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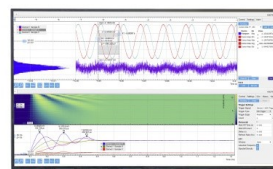
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ABSTRACT

Ab initio multiple spawning (AIMS) offers a reliable strategy to describe the excited-state dynamics and nonadiabatic processes of molecular systems. AIMS represents nuclear wavefunctions as linear combinations of traveling, coupled Gaussians called trajectory basis functions (TBFs) and uses a spawning algorithm to increase as needed the size of this basis set during nonadiabatic transitions. While the success of AIMS resides in this spawning algorithm, the dramatic increase in TBFs generated by multiple crossings between electronic states can rapidly lead to intractable dynamics. In this Communication, we introduce a new flavor of AIMS, coined *ab initio* multiple spawning with informed stochastic selections (AIMSWISS), which proposes a *parameter-free* strategy to beat the growing number of TBFs in an AIMS dynamics while preserving its accurate description of nonadiabatic transitions. The performance of AIMSWISS is validated against the photodynamics of ethylene, cyclopropanone, and fulvene. This technique, built upon the recently developed stochastic-selection AIMS, is intended to serve as a computationally affordable starting point for multiple spawning simulations.

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I. INTRODUCTION

Simulating the excited-state dynamics of molecules is a highly complex computational task that ultimately necessitates letting go of an approximation at the heart of almost all of ground-state chemistry—the Born–Oppenheimer approximation (BOA).^{1,2} After being electronically excited, a molecule will relax and reach regions of configuration space where two or more electronic states come close in energy, at which point a coupling between nuclear and electronic motions—the so-called nonadiabatic couplings—will mark the breakdown of the BOA. In most cases, moving beyond this approximation means employing the Born–Huang representation of the molecular wavefunction. This representation engenders the common picture of photochemistry in which nuclear wavepackets move on distinct electronic potential energy surfaces (PESs) and can transfer amplitude between each other due to nonadiabatic couplings.³ Starting with the seminal work of Heller,^{4,5} a prominent approach to solving the resulting coupled time-dependent Schrödinger equation has been to expand the nuclear wavepackets in a traveling basis of coupled, frozen multidimensional Gaussians, also known as trajectory basis functions (TBFs). An example of a

method employing such a basis set is full multiple spawning and *ab initio* multiple spawning (FMS and AIMS).^{6–9} In FMS/AIMS, the phase space center of a given TBF moves on a single adiabatic surface along a classical trajectory, and nonadiabatic effects are included by allowing the number of TBFs to increase when needed. As soon as a TBF reaches a region of configuration space in which the nonadiabatic coupling to another state is large enough, it will be able to *spawn* a copy of itself on the coupled state, allowing for a smooth transmission of amplitude from one electronic state to the other. While FMS is, in principle, exact in the limit of a large number of TBFs, AIMS has recourse to approximate couplings between TBFs to perform on-the-fly nonadiabatic quantum dynamics (see Ref. 10 for a detailed test of AIMS approximations). Other methods employing a TBF basis exist and differ from FMS/AIMS in the way the TBFs are propagated in time. Examples are the variational multi-configurational Gaussian (vMCG) method,^{11–13} which utilizes the time-dependent variational principle to propagate the TBFs, and multiconfigurational Ehrenfest (MCE),^{14–16} where TBFs are evolved classically on a mean-field potential.

While the adaptive nature of the TBF basis contributes to the success of FMS/AIMS, it also constitutes one of its drawbacks. In

