

# An Overview of Nonadiabatic Dynamics Simulations Methods, with Focus on the Direct Approach versus the Fitting of Potential Energy Surfaces.

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## Abstract

We review state-of-the-art nonadiabatic molecular dynamics methods, with focus on the comparison of two general strategies: the “direct” one, in which the potential energy surfaces (PES) and the couplings between electronic states are computed during the integration of the dynamics equations; and the “PES-fitting” one, whereby the PES’s and couplings are preliminarily computed and represented as functions of the nuclear coordinates. Both quantum wavepacket dynamics (QWD) and classical trajectory approaches are considered, but we concentrate on methods for which the direct strategy is viable: among the QWD ones, we focus on those based on traveling basis functions. We present several topics in which recent progress has been made: quantum decoherence corrections in trajectory methods, the use of quasi-diabatic representations, the sampling of initial conditions, the inclusion of field-molecule interactions and of spin-orbit couplings in the dynamics. Concerning the electronic structure calculations, we discuss the use of ab initio, density functional and semiempirical methods, and their combination with Molecular Mechanics (QM/MM approaches). Within the semiempirical framework, we provide a concise but updated description of our own method, based on configuration interaction with floating occupation molecular orbitals (FOMO-CI). We discuss the ability of different approaches to provide observables directly comparable with experimental results and to simulate a variety of photochemical and photophysical processes. In the concluding remarks we stress how the border between direct and PES-fitting methods is not so sharp, and we briefly discuss recent trends that go beyond this traditional distinction.

**Keywords:** On the fly nonadiabatic dynamics - Nonadiabatic wavepackets - Nonadiabatic trajectories - Surface hopping - Theoretical photochemistry

# 1 Introduction.

The experimental investigation of the mechanism of chemical reactions and other dynamical processes at molecular level yields rather indirect data, that need a non trivial chain of inferences to be interpreted. The problem is even more complicated when two or more electronic states are involved, with transitions among them, which is typical of photochemical reactions and of charge or energy transfer processes. Steady state experimental techniques provide correlations between reactant and product molecular structures, state populations and vectorial quantities such as fragment velocities, angular momenta or absorbed/emitted photon polarizations [1–3]. Transient spectroscopies with pico- or femtosecond resolution can in principle pinpoint any phase of a dynamical process, but once more the raw data are the object of interpretation and often of controversy [4–6]. The photoisomerization of azobenzene is an example of a relatively simple reaction, for which different mechanisms have been proposed during at least 30 years, in spite of the wealth of experimental and computational data that have been made available (see Cusati *et al* [7] and refs. therein).

The calculation of potential energy surfaces (PES) and of other molecular properties, such as charge distributions and electrostatic potentials, is extremely helpful to devise, select and discard reaction mechanisms. In thermal reactions it is normally sufficient to compare the activation free energies associated with different transition states to determine the preferred pathway. In photochemistry and in other cases where more energy is available for the motion of the nuclei, as in combustion reactions, the accessible nuclear phase space volume is much larger. As a consequence, the determination of minimum energy pathways and critical points, such as optimized conical intersections (CoIn) [8–14], in many cases does not provide an unambiguous indication of the reaction mechanism. Moreover, when the excited state lifetimes are very short (few picoseconds or less), the internal vibrational energy redistribution (IVR) does not reach completion, therefore one cannot assume a statistical behavior based on a microcanonical distribution. A fortiori, thermal equilibration is not warranted, even in condensed phase where the energy transfer from an excited chromophore has a typical time scale of ten picoseconds [15]. As a consequence, the wavepacket dynamics depends on the specific initial conditions and, in some degree, on the details of the excitation process, such as the wavelength, duration and monochromaticity of the light pulse.

For these reasons, in photochemistry and in other fields where radiationless electronic transitions are important, the mere exploration of the PES often

provides no more than a hypothetical rationalization of the experimental observations. Only the results of simulations of the molecular dynamics can be directly compared to spectroscopic transients or reactant/product correlated measurements. As discussed above, when the process of interest is fast the dynamical approach is particularly appropriate, and is computationally viable because its burden normally grows with the simulation time. However, in supramolecular systems and in condensed phase one is often confronted with the overlapping time scales of different processes [15], from ultrafast geometrical relaxation and nonadiabatic dynamics ( $< 1$  ps) to IVR and energy transfers between chromophores and to the environment, from hot ground state processes [16,17] to collective rearrangements [18–20]. Efficient methods that would allow to extend the simulation time scales are therefore actively sought for.

