

Ab Initio Nonadiabatic Quantum Molecular Dynamics

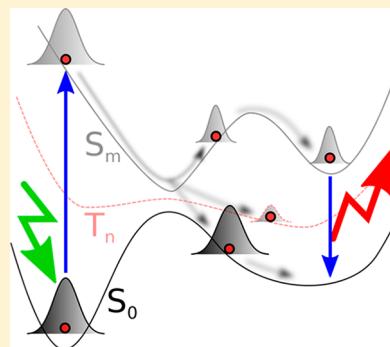
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ABSTRACT: The Born–Oppenheimer approximation underlies much of chemical simulation and provides the framework defining the potential energy surfaces that are used for much of our pictorial understanding of chemical phenomena. However, this approximation breaks down when the dynamics of molecules in excited electronic states are considered. Describing dynamics when the Born–Oppenheimer approximation breaks down requires a quantum mechanical description of the nuclei. Chemical reaction dynamics on excited electronic states is critical for many applications in renewable energy, chemical synthesis, and bioimaging. Furthermore, it is necessary in order to connect with many ultrafast pump–probe spectroscopic experiments. In this review, we provide an overview of methods that can describe nonadiabatic dynamics, with emphasis on those that are able to simultaneously address the quantum mechanics of both electrons and nuclei. Such ab initio quantum molecular dynamics methods solve the electronic Schrödinger equation alongside the nuclear dynamics and thereby avoid the need for precalculation of potential energy surfaces and nonadiabatic coupling matrix elements. Two main families of methods are commonly employed to simulate nonadiabatic dynamics in molecules: full quantum dynamics, such as the multiconfigurational time-dependent Hartree method, and classical trajectory-based approaches, such as trajectory surface hopping. In this review, we describe a third class of methods that is intermediate between the two: Gaussian basis set expansions built around trajectories.



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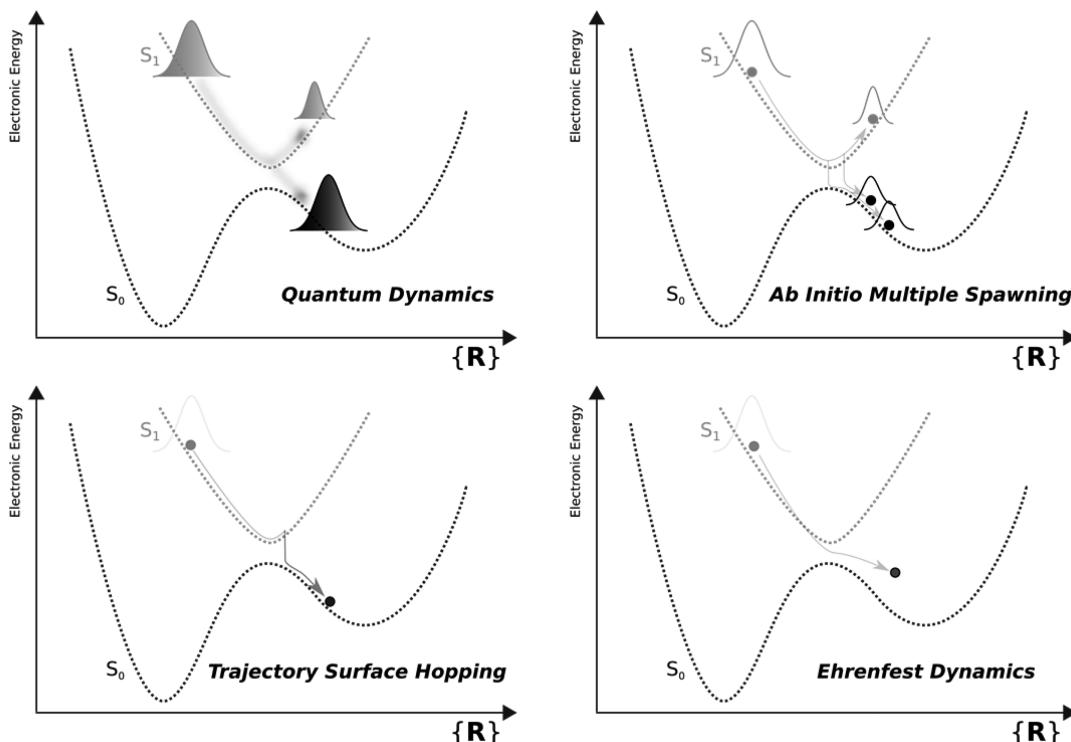


Figure 1. Schematic representation of different methods for excited-state molecular dynamics.

1. INTRODUCTION

In many chemical problems, the electrons respond nearly instantaneously to nuclear motion and the details of electronic dynamics can be ignored. In these cases, the Born–Oppenheimer approximation (BOA) allows us to decouple the electronic and nuclear problems, defining the very concept of the potential energy surface. However, when the dynamics starts on an excited electronic state, there are almost invariably nonadiabatic transitions between electronic states, corresponding to a breakdown of the BOA and demanding a quantum mechanical treatment of both the nuclei and the electrons. There are numerous examples of chemical problems that involve excited electronic states, from photochemistry to electron transfer, with applications in renewable energy, chemical synthesis, and bioimaging. It is thus a major theoretical challenge to describe the quantum mechanical behavior of both electrons and nuclei in the context of nonadiabatic effects and excited-state chemistry.

A number of computational methods have been proposed in the past decades in order to meet the challenge of simulating dynamics beyond the BOA. A schematic representation of some of the most commonly employed nonadiabatic dynamics methods is provided in Figure 1, and numerous reviews of the subject have been published.^{1–4} Methods such as multi-configuration time-dependent Hartree (MCTDH) can provide numerically exact results for molecules with a few tens of nuclear degrees of freedom.^{5,6} MCTDH is often considered as a reference method for excited-state dynamics, when high-accuracy potential energy surfaces and nonadiabatic coupling matrix elements are available. Unfortunately, the method requires precalculated potential energy surfaces (implying the necessity for a computationally challenging global fit) and the limitation to relatively few degrees of freedom requires a reduced dimensionality treatment for most molecules; that is, freezing some of the internal coordinates. Multilayer (ML-

MCTDH)^{7,8} offers a way to circumvent reduced dimensionality in some cases, but further approximations are needed if one is interested in the dynamics of molecules in their full configuration space. In mixed quantum/classical methods,⁹ such as Ehrenfest and trajectory surface hopping dynamics, the nuclei are treated classically. In the former, nuclear forces are directly derived from the time-dependent propagation of an electronic wave function or density matrix, and trajectories evolve on a time-dependent average of the electronic states.^{3,10,11} In surface hopping dynamics,^{12,13} a set of electronic amplitudes are integrated together with the classical trajectories and dictate the probability that the trajectory will hop from one electronic state to the other (additional details on the surface hopping method are given in section 2.2 and section 4.3.1).

These techniques are far from the only way of modeling nonadiabatic molecular dynamics, and we briefly mention semiclassical approaches,^{14,15} quantum-classical Liouville approaches,^{16–19} symmetrical quasi-classical windowing,^{20–24} linearized nonadiabatic dynamics,²⁵ Bohmian dynamics,^{26–31} and exact-factorization-based mixed quantum/classical algorithms.^{32–36}

This review focuses on nonadiabatic dynamics methods that expand the nuclear wave function in terms of a linear combination of traveling Gaussian basis functions.^{37–39} This idea is rooted in the seminal work of Heller.³⁷ Before Heller's work, the most common approach to chemical dynamics was based on a scattering formalism in the energy domain. Heller proposed to use *classically driven Gaussian functions* to describe the semiclassical dynamics of nuclear wavepackets. Heller further introduced a time-dependent perspective on photoabsorption, where the direct propagation of nuclear wave functions replaces the expensive calculation of Franck–Condon factors.^{38,40} In 1981, Heller³⁹ introduced the use of *frozen Gaussians*—that is, Gaussians with a fixed width—as a basis for

the nuclear wave function. This proposal seeded the development of the methods presented in this review.

One particularly compelling feature of Gaussian-based quantum dynamics methods is that they are easily amenable to an ab initio molecular dynamics formulation, where the required electronic structure quantities (such as electronic-state energies and gradients) are calculated on the fly, that is, simultaneously with the nuclear dynamics. Additionally, they can be derived from first principles and made exact in well-defined limits. In principle, the traveling nature of the Gaussian basis functions allows a compact set of basis functions to describe the dynamics, and therefore it can be much more computationally efficient than methods based on a fixed set of basis functions. We focus on full multiple spawning (FMS; section 4) and ab initio multiple spawning (AIMS; section 4.3) methods, but we also discuss other methods based on traveling Gaussian wavepackets such as variational multiconfigurational Gaussian^{41,42} (vMCG; section 5.2) and multiconfigurational Ehrenfest^{43,44} (MCE; section 5.1). The AIMS method avoids precalculated potential energy surfaces and instead solves the electronic Schrödinger equation as needed during the dynamics to obtain these quantities. AIMS constitutes the earliest reported incarnation^{45–47} of ab initio nonadiabatic quantum molecular dynamics. Subsequently, other nonadiabatic dynamics methods have also been used in the context of ab initio molecular dynamics.^{42,48–54}

2. TIME-DEPENDENT MOLECULAR SCHRÖDINGER EQUATION

Ab initio quantum molecular dynamics aims to solve the time-dependent Schrödinger equation (TDSE) for a molecular system (usually in the nonrelativistic limit, as shown here):

$$i\frac{\partial\Psi(\mathbf{r}, \mathbf{R}, t)}{\partial t} = \hat{H}(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}, t) \quad (1)$$

In this equation, \mathbf{r} and \mathbf{R} are the collection of $3N_{\text{el}}$ electronic and $3N$ nuclear coordinates, respectively. We make use of atomic units here and throughout this review: that is, $\hbar = m_e = 1$. The molecular Hamiltonian is given as

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_{\text{nuc}} + \hat{T}_e + \hat{V}_{e-e}(\mathbf{r}) + \hat{V}_{e-n}(\mathbf{r}, \mathbf{R}) + \hat{V}_{n-n}(\mathbf{R}) \\ = \hat{T}_{\text{nuc}} + \hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) \quad (2)$$

where $\hat{T}_{\text{nuc}} = -\sum_{\gamma}^N (1/2M_{\gamma})\nabla_{\mathbf{R}_{\gamma}}^2$ is the nuclear kinetic energy operator and the γ th nucleus has bare mass M_{γ} . The electronic Hamiltonian $\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})$ contains the electronic kinetic energy operator as well as all the Coulomb operators involving electrons and nuclei.

2.1. Representations of the Molecular Wave Function

The Born–Huang representation^{55,56} is a formally exact separation of the molecular wave function into electronic and nuclear contributions:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{J=1}^{\infty} \Omega_J(\mathbf{R}, t)\Phi_J(\mathbf{r}; \mathbf{R}) \quad (3)$$

where the subscript J denotes the electronic state and $\Omega_J(\mathbf{R}, t)$ is the time-dependent nuclear wave function associated with the J th electronic state. The electronic part in eq 3 is expanded in an orthonormal electronic basis, $\{\Phi_J(\mathbf{r}; \mathbf{R})\}$. Often one chooses the adiabatic representation, meaning that the electronic basis

consists of eigenfunctions of the time-independent electronic Schrödinger equation for a given nuclear configuration \mathbf{R} :

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Phi_J(\mathbf{r}; \mathbf{R}) = E_J(\mathbf{R})\Phi_J(\mathbf{r}; \mathbf{R}) \quad (4)$$

where $E_J(\mathbf{R})$ is the J th eigenvalue at a given nuclear position \mathbf{R} . These eigenvalues correspond to the adiabatic potential energy surface for the J th electronic state. Diabatic representations, where the electronic states are not eigenfunctions of the electronic Hamiltonian, are also possible (and in some cases advantageous).^{57–59} For simplicity, we focus on the adiabatic representation throughout most of this article.

In principle, the Born–Huang expansion is formally exact only when an infinite number of electronic states are included. In practice, an excellent approximation is often obtained with a few electronic states. Several alternative formulations exist that simplify the Born–Huang representation by restricting it to a single product. The most common is the Born–Oppenheimer approximation (BOA). In the BOA, the Born–Huang summation in eq 3 is limited to a single time-independent electronic term: $\Psi(\mathbf{r}, \mathbf{R}, t) \approx \Omega_J(\mathbf{R}, t)\Phi_J(\mathbf{r}; \mathbf{R})$, where J is often taken as the ground electronic state. (Note that this approximation is also known as the Born–Huang approximation, and that the Born–Oppenheimer *adiabatic* approximation further implies the neglect of diagonal Born–Oppenheimer corrections.⁴²) Effectively, the BOA assumes that the electrons relax instantaneously as the nuclei move; that is, that the electrons and nuclei are perfectly correlated.^{60,61} However, this correlation is restricted to a single electronic state and therefore breaks down when two electronic states become nearly or exactly degenerate. Although this breakdown of the BOA is rarely a major concern on the ground electronic state, it is practically the rule for molecules undergoing dynamics on excited electronic states, for example, in many ultrafast pump–probe-type experiments.

An alternative single-product formulation leads to the time-dependent self-consistent field (TDSCF) equations. In this approximation, the molecular wave function is given by $\Psi(\mathbf{r}, \mathbf{R}, t) \approx \Omega(\mathbf{R}, t)\Phi(\mathbf{r}, t)$; that is, a product of time-dependent nuclear and electronic wave functions.^{9,62,63} At first glance, this might seem similar to the BOA, but it is actually very different. Because the electronic wave function does not depend on the nuclear coordinates, the electronic and nuclear degrees of freedom are completely uncorrelated in this wave function ansatz. Indeed, when the TDSCF ansatz is inserted into the TDSE (eq 1), it leads to a set of coupled mean-field equations for both the electronic and the nuclear wave functions. Taking a classical limit for the nuclear degrees of freedom then leads to Ehrenfest dynamics. For more details on the classical limit leading to Ehrenfest dynamics and its implication for mixed quantum/classical dynamics, the reader is referred to previous work.^{9–11,64,65}

A final single-product formulation that bears mention is the exact factorization approach. As its name suggests, this formulation is formally exact, in spite of its restriction to a single product. This feat is accomplished^{66–69} by allowing *both* the nuclear and electronic wave functions to be explicitly time-dependent: $\Psi(\mathbf{r}, \mathbf{R}, t) = \Omega(\mathbf{R}, t)\Phi(\mathbf{r}, t; \mathbf{R})$. The explicit time dependence of the electronic wave function results in a potential energy surface that depends on *both* nuclear coordinates and time, as well as a time-dependent vector potential.^{32,70–75} Unlike the BOA ansatz, the electronic wave function is time-dependent. Unlike the TDSCF ansatz, the

electronic wave function depends parametrically on the nuclear degrees of freedom. Even though this single-product formulation is formally exact, it is unclear how to formulate an efficient and accurate implementation, and this is currently a topic of considerable research effort.³⁶

2.2. Coupled Time-Dependent Nuclear Equations

Upon insertion of the Born–Huang representation of eq 3 into the time-dependent Schrödinger equation (eq 1), left multiplication by $\Phi_i^*(\mathbf{r}; \mathbf{R})$, and integration over the electronic coordinates, we obtain a set of coupled equations of motion for the nuclear wave functions $\Omega_i(\mathbf{R}, t)$:

$$\begin{aligned} i \frac{\partial \Omega_i(\mathbf{R}, t)}{\partial t} &= [\hat{T}_{\text{nuc}} + E_i(\mathbf{R})] \Omega_i(\mathbf{R}, t) \\ &- \sum_j^{\infty} \left[\sum_{\rho=1}^{3N} \left(\frac{1}{M_\rho} \langle \Phi_i | \frac{\partial}{\partial R_\rho} | \Phi_j \rangle_r \frac{\partial}{\partial R_\rho} + \frac{1}{2M_\rho} \langle \Phi_i | \frac{\partial^2}{\partial R_\rho^2} | \Phi_j \rangle_r \right) \right] \Omega_j(\mathbf{R}, t) \end{aligned} \quad (5)$$

where ρ indexes the $3N$ nuclear coordinates. The first term of eq 5 describes adiabatic evolution of the nuclear component $\Omega_i(\mathbf{R}, t)$ on the I th electronic state corresponding to the potential energy surface $E_i(\mathbf{R})$. The second term, that is, the second line of eq 5, describes coupling with other electronic states through the first- and second-order nonadiabatic derivative couplings: $d_{ij}(\mathbf{R}) = \langle \Phi_i | \nabla_{\mathbf{R}} | \Phi_j \rangle_r$ and $D_{ij}(\mathbf{R}) = \langle \Phi_i | \nabla_{\mathbf{R}}^2 | \Phi_j \rangle_r$. These quantities couple the electronic states through nuclear motion and are critical in nonadiabatic dynamics. When the nonadiabatic coupling terms are neglected in eq 5, we obtain the so-called Born–Oppenheimer adiabatic approximation,^{42,56} which leads to Born–Oppenheimer molecular dynamics after taking a classical limit for the nuclear degrees of freedom.¹⁰ When only the diagonal second-order couplings are retained, we obtain an adiabatic equation of motion for the nuclei that corresponds to inserting the BOA ansatz (discussed above) in the TDSE (with a mass-dependent potential energy surface).

Diabatic electronic representations rotate the electronic states such that the nonadiabatic couplings are small (ideally they would vanish, but this is not possible for polyatomic molecules).^{57–59,76,77} This rotation necessarily leads to finite off-diagonal elements in the electronic Hamiltonian; that is, any rotation that diagonalizes the kinetic part of the Hamiltonian will undiagonalize the potential part.⁷⁸ In a diabatic representation, electronic transitions are primarily promoted by the off-diagonal elements in the electronic Hamiltonian (as opposed to the nonadiabatic derivative couplings that promote transitions in the adiabatic representation).

In conventional quantum dynamics simulations, the (nuclear) wave functions and Hamiltonian elements are represented on a fixed grid (see section 3). Numerically exact solution of the TDSE can be obtained, given that electronic energies and coupling terms are known along the selected coordinates of the molecular configuration space.^{79–81}

A very different philosophy is to approximate the dynamics of the nuclear wavepackets by a swarm of classical trajectories, which can, for example, *hop* from one electronic state to the other based on a stochastic algorithm. This technique, referred to as *surface hopping*, was first proposed in 1971 by Tully and Preston¹² and further refined by Tully in 1990¹³ as the fewest-switches algorithm. As trajectory surface hopping (TSH) is based on independent classical trajectories, it is well suited to *on-the-fly* dynamics, where the required electronic structure

quantities are computed at each time step of a trajectory. The reliance on classical trajectories also enables dynamical simulations of molecules in their full dimensionality (since the effort in classical propagation scales weakly with the number of degrees of freedom). Unfortunately, TSH cannot be fully derived from first principles. Numerous quasi-derivations have been proposed,^{31,82–85} based on different starting formalisms. However, in each of these at least one step is uncertain, and this makes it difficult to clearly delineate situations where TSH will or will not succeed. Some limitations are well-known and widely discussed. For example, the predicted dynamics from TSH depend (often quite strongly) on the electronic representation that is used (with the adiabatic representation being preferred).⁹ In contrast, the exact solution of the TDSE is independent of the electronic representation used. Decoherence of nuclear wavepackets is also a problem^{1,13,86–91} in TSH, although a number of different fixes have been proposed to overcome this limitation.^{92–99} A number of recent reviews on the TSH are available.^{11,90,100–102}

In the remainder of this review, we focus on basis-set expansions of eq 5, resulting in expressions for molecular quantum dynamics simulation that lead to well-controlled approximations.