many cases, an electronically excited molecule will pass through multiple nonadiabatic regions until it fully relaxes into the ground state, leading to the creation of a large number of TBFs in the context of an AIMS simulation. Such an increase in TBFs can lead to a dramatic computational cost, since, in principle, the number of electronic structure calculations per time step is $N_{\text{TBF}}(t) \times (N_{\text{TBF}}(t) + 1)/2$ [with $N_{\text{TBF}}(t)$ being the number of TBFs at time t]. It has been recently pointed out that propagating all TBFs together for the entire dynamics is unnecessary as newly created TBFs will, in most cases, quickly become uncoupled to their ancestor TBFs.¹⁷ A new method has been developed within the multiple spawning framework by leveraging this quick decoupling, called stochastic-selection *ab initio* multiple spawning (SSAIMS). SSAIMS detects uncoupled (groups of) TBFs during the dynamics and randomly selects only one of them to continue the propagation. The coupling between TBFs is measured either by their Hamiltonian matrix elements (ESSAIMS) or by their overlap (OSSAIMS). As soon as (groups of) TBFs become uncoupled, a stochastic algorithm chooses one of them based on their coherent population. The dynamics is stopped for all (groups of) TBFs that are not selected, whereas the coefficients of the remaining TBFs are renormalized and the dynamics continues with this reduced basis set. Multiple runs have to be performed for every initial condition to converge the stochastic process, using different seeds for the random number generator. This convergence is necessary to ensure an accurate description of the dynamics, where small populations of TBFs are not overlooked. For more details on SSAIMS, the interested reader is referred to Ref. 17.

While SSAIMS offers a strategy to limit the number of TBFs in an AIMS dynamics, it comes at the cost of introducing a new parameter measuring the coupling between TBFs. This parameter is system dependent and has to be optimized to achieve the desired balance between accuracy and efficiency—a particularly cumbersome process when investigating larger molecular systems. In this Communication, we introduce a method called *ab initio* multiple spawning with informed stochastic selections (AIMSWISS), which uses the idea of SSAIMS but determines the coupling parameters on-the-fly without any user input. AIMSWISS can be seen as a TBF-greedy version of AIMS—its primary goal being to keep the number of TBFs as small as possible—and a sweet spot between efficiency and accuracy for a multiple spawning simulation. After discussing the details of the AIMSWISS algorithm, we exemplify its performances with the photodynamics of ethylene, fulvene, and cyclopropane.

II. METHOD

In this work, we wish to depart from the simple “one parameter fits all” idea inherent to SSAIMS and propose instead a strategy where each pair of TBFs will have a personalized coupling parameter. To achieve this goal, we propose to focus our attention on the time needed for the overlap of two TBFs to decrease by a certain amount. This idea is reminiscent of earlier work on the overlap between two multidimensional frozen Gaussians moving on different adiabatic PESs, in particular by Schwartz *et al.*¹⁸ They showed that when the two TBFs have the same initial conditions, the real part of their overlap approximately decays as a Gaussian in time within the short time limit. The decay time of the overlap then takes on a simple form (using atomic units),

$$\tau_D = \left[\frac{1}{4} \left(\mathbf{F}_{i,0}^{(K)} - \mathbf{F}_{j,0}^{(L)} \right)^T \boldsymbol{\alpha}^{-1} \left(\mathbf{F}_{i,0}^{(K)} - \mathbf{F}_{j,0}^{(L)} \right) \right]^{-1/2}, \quad (1)$$

where $\boldsymbol{\alpha}$ represents the width matrix (identical for the two multidimensional frozen Gaussians) and $\mathbf{F}_{i,0}^{(K)}$ represents the nuclear forces acting on the phase space center of the i th frozen Gaussians moving on electronic state K (see the [supplementary material](#) or Ref. 18 for a derivation of this equation). This “Schwartz model” assumes that it is sufficient to know the initial nuclear-force difference to predict how and when two multidimensional frozen Gaussians, i.e., TBFs in an AIMS context, will separate. Interestingly, the central assumption of the Schwartz model, namely that the two TBFs have the same initial conditions, is similar to what happens during a spawning event in AIMS, in which the child TBF is an exact copy of its parent in configuration space, propagating on a different electronic state. Hence, there is much reason to assume that the Schwartz model could apply for the parent–child TBF pairs of AIMS as well. To test whether the model could be applied to predict the overlap decay of an arbitrary parent–child TBF pair, we calculated the AIMS dynamics for three different molecules—ethylene, fulvene, and cyclopropanone—and monitored the overlap decay between all pairs of TBFs. These molecular systems were chosen because they probe different types of excited-state dynamics and nonadiabatic processes (described below and in more detail in Refs. 19 and 20). State-averaged complete active space (SA-CASSCF) was used for the electronic structure of all molecules (for more information, see computational details in the [supplementary material](#)).