In this review paper we discuss the principles and computational strategies of direct methods in the field of nonadiabatic molecular dynamics, and we compare them with the more traditional approaches based on the preliminary determination of the potential energy surfaces and other electronic quantities. In this context the word “direct” is a synonym of “on the fly”, and means that the electronic problem is solved by quantum chemistry methods at every time step of the molecular dynamics. By contrast, the standard approach that was the norm till about 10 years ago and is still in use, consists of three steps: (i) the determination of the relevant regions of the PES’s and of the couplings between electronic states for a (possibly large) number of molecular geometries; (ii) the fitting or interpolation of such quantities as functions of the nuclear coordinates; (iii) the simulation of the dynamics, that makes use of the information about the electronic structure determined and processed in the two preliminary steps. We shall indicate this strategy with the shorthand “PES-fitting”. The direct methods allow to bypass steps (i) and (ii), which can be two serious bottlenecks because of theoretical and computational reasons. They have been used in ground state molecular dynamics since the pioneering work of Leforestier [21]. The introduction of the Car-Parrinello method [22–25] fueled a rapid increase in the popularity of direct methods, especially in condensed phases and wherever accurate force fields are difficult to devise.

The direct strategy can be applied to classical trajectory methods but also to quantum dynamics with traveling localized basis functions, therefore in this review paper we shall concentrate on these approaches. In the next section we shall examine the methods and algorithms for nonadiabatic dynamics and we shall highlight the strong and weak points of the direct and PES-fitting strategies. The rather blurred border between the two approaches will be focused in

section 3, where we shall discuss the electronic structure methods in use for excited states and their applicability to direct dynamics. In particular, we shall provide a unified description of the semiempirical method we proposed almost 15 years ago [26,27], that has undergone improvements and variants described in several papers over the years [28–37]. In section 4 we shall stress the importance of computing observables to be compared with the experimental results, but also mechanistic descriptors to support the qualitative understanding of the dynamic processes. In the same section, a non-exhaustive list of recent applications will be supplied.

## 2 Quantum wavepackets and classical trajectories.

### 2.1 Molecular quantum dynamics.

In quantum wavepacket dynamics (QWD), a non-stationary state can be written in terms of a set of electronic wavefunctions  $\varphi_k$  and of nuclear wavepackets  $\chi_k$ , as

$$\Psi(\mathbf{q}, \mathbf{Q}, t) = \sum_k \varphi_k(\mathbf{q}; \mathbf{Q}) \chi_k(\mathbf{Q}, t) \quad (1)$$

Here  $\mathbf{q}$  and  $\mathbf{Q}$  are the electronic and nuclear coordinates, respectively. The  $\varphi_k(\mathbf{q}; \mathbf{Q})$  wavefunctions depend parametrically on the nuclear positions and are taken to be an orthonormal set, i.e.  $\langle \varphi_k | \varphi_l \rangle = \delta_{kl}$ . On the contrary, the square norm of each nuclear wavepacket  $\chi_k(\mathbf{Q}, t)$ , i.e. the population  $P_k$  of the associated state  $|\varphi_k\rangle$ , depends on time and varies between 0 and 1 ( $\sum_k P_k = 1$ ). Here and in the following we shall use Dirac's notation for the integration over the electronic coordinates only. The time-dependent Schrödinger equation (TDSE)

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{\mathcal{H}} \Psi(\mathbf{q}, \mathbf{Q}, t) \quad (2)$$

then takes the form

$$\begin{aligned} i\hbar \frac{\partial \chi_k}{\partial t} = & \left( \hat{T}_{nuc} + H_{kk}^{(el)} - \sum_r \frac{\hbar^2}{2m_r} T_{kk}^{(r)} \right) \chi_k(\mathbf{Q}, t) + \\ & + \sum_{l(\neq k)} \left[ H_{kl}^{(el)} - \sum_r \frac{\hbar^2}{2m_r} \left( 2G_{kl}^{(r)} \frac{\partial}{\partial Q_r} + T_{kl}^{(r)} \right) \right] \chi_l(\mathbf{Q}, t) \end{aligned} \quad (3)$$

This expression is obtained under the assumption that the  $Q_r$  are fixed orthogonal coordinates and the  $m_r$  the corresponding reduced masses. In the particular case of Cartesian coordinates, the  $m_r$  are simply the nuclear masses.  $\hat{T}_{nuc}$  is the nuclear kinetic energy operator and

$$H_{kl}^{(el)}(\mathbf{Q}) = \langle \varphi_k | \hat{\mathcal{H}}_{el} | \varphi_l \rangle \quad (4)$$

is a matrix element of the electronic Hamiltonian  $\hat{\mathcal{H}}_{el} = \hat{\mathcal{H}} - \hat{T}_{nuc}$ .  $G_{kl}^{(r)}$  and  $T_{kl}^{(r)}$  are the “dynamic” or “derivative” nonadiabatic couplings (DNAC), originated by the application of the  $\hat{T}_{nuc}$  operator to the electronic wavefunctions:

$$G_{kl}^{(r)}(\mathbf{Q}) = \left\langle \varphi_k \left| \frac{\partial}{\partial Q_r} \right| \varphi_l \right\rangle \quad (5)$$

and

$$T_{kl}^{(r)}(\mathbf{Q}) = \left\langle \varphi_k \left| \frac{\partial^2}{\partial Q_r^2} \right| \varphi_l \right\rangle \quad (6)$$