3. AB INITIO QUANTUM DYNAMICS WITH A BASIS SET

The nuclear wave function for electronic state J can be written as a linear combination of N_J basis functions, denoted as $\{\chi_i^{(J)}\}_{i=1}^{N_J}$, whose elements are defined as $\chi_i^{(J)} \equiv \chi_i^{(J)}(\mathbf{R}; a_{i,1}^{(J)}(t), \dots, a_{i,N_p}^{(J)}(t))$; that is, the basis set only has explicit time dependence through its N_p parameters, denoted by $a_{i,1}^{(J)}(t), \dots, a_{i,N_p}^{(J)}(t)$. The superscript (J) is to be understood as an electronic-state label for the basis functions. Expanded in this basis, the Born–Huang representation of eq 3 reads:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_J^{\infty} \sum_i C_i^{(J)}(t) \chi_i^{(J)} \left(\mathbf{R}; a_{i,1}^{(J)}(t), \dots, a_{i,N_p}^{(J)}(t) \right) \Phi_j(\mathbf{r}; \mathbf{R}) \quad (6)$$

with complex time-dependent expansion coefficients $\{C_i^{(J)}\}_{i=1}^{N_J}$ for each basis function on each electronic state. Combination of eq 6 with the TDSE (eq 1) will be the common starting point for the description of different nonadiabatic quantum dynamics methods.

We mentioned previously that the coupled time-dependent nuclear equations can be solved on a grid (quantum dynamics). The grid can be formulated in such a way that it appears as a choice of basis set for the expression of the nuclear wave function, for example, as a series of δ -functions (or sinc functions) centered on each of the grid points. When this grid has a direct product structure, the basis is greatly simplified and a given nuclear wave function on state J with f nuclear degrees of freedom becomes⁵

$$\Omega_J(R_1, \dots, R_f, t) = \sum_{j_1, \dots, j_f=1}^{N_1, \dots, N_f} C_{j_1, \dots, j_f}^{(J)}(t) \prod_{\kappa=1}^f \chi_{j_\kappa}^{(\kappa)}(R_\kappa) \quad (7)$$

where $\chi_{j_\kappa}^{(\kappa)}(R_\kappa)$ represents one of the N_f functions used to describe the f th nuclear degree of freedom. These functions can be considered a dual-space representation connecting physical

space and function space, and this is the perspective taken explicitly in discrete variable (DVR)^{79,103} and finite basis (FBR)⁷⁹ representations. (Note that we keep \mathbf{R} as a generic label for the Cartesian nuclear coordinates. Internal coordinates can also be used, but we do not discuss the implications of such representations in this review.)

The curse of dimensionality in quantum dynamics clearly appears in eq 7, as the size of the problem grows as N^f if each of the f degrees of freedom is described by N functions. The multiconfiguration time-dependent Hartree (MCTDH) method^{5,6,104} proposes a clever way to alleviate the problem: the grid functions, now called single-particle functions (SPFs), acquire a time dependence that allows for a considerable reduction in the number of time-independent grid points:

$$\Omega_j(R_1, \dots, R_f, t) = \sum_{j_1, \dots, j_f=1}^{n_1, \dots, n_f} C_{j_1, \dots, j_f}^{(j)}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(R_\kappa, t) \quad (8)$$

where a SPF is constructed from the primitive functions as $\varphi_{j_\kappa}^{(\kappa)}(R_\kappa, t) = \sum_{i_\kappa=1}^{N_\kappa} c_{i_\kappa j_\kappa}^{(\kappa)}(t) \chi_{i_\kappa}^{(\kappa)}(R_\kappa)$. MCTDH becomes equivalent to a numerically exact (within the primitive basis set) solution of the time-dependent Schrödinger equation when $n_1, \dots, n_f = N_1, \dots, N_f$.

Another commonly employed basis set, which will be described in great detail, is composed of multidimensional Gaussian functions with explicit time-dependent parameters given by

$$[a_{i,1}^{(j)}(t), \dots, a_{i,N_p}^{(j)}(t)] \equiv [\bar{\mathbf{R}}_i^{(j)}(t), \bar{\mathbf{P}}_i^{(j)}(t), \boldsymbol{\alpha}_i^{(j)}(t), \bar{\gamma}_i^{(j)}(t)] \quad (9)$$

Inserting eq 6 with this definition in the TDSE, multiplying on the left by $[\chi_j^{(l)}(\mathbf{R}; a_{j,1}^{(l)}(t), \dots, a_{j,N_p}^{(l)}(t)) \Phi_l(\mathbf{r}; \mathbf{R})]^*$, and integrating over both electronic and nuclear coordinates leads to general equations of motion for the expansion coefficients:

$$\dot{\mathbf{C}} = -i\mathbf{S}^{-1}[(\mathbf{H} - i\dot{\mathbf{S}})\mathbf{C}] \quad (10)$$

Equation 10 is simply the time-dependent Schrödinger equation expressed in a time-dependent nonorthogonal basis set, where $(\mathbf{S})_{ji}^H = \langle \chi_j^{(j)} | \chi_i^{(i)} \rangle_{\mathbf{R}}$, $(\mathbf{H})_{ji}^H = \langle \chi_j^{(j)} | \hat{H} | \Phi_i^{(i)} \rangle_{\mathbf{r}, \mathbf{R}}$, and $\dot{\mathbf{S}}$ is an overlap matrix including the time derivatives of the basis functions, which will be defined more precisely in section 4.1. The finite basis represents the only approximation made so far, and eq 10 fully accounts for the coupling between nuclear motion and electronic states.

From the form of eq 10, it becomes immediately clear that the basis functions are mutually *coupled*, in both intra- and interstate fashions. However, several questions about solutions and approximations to this equation arise at this stage: How should we define equations of motion for the time-dependent parameters of the basis, and how do they influence the dynamics? How can we compute or approximate the matrix elements in eq 10? Answering these questions is the goal of the following sections, and we will see that it defines a hierarchy for nonadiabatic quantum dynamics methods.^{4,105–107}

4. FULL MULTIPLE SPAWNING

Full multiple spawning (FMS) constitutes a framework for nonadiabatic dynamics, where nuclear wave functions are represented by an adaptive linear combination of frozen Gaussian functions that follow classical trajectories. In a complete basis, FMS would be exact. Applying a series of

well-controlled approximations leads to the ab initio multiple spawning (AIMS) method which is well-suited to on-the fly excited-state dynamics of molecules. We first discuss the FMS method; AIMS will be treated in section 4.3.

4.1. Equations of Motion

In FMS,^{108–112} the time-dependent nuclear wave function for each electronic state J is represented as a linear combination of multidimensional, frozen Gaussian basis functions with complex time-dependent coefficients:

$$\begin{aligned} \chi_i^{(j)}(\mathbf{R}; a_{i,1}^{(j)}(t), \dots, a_{i,N_p}^{(j)}(t)) \\ \equiv \chi_i^{(j)}(\mathbf{R}; \bar{\mathbf{R}}_i^{(j)}(t), \bar{\mathbf{P}}_i^{(j)}(t), \bar{\gamma}_i^{(j)}(t), \boldsymbol{\alpha}) \end{aligned} \quad (11)$$

In the language of FMS, $\chi_i^{(j)}$ are called trajectory basis functions (TBFs); each one is labeled with a compound index denoting the corresponding electronic state J and, because there can be many TBFs on each electronic state, also by a second index i . As previously described, the frozen Gaussian is centered at position $\bar{\mathbf{R}}_i^{(j)}(t)$ and momenta $\bar{\mathbf{P}}_i^{(j)}(t)$, both of which evolve in time. The time-independent width of the Gaussian is denoted as $\boldsymbol{\alpha}$, and $\bar{\gamma}_i^{(j)}(t)$ is a phase.

Each multidimensional Gaussian basis function $\chi_i^{(j)}(\mathbf{R}; \bar{\mathbf{R}}_i^{(j)}(t), \bar{\mathbf{P}}_i^{(j)}(t), \bar{\gamma}_i^{(j)}(t), \boldsymbol{\alpha})$ is a product of one-dimensional Gaussian basis functions, one for each nuclear degree of freedom ρ :

$$\begin{aligned} \chi_i^{(j)}(\mathbf{R}; \bar{\mathbf{R}}_i^{(j)}(t), \bar{\mathbf{P}}_i^{(j)}(t), \bar{\gamma}_i^{(j)}(t), \boldsymbol{\alpha}) \\ = e^{i\bar{\gamma}_i^{(j)}(t)} \prod_{\rho=1}^{3N} \chi_{i\rho}^{(j)}(R_\rho; \bar{R}_{i\rho}^{(j)}(t), \bar{P}_{i\rho}^{(j)}(t), \alpha_\rho) \\ \chi_{i\rho}^{(j)}(R_\rho; \bar{R}_{i\rho}^{(j)}(t), \bar{P}_{i\rho}^{(j)}(t), \alpha_\rho) \\ = \left(\frac{2\alpha_\rho}{\pi} \right)^{1/4} \exp \left[-\alpha_\rho (R_\rho - \bar{R}_{i\rho}^{(j)}(t))^2 + i\bar{P}_{i\rho}^{(j)}(t) \right. \\ \left. (R_\rho - \bar{R}_{i\rho}^{(j)}(t)) \right] \end{aligned} \quad (12)$$

In its usual form, FMS prescribes that a TBF on electronic state J follows a *classical trajectory*, evolving adiabatically on the potential energy surfaces given by $E_J(\mathbf{R})$, the eigenvalue of the time-independent electronic Schrödinger equation in eq 4. Hence, the time-dependent positions and momenta associated with each Gaussian basis function are propagated by use of Hamilton's equations of motion:

$$\frac{\partial \bar{R}_{i\rho}^{(j)}(t)}{\partial t} = \frac{\bar{P}_{i\rho}^{(j)}(t)}{M_\rho} \quad (14)$$

$$\frac{\partial \bar{P}_{i\rho}^{(j)}(t)}{\partial t} = -\frac{\partial E_J(\mathbf{R})}{\partial R_{i\rho}} \Big|_{R_{i\rho} = \bar{R}_{i\rho}^{(j)}(t)} \quad (15)$$

The time-dependent phase $\bar{\gamma}_i^{(j)}(t)$ is obtained from semiclassical arguments, namely, by integrating the classical Lagrangian:

$$\frac{\partial \bar{\gamma}_i^{(j)}(t)}{\partial t} = \sum_{\rho=1}^{3N} \frac{(\bar{P}_{i\rho}^{(j)}(t))^2}{2M_\rho} - E_J(\bar{\mathbf{R}}_i^{(j)}(t)) \quad (16)$$

The Born–Huang expansion obtained by inserting the FMS representation is

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_J^{\infty} \sum_i^{N_j(t)} C_i^{(J)}(t) \chi_i^{(J)}(\mathbf{R}; \bar{\mathbf{R}}_i^{(J)}(t), \bar{\mathbf{P}}_i^{(J)}(t), \bar{\gamma}_i^{(J)}(t), \boldsymbol{\alpha}) \Phi_j(\mathbf{r}; \mathbf{R}) \quad (17)$$

Upon comparison to eq 6, the major differences are the specific use of a Gaussian basis set and the time dependence of the number of terms used to describe the nuclear wave function in state $J, N_j(t)$. The central idea of FMS is to use an *adaptive* basis set to better describe the nonadiabatic dynamics and to prevent limitations arising from a fixed number of basis functions. The number of TBFs will indeed increase during the dynamics due to *spawning processes* (see section 4.2 for a complete description). Interesting alterations of eq 17 have recently been proposed, where the global adiabatic electronic wave functions are replaced by electronic wave functions evaluated at the center of the corresponding Gaussian function¹¹³ or by time-dependent quasi-diabatic electronic wave functions.¹¹⁴ As we will see, in AIMS, a similar interpretation arises naturally.

Inserting eq 17 into the time-dependent Schrödinger equation—multiplying on the left by $[\chi_k^{(I)}(\mathbf{R}; \bar{\mathbf{R}}_k^{(I)}(t), \bar{\mathbf{P}}_k^{(I)}(t), \bar{\gamma}_k^{(I)}(t), \boldsymbol{\alpha}) \Phi_I(\mathbf{r}; \mathbf{R})]^*$ and integrating over both nuclear and electronic coordinates—leads to equations of motion for the complex coefficients (or amplitudes) $\{C_i^{(I)}(t)\}_{i=1}^{N_j(t)}$. This projection defines a spectral method (defined entirely in the space of basis functions), but pseudospectral Gaussian methods (defined in a dual space of basis functions and physical space grid points) have also been proposed.¹¹⁵ These equations of motion are similar to the general one given in eq 10. Focusing on the amplitudes for TBFs associated with the I th electronic state, one obtains

$$\frac{d\mathbf{C}^I}{dt} = -i(\mathbf{S}_{II}^{-1}) \left[(\mathbf{H}_{II} - i\dot{\mathbf{S}}_{II}) \mathbf{C}^I + \sum_{J \neq I} \mathbf{H}_{IJ} \mathbf{C}^J \right] \quad (18)$$

where boldface symbols indicate matrices or vectors in the space of Gaussian basis functions.¹¹⁶ The nuclear overlap matrices in eq 18 are a direct consequence of the time-dependent and non-orthonormal Gaussian basis, and the elements are defined as

$$(\mathbf{S}_{II})_{ki} = \langle \chi_k^{(I)} | \chi_i^{(I)} \rangle_{\mathbf{R}} \quad (19)$$

$$(\dot{\mathbf{S}}_{II})_{ki} = \left\langle \chi_k^{(I)} \left| \frac{\partial}{\partial t} \chi_i^{(I)} \right. \right\rangle_{\mathbf{R}} \quad (20)$$

The Hamiltonian matrix \mathbf{H} contains both inter- and intrastate couplings between TBFs. As an example, the Hamiltonian matrix element between TBF k evolving on state J and TBF i evolving on state I is given as

$$\begin{aligned} H_{ki}^{JI} &= \left\langle \chi_k^{(J)} \Phi_j \left| \hat{H} \right| \chi_i^{(I)} \Phi_I \right\rangle_{\mathbf{R}, \mathbf{r}} \\ &= \left\langle \chi_k^{(J)} \left| \hat{T}_{\text{nuc}} \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \delta_{JI} + \left\langle \chi_k^{(J)} \left| E_I \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \delta_{JI} - 2D_{ki}^{JI} - G_{ki}^{JI} \end{aligned} \quad (21)$$

where we used the molecular Hamiltonian given in eq 2 and the definition of adiabatic electronic states $E_I(\mathbf{R}) = \langle \Phi_I | \hat{H}_{\text{el}}(\mathbf{R}) | \Phi_I \rangle_{\mathbf{r}} \delta_{JI}$. The last two terms of eq 21 are linked to the nuclear kinetic energy operator:

$$D_{ki}^{JI} = \left\langle \chi_k^{(J)} \left| \sum_{\rho=1}^{3N} \langle \Phi_I | \frac{\partial}{\partial R_{\rho}} | \Phi_I \rangle_{\mathbf{r}} \frac{1}{2M_{\rho}} \frac{\partial}{\partial R_{\rho}} \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \quad (22)$$

$$G_{ki}^{JI} = \left\langle \chi_k^{(J)} \left| \sum_{\rho=1}^{3N} \frac{1}{2M_{\rho}} \langle \Phi_I | \frac{\partial^2}{\partial R_{\rho}^2} | \Phi_I \rangle_{\mathbf{r}} \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \quad (23)$$

where we recognize the first- and second-order nonadiabatic coupling terms described in section 2.2, sandwiched between TBFs.

We note that the time-dependent phase $\bar{\gamma}_i^{(J)}(t)$ could easily be absorbed into the FMS complex amplitudes. However, the definition of this phase and its semiclassical evolution leads to an interaction picture for the propagation of the complex coefficients. By using the equation of motion for the phase given in eq 16, oscillations in the complex amplitudes are reduced (increasing the time step that can be used in the integration of the equations of motion) and changes in the complex amplitudes are largely confined to times when TBFs are coupled (simplifying the interpretation of simulation results).

Couplings between TBFs described by the Hamiltonian matrix can be summarized as follows. Diagonal elements of \mathbf{H} correspond to the energy of each TBF, while off-diagonal elements give rise to the coupling between TBFs (Figure 2).

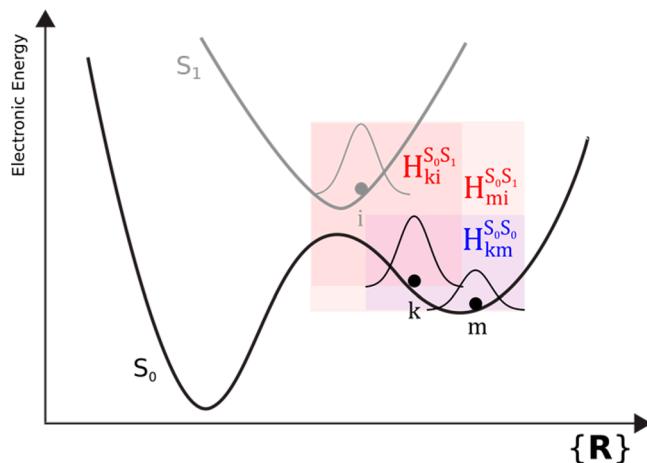


Figure 2. Schematic representation of matrix elements coupling between TBFs in FMS. The blue colored area indicates TBFs coupled by intrastate coupling, while the red area indicates TBFs coupled by interstate coupling.

For instance, two TBFs, k and m , evolving on the same electronic state (S_0) will be coupled through the nuclear kinetic energy operator and the electronic energy, as well as through diagonal Born–Oppenheimer terms (blue area in Figure 2):

$$\begin{aligned} H_{km}^{S_0S_0} &= \left\langle \chi_k^{(S_0)} \left| \hat{T}_{\text{nuc}} \right| \chi_m^{(S_0)} \right\rangle_{\mathbf{R}} + \left\langle \chi_k^{(S_0)} \left| E_{S_0} \right| \chi_m^{(S_0)} \right\rangle_{\mathbf{R}} \\ &\quad - \left\langle \chi_k^{(S_0)} \left| \sum_{\rho=1}^{3N} \frac{1}{2M_{\rho}} \langle \Phi_{S_0} | \frac{\partial^2}{\partial R_{\rho}^2} | \Phi_{S_0} \rangle_{\mathbf{r}} \right| \chi_m^{(S_0)} \right\rangle_{\mathbf{R}} \end{aligned} \quad (24)$$

The coupling between TBFs k and i evolving on different electronic states (S_0 and S_1) is mediated by nonadiabatic coupling terms (red area in Figure 2):

$$H_{ki}^{S_0 S_1} = - \left\langle \chi_k^{(S_0)} \left| \sum_{\rho=1}^{3N} \left\langle \Phi_{S_0} \left| \frac{\partial}{\partial R_\rho} \right| \Phi_{S_1} \right\rangle_{\mathbf{r}} \frac{1}{M_\rho} \frac{\partial}{\partial R_\rho} \right| \chi_i^{(S_1)} \right\rangle_{\mathbf{R}} - \left\langle \chi_k^{(S_0)} \left| \sum_{\rho=1}^{3N} \frac{1}{2M_\rho} \left\langle \Phi_{S_0} \left| \frac{\partial^2}{\partial R_\rho^2} \right| \Phi_{S_1} \right\rangle_{\mathbf{r}} \right| \chi_i^{(S_1)} \right\rangle_{\mathbf{R}} \quad (25)$$

The second-derivative coupling terms given in eq 23 are often neglected.^{46,117} It is important to note, however, that the molecular Hamiltonian is no longer Hermitian without these terms,⁵⁶ and hermiticity has to be enforced by construction.¹¹⁸ Furthermore, the potential influence of second-order nonadiabatic couplings and diagonal Born–Oppenheimer corrections on nonadiabatic dynamics has recently been highlighted.^{61,114,119–122}

The physical interpretation of the first-order term, D_{kb}^H , is that changes in the nuclear coordinates induce coupling between electronic states (because the electronic states change character as the nuclei move). In the diabatic representation, these terms vanish and the coupling is instead described by the off-diagonal elements of the electronic Hamiltonian. However, both descriptions are interchangeable. An advantage of the adiabatic representation is its uniqueness, being determined by the solution of the electronic Schrödinger equation alone. In contrast, diabatic representations are normally not unique and usually require global information about the potential energy surfaces that can be difficult to reconcile with on-the-fly treatments. In the context of surface hopping, a locally diabatic compromise between the two representations has been proposed.^{123,124} This locally diabatic representation might also prove useful in other nonadiabatic dynamics methods, but this has not yet been explored.

