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Communication: XFAIMS—eXternal Field Ab Initio Multiple Spawning for electron-nuclear dynamics triggered by short laser pulses

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INTRODUCTION

Over the last decade, the development of attosecond and few cycle femtosecond IR pulses paved the way for probing electronic motion in atoms and molecules.1–3 Pump-probe schemes combining an IR pulse with an isolated attosecond pulse,4,5 or attosecond pulse trains,6,7 have been used to induce and probe dynamics in small molecules. Despite the attosecond moniker, the time scale of such experiments usually spans several tens of femtoseconds or more because of the longer IR pulse or train of attosecond pulses used to either excite or probe the molecule. This leads to a complex interplay between electronic and nuclear dynamics that complicates analysis even for diatomic molecules.8 Furthermore, the electronic dynamics is usually probed indirectly through fragmentation patterns. Unraveling the complex laser-induced electron-nuclear dynamics requires methods that model the entire experiment from laser excitation through relaxation or fragmentation.

Several methods are able to describe the correlated electronic-nuclear dynamics induced by a laser pulse, including numerically exact grid-based methods.9 However, most of these are limited to diatomic10–12 or small polyatomic13 molecules. For larger molecules, real-time time-dependent density functional theory (TDDFT)14–17 and trajectory surface hopping18–22 have been used to model field-induced dynamics. In RT-TDDFT, electron-nuclear dynamics is modeled using a mean-field Ehrenfest approach. Unfortunately, RT-TDDFT cannot accurately describe fragmentation or nonadiabatic dynamics that can occur after the pulse. Surface hopping19,22,23 using the “fewest-switches” algorithm24 (TSH) requires a double averaging of the trajectories: over the initial conditions and over the hopping events. Therefore a large number of trajectories are required to obtain a converged branching ratio,25–27 or pulse-induced population transfer, especially if this excited population is small. Furthermore, TSH neglects certain phase interferences that might be dynamically important.

In this communication, we present eXternal Field Ab Initio Multiple Spawning (XFAIMS), based on the AIMS method.28–30 XFAIMS models a complete photochemical experiment, from the excitation of a molecule by one or several laser pulses to subsequent nonradiative relaxation or fragmentation. We compare XFAIMS to numerically exact grid-based quantum dynamics for the photoexcitation of LiH from its ground electronic state S_0 to its first excited state S_1. The high anharmonicity of the S_1 potential energy curve (Fig. 1) makes the description of correlated electron-nuclear dynamics challenging, especially when the S_1 nuclear wavepacket leaves the Franck-Condon (FC) region. We further investigate the electron-nuclear dynamics triggered by either a subfemtosecond UV pulse or a 10 fs IR pulse. Finally, XFAIMS is applied to the full-dimensional simulation of photoexcitation in a polyatomic-sulfine (H_2CSO).31,32

THEORY

As in AIMS,28,29,33 the time-dependent nuclear wavefunctions in XFAIMS are expanded in a basis of state-specific Gaussian nuclear basis functions with frozen width (α), called trajectory basis functions (TBPs),28,33

\[
\Psi(r, R, t) = \sum_i \sum_j C_i^j(t) \times \chi_i^j(\mathbf{R}; \mathbf{R}_i^j(t), \mathbf{P}_i^j(t), \mathbf{P}_i^j(t), \alpha) \phi_i(r; \mathbf{R}).
\]
The Hamiltonian matrix coupling the different TBFs can be separated into interstate (TBFs on different electronic states) and intrastate (TBFs on the same electronic state) parts. The intrastate coupling elements are composed of the (field-free) electronic energy, the nuclear kinetic energy, and the field-induced coupling that involves the scalar product of the electric field with the electronic and nuclear dipole moment (computed as described previously)\textsuperscript{34},

\[
\left( \mathbf{H}_{II}^{\text{ intra}} \right)_{kl} = \left\langle \chi_{k}^{l} \mid E_{II}^{*} \mid \chi_{l}^{l} \right\rangle - \left\langle \chi_{k}^{l} \mid \sum_{\rho}^{3N} \frac{\partial^2}{2m_{l}\partial R_{\rho}^2} \mid \chi_{l}^{l} \right\rangle_{R} - \bar{E}(t) \cdot \left\langle \chi_{k}^{l} \mid \mu_{\text{elec}}^{\text{rice}} \right\rangle_{R} \cdot \left\langle \chi_{l}^{l} \right\rangle_{R}.
\]

where the index \( \rho \) runs over the 3N coordinates of the molecule with N atoms. The time-dependent electric field of the pulse, \( \bar{E}(t) \), is derived from the derivative of the vector potential,

\[
\bar{E}(t) = -\frac{1}{c} \frac{d \bar{A}(t)}{dt}.
\]