We note that, provided the  $\varphi_k$  are real functions, the diagonal matrix elements  $G_{kk}^{(r)}$  vanish. The two terms in the rhs of eq. (3) can be called the “wavepacket propagation” and the “coupling” term, respectively. The nuclear motion depends mainly on the first term, that contains the potential energy function  $H_{kk}^{(el)}(\mathbf{Q})$ , i.e. the PES of state  $k$ , along with the small corrections due to the second derivative matrix elements  $T_{kk}^{(r)}(\mathbf{Q})$  (normally neglected). The radiationless transitions, i.e. the transfers of population between electronic states, are due to the coupling term, that anyway also affects the shape and displacement of the wavepackets. This term in general contains both the electronic matrix elements  $H_{kl}^{(el)}(\mathbf{Q})$  and the DNAC’s  $G_{kl}^{(r)}(\mathbf{Q})$  and  $T_{kl}^{(r)}(\mathbf{Q})$  but can be simplified by choosing either the adiabatic or a diabatic representation (see section 2.4): in the first case, which is more common, the PES  $H_{kk}^{(el)}(\mathbf{Q})$  is an eigenvalue of the electronic Hamiltonian and the off-diagonal matrix elements  $H_{kl}^{(el)}(\mathbf{Q})$  vanish. To solve the TDSE, one must choose a representation of the  $\chi_k(\mathbf{Q}, t)$  wavepackets, either on a grid or by expansion on a suitable basis set, in order to discretize the differential equation (3). Then, a numerical integration scheme is applied, to propagate the solution by successive time steps  $\Delta t$  up to the duration  $T_S$  of the physical process to be simulated (see again subsection 2.4).

In order to propagate the molecular wavefunction one must know the  $\mathbf{H}^{(el)}(\mathbf{Q})$ ,  $\mathbf{G}^{(r)}(\mathbf{Q})$  and  $\mathbf{T}^{(r)}(\mathbf{Q})$  matrices at least in the region of the nuclear coordinate space where the values of the  $\chi_k(\mathbf{Q}, t)$  wavepackets are not negligible, which is a manifestation of the non-local nature of quantum mechanics.

This fundamental fact has a direct bearing on the implementation of QWD computational methods, and in principle would forbid the application of the on the fly strategy. Consider for instance the Multi-Configurational Time-Dependent Hartree method (MCTDH), one of the most successful approaches to QWD [38–40]. The gist of MCTDH is to expand the wavepackets on a basis of multi-dimensional “configurations”  $\Phi_I$ :

$$\chi_k(\mathbf{Q}, t) = \sum_I A_{I,k}(t) \Phi_I(\mathbf{Q}, t) \quad (7)$$

A configuration is a product of “single particle functions” (SPF), each depending on a single nuclear coordinate:

$$\Phi_I(\mathbf{Q}, t) = \prod_r \xi_{I,r}(Q_r, t) \quad (8)$$

In turn, each SPF  $\xi_{I,r}(Q_r, t)$  can be expanded on a fixed basis set of one-dimensional functions. The time-dependence of  $\chi_k(\mathbf{Q}, t)$  is then carried by the  $A_{I,k}$  coefficients and by those of the SPF expansions. Two configurations differ because of the SPFs they are built with, and can represent alternative dynamical processes, for instance the evolution towards specific reaction channels. If the PES’s are expressed as sums of products of single coordinate factors the necessary multidimensional integrals can be computed very efficiently; while this mathematical form is sufficiently general for many applications, using it definitely implies a PES-fitting approach, well described in a recent paper by Meyer [40].

However, if a wavepacket is sufficiently localized, i.e. is not spread or fractioned on very different regions of the PES, its dynamics can be approximated in terms of local quantities, such as the lowest order derivatives of the potential (see for instance the discussion of Ehrenfest theorem in Tannor’s textbook [6]). Moreover, if the potential is bound and its anharmonicity is not too large, the wavepacket remains localized while it oscillates many times around the equilibrium position, and several interesting dynamical properties can be easily predicted, as shown by Heller and coworkers [41–44]. Their pioneering work is at the root of methods for nonadiabatic QWD, based on the expansion of the wavepackets on localized traveling basis functions of gaussian shape. Two such methods, the Full Multiple Spawning (FMS) by Martínez and coworkers [45–54] and the variational Multiconfiguration Gaussian wavepacket method (vMCG) by Worth and coworkers [55–60], or its variant G-MCTDH [61], can be presented using the MCTDH formalism outlined above. In both approaches an SPF is a complex gaussian function with a fixed width but with time-dependent central values  $\bar{Q}_{I,r}(t)$  and  $\bar{P}_{I,r}(t)$  of the

coordinate and of the associated momentum:

$$\xi_{I,r} = \left(\frac{2\alpha_r}{\pi}\right)^{1/4} \exp[-\alpha_{I,r}(Q_r - \bar{Q}_{I,r})^2 + i\bar{P}_{I,r}(Q_r - \bar{Q}_{I,r})/\hbar] \quad (9)$$