If the basis set is large enough and all matrix elements are computed exactly, FMS provides an exact solution to the molecular time-dependent Schrödinger equation. The exactness of the dynamics in the limit of a complete basis set does not depend on the equations of motion used for the basis functions (and even a fixed set of basis functions would lead to the exact answer). However, the choice of equations of motion for the basis functions is expected to influence convergence substantially.

4.2. Adapting the Size of the Basis Set by Use of the Spawning Algorithm

In FMS, the initial wave function at time $t = 0$ is prepared as a linear combination of N_{ini} coupled TBFs, called initial parent TBFs (see Figure 3). To better understand how FMS adapts the basis set, it is useful to rewrite the FMS Born–Huang representation of eq 17 to make the initial number of parent TBFs explicit:¹²⁵

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{\beta}^{N_{\text{ini}}} \tilde{\Psi}_{\beta}(\mathbf{r}, \mathbf{R}, t) = \sum_{\beta}^{N_{\text{ini}}} \sum_{J}^{\infty} \sum_{i}^{N_J^{\beta}(t)} C_{i\beta}^{(J)}(t) \chi_{i\beta}^{(J)}(\mathbf{r}; \bar{\mathbf{R}}_{i\beta}^{(J)}(t), \bar{\mathbf{P}}_{i\beta}^{(J)}(t), \bar{\gamma}_{i\beta}^{(J)}(t), \boldsymbol{\alpha}) \Phi_j^{\beta}(\mathbf{r}; \mathbf{R}) \quad (26)$$

This equation highlights the fact that all initial parent TBFs are coupled to each other from the very beginning of the FMS dynamics, and they are also all coupled to any additional TBFs created during the simulation (see Figure 3a). For example, if a simulation starts at time $t = 0$ in the S_1 electronic state with 10 parent TBFs, eq 26 will read

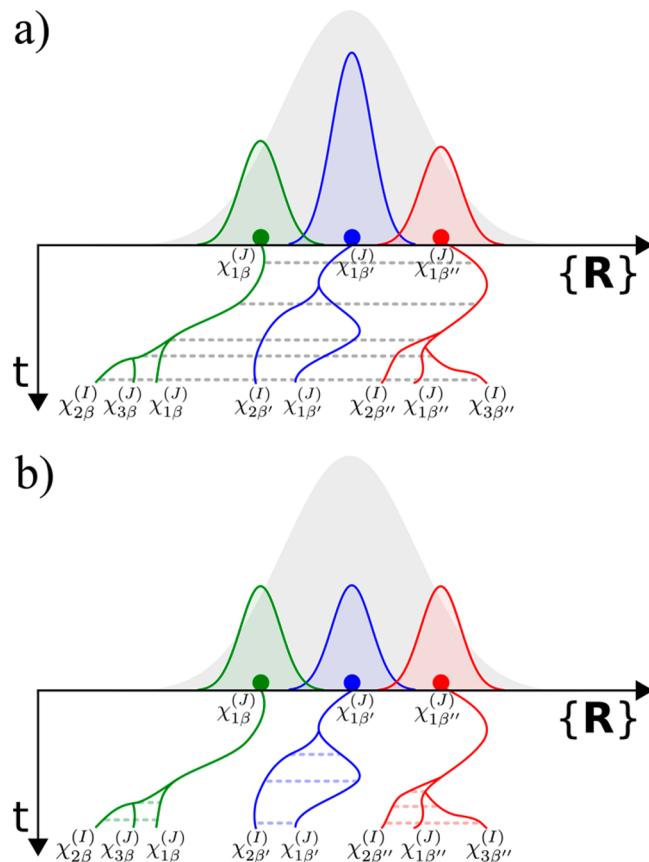


Figure 3. Coupling pattern between parent TBFs and their respective children, (a) without and (b) within the independent first-generation approximation. The gray dashed horizontal lines represent the couplings between different TBFs that are included in the calculation.

$$\Psi(\mathbf{r}, \mathbf{R}, t_0) = \sum_{\beta=1}^{10} C_{1\beta}^{(S_1)}(t_0) \chi_{1\beta}^{(S_1)}(\mathbf{r}; \bar{\mathbf{R}}_{1\beta}^{(S_1)}(t_0), \bar{\mathbf{P}}_{1\beta}^{(S_1)}(t_0), \bar{\gamma}_{1\beta}^{(S_1)}(t_0), \boldsymbol{\alpha}) \Phi_{S_1}^{\beta}(\mathbf{r}; \mathbf{R}) \quad (27)$$

While this notation may appear cumbersome, it helps distinguish between the original N_{ini} parent TBF and their respective child TBFs, labeled as $i = \{1, \dots, N_J^{\beta}(t)\}$. The value of each complex amplitude is obtained by projection on the desired (exact) initial wave function (or the best available approximation) at time $t = 0$:

$$C_{1\beta}^{(J)}(t=0) = \sum_{\beta}^{N_{\text{ini}}} (\mathbf{S}_J^{-1})_{1\beta' 1\beta} \left\langle \chi_{1\beta}^{(J)}(t=0) \middle| \Omega_J^{\text{exact}}(t=0) \right\rangle_{\mathbf{R}} \quad (28)$$

The natural question at this stage is *when* and *how* should the basis set be adaptively expanded? From the initial conditions provided by eq 27, it is clear that the description of nonadiabatic events requires the creation of TBFs in different electronic states. Hence, the spawning algorithm should generate new TBFs whenever an existing TBF approaches a nonadiabatic coupling region.

The spawning algorithm, in its most common implementation,¹²⁶ works as follows (Figure 4): at every time step, each TBF of a FMS run monitors the strength of the nonadiabatic coupling between its assigned electronic state (the running state) and any other electronic state considered in the dynamics

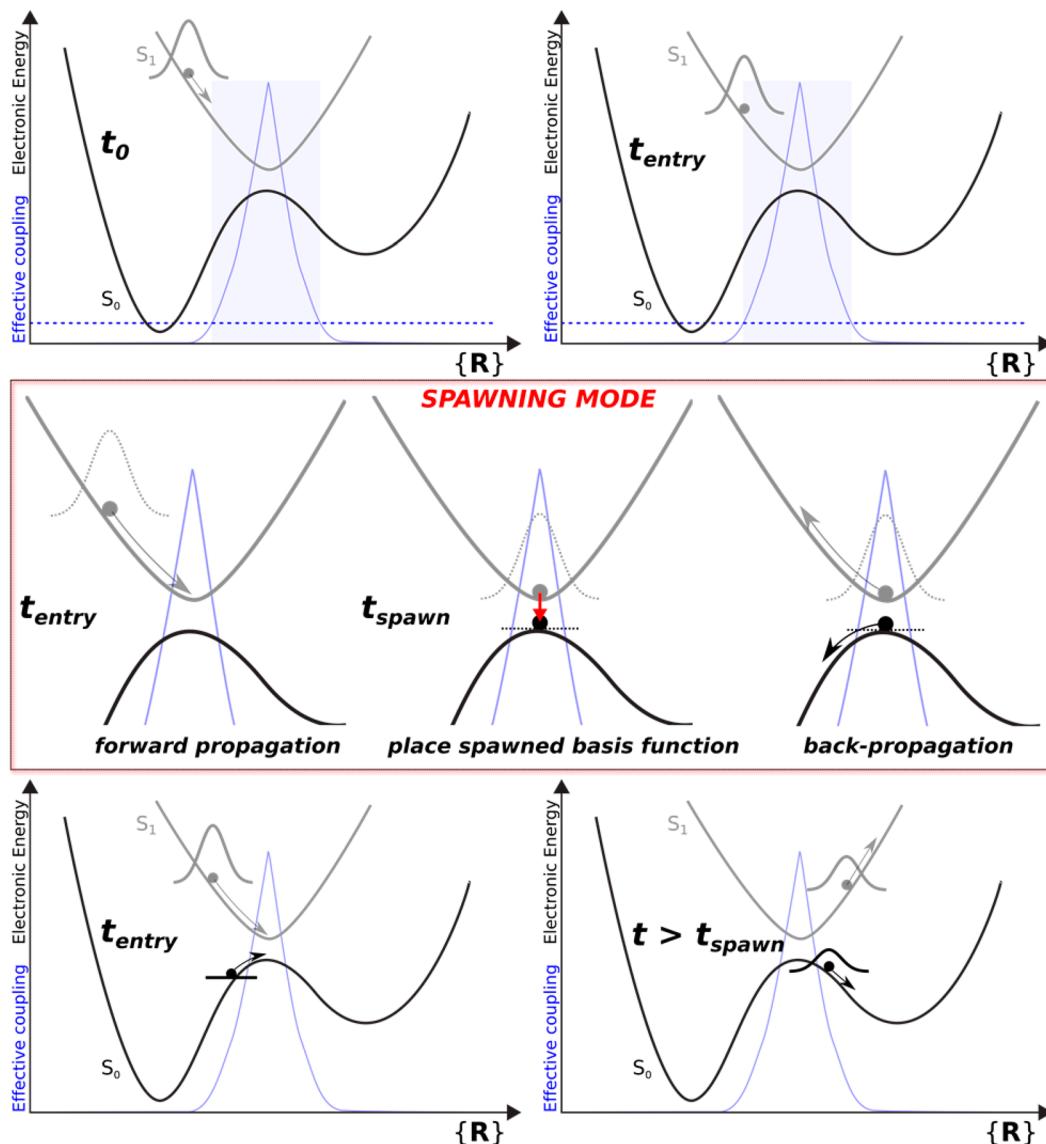


Figure 4. Schematic representation of the simplest spawning algorithm in FMS.

(an energy threshold can be set to prevent the calculations of nonadiabatic coupling vectors for states that are energetically distant from the running state). In the adiabatic representation, the most common metric for the coupling strength between a TBF on state I at position $\bar{\mathbf{R}}_i$ and the electronic state J is simply

$$\Lambda_{IJ}^{\text{eff}}(\bar{\mathbf{R}}_i) = |\mathbf{d}_{IJ}(\bar{\mathbf{R}}_i)| \quad (29)$$

that is, the norm of the nonadiabatic coupling vector. Another commonly employed criterion accounts for the projection of the nonadiabatic coupling vectors on the TBF classical velocities:

$$\Lambda_{IJ}^{\text{eff}}(\bar{\mathbf{R}}_i) = |\mathbf{d}_{IJ}(\bar{\mathbf{R}}_i) \cdot \dot{\bar{\mathbf{R}}}_i| \quad (30)$$

The latter choice is a closer approximant of the off-diagonal matrix element that governs the propensity for nonadiabatic transitions, à la Landau and Zener,^{127–129} and thus one might expect it to be preferred. However, it is also more oscillatory than the choice in eq 29, which can be numerically cumbersome. Both choices have been used successfully, and we do not distinguish between them in what follows. If a TBF reaches a region where Λ^{eff} exceeds a predefined threshold

(horizontal dashed blue line in Figure 4), the entire FMS propagation is frozen and the TBF enters a spawning mode (middle panel in Figure 4); this time in the dynamics is called the entry time (t_{entry}). When the dynamics is in spawning mode, the propagation of the complex amplitudes is suspended (dotted lines for the TBF in Figure 4), and only the spawning parent TBF continues its classical propagation, which is being used at this stage as a probe for nonadiabaticity. The TBF monitors the strength of Λ^{eff} as it propagates from t_{entry} and stops when Λ^{eff} reaches a maximum.¹³⁰ At this time, called the spawning time t_{spawn} , a new TBF is spawned on the coupled state if and only if (1) energy conservation can be ensured—the kinetic energy should be sufficient to balance a gain of potential energy^{112,131–133}—and (2) the newly created TBF (child TBF) has sufficient overlap with the parent TBF.¹³⁴ If the spawn is successful, the child TBF inherits all the properties of its parent TBF, except for a rescaled momentum (p -jump) and a complex coefficient set to 0. At this point, the child TBF needs to be back-propagated in time from t_{spawn} to t_{entry} , as it evolves on a different electronic state. Once the back-propagation is complete, the dynamics leaves the spawning

mode and the integration of the complex amplitudes can resume. The equations of motion now include the additional complex amplitude for the child TBF, having a value of 0 at t_{entry} and the corresponding coupling and overlap terms.

We note that frustrated spawns can take place when a child TBF should be created in a classically forbidden region with respect to the parent TBF; that is, a region where the classical kinetic energy of the parent TBF is not enough to compensate for the change of potential energy associated with the creation of a child TBF on an upper electronic state. Normally, these are handled by steepest-descent minimization until the potential energy decreases sufficiently to allow TBF placement.^{126,131} In this sense, spawning can involve both position and momentum jumps of the child TBF relative to its parent TBF. In any case, it is important to realize that frustrated spawns do *not* affect detailed balance in FMS—as frustrated hops do in TSH^{87,135–137}—because evolution of the complex amplitudes in FMS follows the time-dependent Schrödinger equation.¹³¹

4.3. Ab Initio Multiple Spawning

FMS is well suited to on-the-fly evaluation of the potential energy surfaces and nonadiabatic couplings since it is based on trajectories. However, there are two central approximations that are employed to transform FMS into ab initio multiple spawning (AIMS).

The critical bottleneck that hampers the use of FMS for molecules without pretabulated potential energy surfaces is evaluating the integrals that form the Hamiltonian matrix in eq 21. Calculating the terms containing the electronic energy and the nonadiabatic coupling vectors implies integration over the entire nuclear configuration space. Hence, numerically exact matrix elements can be obtained only if the potential energy surfaces and nonadiabatic couplings are known over all the space covered by the nuclear coordinates of interest.

However, the TBFs are spatially localized, and this localization can be exploited to approximate the required integrals. The product of any two TBFs will itself be another Gaussian basis function, located at a centroid position between the two TBFs. This is shown schematically in Figure 5. One can

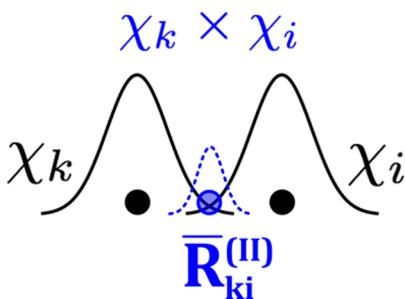


Figure 5. Definition of the centroid between two TBFs, used to calculate integrals in the saddle-point approximation.

then Taylor expand the electronic energy and/or nonadiabatic coupling about this centroid and evaluate the resulting integral analytically.^{112,126,138,139} As an example, we consider the expansion of the intrastate coupling term—containing the electronic energy—between two TBFs k and i with centroid position $\bar{\mathbf{R}}_{ki}^{(II)} = (\bar{\mathbf{R}}_k^{(I)} + \bar{\mathbf{R}}_i^{(I)})/2$; that is, at the maximum of the product $|(\chi_k^{(I)})^* \chi_i^{(I)}|$:

$$\begin{aligned} E_I(\mathbf{R}) = E_I(\bar{\mathbf{R}}_{ki}^{(II)}) &+ \sum_{\rho}^{3N} (R_{\rho} - \bar{R}_{\rho,ki}^{(II)}) \frac{\partial E_I(\mathbf{R})}{\partial R_{\rho}} \Bigg|_{R_{\rho}=\bar{R}_{\rho,ki}^{(II)}} \\ &+ \frac{1}{2} \sum_{\rho,\rho'}^{3N} (R_{\rho} - \bar{R}_{\rho,ki}^{(II)}) \frac{\partial^2 E_I(\mathbf{R})}{\partial R_{\rho} \partial R_{\rho'}} \Bigg|_{R_{\rho}=\bar{R}_{\rho,ki}^{(II)}, R_{\rho'}=\bar{R}_{\rho',ki}^{(II)}} (R_{\rho'} - \bar{R}_{\rho',ki}^{(II)}) + \dots \end{aligned} \quad (31)$$

Upon inserting this expansion into the corresponding Hamiltonian integral, we obtain

$$\begin{aligned} \langle \chi_k^{(I)} | E_I | \chi_i^{(I)} \rangle_{\mathbf{R}} &= E_I(\bar{\mathbf{R}}_{ki}^{(II)}) \langle \chi_k^{(I)} | \chi_i^{(I)} \rangle_{\mathbf{R}} \\ &+ \sum_{\rho}^{3N} \frac{\partial E_I(\mathbf{R})}{\partial R_{\rho}} \Bigg|_{R_{\rho}=\bar{R}_{\rho,ki}^{(II)}} \langle \chi_k^{(I)} | (R_{\rho} - \bar{R}_{\rho,ki}^{(II)}) | \chi_i^{(I)} \rangle_{\mathbf{R}} \\ &+ \frac{1}{2} \sum_{\rho,\rho'}^{3N} \frac{\partial^2 E_I(\mathbf{R})}{\partial R_{\rho} \partial R_{\rho'}} \Bigg|_{R_{\rho}=\bar{R}_{\rho,ki}^{(II)}, R_{\rho'}=\bar{R}_{\rho',ki}^{(II)}} \\ &\times \langle \chi_k^{(I)} | (R_{\rho} - \bar{R}_{\rho,ki}^{(II)}) (R_{\rho'} - \bar{R}_{\rho',ki}^{(II)}) | \chi_i^{(I)} \rangle_{\mathbf{R}} + \dots \end{aligned} \quad (32)$$

Hence, the Hamiltonian matrix element has been expressed as a product of analytically soluble integrals (moments of Gaussian functions) multiplied by electronic structure contributions evaluated at the centroid.¹⁴⁰ This type of expansion has been commonly used in combination with Gaussian basis sets. In AIMS, the Taylor series is often truncated after zeroth order, all second-order nonadiabatic coupling terms are neglected, and eq 21 is therefore approximated as

$$\begin{aligned} H_{ki}^{II} \approx \langle \chi_k^{(I)} | \hat{T}_{\text{nuc}} | \chi_i^{(I)} \rangle_{\mathbf{R}} \delta_{II} &+ E_I(\bar{\mathbf{R}}_{ki}^{(II)}) \langle \chi_k^{(I)} | \chi_i^{(I)} \rangle_{\mathbf{R}} \delta_{II} \\ &- \sum_{\rho=1}^{3N} \frac{1}{M_{\rho}} \langle \chi_k^{(I)} | \frac{\partial}{\partial R_{\rho}} | \chi_i^{(I)} \rangle_{\mathbf{R}} \langle \Phi_I | \frac{\partial}{\partial R_{\rho}} | \Phi_I \rangle_{\mathbf{r}} \Bigg|_{R_{\rho}=(\bar{\mathbf{R}}_{ki}^{(II)})_{\rho}} \end{aligned} \quad (33)$$