First of all, we note that the qualitative feature of a Gaussian overlap decay for parent and child TBFs, proposed in the Schwartz model, is effectively observed in AIMS (see Fig. S2 in the [supplementary material](#)). How well do the decay times between pairs of TBFs obtained with AIMS compare to those predicted by the Schwartz model? To answer this question, the squared magnitude of the overlap was calculated for every parent–child TBF pair. This was achieved by calculating a Gaussian profile with decay time τ_D from Eq. (1), using the nuclear forces of the parent and child TBFs at the spawning time, and multiplying it with the initial squared modulus overlap of the pair. The time for this Schwartz model overlap to reach 10% of its initial value can then be compared to the time taken for the squared magnitude of the overlap observed in AIMS to decay to the same percentage (Fig. 1). We observe a considerable correlation between the two quantities and, more importantly, that the model overestimates the AIMS overlap decay time more often than it underestimates it. (For a detailed investigation of the outliers for ethylene in this correlation plot, see Figs. S3 and S4 in the [supplementary material](#).) We note that the photodynamics of fulvene leads to rare reoverlap events between TBFs, which are visible in the correlation plot.

Motivated by these results, we propose the following strategy to integrate the Schwartz model into SSAIMS: instead of looking at a single (user-defined) parameter to measure the decoupling between TBFs, we can define for each pair of parent–child TBFs an approximate short-coherence time based on the Schwartz model—using as information only the nuclear forces on the TBFs at the spawning point. The resulting AIMSWISS method works in the following way (see Fig. 2 for a schematic depiction of the following steps): (a) after each successful spawning event, a new parent–child pair is created and the fully coupled family of TBFs is propagated in time from

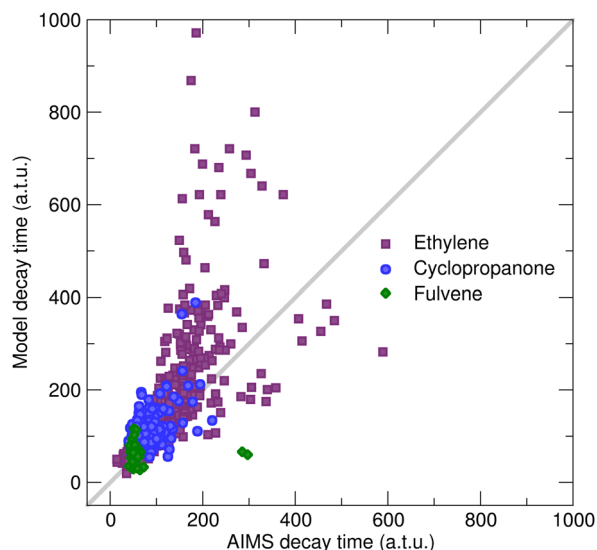


FIG. 1. Correlation between the decay times provided by the Schwartz model and AIMS dynamics for ethylene (violet squares), cyclopropanone (blue circles), and fulvene (green diamonds). The gray line represents an ideal correlation between the Schwartz model and the actual AIMS decay times.

t_{entry} onward; (b) when the spawning time t_{spawn} of the newly created child TBF is reached, the nuclear forces of this newcomer and its parent are used to calculate τ_D from Eq. (1); (c) τ_D is used to determine the simulation time at which the Gaussian profile of the absolute value squared overlap (represented by the blue curve in Fig. 2) drops to $\exp(-1)$ of its initial value; (d) at the time $t_{\text{SS}} = t_{\text{spawn}} + \tau_D$, the pair is then considered fully separated and two disconnected