This is a very effective way to avoid the expansion in a fixed basis set, that becomes very expensive for large amplitude motions, such as bond dissociations. A configuration, usually called a basis function in FMS, is then a product of gaussians that peaks at  $\bar{\mathbf{Q}}_I(t)$ , the vector collecting the gaussian centers for all coordinates, with the central momentum vector  $\bar{\mathbf{P}}_I(t)$ .

In FMS the basis function centers  $\bar{\mathbf{Q}}_I(t)$  and momenta  $\bar{\mathbf{P}}_I(t)$  describe classical trajectories, governed by Newton's equations, as gaussian wavepackets would do in a harmonic potential. A calculation is normally started with one or several basis functions and more are added when necessary to represent the time-dependent wavefunction. More specifically, at each time step, for any basis function traveling on a given PES the effective couplings with other electronic states are computed and if one is found larger than a given threshold, one or more new basis functions are spawn on the appropriate PES. Besides electronic transitions, also tunneling requires to spawn new functions where Newton's equations would never allow the existing ones to travel: an ad hoc procedure has been proposed [48]. An optimal spawning algorithm has been introduced [52] in order to improve the computational accuracy obtained with a given dimension of the basis set. With the same aim, a set of optimal width parameters  $\alpha$  for the most common atoms have been determined [54]. Once the basis set of configurations  $\Phi_I$  has been defined, the time-dependent variational principle (TDVP) [62]

$$\left\langle \delta\Psi \left| i\hbar \frac{\partial}{\partial t} - \hat{\mathcal{H}} \right| \Psi \right\rangle = 0 \quad (10)$$

is applied to determine the  $A_{I,k}(t)$  coefficients. To this aim, one needs the matrix elements of the wavepacket propagation and coupling terms contained in eq. (3). While the kinetic energy matrix elements between gaussian functions are given by simple analytical formulas, the PES's and the couplings require a numerical integration.

The on the fly version of FMS, most often called AIMS ("ab initio multiple spawning"), resorts to a further approximation besides the truncation of the basis set and the numerical propagation of the time-dependent solution. In fact, the integrals are computed by a saddle-point approximation. For instance, considering the matrix elements of the potential  $H_{kk}^{(el)}(\mathbf{Q})$ , the first-

order approximation is

$$\langle \Phi_I | H_{kk}^{(el)} | \Phi_J \rangle \simeq \langle \Phi_I | \Phi_J \rangle H_{kk}^{(el)}(\bar{\mathbf{Q}}_{IJ}) \quad (11)$$

and the second-order one is

$$\langle \Phi_I | H_{kk}^{(el)} | \Phi_J \rangle \simeq \langle \Phi_I | \Phi_J \rangle H_{kk}^{(el)}(\bar{\mathbf{Q}}_{IJ}) + \sum_r \langle \Phi_I | Q_r - \bar{Q}_{IJr} | \Phi_J \rangle \left( \frac{\partial H_{kk}^{(el)}}{\partial Q_r} \right)_{\mathbf{Q}=\bar{\mathbf{Q}}_{IJ}} \quad (12)$$

Here  $\bar{\mathbf{Q}}_{IJ}$  is the centroid of the product  $\Phi_I(\mathbf{Q})\Phi_J(\mathbf{Q})$ . Using the second-order approximation for the PES and the first-order one for the couplings, at each time step one has to compute the PES and its gradient at each basis function center  $\bar{\mathbf{Q}}_I$  and at all the centroids  $\bar{\mathbf{Q}}_{IJ}$  of  $\Phi_I, \Phi_J$  pairs traveling on the same PES, and the coupling at the centroids of  $\Phi_I, \Phi_J$  pairs on different PES's (notice that the gradients at the  $\bar{\mathbf{Q}}_I$  geometries are also needed to propagate the Newtonian trajectories). In discussing the computational burden of direct dynamics methods, we shall assume that it is essentially due to the electronic structure calculations, although in some cases the contribution of the solution of the propagation equations is not negligible. In principle, the computing time with  $M$  basis functions would then be equivalent to  $M(M+1)/2$  electronic structure calculations per time step. However, when two basis functions are far apart and their overlap is very small, their matrix elements can be neglected, at least according to the saddle-point approximation. Since this situation is likely to occur more often the larger is  $M$ , the increase in computational time can be closer to linear than to quadratic in  $M$ . On the other hand, since the number of basis functions increases in time because of the spawning, the total cost increases more than linearly with the simulation time  $T_S$ . It is worth noting that this feature is not peculiar of FMS/AIMS, but is rather connected to the intrinsic behavior of molecular quantum wavepackets. A wavepacket initially localized in a limited region of a PES, at later times tends to occupy an increasing fraction of the energetically accessible volume in the nuclear configuration space. Electronic transitions add a further dimension to the spreading of wavepackets. As a consequence, a fixed basis set or grid representation that would yield accurate ("converged") results for a given simulation time  $T_S$ , may turn out inadequate at longer times; the same may occur with a fixed number of traveling basis functions, as in vMCG.