This appears to require $N_{\text{TBF}} \times (N_{\text{TBF}} + 1)/2$ electronic structure calculations; that is, at the position of each TBF and the centroids for each pair of TBFs.¹²⁶ However, this is a gross overestimate because the overlap (and higher moment) integrals decay quickly with distance between TBFs. Thus, one needs only to calculate electronic energies and/or nonadiabatic couplings for pairs of TBFs that are close to each other, and the effective computational effort is normally nearly linear in N_{TBF} . This zeroth-order saddle-point approximation facilitates an on-the-fly solution of the FMS equations of motion, where any electronic structure information is computed as needed at each integration time step. Higher-order saddle-point approximations are also possible, by calculating first and/or second derivatives of the electronic energies and/or nonadiabatic coupling matrix elements.¹⁴¹ However, this has rarely been pursued because of the considerable expense associated with derivatives of the nonadiabatic coupling matrix elements or second derivatives of the electronic energy. A promising alternative that has been recently suggested uses Gaussian process regression to calculate these matrix elements.¹³⁹

If one is interested in the excited-state dynamics of a rather high-dimensional molecular system, another simplification of the FMS equations of motion is useful. At time $t = 0$, all N_{ini} initial parent TBFs are coupled together and reproduce the

molecular wave function; see eq 26 and Figure 3a. Instead of considering that all parent TBFs are coupled from time $t = 0$, we can invoke the independent first generation (IFG) approximation. The initial nuclear wavepacket will usually spread rapidly in phase space at the beginning of the dynamics, implying that the initially coupled TBFs will soon become uncoupled and evolve independently. To a good approximation, we can therefore consider that they are, from time $t = 0$, uncoupled (Figure 3b). Hence, each parent TBF is sampled—positions and momenta from a Wigner distribution, amplitude set to 1 for the initial state—and run independently (compare upper and lower panels in Figure 3). In other words, we consider that the evolution of complex amplitudes is not coupled if they belong to a different parent β ($S_{k\beta'|\beta}^{IJ} \approx S_{k\beta}^{IJ} \delta_{\beta'\beta}$ and $H_{k\beta'|\beta}^{IJ} \approx H_{k\beta}^{IJ} \delta_{\beta'\beta}$, $\forall I, J$).^{112,125}

In summary, when the saddle-point approximation of zeroth-order is used to approximate the Hamiltonian matrix elements, and the independent first generation uncouples the initial TBFs, FMS becomes fully compatible with on-the-fly non-adiabatic dynamics and is usually called ab initio multiple spawning (Figure 6).^{111,112,132,142}

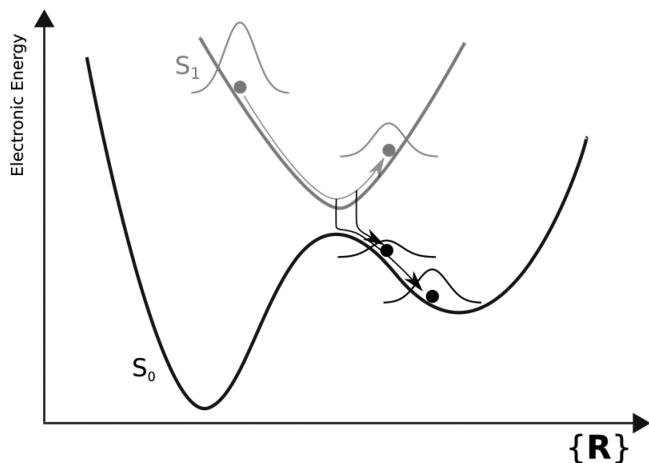


Figure 6. Schematic representation of an AIMS run, where an initial TBF on S_1 spawns two new TBFs on S_0 .

4.3.1. Links between Trajectory Surface Hopping and Ab Initio Multiple Spawning.

In section 4.3, we mentioned the IFG approximation, which implies that TBFs originating

from different initial conditions are considered as independent during the nuclear dynamics, while those originating from the same initial condition remain fully coupled. Trajectory surface hopping^{9,12,13} (TSH) can be seen as a method pushing the IFG a step further by invoking the so-called independent trajectory approximation (ITA). TSH uses a swarm of totally *independent* classical trajectories, each carrying a set of amplitudes, to represent the dynamics of a nuclear wavepacket. The spawning of additional trajectories is replaced by surface hops (Figure 1), meaning that the electronic state driving the classical nuclear dynamics of a given trajectory can change if a nonadiabatic region is encountered. Such hops are mediated by a stochastic algorithm, based on hopping probabilities expressed in terms of TSH complex amplitudes for each independent trajectory $[\alpha]$. Therefore, the complex amplitudes in TSH evolve coherently along a single trajectory, whose driving electronic state can change along the dynamics.

Despite the fact that it requires the same electronic structure properties as AIMS (electronic energies, forces on the nuclei, nonadiabatic coupling vectors), the TSH algorithm is simplified by the ITA. An important difference is that TSH needs only electronic calculations at the nuclear configuration of the classical trajectory at time t , $\mathbf{R}^{[\alpha]}(t)$. In AIMS, the couplings between the different TBFs arising from a given initial condition necessitate additional electronic energies and non-adiabatic couplings calculations at the position of centroids, as described before. To better illustrate the differences between the equations of motion for the amplitudes of the two methods, let us consider the illustrative example of a molecular system with two electronic states, I and J , at a given time t . The TSH equations of motion for the complex amplitudes along a trajectory $[\alpha]$ are given by eq 34:

$$\begin{pmatrix} \dot{c}_{[\alpha]}^I(t) \\ \dot{c}_{[\alpha]}^J(t) \end{pmatrix} = -i \begin{pmatrix} H_{[\alpha]}^{II} & H_{[\alpha]}^{IJ} \\ H_{[\alpha]}^{JI} & H_{[\alpha]}^{JJ} \end{pmatrix} \begin{pmatrix} c_{[\alpha]}^I(t) \\ c_{[\alpha]}^J(t) \end{pmatrix} \quad (34)$$

where $H_{[\alpha]}^{II} = E_I(\mathbf{R}^{[\alpha]}(t))$ and $H_{[\alpha]}^{IJ} = -i \mathbf{d}_I(\mathbf{R}^{[\alpha]}(t)) \cdot \dot{\mathbf{R}}^{[\alpha]}(t)$.

In AIMS, within the IFG approximation and considering a case where three TBFs evolve on state I and two on state J , the equations have the form given by eq 35. (The system of coupled AIMS equations grows each time a new TBF is spawned.) These two equations highlight the different treatment of the amplitudes in the single-trajectory picture of TSH and in the correlated-TBFs propagation of AIMS. By

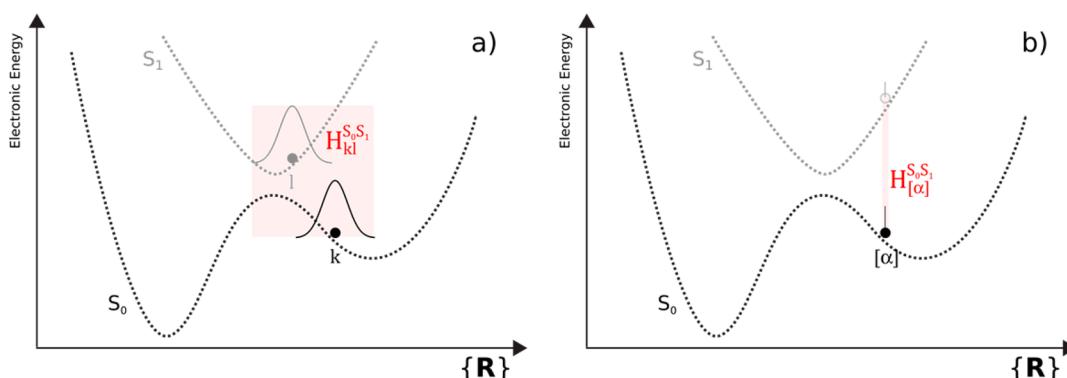


Figure 7. Snapshot of AIMS and TSH dynamics at a given time t . (a) Inter- and intrastate couplings in FMS between two TBFs (l, k) evolving on different electronic states. (b) Coherent propagation of TSH amplitudes (vertical thin line) along the trajectory $[\alpha]$ running on state S_0 (●), implying that the amplitude on state S_1 is constrained to evolve on the support of a trajectory driven by a different electronic state (○).

virtue of the ITA, no intra- or interstate interactions between trajectories are accounted for in TSH. As a direct consequence, the interstate couplings are strictly evaluated at the molecular configuration of trajectory $[\alpha]$ at time t , as given by the term $H_{[\alpha]}^J$, neglecting any form of decoherence of the nuclear wavepackets (Figure 7b). As mentioned before, decoherence is the Achilles' heel for surface hopping¹⁴³ if no ad hoc corrections are added to the amplitudes propagator.

$$\begin{pmatrix} S_{11}^{II} & S_{12}^{II} & S_{13}^{II} & 0 & 0 \\ S_{21}^{II} & S_{22}^{II} & S_{23}^{II} & 0 & 0 \\ S_{31}^{II} & S_{32}^{II} & S_{33}^{II} & 0 & 0 \\ 0 & 0 & 0 & S_{11}^{JJ} & S_{12}^{JJ} \\ 0 & 0 & 0 & S_{21}^{JJ} & S_{22}^{JJ} \end{pmatrix} \begin{pmatrix} \dot{C}_1^{(I)}(t) \\ \dot{C}_2^{(I)}(t) \\ \dot{C}_3^{(I)}(t) \\ \dot{C}_1^{(J)}(t) \\ \dot{C}_2^{(J)}(t) \end{pmatrix} = -i \left\{ \begin{pmatrix} H_{11}^{II} & H_{12}^{II} & H_{13}^{II} & H_{11}^{IJ} & H_{12}^{IJ} \\ H_{21}^{II} & H_{22}^{II} & H_{23}^{II} & H_{21}^{IJ} & H_{22}^{IJ} \\ H_{31}^{II} & H_{32}^{II} & H_{33}^{II} & H_{31}^{IJ} & H_{32}^{IJ} \\ H_{11}^{JJ} & H_{12}^{JJ} & H_{13}^{JJ} & H_{11}^{J2} & H_{12}^{J2} \\ H_{21}^{JJ} & H_{22}^{JJ} & H_{23}^{JJ} & H_{21}^{J2} & H_{22}^{J2} \end{pmatrix} - i \begin{pmatrix} \dot{S}_{11}^{II} & \dot{S}_{12}^{II} & \dot{S}_{13}^{II} & 0 & 0 \\ \dot{S}_{21}^{II} & \dot{S}_{22}^{II} & \dot{S}_{23}^{II} & 0 & 0 \\ \dot{S}_{31}^{II} & \dot{S}_{32}^{II} & \dot{S}_{33}^{II} & 0 & 0 \\ 0 & 0 & 0 & \dot{S}_{11}^{JJ} & \dot{S}_{12}^{JJ} \\ 0 & 0 & 0 & \dot{S}_{21}^{JJ} & \dot{S}_{22}^{JJ} \end{pmatrix} \right\} \begin{pmatrix} C_1^{(I)}(t) \\ C_2^{(I)}(t) \\ C_3^{(I)}(t) \\ C_1^{(J)}(t) \\ C_2^{(J)}(t) \end{pmatrix} \quad (35)$$

5. OTHER FLAVORS OF QUANTUM DYNAMICS WITH GAUSSIAN FUNCTIONS

FMS and AIMS portray the quantum dynamics of nuclear wavepackets by using an adaptive number of coupled Gaussian functions, whose centers and momenta are classically propagated. This results in a separation between the formal propagation of the grid elements (classically evolved Gaussian TBFs) and their associated coefficients (complex amplitudes evolved through the Schrödinger equation). The complex coefficients, as well as the time-dependent phases, do not affect the classical propagation of the TBFs, while the positions and momenta of the TBFs do determine the electronic structure quantities sampled for the integration of the Schrödinger equation.

In this section, we will discuss alternative techniques that differ from AIMS in the way they treat the dynamics of the basis functions and the entanglement between the basis functions and the complex coefficients. This section will mostly focus on ab initio techniques; that is, those that are compatible with on-the-fly dynamics.

5.1. Multiconfigurational Ehrenfest Method

The multiconfigurational Ehrenfest^{43,117,146} (MCE) technique proposes to represent the total molecular wave function as a combination of Ehrenfest wave functions. As discussed in section 2.1, Ehrenfest dynamics emerges from a classical limit of the TDSCF equations, which represents the total molecular wave function as the simple product of a time-dependent electronic and nuclear wave function. As a result, the MCE molecular wave function reads

$$\begin{aligned} \Psi(\mathbf{r}, \mathbf{R}, t) &= \sum_{\beta}^{N_{\text{ini}}} C_{\beta}(t) \psi_{\beta}^{\text{Ehr}}(\mathbf{r}, \mathbf{R}, t) \\ &= \sum_{\beta}^{N_{\text{ini}}} C_{\beta}(t) \chi_{\beta}\left(\mathbf{R}; \bar{\mathbf{R}}_{\beta}(t), \bar{\mathbf{P}}_{\beta}(t), \bar{\gamma}_{\beta}(t), \boldsymbol{\alpha}\right) \Phi_{\beta}^{\text{el}}(\mathbf{r}; \mathbf{R}, t) \end{aligned} \quad (36)$$

That is, the total molecular wave function is given by a combination of Ehrenfest-like molecular wave functions (note that the Gaussian functions do not carry an electronic state label because each one is associated with a distinct coherent

state).^{92,96,99,144,145} In AIMS, even if the IFG is applied, the TBFs resulting from a given initial conditions remain potentially coupled via the intra- or interstate terms, H_{kl}^{II} or H_{kl}^{JJ} (Figure 7a). The TBFs can therefore visit different regions of the molecular configuration space, resulting in an improved description of the separation of nuclear wavepackets in different electronic states.

superposition of electronic states). Equation 36 corresponds to the MCE molecular wave function presented in ref 44, which differs slightly from the one given in the original MCE paper⁴³ and leads to coupling between the trajectories. For the simple case of a two-electronic-state problem, the time-dependent electronic wave function becomes $\Phi_{\beta}^{\text{el}}(\mathbf{r}; \mathbf{R}, t) = c_{\beta}^{(1)}(t)\Phi_{\beta}^{(1)}(\mathbf{r}; \mathbf{R}) + c_{\beta}^{(2)}(t)\Phi_{\beta}^{(2)}(\mathbf{r}; \mathbf{R})$. Hence, a given Gaussian function β in the Ehrenfest wave function may (and often will) correspond to more than one electronic state. This is a major difference from FMS or AIMS, in which a TBF is assigned to a single electronic state. While a single element of the summation in eq 36 would suffer from the mean-field approximation inherent to Ehrenfest dynamics, the multiconfiguration representation allows one to target, in principle, an exact solution of the time-dependent Schrödinger equation.

Equation 36 will give rise to equations of motion for the Gaussian function parameters, the N_{ini} Ehrenfest configuration amplitudes $\{C_{\beta}(t)\}_{\beta=1}^{N_{\text{ini}}}$, and the electronic coefficients $\{c_{\beta}^{(j)}(t)\}_{j=1}^{N_e}$ (one set for each Ehrenfest configuration, where N_e electronic states are considered). One central difference between MCE and FMS is the way the Gaussian functions evolve in time. In MCE, the dynamics follows Ehrenfest trajectories. In regions with strong nonadiabaticity, an Ehrenfest trajectory follows an average potential energy surface, given by a linear combination of the adiabatic potential energy surfaces weighted by the electronic coefficients (Figure 8). In comparison, the classical propagation in FMS/AIMS is purely adiabatic (Figure 6). It is unclear which equations of motion are more accurate, and this will likely depend on both the particular system and the time scale of the nonadiabatic interaction. Another technical yet practically important difference between the two techniques is that MCE does not use an adaptive basis set; that is, all the basis functions required at time t need to be present at time $t = 0$. As the basis functions in MCE evolve according to Ehrenfest dynamics, their spread is expected to be slower, and basis functions will remain coupled longer than with classical trajectories (as in FMS and AIMS). On the other hand, the mean-field potential generated in Ehrenfest dynamics might artificially trap trajectories and prevent a uniform sampling of the phase space visited by the true nuclear wavepacket. To remedy these issues, the ab initio multiple cloning^{147,148} (AIMC) approach was proposed, combining features of MCE

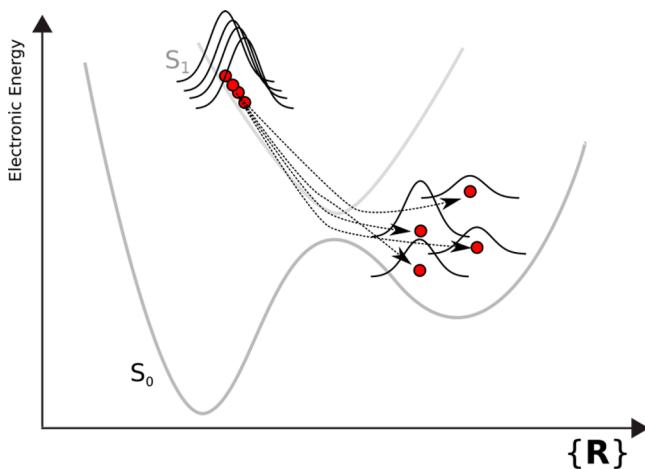


Figure 8. Schematic representation of a MCE run. A swarm of Gaussian functions follow mean-field (Ehrenfest) trajectories.

and AIMS. In AIMC, the basis functions are propagated along Ehrenfest trajectories, but a cloning process—similar to spawning—projects basis functions that are evolving on mean-field surfaces onto adiabatic electronic states, without altering the underlying nuclear wavepacket. As in spawning, the cloning procedure only alters the computational representation of the wave function and does not alter the wave function itself. The AIMC and AIMS methods should both converge to the same result given sufficient basis functions. Indeed, this was demonstrated for the excited-state population after photoexcitation of ethylene.¹⁴⁷ It remains an open question as to which method, AIMS or AIMC, converges more quickly. AIMC was also recently extended to the treatment of tunneling effects,¹⁴⁹ analogous to the procedure used to treat tunneling in AIMS.¹⁵⁰

5.2. Variational Multiconfigurational Gaussian

FMS and AIMS propagate Gaussian basis functions classically, while MCE employs Ehrenfest forces, which might better represent the short-time dynamics of nuclear wavepackets. Is there a way to define optimal trajectories for the basis functions, in the sense that they would represent the optimal support for nuclear wavepackets at any time? The quantum equilibrium hypothesis¹⁵¹ indicates that an ensemble of trajectories, initially represented according to $|\Omega(\mathbf{R}, t_0)|^2$, will remain $|\Omega(\mathbf{R}, t)|^2$ -distributed at any later time t if the ensemble follows quantum trajectories, whose driving equation for nuclei γ is given by

$$\frac{d\mathbf{R}_\gamma(t)}{dt} = \frac{1}{M_\gamma} \left[\frac{\text{Im}\{\Omega^*(\mathbf{R}, t)\nabla_\gamma\Omega(\mathbf{R}, t)\}}{\Omega^*(\mathbf{R}, t)\Omega(\mathbf{R}, t)} \right]_{\mathbf{R}=\mathbf{R}(t)} \\ = \left[\frac{\mathbf{J}_\gamma(\mathbf{R}, t)}{|\Omega(\mathbf{R}, t)|^2} \right]_{\mathbf{R}=\mathbf{R}(t)} \quad (37)$$

Equation 37 expresses a nuclear velocity vector field from the nuclear current density (or quantum flux) $\mathbf{J}(\mathbf{R}, t)$ divided by the nuclear probability density $|\Omega(\mathbf{R}, t)|^2$.^{151,152} An alternative way to define the optimal trajectories for a Gaussian basis set is to determine equations of motion for all the time-dependent parameters through the Dirac–Frenkel variational principle. Rooted in the MCTDH formalism, G-MCTDH proposes to replace some SPF by Gaussian functions.⁴¹ In the limit where all SPF are replaced by Gaussian functions, the method is

called variational multiconfigurational Gaussian (vMCG), which is our focus in this section.^{42,153}

5.2.1. Adiabatic Dynamics within Variational Multiconfigurational Gaussian. Let us consider the general case of a nuclear wave function represented by N_b Gaussian functions (considering no correlation in the width matrix):

$$\Omega(\mathbf{R}, t) = \sum_i^{N_b} C_i(t) \tilde{\chi}_i(\mathbf{R}, t) \\ = \sum_i^{N_b} C_i(t) \exp \left[\sum_\rho^{3N} \zeta_{ip}(t) R_\rho^2 + \xi_{ip}(t) R_\rho + \eta_i(t) \right] \quad (38)$$

Equation 38 exploits the notation for Gaussian functions used in the vMCG literature. The form of Gaussian functions given in eq 38 corresponds to the definition given in eq 13 by using the following correspondences: $\zeta_{ip}(t) = -\alpha_{ip}(t)$, $\xi_{ip}(t) = 2\alpha_{ip}(t)$, $R_{ip}(t) + i\bar{P}_{ip}(t)$, and $\eta_i(t) = \sum_\rho^{3N} [-\alpha_{ip}(t)R_{ip}^2(t) - i\bar{P}_{ip}(t)\bar{R}_{ip}(t)] + \bar{\eta}_i(t)$. These three parameters are grouped into a vector $\Lambda_i(t) = \{\zeta_i(t), \xi_i(t), \eta_i(t)\}$.

