMS method, and detail the two cases we will use to test the combined AIMS–NPI method. In Section 3 we present analysis of the population transfer probabilities computed using the analytical and NPI schemes in these cases and discuss the primary sources of error in transition probabilities computed using AIMS–NPI. Finally, in Section 4, we draw conclusions and discuss future prospects.

2. Methods

2.1. Approximation of the TDC

The NPI scheme approximates the time-derivative coupling at the middle of a time step (time $t_0 + \Delta t/2$) from the adiabatic electronic wavefunctions computed at the beginning and end of that step (times t_0 and $t_0 + \Delta t$, respectively). Specifically, NPI is based on an interpolated wavefunction which is defined continuously as a function of time. At any arbitrary time, τ , within a particular time step, the interpolated electronic wavefunction associated with adiabatic state J , is computed by application of a transformation matrix, $\mathbf{U}(\tau)$, to the adiabatic wavefunction at t_0

$$|\phi_J(\tau)\rangle = \mathbf{U}(\tau)|\phi_J(t_0)\rangle \quad (3)$$

where the diagonal and off-diagonal elements of $\mathbf{U}(\tau)$ are defined, respectively,

$$U_{JJ}(\tau) = \cos\left(\frac{\cos^{-1}(U_{JJ}(t_0 + \Delta t))}{\Delta t}(\tau - t_0)\right) \quad (4)$$

$$U_{JK}(\tau) = \sin\left(\frac{\sin^{-1}(U_{JK}(t_0 + \Delta t))}{\Delta t}(\tau - t_0)\right) \quad (5)$$

and

$$U_{JK}(t_0 + \Delta t) = \langle \phi_J(t_0) | \phi_K(t_0 + \Delta t) \rangle. \quad (6)$$

Thus Eq. (3) describes a linear rotation of the adiabatic states between their known values at times t_0 and $t_0 + \Delta t$. In the present work, these overlaps are computed from adiabatic electronic wavefunctions determined at the complete active space self-consistent field (CASSCF) level of theory [58]. The orbitals at $t_0 + \Delta t$ are rotated to maximize overlap (diabatized) with those at t_0 , and then $U_{JK}(t_0 + \Delta t)$ is approximated as the dot product of the configuration interaction vector of state J at time t_0 with that of state K at time $t_0 + \Delta t$. A similar approach was used in the calculation of TDCs in the context of early AIMD simulations conducted at the complete active space second order perturbation level of theory [59].

The TDC between state J and state K at time τ may then be computed according to

$$\langle \phi_K(\tau) | \partial \phi_J(\tau) / \partial \tau \rangle = \langle \phi_K(t_0) | \mathbf{U}^\dagger(\tau) \frac{\partial}{\partial \tau} \mathbf{U}(\tau) | \phi_J(t_0) \rangle. \quad (7)$$

We approximate the TDC at the center of the time step, $t_0 + \Delta t/2$ as the average of Eq. (7) over the interval $t_0 \leq \tau \leq t_0 + \Delta t$

$$\left\langle \phi_K(t) \left| \frac{\partial \phi_J(t)}{\partial t} \right. \right\rangle_{t_0 + \Delta t/2} \approx \frac{\int_{t_0}^{t_0 + \Delta t} d\tau \langle \phi_K(t_0) | \mathbf{U}^\dagger(\tau) \frac{\partial}{\partial \tau} \mathbf{U}(\tau) | \phi_J(t_0) \rangle}{\Delta t}. \quad (8)$$

Evaluation of the right hand side of Eq. (8) results in a set of relatively simple analytical expressions which require only the overlaps, $U_{JK}(t_0 + \Delta t)$, between all pairs of adiabatic states as input. For

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