The vMCG method differs from FMS/AIMS mainly because the basis functions move according to the TDVP, eq. (10), instead of following Newtonian trajectories. Besides the  $A_{I,k}$  coefficients (as in FMS/AIMS), the TDVP can be applied to the gaussian basis function parameters. An attempt to treat in this way the width parameters  $\alpha_{I,r}$  showed that it is not worth to deal with



the associated numerical difficulties [55], so in practice the gaussian widths are kept fixed as in FMS/AIMS. The gaussian centers  $\overline{\mathbf{Q}}_I$  follow instead “quantum” trajectories determined by the appropriate form of eq. 10, so at each time-step the basis functions are optimally displaced where they are needed to describe the evolving wavefunction. In this way,  $\overline{\mathbf{Q}}_I$  can also reach classically forbidden regions. The optimal adaptation of the vMCG basis functions dispenses with enlarging the configuration basis during the calculation, so the number of basis functions is kept fixed (no spawning). Notice however that the step by step optimal motion of the basis functions does not mean that their positions will be optimal at all times or in a time-averaged sense, even discounting the obvious dependence on the initial positions (see Tannor [6], section 9.6).

Another feature that differentiates vMCG from FMS/AIMS is the use of a diabatic representation for the electronic states and of the local harmonic approximation for the  $\mathbf{H}^{(el)}$  matrix, i.e. an expansion of  $\mathbf{H}^{(el)}(\mathbf{Q})$  up to second order around the center  $\overline{\mathbf{Q}}_I$  of each gaussian basis function. So, the adiabatic energies along with the associated gradients and Hessian matrices are computed only at the  $\overline{\mathbf{Q}}_I$  geometries and then transformed to the diabatic basis (see section 2.4) to evaluate the matrix elements  $\langle \Phi_I | H_{kl}^{(el)} | \Phi_J \rangle$ . The computational cost per time-step is then proportional to the dimension  $M$  of the basis, but this simple scaling property is not sufficient to compare the efficiencies of vMCG and FMS/AIMS. In fact, other factors affect the computing times: in vMCG the Hessian is required, which is more expensive than the gradient; the authors claim that with vMCG one needs a smaller number of basis functions to approximate the exact solution with a given accuracy, thanks to their optimal positioning [58]; on the other hand, the simplest AIMS calculations start with one basis function and  $M$  is increased only when necessary to describe nonadiabatic transitions, so AIMS can be faster (but less accurate) than vMCG in the short time range.

The Multiconfigurational Ehrenfest (MCE) method put forward by Shalashilin [63, 64] is similar to vMCG, but the basis functions travel according to the mean-field ansatz (see next section). The corresponding equations are simpler and of faster solution than the time-dependent variational ones, but the gaussian basis functions are however able to reach classically forbidden regions of the PES’s without ad hoc provisions as in FMS. MCE can also work in the direct way, by using saddle-point formulas as in FMS or simpler approximations [65, 66]. A formal reduction of the G-MCTDH method to the classical Ehrenfest limit is discussed by Römer and Burghardt [67]. Ronto and Shalashilin recently published an interesting comparison of MCE with a technically

improved version of vMCG [68].

## 2.2 Nonadiabatic classical trajectories.

Classical trajectories lend themselves very easily to the direct computational strategy, which is applied to ground state simulations since a long time [21, 22]. Pioneering work in nonadiabatic dynamics dates back to almost 20 years ago [69–72]. One electronic structure calculation is needed at each time-step, so the computational burden is simply proportional to the number of steps  $N_S = T_S/\Delta t$ . Since normally a swarm of many trajectories is run, one must multiply by the number of trajectories  $N_T$ . Independent trajectories can be simultaneously launched on many processors, so parallel computing is trivially and very effectively exploited.