If one uses eq 38 within the Dirac–Frenkel variational principle

$$\left\langle \delta\Omega \left| \left(\hat{H} - i\frac{\partial}{\partial t} \right) \right| \Omega \right\rangle_{\mathbf{R}} = 0 \quad (39)$$

we can extract equations for the propagation of $\{C_i(t)\}_{i=1}^{N_b}$ and $\{\Lambda_i(t)\}_{i=1}^{N_b}$. The form of the equations of motion for the complex amplitudes is similar to eq 10. The fundamental difference between vMCG and FMS/AIMS/MCE occurs in the time-evolution equations for Gaussian parameters:

$$i\dot{\Lambda} = \mathbf{A}^{-1}\mathbf{Y} \quad (40)$$

Elements of matrix \mathbf{A} and of vector \mathbf{Y} are given by

$$A_{k\sigma, i\sigma'} = C_k^*(t) C_i(t) (S_{ki}^{(\sigma\sigma')} - [\mathbf{S}^{(\sigma 0)} \mathbf{S}^{-1} \mathbf{S}^{(0\sigma')}]_{ki}) \quad (41)$$

$$Y_{k\sigma} = \sum_i^{N_b} C_k^*(t) C_i(t) (H_{ki}^{(\sigma 0)} - [\mathbf{S}^{(\sigma 0)} \mathbf{S}^{-1} \mathbf{H}]_{ki}) \quad (42)$$

where

$$S_{ki}^{(\sigma\sigma')} = \left\langle \frac{\partial \tilde{\chi}_k}{\partial \lambda_{k\sigma}} \left| \frac{\partial \tilde{\chi}_i}{\partial \lambda_{i\sigma'}} \right. \right\rangle_{\mathbf{R}} \quad S_{ki}^{(\sigma 0)} = \left\langle \frac{\partial \tilde{\chi}_k}{\partial \lambda_{k\sigma}} \left| \tilde{\chi}_i \right. \right\rangle_{\mathbf{R}} \\ H_{ki}^{(\sigma 0)} = \left\langle \frac{\partial \tilde{\chi}_k}{\partial \lambda_{k\sigma}} \left| \hat{H} \tilde{\chi}_i \right. \right\rangle_{\mathbf{R}}$$

and $\lambda_{k\sigma}$ designates the σ element of the Λ_k matrix. Hence, the variational character of vMCG leads to highly coupled equations for the Gaussian parameters (Figure 9), far from the simple classical or Ehrenfest propagation proposed by FMS/AIMS or MCE. Additional mathematical manipulations can be performed on eq 40 to reach a CX formalism, which presents numerical advantages and highlights the classical and nonclassical parts of the equations of motion. The overall quantum propagation of Gaussian parameters leads to an improved distribution of the basis functions, potentially covering a broader region of phase space than would be possible with the same number of classical trajectories. In addition, nonclassical propagation allows the basis functions to tunnel through barriers. We note that the width can be

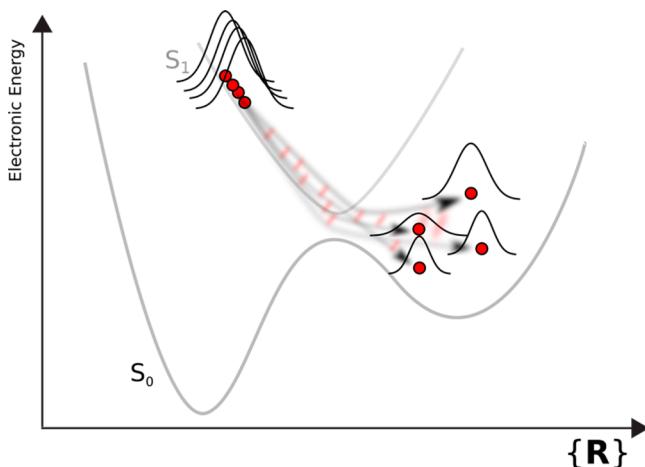


Figure 9. Schematic representation of vMCG nonadiabatic dynamics in the single-set formalism. Blurred lines and arrows symbolize the coupling between Gaussian functions and the resulting nonclassical trajectories.

propagated using the time-dependent variational principle but the dynamics can become numerically unstable, and often frozen widths are used for vMCG simulations (which does not compromise the variational nature of the method).^{42,102}

In direct-dynamics variational multiconfigurational Gaussian (DD-vMCG),^{4,80,154–156} the quantum dynamics is performed on-the-fly by computing electronic structure quantities as needed at each time step. The Hamiltonian matrix elements are computed in a local harmonic approximation (LHA), which differs from the saddle-point approximation discussed before by the fact that the Taylor expansion is performed around the center of the Gaussian function.¹³⁹ Use of the LHA implies the expensive calculation of Hessians, in addition to energies and gradients.

5.2.2. Nonadiabatic Dynamics within Variational Multiconfigurational Gaussian. Two different ways to extend vMCG to nonadiabatic dynamics have been proposed.¹⁰⁶ In the *multiset* formalism, the total molecular wave function is expanded as in FMS, by using a linear combination of Gaussian functions to describe nuclear amplitudes on each electronic state:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j^{\infty} \sum_i^{N_j} C_i^{(j)}(t) \tilde{\chi}_i^{(j)}(\mathbf{R}, t) \Phi_j(\mathbf{r}; \mathbf{R}) \quad (43)$$

In this formalism, each (variationally propagated) Gaussian function evolves on a given electronic state. In contrast, the *single-set* formalism employs a common set of Gaussian functions for all the electronic states; that is, the molecular wave function is represented by

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i^{\infty} \sum_b^{N_b} C_i^{(b)}(t) \tilde{\chi}_i^{(b)}(\mathbf{R}, t) \Phi_b(\mathbf{r}; \mathbf{R}) \quad (44)$$

Hence, the single-set formalism assumes that the nuclear wave functions for all different electronic states can be represented with a common set of N_b Gaussian functions, leading to a substantial reduction of the computational cost for direct dynamics by decreasing the number of Gaussian functions considered for a DD-vMCG run. Inserting eq 43 or eq 44 in the TDSE leads to equations of motion for the set of complex coefficients similar to those in FMS, with more complicated

expressions for the overlap time-derivative matrix elements. Interestingly, it was shown that the *single-set* formalism leads to Ehrenfest dynamics upon applying a single-configuration condition and a classical limit for the Gaussian basis function.¹⁰⁷

6. DISSECTION OF AN AB INITIO MULTIPLE SPAWNING DYNAMICS SIMULATION

The overall target of any ab initio nonadiabatic molecular dynamics is the *in silico* simulation of a complete photochemical or photophysical experiment. Before detailing how AIMS can be used in this context, let us first start by summarizing the important steps of a typical photochemical experiment (Figure 10), highlighting the critical steps that we will need to address in an *in silico* experiment.

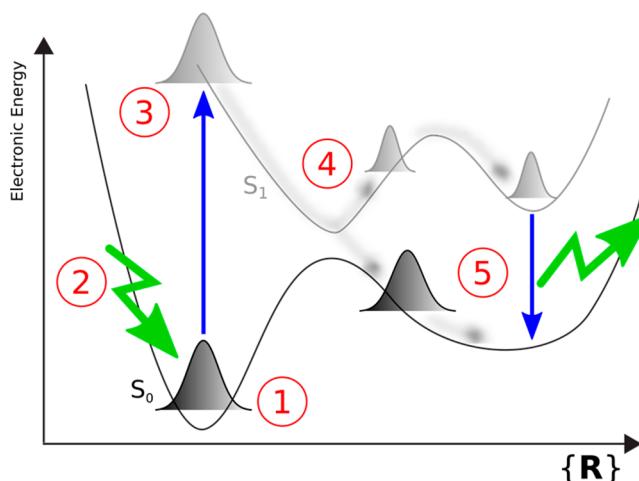


Figure 10. Different steps of an *in silico* photochemical experiment. A molecule in a given initial state (1) is photoexcited (2) and transferred to an excited electronic state (3), from which it relaxes nonadiabatically (4) until it reaches either the ground electronic state or a low-lying excited state (5) from which a radiative process could take place.

A molecular system is initially in its ground electronic state (step 1 in Figure 10). In a fully quantum picture at 0 K, the molecule may furthermore be considered in its ground vibrational eigenstate. We can now imagine an external perturbation (step 2 in Figure 10). For the case of interest here (namely, electronic photoexcitation), we consider that a UV/Vis laser pulse impinges on the molecule. The intensity and length of the laser pulse will obviously be key parameters to determine the photoexcitation process; these questions will be explored. Upon light absorption, the molecule is excited into one of its electronic states, based on selection rules. In cases where an ultrashort laser pulse is used, the original ground vibrational eigenstate is projected onto a new electronic state. As the nuclear wave function is no longer a vibrational eigenstate of the excited electronic state but rather a linear combination of vibrational eigenstates on this new electronic state—that is, a nuclear wavepacket—it will evolve in time. This time-dependent relaxation of the nuclear wavepacket is precisely the point of interest for all the previously described methods. Its accurate description, beyond the Born–Oppenheimer approximation and possibly also beyond the nonrelativistic limit (when spin–orbit coupling is considered), is step 4 in Figure 10. The nuclear wavepacket will likely reach regions where electronic states come close in energy, points

where nuclear motion triggers coupling between electronic states and eventually leads to a splitting of the nuclear wavepacket into different components (in a Born–Huang representation; see section 2.1). These nonradiative processes are fast, typically in the femto- to picosecond regime, and provide us with the time scale for *in silico* nonadiabatic simulations (step 5 in Figure 10). At later times, fluorescence or phosphorescence processes can take place if part of the nuclear wavepacket remains on an excited electronic state.

This section will discuss how the different steps described above can be translated into an *in silico* photochemical experiment. More specifically, we will present some additional features of the overall theory of AIMS described earlier and highlight recent developments aiming at extending AIMS dynamics to a wide variety of photochemical processes.

6.1. Initial Conditions

Often the desired initial state is the molecule either in its ground vibrational state or at a specified temperature. In AIMS, the TBFs follow classical trajectories, and thus rapid convergence depends on a good choice of initial conditions (positions and momenta of the TBFs). The essential issue is that there must be TBFs in regions of phase space that can represent the evolving nuclear wave function. In order to ensure that this is the case at time $t = 0$, we sample the initial nuclear momenta and positions from a phase-space distribution corresponding to the desired initial quantum state. When the molecule is in its ground vibrational state, this implies sampling the positions and momenta for the initial TBFs from a Wigner distribution for the molecule in $\nu = 0$, referred to as Ω_{S_0} . The Wigner distribution is a phase-space distribution corresponding to a desired wave function:^{157,158}

$$W(\mathbf{R}, \mathbf{P}) = \frac{1}{(2\pi)^{3N}} \times \int_{-\infty}^{\infty} d\mathbf{s} \exp(i\mathbf{P} \cdot \mathbf{s}) [\Omega_{S_0, \nu_0}(\mathbf{R} - \mathbf{s}/2) \Omega_{S_0, \nu_0}^*(\mathbf{R} + \mathbf{s}/2)] \quad (45)$$

where Ω_{S_0, ν_0} represents the ground-vibrational and -electronic nuclear wave function for the system with $3N$ dimensions, and \mathbf{s} is a displacement vector. In short, the Wigner function is a pseudo-phase-space distribution, which provides the position (momentum) distribution upon integration over momentum (position).

However, a numerically exact quantum description of the nuclear degrees of freedom is possible only for low-dimensional (or reduced-dimensional) systems. Hence, $\Omega_{S_0, \nu_0}(\mathbf{R})$ is in principle not available for most molecular applications, and the initial conditions need to be sampled from an approximate distribution. One way of extracting initial conditions (nuclear positions and momenta) is to sample them from a thermal distribution, for example, by running a long *ab initio* molecular dynamics in the ground electronic state at a given temperature. While this protocol is easy to set up for molecules, one drawback is that the internal energy distribution for dynamics at 300 K is too narrow with respect to the one expected at the zero-point energy (ZPE) of a molecule.¹⁵⁹ In other words, initial conditions sampled from an *ab initio* molecular dynamics are likely to have a too-narrow distribution in kinetic and potential energy. When projected onto an excited electronic state, such a narrow distribution might alter the outcome of the simulation.¹⁵⁹

One way to approximate a quantum distribution consists in approximating the Wigner distribution in eq 45 by representing $\Omega_{S_0, \nu_0}(\mathbf{R})$ as a product of uncoupled harmonic oscillator (UHO) eigenstates.¹⁶⁰ In other words, one can approximate the ground vibrational eigenstate of a molecule as the one for a combination of uncoupled oscillators, whose frequencies correspond to the molecular normal modes. In this case, an analytical solution exists for the Wigner distribution, which in a normal-mode representation becomes^{159–163}

$$W(\mathbf{R}, \mathbf{P}) \approx \tilde{W}_{\text{UHO}}(\mathbf{R}, \mathbf{P}) = \frac{1}{(\pi)^{3N-6}} \prod_{\rho}^{3N-6} \exp\left(-\frac{R_{\rho}^2}{2\sigma_{R_{\rho}}^2}\right) \exp\left(-\frac{P_{\rho}^2}{2\sigma_{P_{\rho}}^2}\right) \quad (46)$$

where $\sigma_{R_{\rho}}^2 = 1/2\mu_{\rho}\omega_{\rho}$ and $\sigma_{P_{\rho}}^2 = \mu_{\rho}\omega_{\rho}/2$; that is, nuclear positions and momenta are sampled independently. Generating eq 46 is therefore straightforward, as it requires only an equilibrium molecular geometry in the ground electronic state and its corresponding normal-mode analysis: frequency ω and reduced mass μ for each normal mode ρ . Initial positions and momenta can then be randomly sampled from eq 46, where $R_{\rho} = 0$ at the equilibrium geometry. This Wigner sampling can also be used to generate photoabsorption cross sections.^{164,165}

Strong approximations are nevertheless encoded in eq 46 when it is used for molecules. First, we employ a harmonic approximation for all modes, neglecting any anharmonicities, which is likely to be problematic for low-frequency modes, for example.¹⁶⁶ Another critical problem is ZPE leakage: sampling initial conditions from eq 46 does generate a distribution whose average classical energy approaches the $\nu = 0$ energy of the quantum system, but classical degrees of freedom can freely transfer this energy among each other, while such transfer is obviously regulated in quantum mechanics. Hence, energy from a given mode can be transferred to other modes, which leads to an imbalance when it is considered that at least an amount equal to the ZPE should remain in any modes quantum mechanically. An extensive discussion on the sampling of initial conditions for nonadiabatic dynamics can be found in ref 102. We note that employing the Wigner distribution obtained from classical adiabatic switching^{167,168} would allow one to remove the uncoupled and harmonic approximations in the aforementioned sampling.

It is finally important to note that proper sampling of initial conditions is even more critical for methods like MCE and vMCG, which do not use an adaptive basis set and therefore keep the number of basis functions constant during the dynamics. Hence, the choice of the number of TBFs at time $t = 0$, as well as their initial placement, is critical to ensure that the TBFs provide proper support for the nuclear wavepackets at later times. For more details, the reader is referred to ref 117, which discusses sampling in the context of MCE.

Having discussed the choice of initial $\bar{\mathbf{R}}$ and $\bar{\mathbf{P}}$ for the TBFs, one still needs to specify their Gaussian widths. A general protocol was recently proposed¹⁶⁹ to determine the frozen widths from simple frequency calculations in the ground electronic state. The protocol was tested for different molecules, and the typical width obtained for a given atom is quite insensitive to the chemical environment. Furthermore, the resulting electronic population dynamics was found to be quite insensitive to the choice of widths, within the variability

observed due to different bonding environments. Thus, standard values¹⁶⁹ for the widths, depending only on atomic number, can be used.

6.2. Excitation Process

Once the initial conditions are selected, it remains to define how to account for the interaction with an external field triggering the electronic excitation. An obvious solution is to include the external field explicitly in the ab initio multiple spawning simulation (XFAIMS),¹⁷⁰ which allows one to start the dynamics in the ground electronic state and explicitly simulate the photoexcitation process. This approach has also been explored for other trajectory-based nonadiabatic methods.^{171–180} The light/matter interaction term, in the dipole approximation, can easily be included in the Hamiltonian matrix and the spawning algorithm modified accordingly. The influence of laser pulse characteristics [such as intensity, carrier-envelope phase (CEP), or duration] on the excitation process can also be studied in detail.

Nevertheless, first-order perturbation theory provides a justification for a rather simpler protocol to simulate photoexcitation.^{102,103} Let us approximate a molecular system originally in its ground electronic and vibrational state by $\Omega_{S_0, v_0}(\mathbf{R}) = \Omega_{S_0, v_0}^{(0)}(\mathbf{R})$, and apply an external time-dependent electric field $E(t)$, which will couple to the molecule through its transition dipole moment with an excited state S_1 , $\mu_{S_1 S_0}(\mathbf{R})$ (we consider the field aligned with the transition dipole moment for simplicity). The first-order correction to the nuclear wave function contains only a contribution for the excited state part and reads

$$\begin{aligned}\Omega_{S_1}^{(1)}(\mathbf{R}, t) &= \frac{1}{i} \int_0^t dt' \exp[-i\hat{H}_{S_1}(t-t')] [-\mu_{S_1 S_0}(\mathbf{R})E(t')] \\ &\quad \times \exp(-i\hat{H}_{S_0}t')\Omega_{S_0, v_0}(\mathbf{R}) \\ &= -\frac{1}{i} \int_0^t dt' E(t') \exp(-iE_{S_0, v_0}t') \\ &\quad \times \exp[-i\hat{H}_{S_1}(t-t')][\mu_{S_1 S_0}(\mathbf{R})\Omega_{S_0, v_0}(\mathbf{R})]\end{aligned}\quad (47)$$

We therefore have the physical interpretation that, upon excitation, an initial state is given by $\mu_{S_1 S_0}(\mathbf{R})\Omega_{S_0, v_0}(\mathbf{R})$. If in addition one considers a sudden laser pulse, $E(t') = \delta(t' - t_1)$, we obtain

$$\begin{aligned}\Omega_{S_1}^{(1)}(\mathbf{R}, t) &= -\frac{1}{i} \exp(-iE_{S_0, v_0}t_1) \\ &\quad \times \exp[-i\hat{H}_{S_1}(t-t_1)][\mu_{S_1 S_0}(\mathbf{R})\Omega_{S_0, v_0}(\mathbf{R})]\end{aligned}\quad (48)$$

which describes the generation and evolution of the initial state, given by $\mu_{S_1 S_0}(\mathbf{R})\Omega_{S_0, v_0}(\mathbf{R})$, on the excited electronic state S_1 .