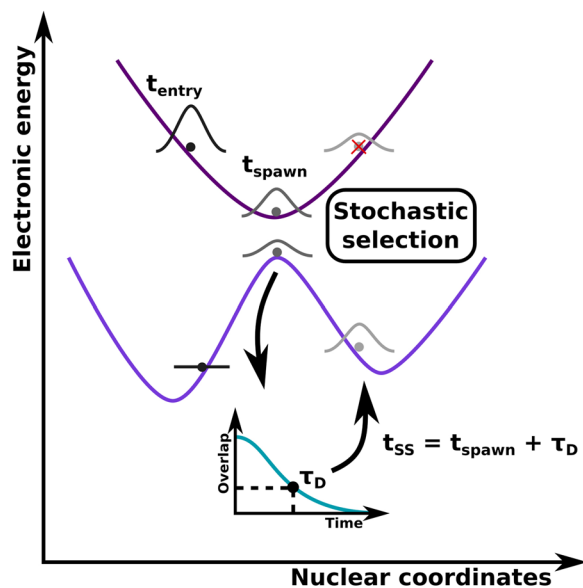


FIG. 2. Schematic representation of the AIMSWISS method. See the main text for details.

groups of TBFs are formed; and (e) the coherent populations of both groups are calculated and a random number is generated. A Monte Carlo procedure then picks one these two groups to continue the dynamics. The group of TBFs that is not chosen is discarded from the simulation and the remaining TBFs are renormalized. Multiple AIMSWISS runs might be required for each initial condition to converge the stochastic-selection algorithm, as done in SSAIMS. The “informed” nature of the stochastic selections in AIMSWISS makes it such that the method can be used for any molecular system without any preparatory runs to determine an adequate selection criterion, in strong contrast to ESSAIMS and OSSAIMS.

Note that since AIMSWISS employs the decay time given in Eq. (1) for every parent–child pair created in the course of the dynamics, the stochastic selection will always select between two different groups of TBFs, that is, one retains either the child TBF and its offspring or the parent TBF and its other progeny. This highlights an important assumption made by AIMSWISS: when parent and child TBFs separate in phase space, their respective offspring separate as well.

We would like to emphasize here some key differences between AIMSWISS and the original SSAIMS algorithm. Whereas (E/O)SSAIMS define the coupling between TBFs via a predefined threshold, AIMSWISS employs an adaptable threshold defined on-the-fly during the dynamics, because it implicitly assumes that TBFs are decoupled when their magnitude squared overlap has decayed to $\exp(-1)$ of its initial value at t_{spawn} . Most implementations of AIMS/FMS apply a velocity rescaling to the child TBF at the spawning time to enforce total (classical) energy conservation—potentially reducing the initial overlap with its parent TBF. Hence, it is assumed that no matter how large or small the initial overlap between parent and child TBFs is, they and their descendants will always be separated after the decay time τ_D has passed. Nevertheless, the overlap between TBFs is monitored during an AIMSWISS run and if it is larger than expected for a pair of TBFs at the moment of the selection, a warning is issued in the output file and the result should be checked with care. It is finally important to realize that there are no other approximations in AIMSWISS than that of selecting the TBFs when considered uncoupled. As such, the AIMS dynamics can be easily recovered in the limit $\tau_D \rightarrow \infty$ (see Fig. S5 in the [supplementary material](#)).

III. RESULTS

In the following, we shall compare the performance of AIMSWISS to that of AIMS and the original formulation of SSAIMS (ESSAIMS) on the three previously introduced molecular systems—ethylene, fulvene, and cyclopropanone (see the [supplementary material](#) for full computational details).

Let us first focus on the population traces produced by AIMSWISS. The S_1 excited-state population decay of ethylene resulting from the AIMSWISS dynamics is almost indistinguishable from that of AIMS [see Fig. 3(a)]. AIMSWISS captures the AIMS dynamics just as well as ESSAIMS ($\epsilon = 10^{-5}$ a.u.), an observation explained by the fact that AIMSWISS and ESSAIMS perform stochastic selections at similar times. Due to the number of runs required per initial conditions (5 here), AIMSWISS and ESSAIMS are actually more computationally expensive than AIMS in the early time of the dynamics (see below for more details on the computational cost of