The most widely used methods are based on the assumption that the system can be described as a set of nuclei moving according to a classical trajectory  $\mathbf{Q}(t)$ , while the electronic wavefunction evolves according to the TDSE:

$$i\hbar \frac{\partial \psi_{el}}{\partial t} = \hat{\mathcal{H}}_{el} \psi_{el}(\mathbf{q}, \mathbf{Q}, t) \quad (13)$$

Classical trajectories can also be used as a tool to approximate quantum dynamics as in the path-integral [73–76] or Bohmian [77–79] approaches. Such methods have been seldom conjugated with a direct strategy, probably because of the very large number of trajectories to be computed and/or the difficulty to manage many coordinates [79]. Among the exceptions we quote the simulation of excess electrons in liquids, treated as a one-electron problem [76], and the study of H+H<sub>2</sub> collisions [78].

Here we shall only consider the electronic TDSE ansatz, that can be realized in different ways. As in QWD, we expand the electronic wavefunction on the  $\varphi_k$  basis:

$$\psi_{el}(\mathbf{q}, \mathbf{Q}, t) = \sum_k C_k(t) \varphi_k(\mathbf{q}; \mathbf{Q}) \quad (14)$$

$\psi_{el}$  depends on time through both the  $C_k(t)$  coefficients and the  $\mathbf{Q}(t)$  nuclear coordinates. The TDSE (13) then becomes

$$\dot{C}_k(t) = - \sum_l C_l(t) \left( \frac{i}{\hbar} H_{kl}^{(el)} + \dot{\mathbf{Q}}^t \mathbf{G}_{kl} \right) = \quad (15)$$

$$= - \sum_l C_l(t) \left( \frac{i}{\hbar} H_{kl}^{(el)} + \left\langle \varphi_k \left| \frac{d}{dt} \right| \varphi_l \right\rangle \right)$$

Here  $\mathbf{G}_{kl}$  is the vector of the DNAC's  $G_{kl}^{(r)}$  between the  $k$  and  $l$  states.  $P_k(t) = |C_k|^2$  is the state probability of state  $\varphi_k$ . As in QWD, the electronic transitions are caused by the electronic couplings  $H_{kl}^{(el)}$  and/or by the dynamic ones, that can be also put in the form of matrix elements of the time derivative operator. When the  $\varphi_k$  are adiabatic states, i.e. eigenstates of  $\hat{\mathcal{H}}_{el}$  with eigenvalues  $U_k$ , the  $\mathbf{H}^{(el)}$  matrix is diagonal:  $H_{kl}^{(el)} = U_k \delta_{kl}$  (see section 2.4).

In eqs. (13-15) the nuclear trajectory  $\mathbf{Q}(t)$  is taken for granted, and there are two main variants of the method depending on how the nuclear motion is coupled with the time evolution of the electronic wavefunction. The Ehrenfest or “mean-field” ansatz [80–88] is embodied by the following expression of the electronic energy, i.e. the potential energy driving the nuclear motion:

$$V(\mathbf{Q}) = \left\langle \psi_{el}(t) \left| \hat{\mathcal{H}}_{el} \right| \psi_{el}(t) \right\rangle = \sum_{k,l} C_k^*(t) C_l(t) H_{kl}^{(el)} \quad (16)$$

By imposing the energy conservation one obtains the forces acting on the nuclei. The force component for the  $r$ -th coordinate is

$$F_r = - \sum_{k,l} C_k^* C_l \frac{\partial H_{kl}^{(el)}}{\partial Q_r} - 2 \sum_{k,l,k'} \Re(C_k^* C_l) G_{k'l}^{(r)} H_{kk'}^{(el)} \quad (17)$$

We see that the force has two terms: one is due to the space-derivative of the state-averaged potential, the other to its time-derivative. The latter is only important when the dynamic coupling between two states  $k$  and  $l$  is large, and is directed as the  $\mathbf{G}_{kl}$  vector. The off-diagonal ( $k \neq l$ ) contributions to the mean-field force (17) are analogous to the coupling term of eq. (3) that affects the wavepacket propagation in QWD. However, as the nuclear motion is represented by one phase space point for all the electronic states, the mean-field trajectory can be dramatically at variance with the behavior of the wavepackets if the latter move far apart from each other. This will happen every time the respective PES's have very different slopes, and is one aspect of the quantum decoherence phenomenon [87]. To take care of this problem one may alter the coefficients  $C_k$  and the state probabilities  $P_k$  with respect to those obtained by integrating eqs. (15), so that the wavefunction  $\psi$  collapses gradually or stepwise to the most populated  $\varphi_k$  state in the weak coupling regions [89–93]. In this way the nuclear motion is ultimately driven by one PES, as in the case of a single wavepacket  $\chi_k$ .