This description of photoexcitation by a short laser pulse implies that we can describe the initial nuclear wavepacket in the excited state as the ground-state eigenstate multiplied by the corresponding transition dipole moment. The Condon approximation proposes that the latter can be considered as a constant in the Franck–Condon region; that is, $\mu_{IS_0}(\mathbf{R}) \approx \mu_{IS_0}$. Hence, a good approximation to this initial state would be to generate a given quantum distribution for the ground state (see Section 6.1) and to simply promote it to the desired excited state. This process is actually the one most commonly employed in trajectory-based and trajectory-guided simulations.

Alterations of this protocol are possible if the nuclear wavepacket is initially distributed among more than one excited electronic state after the pulse. We note that Heller and co-workers¹⁸¹ used this sudden generation of a nuclear wavepacket onto a given electronic state as a way to compute vibrationally resolved electronic absorption spectra, obtained from the Fourier transform of the autocorrelation function of the time-dependent nuclear wavepacket with itself at time $t = 0$.

6.3. Electronic Structure Methods for Excited Electronic States

We give in this section a brief discussion related to electronic structure calculations. Until now, we have indeed always considered that electronic structure quantities like electronic energies, nuclear forces, or nonadiabatic coupling vectors were provided. In AIMS, all these quantities will be computed on-the-fly for each TBF—for their classical propagation, to monitor potential new spawning events, and for the Hamiltonian matrix—but also at the centroid positions between TBFs, to couple TBFs through the Hamiltonian matrix. We here summarize the range of electronic structure methods that were interfaced with AIMS.

Key to all on-the-fly nonadiabatic methods is determining the best compromise between the accuracy of an electronic structure method and its computational efficiency.¹⁸² The level of electronic structure theory should be sufficient to capture the different features of all involved electronic states, not only in the Franck–Condon region but also over a large range of the configuration space visited by the nuclear wavepackets. At the same time, the computational cost should be minimized as much as possible to allow for simulation of realistic molecules over time scales ranging from tens to thousands of femtoseconds.

Numerous excited-state dynamics were carried out with multiconfigurational methods like state-averaged complete active space self-consistent field (SA-CASSCF).¹⁸³ While it largely neglects dynamic correlation for practically accessible active spaces, SA-CASSCF often provides a qualitatively correct picture of excited-states topologies and their crossings and led to numerous successful simulations when combined with AIMS,^{126,184} DD-vMCG,^{42,185–192} or MCE.^{146,193,194} Achieving accurate results with SA-CASSCF depends on judicious choice of the active space (number of orbitals and number of electrons) as well as the number of electronic states included in the averaging procedure. Previous AIMS simulations^{142,195–197} invariably determined these parameters by validation with more accurate methods capable of describing dynamic correlation, and thus the results are often much more reliable than might otherwise be expected from CASSCF with standard choices of active space. Such validation would also benefit other nonadiabatic dynamics methods using SA-CASSCF or other necessarily approximate electronic structure methods.

Multistate complete active space perturbation of second order (MS-CASPT2)¹⁹⁸ includes dynamic correlation effects through perturbation theory in a multistate approach. Its computational cost precluded its use in early nonadiabatic dynamics simulations. However, numerous applications of AIMS/MS-CASPT have now been reported,^{199–205} aided by the development of schemes to obtain analytic gradients²⁰⁶ and nonadiabatic coupling vectors.^{202,207} Recent work shows the direct effect of dynamic correlation on AIMS dynamics for a model of retinal, *trans*-PSB3.²⁰¹ An alternative to MS-CASPT2 is multireference configuration interaction (MRCI), which also

benefits from efficient implementations of analytical gradients and nonadiabatic coupling vectors.^{208,209} MRCI methods, with single or with single and double interactions, have been extensively used in combination with trajectory surface hopping^{101,210,211} and with AIMS dynamics,^{46,142,212,213} but the computational cost limits the size of the molecules that can be simulated. The extended multistate complete active space second-order perturbation theory (XMS-CASPT2), which offers a more robust description of conical intersections than MS-CASPT2,²¹⁶ has recently been used in combination with TSH.²¹⁷

Reparametrized semiempirical methods have enabled highly efficient AIMS simulations for large molecules and condensed phases.^{218,219} Linear-response time-dependent density functional theory (LR-TDDFT)^{220–223} also offers an interesting compromise between efficiency and accuracy for excited-state dynamics.^{11,100,224} However, its practical approximations can lead to severe deficiencies when describing charge-transfer or doubly excited states, as well as conical intersections between the ground and first excited electronic states.^{223,225–227}

AIMS has been interfaced with different electronic structure codes like Columbus,²²⁸ GAMESS,²²⁹ Molpro,¹²⁶ Mopac,²³⁰ and TeraChem.^{231–234} A significant advance toward improving both accuracy and efficiency in excited-state dynamics has recently been obtained by redesigning the algorithms behind excited-state electronic structure methods such as LR-TDDFT,²³⁵ CASCI,²³⁶ SA-CASSCF,^{237,238} and floating occupation molecular orbital (FOMO)-CASCI^{239,240} for use with graphical processing units (GPUs).^{231–234} The first GPU-accelerated AIMS dynamics were recently reported for SA-CASSCF¹⁸⁴ and LR-TDDFT.²⁴¹

6.4. Nonadiabatic Dynamics

Once the initial conditions have been generated and the electronic structure method has been selected, ab initio multiple spawning dynamics per se can be initiated. Within the IFG (section 4.3), each parent TBF is run independently. Hence, a typical AIMS run starts with one TBF in the selected excited electronic state, with nuclear positions and momenta sampled from the appropriate Wigner distribution on the ground state. Electronic structure quantities will be computed on-the-fly. At this early stage where only one TBF is present, electronic energies are used in the equation of motion for the complex coefficients (eq 18), within the saddle-point approximation described in section 4.3, and for the corresponding phase, while nuclear gradients are required for classical propagation of the TBF. Nonadiabatic coupling vectors at the TBF center are also computed to monitor the value of Λ^{eff} and to detect potential spawning regions.

Once a nonadiabatic region is detected, the spawning mode described in section 4.2 is activated, potentially resulting in the generation of a new TBF in the coupled electronic state. The dynamics becomes more involved, as two TBFs have to be propagated classically and coupled through eq 18, which is now composed of (2×2) matrices. Off-diagonal elements of the Hamiltonian matrix are evaluated within the saddle-point approximation (section 4.3), which implies additional electronic structure calculations for the nonadiabatic coupling vectors at the centroid position (if the two TBFs are on different electronic states). Electronic phase is monitored—through overlap of the electronic wave function at the previous and current time steps—and propagated along each TBF to ensure a proper description of interference effects.

The spawning mode described in section 4.2 is the simplest possible and prevents overly rapid growth of the number of TBFs.¹²⁶ Alternative spawning modes have been proposed,^{111,112,125,131,132,242} including a version where TBFs are created not only at the maximum of the function Λ^{eff} but also at the entry point and once the maximum of couplings is passed (this last region is defined by an additional exit threshold).¹¹¹ Three TBFs would therefore be created for a single entrance in the spawning mode, leading to an improved description of the nonadiabatic transfer of amplitudes at a clear increase in computational cost. The spawning mode is primarily an algorithm to ensure proper generation of additional TBFs; the overall amplitude transfer is dictated by the TDSE. This is in contrast to surface hopping, where the hopping algorithm must accurately encode the physics of the nonadiabatic transitions, including not only where the hops occur but also how often. Because of this, many optimizations can be envisaged to maximize the efficiency and accuracy of TBF creation in spawning, while there is less opportunity for such enhancements in surface hopping. The *optimal* spawning method was introduced as an algorithm ensuring a compromise between the best position and the best momentum for the newly created TBF.¹³¹ In optimal spawning, the position and momentum of the new TBF are varied to maximize the overlap between the parent and child TBFs and to minimize their energy difference, hence eliminating any predefined conditions for the generation of the child TBF. We finish this paragraph on a numerical detail regarding the number of TBFs in the simulation. Let us consider an AIMS run where several TBFs are evolving on the same electronic state. As the *classical* propagation of each TBF is performed *independently* from all other TBFs, nothing prevents them from strongly overlapping. However, large overlaps between different TBFs in the same electronic state will lead to linear dependencies in the overlap matrix S , eventually causing numerical instabilities, as the propagation of the complex coefficients in AIMS requires²⁴³ the calculation of S^{-1} (see eq 18).^{244,245} AIMS employs a simple regularization to circumvent this issue,^{108,111} but more involved techniques have been proposed in the broader context of quantum dynamics with Gaussian functions.^{138,246,247}

While the coupling between TBFs as described in AIMS and FMS formally allows for the description of quantum tunneling, the practical use of classical trajectories to propagate the TBFs intrinsically limits them to exploration of classically allowed regions of phase space. Gaussian functions propagated within the vMCG method can, on the other hand, reach nonclassical regions thanks to the quantum propagation of the Gaussian parameters.^{106,248} The spawning idea, nevertheless, offers ways to describe tunneling effects in FMS and AIMS by adding a same-state spawning criterion.^{112,150} A similar strategy to the one described in section 4.2 for nonadiabatic events can be applied (Figure 11): detection of the need for basis-set expansion in the case of tunneling events and generation of initial conditions for the newly spawned TBF, using a simple protocol that takes advantage of the local nature of the TBFs. The detection of tunneling events is based on the idea of labeling tunneling particles, as well as acceptor and donor sites where the tunneling particle might be attached. The same-state spawning algorithm detects potential tunneling events whenever the distance between a tunneling particle and its donor exceeds a given threshold (Figure 11a). At this stage, all the potential acceptor particles are detected, and a set of structures with the tunneling particle placed close to each acceptor

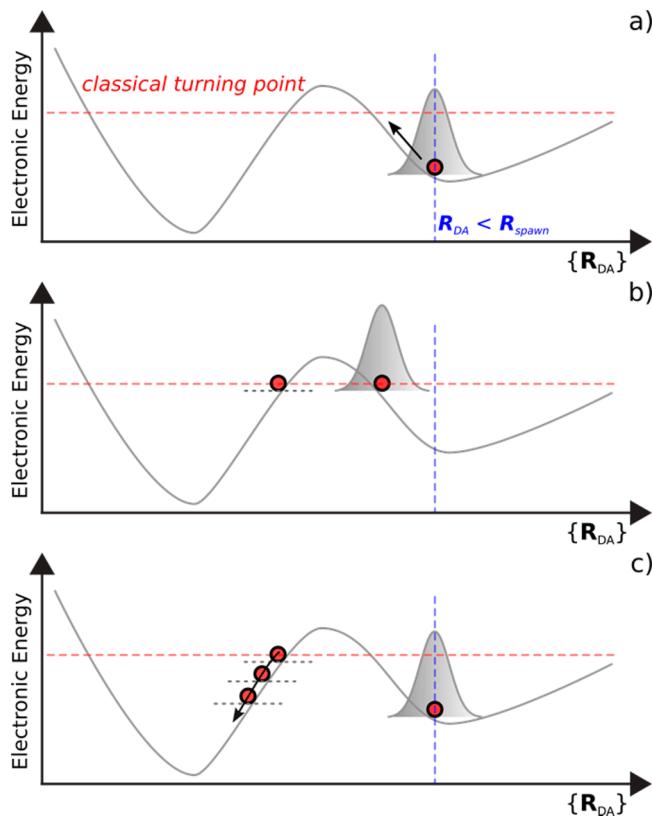


Figure 11. Schematic representation of intrastate spawning algorithm accounting for tunneling effects. (a) A TBF reaches a region where the distance between donor (D) and acceptor (A) is lower than a given threshold, triggering the spawning mode. (b) If tunneling is detected, the TBF evolves until it reaches a classical turning point along the tunneling direction. Then a new TBF with zero amplitude is spawned along the tunneling direction on the other side of the barrier. (c) Back-propagation is performed for both parent and child TBFs. A number of new children TBFs are spawned during the back-propagation step to ensure adequate support for the tunneling process. The multiple spawning dynamics can then restart, including all the newly created TBFs.

particle is generated and minimized. A tunneling vector, connecting the original TBF to the minimized structure, is defined for each structure whose energy is lower than the energy of the current TBF. The original TBF is then propagated classically and monitored, for each minimum. If, during this classical propagation, a geometry is encountered where the tunneling particle is closer to the new minimum than to the original one, the minimum is discarded, as it implies that a classical path is possible. On the other hand, if a turning point along the tunneling vector is found, the TBF is shifted along this vector until the next classical region is found (Figure 11b). Back-propagation is then performed from this current time back to the time when the spawning mode was entered (Figure 11c). A given number of new TBFs will be spawned with zero population during this back-propagation (Figure 11c), and their initial momenta and coordinates are determined from a back-propagated trajectory originating from the point where the new classically allowed region was located. Once the back-propagation is done, the FMS/AIMS run can proceed with the addition of new TBFs.

Photogenerated electron-transfer or long-range energy-transfer processes have been extensively investigated due to their importance for solar-energy harvesting devices. However, the

underlying photophysical mechanisms are challenging due to the potentially weak diabatic coupling between the electronic states describing the energy or electron transfer, leading to the presence of *trivially unavoidable crossings* (TUCs).^{249–252} TUCs can be thought of as conical intersections, for which one of the coordinates in the branching plane only very weakly lifts the degeneracy due to a (nearly or exactly) vanishing diabatic coupling between the electronic states. This implies that TUCs appear in the adiabatic representation as $3N - 7$ dimensional seams of intersection (in contrast, conical intersections form $3N - 8$ dimensional seams), exhibiting extremely large and extremely localized nonadiabatic couplings (Figure 12).

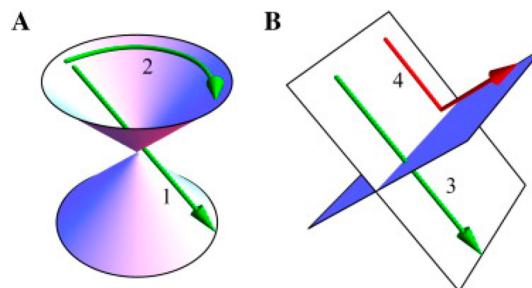


Figure 12. (A) Dynamics around a conical intersection, where (1) diabatic transfer and (2) adiabatic passage of the nuclear wavepacket are both possible. (B) In the case of a trivially unavoidable crossing (TUC), only (3) purely diabatic transfer is possible, because the coupling term is exactly zero or negligible. Reprinted with permission from ref 253. Copyright 2015 Elsevier.

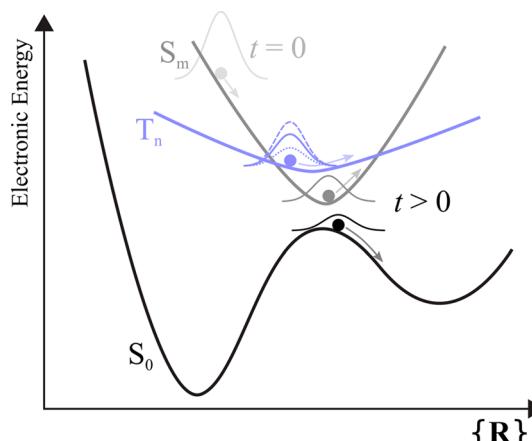


Figure 13. Schematic representation of GAIMS. An initial singlet TBF (gray) is evolving on S_m and will spawn new TBFs on S_0 (black)—by internal conversion—and on the triplet state T_n (blue) as a result of spin–orbit coupling–intersystem crossing. The superimposed Gaussian shapes on the triplet TBF (blue) represent the different sublevels (M_s values) of the triplet state. Reprinted with permission from ref 267. Copyright 2013 AIP Publishing.

A nuclear wavepacket reaching a TUC region will be entirely transferred to the coupled adiabatic state, preserving its diabatic character. This phenomenon is especially surprising when it leads to significant nonadiabatic transitions from a lower electronic state to an upper electronic state and has been called upfunneling or diabatic trapping in these cases.^{46,254–257} Certain nonadiabatic molecular dynamics methods can miss those localized regions for numerical reasons, and one way to monitor the presence of TUCs is by looking for abrupt changes

in the electronic wave function of the running state (via wave function overlap at different time steps), testing for a rapid change of the corresponding electronic character.^{126,258,259} On the basis of those considerations and the development of a norm-preserving interpolation strategy for calculation of time-derivative couplings,²⁶⁰ AIMS was adapted to efficiently detect and properly describe TUCs.²⁵³

Until now, we have only discussed *internal conversion* processes, which are nonradiative transitions between electronic states sharing the same spin multiplicity. Different nonadiabatic methods like TSH^{166,175,176,261–264} or MCTDH²⁶⁵ were extended to include *intersystem crossing* events; that is, transitions that involve spin changes mediated by spin–orbit coupling.²⁶⁶ A recent extension of AIMS, termed *generalized ab initio multiple spawning* (GAIMS),²⁶⁷ uses TBFs that encode, in addition to an electronic state, a given spin state and projection (depicted in Figure 13 by different line style for the TBF evolving on the triplet state T_n). The coupling pattern between TBFs is more complex due to the addition of spin–orbit coupling and the appearance of spin sublevels for each electronic state, but the formalism is easily extended to accommodate spin variables. The spawning algorithm is simply modified by monitoring an effective diabatic coupling between states of different spin multiplicity, containing spin–orbit coupling.

We have so far made no mention of the molecular environment, that is, whether the chromophore was in isolation, surrounded by solvent, or embedded in a protein matrix. The challenge of describing the environment of an excited molecule has stimulated the development of various techniques, from implicit solvent models adapted to the calculation of electronically excited states^{268–271} to explicit solvent methods, ranging from a purely classical description (quantum mechanical/molecular mechanical, QM/MM) to more accurate models like polarizable force fields, effective fragment potentials,²⁷² fragment molecular orbitals,²⁷³ or embedding strategies.^{274–276} The QM/MM technique is by far the most common way of explicitly including the effect of neighboring molecules in the excited state of a molecule^{277–282} and has been implemented within different nonadiabatic dynamics schemes.^{219,230,283–285} While a purely classical QM/

MM description with the usual fixed-charge empirical force fields offers a cost-effective way of coupling the molecule of interest to its environment, it neglects the role of rapid electronic polarization of the solvent in response to changes in the electronic character of the photoexcited molecule. Techniques such as polarizable force fields²⁸⁶ include a description of these effects, at a larger computational cost. AIMS dynamics can easily be combined with QM/MM to account for the role of solvent or protein environment.^{126,219,230,287–289} All atoms in the simulation take part in the TBFs, and spawning results in new TBFs with a quantum mechanical description encompassing the entire solute/solvent system. In other words, despite the classical treatment of the environment from an electronic perspective, the AIMS nuclear dynamics treats all nuclei quantum mechanically. Hence, AIMS with QM/MM accounts for the effect of the environment on coherence/decoherence of nuclear wavepackets on different electronic states.