In the simulations below, we used a Gaussian-shaped pulse,

\[
\bar{A}(t) = \bar{e} (c f_0 / \omega) \exp \left[ - \frac{(t - t_0)^2}{2\sigma^2} \right] \sin (\omega t + CEP),
\]

where \( \bar{e} \) is the polarization vector, \( c \) is the speed of light, \( t_0 \) is the time at which the pulse is centered, \( f_0 \) is the field strength, \( \omega \) is the carrier frequency, and the pulse length is given by \( \sigma \). The full width at half maximum (FWHM) of the pulse is 2.35\( \sigma \). The carrier envelope phase (CEP) is the phase difference between the pulse envelope and the oscillation of the electric field. For few cycle pulses, the CEP controls the waveform (sub-femtosecond evolution) of the pulse and can affect the dynamics.\textsuperscript{35,36}

The interstate coupling includes the nonadiabatic coupling matrix elements (\( \mathbf{d}_{II} \)) and the coupling between electronic states due to the electric field (intra- and interstate second-order nonadiabatic couplings are neglected),

\[
\left( \mathbf{H}_{II}^{\text{ inter}} \right)_{kl} = - \left\langle \chi_{k}^{l} \right\rangle_{R} \sum_{\rho}^{3N} \frac{1}{m_{l}} \frac{\partial}{\partial R_{\rho}} \left\rangle \left\langle \chi_{l}^{l} \right\rangle_{R}.
\]

The transfer of amplitude between electronic states during the pulse depends on the transition dipole moment modulated by \( \bar{E}(t) \) and the nuclear overlap between the TBFs. Eq. (2) is equivalent to the exact TDSE in the limit of a large number of TBFs and is at the heart of the Full Multiple Spawning (FMS) method. In practice, two central approximations are required for molecular applications. First, a zeroth-order saddle-point approximation (SPA) is used to evaluate the Hamiltonian matrix elements. Second, the initial (parent) TBFs are considered uncoupled and will be run independently. It is however important to note that all the children TBFs produced by a given parent TBF will be coupled, i.e., only the TBFs produced by different parents are uncoupled. This independent first generation (IFG) approximation is based on the observation that for multidimensional systems, the initial nuclear wavepacket is expected to rapidly spread over the molecular configuration space, i.e., parent TBFs will rapidly separate. Combining the SPA and IFG approximations with on-the-fly
The population of an electronic state $I$ is given by

$$n_I(t) = \sum_{\tilde{J}'} \sum_{\tilde{J}} C_{\tilde{J}'}^{\tilde{J}} (t) C_{\tilde{J}}^{\tilde{J}} (t) S_{\tilde{J}'}^{\tilde{J}}$$

and the time-dependent dipole moment by

$$\vec{\mu}(t) = \sum_{I'} \sum_{J} C_{I'}^{J} (t) C_{J}^{J} (t) \times \left[ \vec{\mu}_{\text{elec}} \left( \mathbf{R}_{I'}^{\text{centroid}} \right) S_{I'}^{J} + \vec{\mu}_{\text{nuc}} \left( \mathbf{R}_{I'}^{\text{centroid}} \right) \delta_{I,J} \right],$$

where $N_i$ is the number of electronic states and the SPA has been invoked. The time-dependent dipole moment reflects the density of the coherent superposition of states. Due to interferences between electronic states, the dipole continues oscillating after the pulse is over with an amplitude that is modulated by the overlap between TBFs (Fig. 2(b)).

**TEST APPLICATION**

We first compare the XFAIMS method to grid-based numerically exact quantum dynamics simulations for the photoexcitation of the heteronuclear diatomic LiH (Fig. 1) by a short UV resonant pulse or an 8.5 fs IR pulse. For the grid simulations, potential energy surfaces are pre-computed at the SA2-CASSCF(4/6)-6-31G level for S0 and S1. In XFAIMS, the electronic structure is computed on-the-fly with MOLPRO at the same level of theory. The S1 state has an anharmonic potential with an equilibrium LiH distance of 2.44 Å compared to 1.66 Å on S0. We include only two electronic states in this example, but more states should be included if strong pulses are used and ionization needs to be described. The simulations below are carried out for aligned molecules.