A more drastic departure from the mean-field model is represented by the

surface hopping (SH) philosophy [31, 84–88, 94–115]. Here the nuclei always move on the PES of a given state  $k$  (the “current” state), so  $V(\mathbf{Q}) = H_{kk}^{(el)}(\mathbf{Q})$ , but the system can make transitions (“hops”) to other states according to the time-dependent probabilities  $P_l$ . When and to which state to hop is chosen by a stochastic algorithm, of which several versions exist. The most widely used is Tully’s “fewest switches” (FSSH) [100], which is devised to distribute the trajectories among the electronic states in agreement with the computed state probabilities, by performing a minimum number of hops. According to eq. (15), the time-derivative of  $P_k$  can be put in the form

$$\dot{P}_k = \sum_{l(\neq k)} (P_l B_{l \rightarrow k} - P_k B_{k \rightarrow l}) \quad (18)$$

Assuming the matrix elements  $H_{kl}^{(el)}$  and  $\langle \varphi_k | d/dt | \varphi_l \rangle$  are real, the transition rate  $B_{k \rightarrow l}$  is

$$B_{k \rightarrow l} = \frac{\max\{0, B_{kl}\}}{P_k} \quad B_{l \rightarrow k} = \frac{\max\{0, -B_{kl}\}}{P_l} \quad (19)$$

with

$$B_{kl} = 2\Re(C_k^* C_l) \left\langle \varphi_k \left| \frac{d}{dt} \right| \varphi_l \right\rangle - \frac{2}{\hbar} \Im(C_k^* C_l) H_{kl}^{(el)} \quad (20)$$

In FSSH the probability to hop from the current state  $k$  to  $l$  is

$$T_{k \rightarrow l} = \frac{\int_t^{t+\Delta t} P_k B_{k \rightarrow l} dt}{P_k(t)} \quad (21)$$

We see that hops are performed only when there is a positive  $B_{k \rightarrow l}$  transition rate, with a frequency proportional to  $B_{k \rightarrow l}$ , which realizes the physical requirement of “fewest switches”. Calling  $\Pi_l$  the fraction of trajectories on state  $l$ , and  $\langle P_l \rangle$  the state probability averaged over all trajectories, it can be shown that FSSH yields  $\Pi_l = \langle P_l \rangle$  at any time, if the probabilities  $P_l(t)$  for a single trajectory do not depend on the number and timing of hops [31]. This is approximately true when a trajectory is not much affected by the PES on which it is running, for instance in very energetic collisions or fast photodissociations. In general, however, changing the current PES also changes the course of the trajectory and the transition probabilities, so  $\Pi_l$  and  $\langle P_l \rangle$  may differ considerably, especially when a strong coupling region is crossed several times, or for any other reason a  $B_{kl}$  transition rate oscillates in time between positive and negative values [31]. This drawback is intimately connected to the quantum decoherence issue. Under this respect the surface hopping trajectories behave better than the mean-field ones, but the TDSE still incorporates

the assumption that one phase space point represents the nuclear dynamics for all electronic states. An analysis of this issue and of other minor flaws of SH has been presented by Subotnik and coworkers on the basis of semiclassical quantum Liouville theory [110]. Quantum decoherence corrections in the spirit outlined above have been proposed also in the SH framework, and greatly improve the consistency between the  $\Pi_l$  and  $\langle P_l \rangle$  populations [31,32,37,112,113]. Energy conservation is usually enforced in SH by compensating the change of the potential energy due to a hop with an opposite change in the kinetic energy [105,106]. This way, the total energy is constant for each trajectory, but we note that mimicking the behavior of quantum wavepackets would only require energy conservation for the whole swarm.

Nonadiabatic trajectory treatments of model and real systems have been compared with accurate or approximate QWD calculations [31,32,37,108,116–127]. Surface hopping usually yields results in at least semi-quantitative agreement with QWD, when the simulation is not focused on specific quantum effects concerning the nuclear dynamics. Trends in lifetimes, quantum yields and energy disposal are correctly reproduced. The quantization of molecular vibrations is unavoidably disregarded by trajectory methods, but the vibrational frequencies are easily recognized by Fourier or related analysis methods. In specific problems, an important issue is the “leaking” of zero-point energy (ZPE), i.e. the fact that the energy belonging to some vibrational modes can fall below their ZPE’s and be used to travel along other modes up to transition states, dissociation limits or CoIn’s that would otherwise be inaccessible. Some of the envisaged corrections [128,129] consist in discarding the trajectories that violate the ZPE constraints when computing statistical averages, or in altering the trajectories to avoid the ZPE forbidden regions of the nuclear phase space [130,131]. The latter approach has been also applied to nonadiabatic dynamics [132]. With such methods the computational cost of direct dynamics increases, because local normal modes must be determined along a trajectory. More drastic ways to reduce the ZPE leak are to freeze the vibrational modes that contribute most to the problem, or to correct the PES’s for the ZPE of non reactive modes [133,134]. Acting on the initial conditions is another option, as we shall see in the next section. Tunneling is also missing in nonadiabatic trajectory methods, but ad hoc corrections could be introduced as in ground state dynamics [135,136]. While vibrational quantization, ZPE leaking and tunneling are important issues in ground state dynamics as well as in the excited states, the geometric phase [137–139], being connected to the presence of a conical intersection, is a specifically multistate quantum effect that is not taken into account by independent trajectory approaches [117,118].