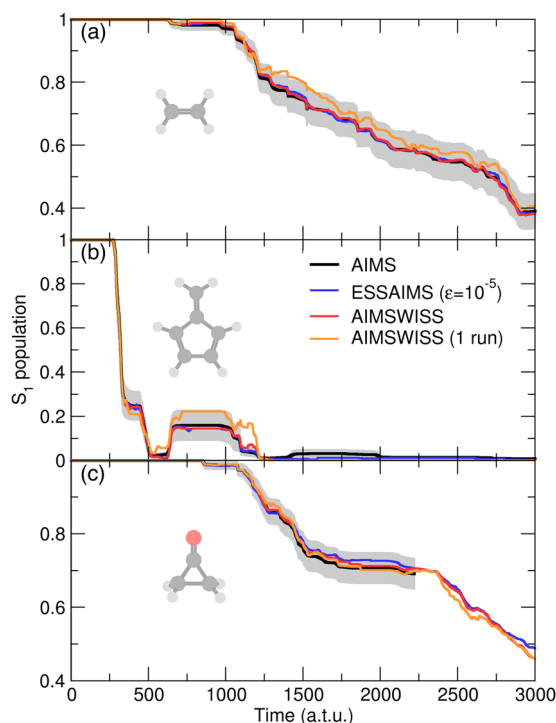


FIG. 3. Photodynamics of (a) ethylene, (b) fulvene, and (c) cyclopropanone. The S_1 population decays for all three molecules were obtained with AIMS (black curve), ESSAIMS (blue curve, $\epsilon = 10^{-5}$ a.u.), AIMSWISS (light red curve), and AIMSWISS with one run per initial condition (orange curve). The gray error bars represent the standard error for the AIMS result.

AIMSWISS). Hence, we can examine the population trace obtained with AIMSWISS by running each initial condition only once. The S_1 population dynamics resulting from this cheap AIMSWISS dynamics matches that of AIMS within its standard error for most of the simulation time [see the orange curve in Fig. 3(a)].

In contrast to the rather simple photodynamics of ethylene, fulvene exhibits a more complex nuclear dynamics^{21–24} due to its sloped conical intersection that causes reflection of the nuclear wavepackets and multiple nonadiabatic transitions between the S_1 and S_0 states—a challenge for methods based on independent trajectories.¹⁹ Hence, the nonadiabatic dynamics of fulvene constitutes a stringent test for AIMSWISS. Comparing the excited state population resulting from AIMS with that of AIMSWISS, we observe that the AIMSWISS result lies within the standard error of the AIMS reference for most of the dynamics [see Fig. 3(b)]. At around 600 and 1200 atomic time units (atu), the S_1 population predicted by AIMSWISS marginally deviates from the standard error of the AIMS population trace. Furthermore, the last repopulation of the excited state, observed for AIMS at around 1500 atu, is not fully captured by AIMSWISS. Interestingly, AIMSWISS performs as well as ESSAIMS ($\epsilon = 10^{-5}$ a.u.) for this challenging system, both results being nearly indistinguishable, even for the last recurrence. Using only one run per initial condition, the AIMSWISS population trace deviates more significantly from the reference AIMS average trace [see the orange curve in Fig. 3(b)],

even though it lies within the standard error of AIMS up until 1000 atu and reproduces its quantitative behavior—in contrast to other methods like surface hopping.¹⁹ The deviations from the standard error of AIMS at around 600 and 1200 atu, already observed in AIMSWISS with multiple runs, are further exacerbated. We note that the AIMSWISS warning described in Sec. II is actually triggered in fulvene and the user is informed in most runs that the first or second parent–child TBF pair is prematurely selected (based on their overlap). Hence, in a normal usage of AIMSWISS, the user would be made aware of a possible issue with the underlying approximations of the method—such a red flag would imply that the simulation should be thoroughly verified and the use (E/O)SSAIMS (with conservative selection parameters) or if possible AIMS considered.