6.5. Convergence and Analysis of Results

The AIMS dynamics resulting from a given parent TBF is often denoted as an AIMS run. Within the IFG approximation, one should average over many such runs to obtain converged results. The convergence of the results for any given observable can be determined by statistical analyses, analogous to standard ones used for classical trajectories. In low-dimensional model systems, convergence of the population dynamics with FMS has been demonstrated^{111,242} after a few tens of initial conditions or AIMS runs.

The analysis of a set of AIMS runs is somewhat more involved than methods based on classical trajectories such as surface hopping. In TSH, each trajectory has an equivalent weight in the simulation and all intertrajectory coupling is neglected. Thus, the value of any observable is obtained by simple unweighted averaging of the observable over all trajectories. In FMS and AIMS, one needs to consider all coupled TBFs together, and different TBFs will usually have different weights. For a general operator \hat{O} , the FMS time-dependent expectation value based on eq 26 gives eq 49. Within the IFG, where the different initial conditions are uncoupled, eq 49 becomes eq 50.

$$O(t) = \frac{\langle \Psi(t) | \hat{O} | \Psi(t) \rangle_{\mathbf{R}, \mathbf{r}}}{\langle \Psi(t) | \Psi(t) \rangle_{\mathbf{R}, \mathbf{r}}} = \frac{\sum_{\beta\beta'}^{N_{\text{ini}}} \sum_{JI}^{N_{\text{state}}} \sum_{ij}^{N_j^{\beta}(t) N_I^{\beta'}(t)} [C_{i\beta}^{(J)}(t)]^* C_{j\beta'}^{(I)}(t) \langle \Phi_J^{\beta} \chi_{i\beta}^{(J)}(t) | \hat{O} | \chi_{j\beta'}^{(I)}(t) \Phi_I^{\beta'} \rangle_{\mathbf{R}, \mathbf{r}}}{\sum_{\beta\beta'}^{N_{\text{ini}}} \sum_{JI}^{N_{\text{state}}} \sum_{ij}^{N_j^{\beta}(t) N_I^{\beta'}(t)} [C_{i\beta}^{(J)}(t)]^* C_{j\beta'}^{(I)}(t) S_{ij\beta\beta'}^{JI}(t) \delta_{JI}} \quad (49)$$

$$O(t) \approx \frac{1}{N_{\text{ini}}} \sum_{\beta}^{N_{\text{ini}}} \left[\frac{\sum_{JI}^{N_{\text{state}}} \sum_{ij}^{N_j^{\beta}(t) N_I^{\beta}(t)} [C_{i\beta}^{(J)}(t)]^* C_{j\beta}^{(I)}(t) \langle \Phi_J^{\beta} \chi_{i\beta}^{(J)}(t) | \hat{O} | \chi_{j\beta}^{(I)}(t) \Phi_I^{\beta} \rangle_{\mathbf{R}, \mathbf{r}}}{\sum_{JI}^{N_{\text{state}}} \sum_{ij}^{N_j^{\beta}(t) N_I^{\beta}(t)} [C_{i\beta}^{(J)}(t)]^* C_{j\beta}^{(I)}(t) S_{ij\beta\beta}^{JI}(t) \delta_{JI}} \right] \quad (50)$$

For a given AIMS run β , the population in electronic state I , that is, $\hat{O} \equiv \hat{P}_I^{\beta} = |\Phi_I^{\beta}\rangle\langle\Phi_I^{\beta}|$, is therefore

Table 1. Summary of AIMS Calculations Reported in the Literature

molecule	electronic structure method ^a	refs	molecule	electronic structure method ^a	refs	
azobenzene	SA-CASSCF	297	11- <i>cis</i> -retinal protonated Schiff base	QM/MM ^c	219	
azobenzene	semiempirical	218	<i>all-trans</i> -retinal protonated Schiff base	QM/MM ^c	288	
bridged azobenzene	SA-CASSCF	298	31-atom retinal protonated Schiff base	QM/MM ^c	289	
<i>trans</i> - <i>p</i> -coumaric acid chromophore	SA-CASSCF	255	retinal model PSB3	MS-CASPT2	201	
<i>trans</i> - <i>p</i> -coumaric acid chromophore	SA-CASSCF + point charge	299	(<i>p</i> -hydroxybenzylidene) imidazolidinone	QM/MM ^c	230	
malonaldehyde	SA-CASSCF	195, 300	(<i>p</i> -hydroxybenzylidene) imidazolidinone	QM/MM ^b	219	
propanal cation	SA-CASSCF	301, 302	(<i>p</i> -hydroxybenzylidene) imidazolidinone	SA-CASSCF	310	
uracil and thymine	SA-CASSCF	196	(<i>p</i> -hydroxybenzylidene) imidazolidinone	SA-CASSCF	311, 312	
methyl salicylate	CASPT2	199	1,3-cyclohexadiene	SA-CASSCF	313–315	
<i>o</i> -hydroxybenzaldehyde	SA-CASSCF	303	silicon cluster models	SA-CASSCF	267	
cytosine	SA-CASSCF	304	thioformaldehyde	SA-CASSCF-SO	316	
butadiene	SA-CASSCF	197	GeH ₂	SA-CASSCF-SO	184	
benzene	SA-CASSCF	305	provitamin D ₃	GPU-SA-CASSCF	241	
<i>trans</i> -azomethane	SA-CASSCF	229	4-(<i>N,N</i> -dimethylamino) benzonitrile (DMABN)	GPU-LR-TDDFT	320	
polyenes	MS-CASPT2	203	N ₂ CO	SA-CASSCF	317	
hexamethylcyclopentadiene	MS-CASPT2	306	cyclobutanone	SA-CASSCF	318	
ethylene	MR-CI	212, 307	cyclopropenone	SA-CASSCF	319	
ethylene	HF-Occupation-Averaged (OA)-CASSCF	142	2-(2'-hydroxyphenyl) benzothiazole	GPU-FOMO-CASCI	321	
ethylene cation tetramethylethylene	SA-CASSCF	126	2-(2'-hydroxy-5'-methylphenyl)benzotriazole	GPU-FOMO-CASCI	322	
ethylene cation tetramethylethylene	QM/MM ^b	126, 287	H ₂ CSO sulfine	MS-CASPT2	322	
ethylene cation tetramethylethylene	MS-CASPT2	200, 202, 204, 205	^a SA, state-averaged; CAS, complete active space; SCF, self-consistent field; PT2, second-order perturbation theory; MS, multistate; MR, multireference; CI, configuration interaction; HF, Hartree–Fock; QM/MM, quantum mechanical/molecular mechanical; LMO/GVB, localized molecular orbital/generalized valence bond; SO, spin-orbit coupling; GPU, graphical processing unit-accelerated; LR-TDDFT, linear-response time-dependent density functional theory; FOMO, floating occupation molecular orbital. ^b Here the QM method is SA-CASSCF. ^c Here the QM method is semiempirical. ^d Here the QM part comprises the chromophore, three amino acids, and eight water molecules.			
ethylene cation tetramethylethylene	MR-First-Order Configuration Interaction (FOCI)	308				
ethylene cation tetramethylethylene	SA-CASSCF	309				
ethylene cation tetramethylethylene	SA-CASSCF (QM/MM)	287				
cyclobutene	HF-OA-CAS	142				
sodium iodide	LMO/GVB	45				
Li (2p) + H ₂	MR-CI	46				
(<i>p</i> -hydroxybenzylidene) acetone	QM/MM ^b	219				
4-hydroxybenzylidene-1,2-dimethylimidazolinone	QM/MM ^{c,d}	219				

$$\begin{aligned}
 P_I^\beta(t) &= \sum_{JK}^{N_{\text{state}}} \sum_{jk}^{N_I^\beta(t) N_K^\beta(t)} [C_{j\beta}^{(J)}(t)]^* C_{k\beta}^{(K)}(t) \\
 &\quad \times \left\langle \Phi_J^\beta \chi_{j\beta}^{(J)}(t) \middle| \hat{P}_I^\beta \right| \chi_{k\beta}^{(K)}(t) \Phi_K^\beta \right\rangle_{\mathbf{R}, \mathbf{r}} \\
 &= \sum_{ij}^{N_I^\beta(t)} [C_{i\beta}^{(I)}(t)]^* C_{j\beta}^{(I)}(t) \left\langle \chi_{i\beta}^{(I)}(t) \middle| \chi_{j\beta}^{(I)}(t) \right\rangle_{\mathbf{R}} \\
 &= \sum_{ij}^{N_I^\beta(t)} [C_{i\beta}^{(I)}(t)]^* C_{j\beta}^{(I)}(t) S_{i\beta j\beta}^{II}(t)
 \end{aligned} \tag{51}$$

where we neglect the denominator since the wave function is normalized and this normalization is preserved by FMS and AIMS. After averaging over all the initial conditions, we obtain

$$P_I(t) = \frac{1}{N_{\text{ini}}} \sum_{\beta}^{N_{\text{ini}}} \sum_{ij}^{N_I^\beta(t)} [C_{i\beta}^{(I)}(t)]^* C_{j\beta}^{(I)}(t) S_{i\beta j\beta}^{II}(t) \tag{52}$$

More care is required for operators that depend explicitly on the nuclear positions. As an example, we consider the case of

the dipole moment operator $\hat{\mu} \equiv \hat{\mu} = \sum_{\alpha}^N Z_{\alpha} \hat{\mathbf{R}}_{\alpha} - \sum_{\lambda}^{N_{\text{elec}}} \hat{\mathbf{r}}_{\lambda} = \hat{\mu}_{\text{N}} + \hat{\mu}_{\text{e}}$, which (within the IFG) becomes

$$\begin{aligned}
 \mu(t) &= \frac{1}{N_{\text{ini}}} \sum_{\beta}^{N_{\text{ini}}} \sum_{JI}^{N_{\text{state}}} \sum_{ij}^{N_I^\beta(t) N_J^\beta(t)} [C_{i\beta}^{(J)}(t)]^* C_{j\beta}^{(I)}(t) \\
 &\quad \times \left[\left\langle \chi_{i\beta}^{(J)}(t) \middle| \hat{\mu}_{\text{N}} \right| \chi_{j\beta}^{(I)}(t) \right]_{\mathbf{R}} \delta_{JI} + \left\langle \chi_{i\beta}^{(J)}(t) \middle| \boldsymbol{\mu}_{JI}^{\text{e}\beta} \right| \chi_{j\beta}^{(I)}(t) \right]_{\mathbf{R}}
 \end{aligned} \tag{53}$$

where $\boldsymbol{\mu}_{JI}^{\text{e}\beta}(\mathbf{R}) = \langle \Phi_J^\beta | \hat{\mu}_{\text{e}} | \Phi_I^\beta \rangle_{\mathbf{r}}$ is the electronic (transition) dipole moment and exhibits a nuclear dependence through the parametric \mathbf{R} dependence of the electronic wave functions. Therefore, while the integral depending on $\hat{\mu}_{\text{N}}$ in eq 53 can be evaluated analytically, the term depending on the electronic (transition) dipole moment, $\boldsymbol{\mu}_{JI}^{\text{e}\beta}$, requires knowledge of this electronic quantity over the entire nuclear configuration space. The saddle-point approximation can be used here, resulting in the final equation:

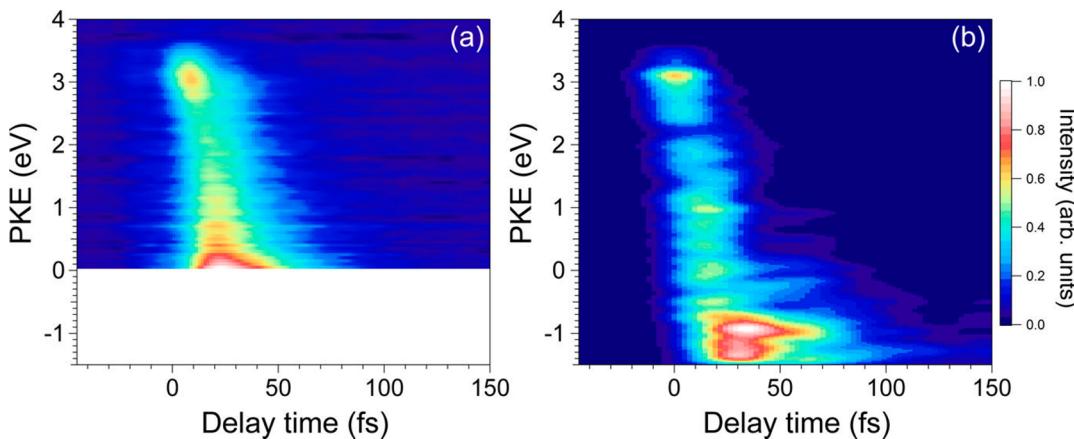


Figure 14. (a) Experimental and (b) AIMS-predicted time-resolved photoelectron kinetic energy spectra. The white area in panel a arises because the probe photon energy used in the experiment did not exactly match what was used in the prior AIMS simulations. Reprinted from ref 296. Copyright 2015 American Chemical Society.

$$\mu(t) = \frac{1}{N_{\text{ini}}} \sum_{\beta}^{N_{\text{ini}}} \sum_{II}^{N_{\text{state}}} \sum_{ij}^{N_j^{\beta}(t) N_I^{\beta}(t)} [C_{i\beta}^{(I)}(t)]^* C_{j\beta}^{(I)}(t) \times \left[\langle \chi_{i\beta}^{(I)}(t) | \hat{\mu}_N | \chi_{j\beta}^{(I)}(t) \rangle_R \delta_{II} + \mu_{II}^{\epsilon\beta} (\bar{R}_{ij}^{(II)}) S_{i\beta j\beta}^{II}(t) \right] \quad (54)$$

$$\sum_I^{N_{\text{state}}} \sum_j^{N_I^{\beta}(t)} |C_{j\beta}^{(I)}(t)|^2$$

which requires calculations of additional quantities (dipole moments) at the centroid positions between each pair of TBFs. Many of these will not need to be evaluated because the overlap integral is small when the TBFs are far from each other.

We denote the analysis in eq 49 as a *fully coherent analysis* because it includes all the phase relationships and interferences between pairs of TBFs included in the FMS or AIMS dynamics. Within the IFG, interferences between TBFs resulting from different initial parent TBFs are neglected, and this should also be reflected in the subsequent analysis. This leads to eq 50, which neglects off-diagonal matrix elements corresponding to TBFs that belong to different parent initial conditions. In many cases, the overlap between TBFs decays rapidly, even for TBFs originating from the same initial condition. When the overlap between TBFs is very small, a *fully incoherent analysis* can be a good approximation to eq 49 when only diagonal terms are considered (eq 55):

$$O(t) \approx \frac{1}{N_{\text{ini}}} \times \sum_{\beta}^{N_{\text{ini}}} \left[\frac{\sum_I^{N_{\text{state}}} \sum_j^{N_I^{\beta}(t)} |C_{j\beta}^{(I)}(t)|^2 \langle \Phi_I^{\beta} \chi_{j\beta}^{(I)}(t) | \hat{\rho} | \chi_{j\beta}^{(I)}(t) \Phi_I^{\beta} \rangle_R}{\sum_I^{N_{\text{state}}} \sum_j^{N_I^{\beta}(t)} |C_{j\beta}^{(I)}(t)|^2} \right] \quad (55)$$

In this case, one should always include the normalization factor in the denominator because the dynamics always includes explicit calculation of the TBF overlap arising from the nonorthogonality of the Gaussians. Therefore, the equality

$$\sum_{II}^{N_{\text{state}}} \sum_{ij}^{N_I^{\beta}(t) N_J^{\beta}(t)} [C_{i\beta}^{(I)}(t)]^* C_{j\beta}^{(I)}(t) S_{i\beta j\beta}^{II}(t) \delta_{II} = 1$$

is guaranteed by the dynamics, and the term

can deviate from unity. We note that the expression

$$n_{j\beta}^{(I)}(t) = \sum_i^{N_I^{\beta}(t)} \text{Re} \left[(C_{i\beta}^{(I)})^* S_{i\beta j\beta}^{II} C_{j\beta}^{(I)} \right]$$

is often called the TBF population, reducing to $n_{j\beta}^{(I)}(t) = |C_{j\beta}^{(I)}(t)|^2$ when all inter-TBF overlaps are negligible.²⁹⁰

The rapid decay of the overlap between TBFs—implying that their interference is no longer important—can be exploited and used to define a death process for the TBFs in an AIMS run. Whenever groups of TBFs (or single TBFs) become uncoupled, their dynamics could be carried out independently with no ill effects. Therefore, we can stochastically select one of these groups to carry on the dynamics. Upon averaging many such cases, the overall dynamics will be equivalent to a traditional AIMS run. This stochastic selection AIMS substantially limits the number of TBFs propagated during an AIMS run while preserving an accurate description of nonadiabatic transfer (as TBFs in those regions are by definition strongly coupled).

7. SELECTED APPLICATIONS OF AB INITIO NONADIABATIC QUANTUM MOLECULAR DYNAMICS

We now turn to selected applications of AIMS, AI-MCE, and (DD-)vMCG to molecular photochemistry and photophysics. These examples aim at showcasing the descriptive—and in some cases demonstrably predictive—power of current ab initio nonadiabatic quantum molecular dynamics techniques.

7.1. Ab Initio Multiple Spawning

AIMS has been applied to the photochemistry of a large number of molecules, as testified by Table 1. Ethylene (C_2H_4) constitutes a typical example of the accuracy achieved by AIMS, not only to describe the nonadiabatic molecular quantum dynamics of this molecule but also to reproduce and predict experimental observables. The excited-state dynamics of this prototypical molecule for double-bond isomerization has been studied by a range of methods.^{142,200,202,204,205,212,291–295} When combined with MS-CASPT2,²⁰⁰ AIMS offers unprecedented

accuracy to describe the excited-state dynamics and lifetime of ethylene upon photoexcitation to its $\pi\pi^*$ electronic state.²⁰⁵ Direct comparison with experimental observables has been achieved by predicting a femtosecond time-resolved photoelectron spectrum from AIMS dynamics, which was in excellent agreement with the measured total ion yield from a vacuum UV/vacuum UV pump–probe experiment. Not only did AIMS/MS-CASPT2 reproduce experimental observables but it also shed light on long-standing discrepancies between theory and experiment about ethylene excited-state lifetime. Indeed, excited-state dynamics simulations have predicted a lifetime ranging from 89 to 180 fs for the S_1 electronic state of ethylene, whereas experimental measurements indicate a faster relaxation of 50 fs or less. Calculations of the total ion yield based on MS-CASPT2/AIMS, however, revealed that the photoexcited ethylene visits regions of the S_1 configuration space where the experimental 7.7 eV probe pulse was insufficiently energetic to induce ionization. Therefore, experimental lifetimes based on the decay of the measured photoion yield could not be directly related to the actual population decay from S_1 but instead provided a lower bound. AIMS was also used to predict a time-dependent photoelectron kinetic energy distribution (right panel of Figure 14).²⁰² The corresponding experiment was performed several years later (left panel of Figure 14)²⁹⁶ and largely reproduced the predicted ultrafast decrease of the photoelectron kinetic energy (PKE) spectra predicted by AIMS.