We compared the dynamics of LiH excited by a 0.85 fs one-cycle UV resonant attopulse predicted by different methods. For the grid simulation, we started the dynamics on S0 from the ground vibrational eigenstate of S0 while for XFAIMS we started from a swarm of 100 Wigner-sampled initial conditions, using the IFG approximation. We also ran XFAIMS dynamics starting from a set of 5 initially coupled TBFs with LiH distance ranging from 1.60 Å to 1.72 Å and no initial momentum. Finally, we also ran XFAIMS at a frozen nuclear geometry starting from the equilibrium geometry of LiH.
We observed in all cases nearly identical population transfer during the pulse (Fig. 2(a)), and backtransfer from S\textsubscript{1} to S\textsubscript{0} is also well described. This was expected since the pulse is short (0.85 fs) and there is no significant nuclear motion during the pulse. However, the nuclear motion plays a major role on the dipole moment after the end of the pulse (Fig. 2(b)). When the nuclei are frozen, the dipole moment incorrectly oscillates with constant amplitude due to interferences between the two electronic states of the coherent superposition built by the pulse. The numerically exact grid simulation including nuclear motion shows that the amplitude of the time-dependent dipole moment should decrease with time as the wavepacket on S\textsubscript{1} leaves the Franck-Condon (FC) region.\textsuperscript{12} XFAIMS with moving nuclei and the IFG approximation yields a time-dependent dipole moment that agrees with the grid simulation for early and late times. At intermediate times (5-10 fs), the amplitude of dipole moment oscillations is underestimated. A more accurate XFAIMS description is achieved by starting from five initially coupled TBFs on S\textsubscript{0}. This simulation both releases the IFG approximation and better describes the initial nuclear wavefunction, leading to quantitative agreement with the grid simulation.

The S\textsubscript{1} state is bound, so the wavepacket returns to the FC region after reaching the outer turning point, leading to interferences with the S\textsubscript{0} wavepacket.\textsuperscript{12,39,46} This is reflected in the strong oscillations of the dipole moment between 70 and 80 fs (Fig. 2(c)). XFAIMS somewhat underestimates the amplitude of these oscillations, potentially due to the IFG approximation, but the oscillations remain in phase with exact results even after 80 fs. The Fourier transform of the dipole moment (Fig. 2(d)) exhibits a broad peak centered at the S\textsubscript{0} to S\textsubscript{1} excitation energy, superimposed on a vibrational progression corresponding to excitation from S\textsubscript{0} to vibrationally excited states of S\textsubscript{1}, as reported previously.\textsuperscript{12,39}

We also assessed XFAIMS for a longer and more realistic pulse where nuclear motion is significant during the pulse (Fig. 3). We choose a weak (3 \times 10^{-12} W/cm\textsuperscript{2}) 8.5 fs 800 nm IR pulse that populates S\textsubscript{1} through 2 photon transitions. As for the short pulse, XFAIMS simulations start from 100 uncoupled Wigner-sampled initial conditions. The population transfer and time-dependence of the dipole moment are again in good agreement with the grid simulation (Fig. 3). As in the case of the short pulse, the XFAIMS-computed time-dependent dipole moment is somewhat underestimated at intermediate times (15-20 fs). However, the XFAIMS and exact time-dependent dipole moments are overall in excellent agreement.

As a last example, we use XFAIMS to model polyatomic electron-nuclear dynamics, which is the raison d’être of this method. We investigated the effect of nuclear motion on population transfer of H\textsubscript{2}CSO during photoexcitation to S\textsubscript{1} by short (0.85 fs) and longer (2.54 fs) resonant perpendicularly polarized UV pulses (Fig. 4). The S\textsubscript{0} and S\textsubscript{1} electronic states are computed on-the-fly with SA2-CASSCF(4/3)/6-31G(d). The short pulse (Fig. 4(a)) leads to similar population transfer when the nuclei are frozen or allowed to move. For the longer pulse (Fig. 4(b)), population transfer is significantly overestimated when the nuclei are frozen.

**CONCLUSIONS**

XFAIMS efficiently and accurately describes the coupled electron-nuclear dynamics from laser excitation through fragmentation/relaxation. Good agreement with numerically exact quantum dynamics was achieved for the excitation of LiH molecule by resonant and non-resonant short and long pulses. We demonstrated the applicability of the method to a polyatomic molecule. XFAIMS paves the way towards complete in silico photochemical experiments of large molecules, especially given the emergence of GPU-accelerated electronic structure calculations.\textsuperscript{47}

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