Finally, AIMSWISS was tested with the photodynamics of cyclopropanone. This molecule shows dissociation following its relaxation into the ground state, and a TBF evolving on this state is likely to reach a region of configuration space in which the active space becomes unstable.²⁰ Even if this TBF is only weakly coupled to the other TBFs, the coupled nature of an AIMS dynamics implies that such an electronic structure instability for a single TBF will cause the full dynamics to stop [black line in Fig. 3(c)]. We showed in an earlier work²⁰ that SSAIMS is able to extend the dynamics beyond this point by discarding TBFs from the simulation before they can cause a fatal issue [see Fig. 3(c)]. The S_1 population dynamics resulting from AIMSWISS as well as ESSAIMS ($\epsilon = 10^{-5}$ a.u.) lies within the standard error of the population trace calculated with AIMS. [The reader is referred to Fig. S6 in the [supplementary material](#) for a plot showing the agreement between AIMSWISS and ESSAIMS ($\epsilon = 10^{-5}$ a.u.) up to 12 500 atu.] The AIMSWISS population decay using only one run per initial condition agrees closely with the converged AIMSWISS run as well as the population dynamics of ESSAIMS ($\epsilon = 10^{-5}$ a.u.) in the range from 0 to 3000 atu.

We showed that AIMSWISS, despite its simplicity, can provide population decays in close agreement with AIMS and ESSAIMS, even for challenging photodynamical processes. We now want to address the question of its computational effort. To facilitate a comparison of the computational cost for the different methods discussed in this work—AIMS, AIMSWISS, and ESSAIMS ($\epsilon = 10^{-5}$ a.u.)—we propose to employ a *theoretical number of electronic structure calls per time step*. This value represents the worst case scenario in a multiple spawning dynamics, where the Hamiltonian matrix elements are not screened and all elements are always calculated. Since the number of active TBFs differs from one initial condition to another and between different runs, the number of electronic structure (ES) calls was calculated via $N_{\text{ES}}(t) = \sum_{j=1}^{n_{\text{run}}} \sum_{k=1}^{N_{\text{init}}} N_{\text{TBF}}^{kj}(t) \times (N_{\text{TBF}}^{kj}(t) + 1)/2$, where $N_{\text{TBF}}^{kj}(t)$ is the number of TBFs at time t of the j th run for the k th initial condition. We note that $n_{\text{run}} = 1$ for AIMS or AIMSWISS (1 run).

In the case of ethylene, we observe that AIMSWISS predicts a slightly faster decoupling of the TBFs than ESSAIMS ($\epsilon = 10^{-5}$ a.u.), which reduces its theoretical number of ES calls [see Fig. 4(a)]. The number of ES calls of AIMS starts at around 1000 atu to increase linearly from 54 to over 600 (the growing complexity of a typical AIMS run is further discussed in Fig. S1 of the [supplementary material](#)). AIMSWISS and ESSAIMS ($\epsilon = 10^{-5}$ a.u.) start off with 223 ES calls (as a result of the number of runs per initial condition). A difference in the number of TBFs preserved by the two methods is

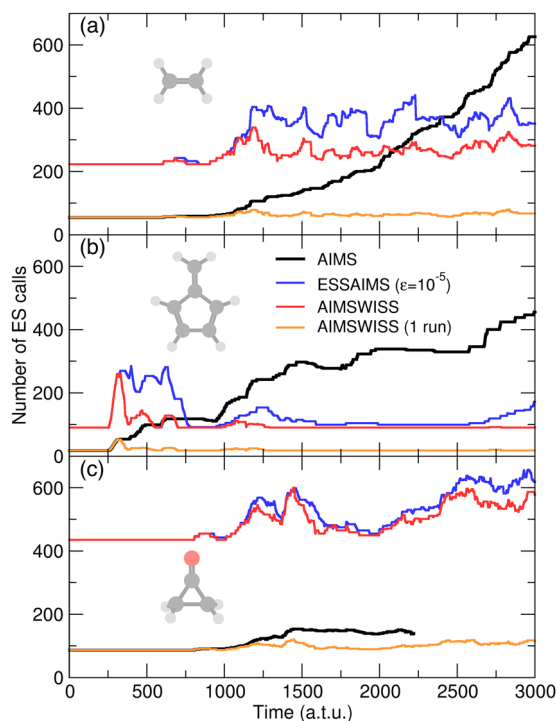


FIG. 4. Theoretical number of electronic structure calculations at each time step for (a) ethylene, (b) fulvene, and (c) cyclopropanone. The following methods are compared: AIMS (black curve), ESSAIMS (blue curve, $\epsilon = 10^{-5}$ a.u.), AIMSWISS (light red curve), and AIMSWISS with one run per initial condition (orange curve).

observed from around 1200 atu, as evidenced by the variation in the number of ES calls, which increases for ESSAIMS to ~ 400 and oscillates around this value, while for AIMSWISS, it reaches a maximum of ~ 340 and stays below this value for the rest of the dynamics. The greediness of AIMSWISS for TBFs is apparent for the AIMSWISS dynamics employing only one run per initial condition, as the number of ES calls remains below 100 for the totality of the dynamics. We recall that despite such a small number of TBFs employed by AIMSWISS (1 run), its population decay dynamics was in good agreement with the AIMS reference.