Combining AIMS with GPU-accelerated electronic structure calculations paved the way for simulations of excited-state dynamics in large molecular systems. AIMS coupled to GPU-accelerated SA-CASSCF reproduced the experimentally observed biexponential decay of photoexcited provitamin D₃, a molecule with 51 atoms.¹⁸⁴ The experimental time scales were also reproduced, and the calculations indicated (in contradiction to previous³²³ surface hopping simulations based on time-dependent density functional theory) that the biexponential behavior is unconnected with the nature of the photoproduct (ring-closed or ring-opened). Instead, this arises from nonequilibrium relaxation in the first excited state. The fast exponential decay is due to a first encounter of the nuclear wavepacket with the S_1/S_0 conical intersection immediately after photoexcitation, when the wavepacket is still far from equilibrium. The longer decay takes place after the remaining part of the nuclear wavepacket on S_1 has relaxed. Subsequent experiments confirmed this explanation.³²⁴

Applications of AIMS are not limited to organic molecules. A series of studies on nonradiative recombination in silicon nanocrystals employed AIMS to simulate the excited-state dynamics of cluster models of characteristic silicon epoxide defects containing up to nine Si atoms.^{313,314} AIMS/SA-CASSCF nonadiabatic dynamics identified fast relaxation mediated by conical intersections between S_1 and S_0 (see Figure 15 for $\text{Si}_8\text{H}_{12}\text{O}$), hence proposing recombination pathways in the presence of epoxides. Importantly, reaching the conical intersection implies a photochemical ring-opening mechanism, whose mechanism slightly differs between the studied clusters. Such ultrafast decay to the ground state is also predicted for similar silicon nanocrystals with a single surface silanol group.³¹⁵ This work demonstrates that the importance of conical intersections in photochemical dynamics may extend to solid-state and surface problems.

What is the importance of spin–orbit coupling in deactivation processes of organic and inorganic molecules?

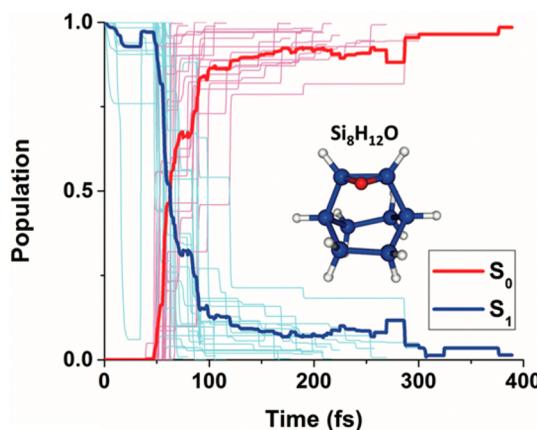


Figure 15. AIMS/SA-CASSCF excited-state dynamics of $\text{Si}_8\text{H}_{12}\text{O}$. Reprinted with permission from ref 313. Copyright 2013 AIP Publishing.

This question has triggered the extension of a number of theoretical methodologies for excited-state dynamics, including TSH^{175,176,261–264} and AIMS.^{267,316} The intersystem crossing process between the triplet state $^3\text{B}_1$ and the singlet state $^1\text{A}_1$ in GeH_2 was investigated with AIMS,³¹⁶ and the nonadiabatic dynamics results were compared to statistical nonadiabatic transition-state theory. The lifetime of the $^3\text{B}_1$ state was found to be shorter with AIMS, an observation explained by the fact that transitions can take place at any point of configuration space in the neighborhood of the intersection seam, while statistical nonadiabatic transition-state theory restricts transitions to occur at the minimum-energy crossing point.

When combined with a QM/MM formalism, AIMS dynamics can provide information on the role of solvent or counterions in excited-state dynamics. Retinal protonated Schiff base (RPSB) is the active chromophore found in rhodopsin proteins, which convert light energy into mechanical energy through photoisomerization. The photodynamics of RPSB is highly sensitive to the environment of the molecule: while the isomerization of RPSB in methanol takes from 2 to 10 ps, it only requires hundreds of femtoseconds in proteins. Recent work compared AIMS simulations in gas and condensed (using QM/MM) phases for a large analogue of RPSB.²⁸⁹ The QM/MM setup comprises the RPSB analogue as well as 85 MM methanol molecules. The electronic structure was treated at the semiempirical FOMO-CASCI level, and 30 (40) initial conditions were used for the gas-phase (methanol) simulation, running for up to 10 ps. The S_1 population decay predicted by AIMS/MM is an order of magnitude slower than that obtained in gas phase (Figure 16), in agreement with experimental evidence. This tremendous slowdown of the nonradiative deactivation is largely due to electrostatic effects that generate rotational barriers in methanol (effectively a type of solvent friction).³²⁵ The final distribution of photoproducts is, however, similar in the two sets of simulations. Interestingly, the addition of a counterion in the AIMS/MM simulation does not significantly alter the result and can be rationalized by the efficient Coulombic screening provided by the surrounding solvent molecules.

Another retinal model, PSB3, was recently used in a different context: namely, to study the role of dynamical correlation effects in excited-state dynamics.²⁰¹ This study compared two sets of gas-phase AIMS simulations, one employing SA3-CASSCF(6/6)/6-31G (100 initial conditions) and the other

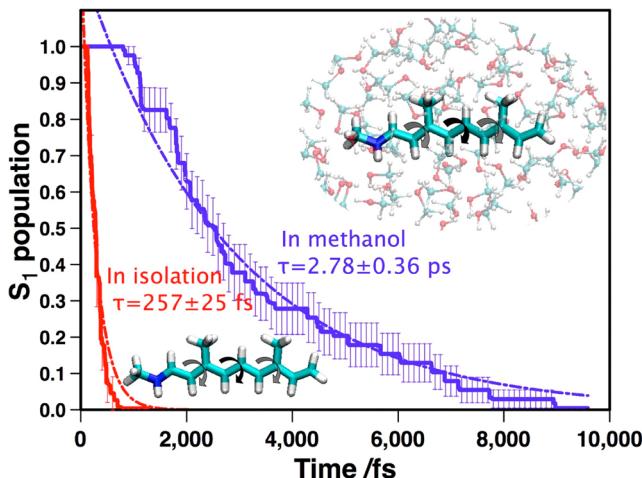


Figure 16. S_1 population decay of RPSB predicted by AIMS in gas phase (red) and in methanol (blue). Reprinted from ref 289. Copyright 2015 American Chemical Society.

employing SA3-MS-CASPT2(6/6)/6-31G (46 initial conditions). Optimizations of local minima on S_1 and S_0/S_1 minimum-energy conical intersections (MECIs) with the two electronic structure methods already revealed some major differences that are reflected in the dynamics simulations. While torsion around the central double bond is observed in both cases, the MS-CASPT2 nonadiabatic dynamics through the isomerization MECI proceeds more efficiently, leading to an increased population of the cis ground state (78.5%). This result is in contrast with the almost 1:1 ratio between cis and trans predicted by the AIMS/SA-CASSCF dynamics.

Besides the description of a molecular environment, AIMS can also incorporate coupling between an external field and a molecule. By use of a Floquet formalism (often useful for simulations in the strong-field regime), this extension of AIMS allows the study of light-induced conical intersections^{326,327} that were used to alter the outcome of photoinduced ring opening in 1,3-cyclohexadiene.^{311,312} The addition of the external field generates a light-induced conical intersection that can intercept the molecule in its S_1 state before it reaches the (field-free) conical intersection between S_1 and S_0 . Such early interception of the nuclear wavepacket leads to the formation of cyclohexadiene in the ground state, and therefore lowers the amount of ring-opened hexatriene photoproduct. The AIMS simulations predict that the maximal impact of this control occurs at 50 fs after photoexcitation, in agreement with experiment (Figure 17).

7.2. Ab Initio Multiconfigurational Ehrenfest and Ab Initio Multiple Cloning

Despite their rather recent development, AI-MCE and AIMC have also been applied to a variety of different molecular systems (Table 2). A variant of AI-MCE called MCE-TDDB (multiconfigurational Ehrenfest time-dependent diabatic basis), that uses a diabatic basis for the matrix elements between Gaussian functions, was used to simulate the dynamics of a chromophore composed of two- and three-ring linear polyphenylene ethynylene units. This type of molecule is a building block of the larger molecular arrangement known as the nanostar. The on-the-fly dynamics employed the collective electron oscillator method³²⁸ for the required electronic structure quantities, based on the semiempirical method

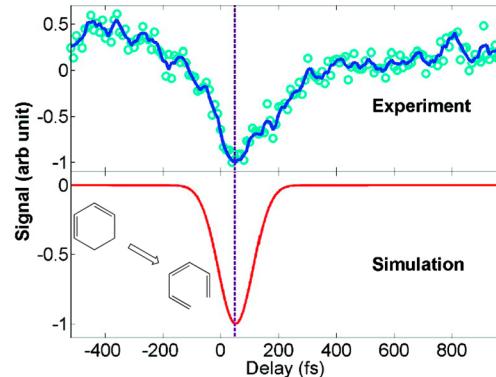


Figure 17. Comparison between AIMS predicted effect of control pulse on branching ratio (lower panel) for hexatriene (HT) with experimental result (upper panel). Adapted from ref 311. Copyright 2012 American Chemical Society.

Table 2. Summary of AI-MCE and AIMC Calculations Reported in the Literature

molecule	electronic structure method	refs
ethylene	AI-MCE/SA-CASSCF	146, 194
ethylene	AIMC/SA-CASSCF	147
phenylene ethynylene dendrimer	AI-MCE/collective electron oscillator	259
pyrrole	AI-MCE/SA-CASSCF	193
pyrrole	AIMC/SA-CASSCF	148

AM1³²⁹ and on single-excitation configuration interaction (CIS). The results from MCE-TDDB dynamics were compared with similar simulations performed with an equivalent of TSH called nonadiabatic excited-state molecular dynamics (NA-ESMD)^{330,331} (100 trajectories) and Ehrenfest dynamics (Figure 18). While the excited-state population dynamics generated by MCE-TDDB and Ehrenfest dynamics are in close agreement, the final population in S_1 given by NA-ESMD is either overestimated (classical population) or underestimated (quantum population). The discrepancy between these two variants of NA-ESMD points toward an internal inconsistency,^{87,89,92,102} potentially due to a decoherence problem. Including decoherence corrections³³² in NA-ESMD led to a faster increase of the S_1 quantum population.

Total kinetic energy release (TKER) spectra and velocity map imaging (VMI) of pyrrole were also simulated on the basis of AIMC/SA-CASSCF dynamics. Due to the efficiency of AIMC/SA-CASSCF, enough statistics could be obtained to resolve fine details in both quantities. While the major features of the computed TKER spectra match the experimental ones, the use of SA-CASSCF led to a slight blue shift in the TKER spectra. However, additional MS-CASPT2 calculations indicate that excellent agreement with experiment would be achieved by including dynamic electron correlation. The AIMC-generated VMI exhibits an isotropic distribution in the low-energy region and clear anisotropy in the high-energy region, in agreement with experimental observations.

7.3. Direct-Dynamics Variational Multiconfigurational Gaussian

The seminal article on the vMCG method⁴² applied it to the excited-state dynamics of butatriene cation, both with reduced-dimensionality models and with a full-dimensional direct dynamics simulation. As a first validation of the vMCG method, a comparison between vMCG and full quantum

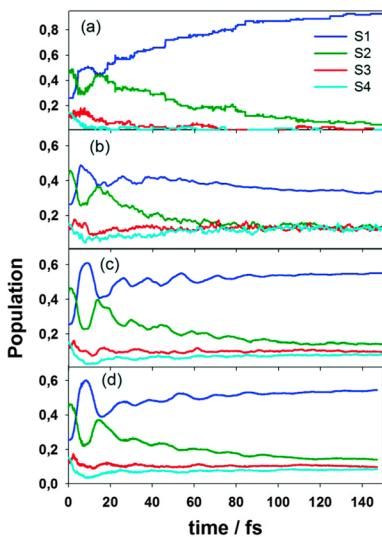


Figure 18. (a) Nonadiabatic excited-state molecular dynamics (classical population), (b) nonadiabatic excited-state molecular dynamics (quantum population), (c) Ehrenfest dynamics, and (d) multiconfigurational Ehrenfest time-dependent diabatic basis. Classical population refers to the proportion of trajectories running in a given electronic state, while quantum population refers to the quantum amplitudes attached to each trajectory, averaged for each state over the entire swarm. Reprinted with permission from ref 259. Copyright 2016, published by the PCCP Owner Societies.

dynamics was presented for a five-dimensional model Hamiltonian. Despite the small number of Gaussian functions (16 functions for each state) employed, vMCG agrees nicely at short times (<30 fs) with the full quantum result when the time dependence of the reduced density for the lowest state in the simulation is compared, as shown in Figure 19. Dynamics calculations were also carried out with on-the-fly computation of potential energy surfaces at the CASSCF/3-21G* level of

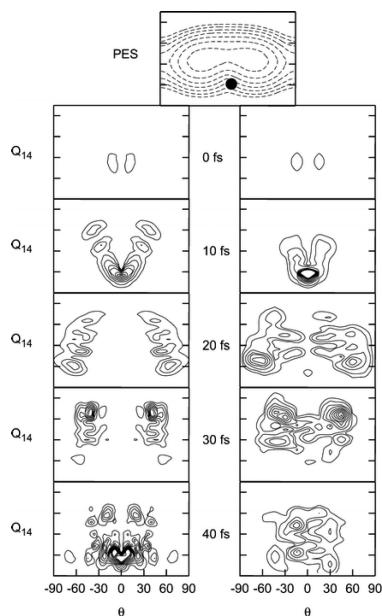


Figure 19. Comparison between (left) full quantum dynamics and (right) vMCG for the projection of a nuclear wavepacket on two principal coordinates in the decay of butatriene cation. Reprinted with permission from ref 42. Copyright 2004 Royal Society of Chemistry.

theory (employing a combination of CASSCF far from the coupling region with SA-CASSCF in the coupling region).¹⁰⁵

DD-vMCG has been applied to a number of different molecular systems (Table 3). For example, DD-vMCG was

Table 3. Summary of DD-vMCG Calculations Reported in the Literature

molecule	electronic structure method	refs
fulvene	CASSCF	185, 188
trimethine cyanine	CASSCF	153, 186
formaldehyde	CASSCF	189,192
butatriene cation	CASSCF	42
benzene	CASSCF	190
thymine	CASSCF	187
NOCl	CASSCF	156

employed to perform an *in silico* experiment on formaldehyde photodynamics. When the excited-state dynamics were initiated from the top of a transition state in S_1 , different photo-dissociation outcomes, that is, $H_2 + CO$ versus $H + HCO$, were generated by altering the initial momentum of the nuclear wavepacket (Figure 20). The transition state on S_1 lies rather high in energy, but it allows for deactivation through a S_1/S_0 conical intersection.

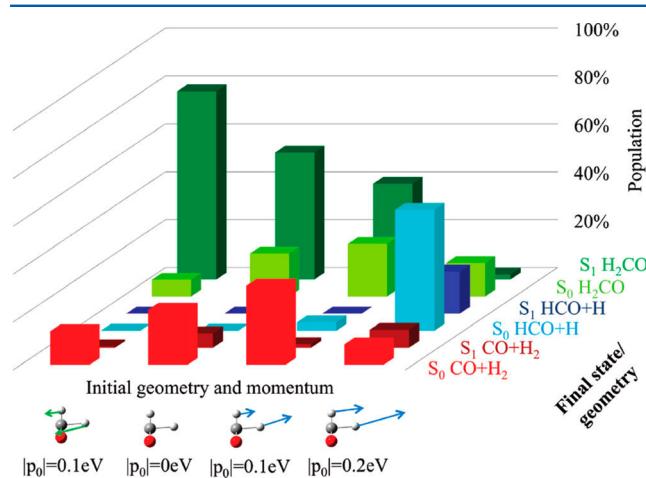


Figure 20. Different distributions of final populations can be obtained by altering the initial geometry and momentum in formaldehyde dynamics. Reprinted from ref 192. Copyright 2010 American Chemical Society.

When the initial momentum is directed along the transition vector pointing toward the reactant (first case in Figure 20), most of the S_1 formaldehyde population is re-formed, as expected. Starting at the TS with no initial momentum produces more $CO + H_2$ in the ground state. If the initial momentum is directed toward the product, a significant population of $CO + H_2$ on S_0 builds up (third case in Figure 20). Finally, adding even more energy in the mode directed toward product eventually leads to an increase of $HCO + H$ on the ground state. The authors proposed that the ratio between $CO + H_2$ and $HCO + H$ depends on a competition between two different momenta: that of the nuclear wavepacket when it arrives in the coupling region and the momentum acquired by the wavepacket as a result of the nonadiabatic crossing. Hence, this *in silico* experiment shows how the momentum at the conical intersection can bias the generation of photoproducts.

8. SUMMARY AND OUTLOOK

Gaussian-based nonadiabatic quantum molecular dynamics offers an important alternative to more traditional trajectory-based methods for the simulation of excited-state dynamics. The different methods presented in this review are derived from first principles, and their approximations are well understood. The use of coupled traveling Gaussian functions to represent nuclear wavepackets leads to a good representation of quantum effects, such as interference and decoherence, and at the same time offers the possibility to propagate the trajectory basis functions on-the-fly without requiring a priori knowledge of the expected dynamics or outcomes.

Ab initio nonadiabatic quantum molecular dynamics methods are, however, always based on a compromise between the efficiency of the overall computational task to treat the photochemical or photophysical process of interest and its accuracy. On one hand, the development of more efficient electronic structure methods for excited states, the optimization of existing algorithms, or the use of new computing technologies such as GPUs will surely permit the accurate simulation of larger systems. On the other hand, the past decade has witnessed important growth in the development of novel methods and algorithms for nondiabatic molecular dynamics. A strong stimulation has indeed been provided not only by recent new spectroscopic techniques that achieve the simultaneous time and spatial resolution needed to produce direct molecular movies of photochemical events but also by the increasing need for excited-state calculations in important applications such as renewable energy, light-driven molecular machines, and atmospheric chemistry.

ASSOCIATED CONTENT

Special Issue Paper

This paper is an additional review for *Chem. Rev.* **2017**, *117*, issue 16, “Ultrafast Processes in Chemistry”.

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Notes

The authors declare no competing financial interest.

Biographies

Basile F. E. Curchod obtained a Ph.D. in theoretical chemistry in 2013 at EPFL (Lausanne, Switzerland), under the direction of Dr. Ivano Tavernelli and co-direction of Professor Ursula Röthlisberger. In early 2014, he was awarded an Early PostDoc grant from the Swiss National Science Foundation to join the group of Professor Todd J. Martínez at Stanford University. In December 2015, he initiated a short postdoctoral stay in the Theory Group, directed by Professor Eberhard K. U. Gross, at the Max Planck Institute in Halle, Germany. He was then awarded a Marie Skłodowska-Curie Research Fellowship to join, in May 2016, the Centre for Computational Chemistry at the University of Bristol. Since November 2017, he has been an assistant professor in theoretical chemistry at Durham University.

Todd J. Martínez holds a B.A. in chemistry from Calvin College (1989) and a Ph.D. in chemistry from UCLA (1994). He was a

Fulbright Junior Researcher and UC President's Postdoctoral Fellow at UCLA and Hebrew University before joining the faculty at the University of Illinois, Urbana–Champaign, in 1996. He has been the Ehrensam and Franklin Professor in the departments of Chemistry and Photon Sciences at Stanford University and SLAC National Accelerator Laboratory since 2009.

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