For the fulvene dynamics, comparing the number of ES calls per propagation step obtained from AIMSWISS [see Fig. 4(b)] with the resulting S_1 population trace paints an interesting picture. At the onset of each population decay (or recurrence) event, AIMSWISS allows the basis set to grow via spawning, which engenders an increase in the amount of ES calls. However, once this change of population is achieved, AIMSWISS collapses the basis set nearly back to its original size. Thus, peaks in the number of ES calls can be observed at 310, 460, 630 atu, and finally at around 1000 atu [see Fig. 4(b)]. ESSAIMS ($\epsilon = 10^{-5}$ a.u.) is less aggressive in its stochastic-selection process, leading to a number of ES calls that rises to 300 at around 250 atu and oscillates near this value until the basis set is fully reduced to a single TBF per initial condition at around 800 atu. Both methods, in their converged form, become less computational expensive than AIMS at around 700 atu, even if AIMSWISS arrives at this point slightly earlier than ESSAIMS ($\epsilon = 10^{-5}$ a.u.).

When comparing the number of ES calls between the three different methods for the cyclopropanone dynamics, one observes that this number is smaller for AIMS than for the fully converged methods based on stochastic selections [see Fig. 4(c)]. However, this is the price to pay for describing the S_1 population decay beyond what is possible for AIMS, and we note that AIMSWISS (1 run) is stable for the entire dynamics and rapidly cheaper than AIMS. Once again, the aggressive selection performed by AIMSWISS makes that its number of ES calls per time step is smaller than that of ESSAIMS ($\epsilon = 10^{-5}$ a.u.).

We finally note that earlier work showed that the number of ES calls of ESSAIMS ($\epsilon = 10^{-5}$ a.u.) for the photodynamics of fulvene and cyclopropanone was close to that of converged trajectory surface hopping dynamics.²⁰ Based on the results presented here, we can infer that AIMSWISS will also be competitive with surface hopping while preserving the accurate description of nonadiabatic transitions offered by coupled TBFs.

IV. CONCLUSION

In this Communication, we introduced the AIMSWISS approach, which offers a simple strategy to reduce the number of TBFs produced in a multiple spawning dynamics while preserving the accuracy of employing coupled TBFs during nonadiabatic events. In contrast to SSAIMS, AIMSWISS uses adaptable parameters to select TBFs that are determined on-the-fly with no input from the user. Furthermore, a simple diagnostic of the quality of AIMSWISS can be encoded to warn the user of a potential failure of its underlying approximations. The population time traces calculated with AIMSWISS for the photodynamics of ethylene, fulvene, and cyclopropanone are in close agreement with both ESSAIMS and AIMS. The computational effort associated with AIMSWISS is lower than that of ESSAIMS due to a more aggressive selection strategy, making AIMSWISS competitive with the mixed quantum/classical method trajectory surface hopping. As such, we believe that AIMSWISS can serve as the simplest and cheapest entry door for excited-state dynamics within the multiple spawning framework. AIMSWISS is particularly suited for exploratory excited-state dynamics in preparation for a more rigorous AIMS simulation, the photodynamics of a large molecular system, or the nonadiabatic dynamics of a molecule involving an important number of coupled electronic states. The strategy described here to select important TBFs could also be of interest for other recent methods based on coupled trajectories.^{25,26}

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for computational details of the calculations presented in this work, information about the complexity of an AIMS run, a derivation of the Schwartz decay time, analysis of the outliers in the correlation plot, the full population decay of cyclopropanone obtained with AIMSWISS and ESSAIMS, and a study of how AIMSWISS can be converged toward AIMS.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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