In general, the agreement of nonadiabatic trajectory results with QWD improves when quantum decoherence corrections are applied [31, 32, 37, 124, 125]. The evaluation of quantum decoherence effects in principle requires to calculate independent trajectories on different PES's [32], as the localized wavepacket methods do. In direct trajectory methods this would considerably increase the computational burden, because at each time step one would solve the electronic structure problem at several geometries instead of one. Therefore, all the proposed decoherence methods avoid the determination of multiple trajectories by resorting to different approximations [31, 32, 37, 89–93, 112], even in formulations based on the explicit identification of representative points with localized wavepackets (ODC, overlap-based decoherence) [32, 36, 37].

### 2.3 Initial conditions and electronic excitation.

The issue of initial conditions (IC) in simulations of excited state dynamics presents rather different problems in QWD and in trajectory methods. In general, the molecular process of interest may start from a well defined quantum state or from a statistical mixture, either of microcanonical or of canonical type. For instance, one may simulate state selective photochemistry in isolated molecules, starting with a single metastable excited vibronic state that undergoes IVR and/or radiationless electronic transitions. However, if IVR is the fastest process, it may be bypassed by using IC's that describe the resulting microcanonical distribution of vibrational states. If instead temperature effects are relevant in a photochemical process, one will need to combine the canonical distribution for the ground electronic state with a modelization of the excitation process.

In QWD, a single initial quantum state can be adequately described by the normal mode or better approximations. In many cases, a simple Franck-Condon excitation [120] or variants thereof [140] are assumed, i.e. the vibrational wavepacket is transferred without modification from the ground electronic state to the excited one before starting the propagation. The field-molecule coupling can also be explicitly taken into account to describe photon absorption and emission, as in MCTDH optimal control studies [141]. With a fixed basis set, the description of the initial state is a lesser problem with respect to the solution of the TDSE. The same is true for vMCG [55], because at  $t = 0$  all the traveling basis functions are clustered in the region spanned by  $\chi(\mathbf{Q}, 0)$ , which is then expanded in this basis with sufficient accuracy. One can similarly start an FMS calculation with a sufficient number of basis functions, so as to represent adequately the initial  $\chi(\mathbf{Q}, 0)$  [45]. In direct AIMS simulations,

however, one may prefer not to give up the important advantage of starting the calculation with one basis function, and to increase the dimension of the basis only when needed through the spawning procedure; then, the same basis functions that would be chosen to expand the initial wavepacket  $\chi(\mathbf{Q}, 0)$  are propagated one by one; of course in this way the coupling between the basis functions is neglected and AIMS gets one step closer to trajectory methods [45]. If a statistical, rather than quantum mechanical, distribution of IC's is sought for, the centroids of the basis functions (positions and momenta) will be sampled according to the given distribution, just as with classical trajectories [116] (see below).

Methods based on classical nuclear dynamics usually require to run a swarm of trajectories with different IC's, no matter what physical process is dealt with. In particular, surface hopping (but not mean-field) methods need large numbers of trajectories because of the stochastic nature of the model. Even when the time evolution starts with a single, well identified, quantum state, mimicking the wavepacket motion by classical dynamics requires to sample the IC's from the quantum mechanical (QM) distributions  $\rho_Q(\mathbf{Q})$  and  $\rho_P(\mathbf{P})$  of positions and momenta. Assuming as the starting point of a nuclear trajectory just the QM averages of positions and momenta is quite erroneous, as one can clearly see by considering a symmetric molecule, in which case all antisymmetric modes would be inactive (barring the possibility of numerical errors in the trajectory integration). This makes apparent that the zero point motion and the ZPE must be taken into account to some extent also in trajectory simulations.

In 1932 Wigner [142, 143] showed that the quantum mechanical averages of  $\mathbf{Q}$  and  $\mathbf{P}$  dependent quantities can be obtained in a classical framework by using a suitably defined pseudo-distribution  $\rho_W(\mathbf{Q}, \mathbf{P})$ , later called the Wigner distribution. For a single pair of conjugated variables we have

$$\rho_W(Q, P) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \chi(Q - X/2)\chi^*(Q + X/2) e^{iPX/\hbar} dX \quad (22)$$

$\rho_W(Q, P)$  is consistent with the  $\rho_Q(Q)$  and  $\rho_P(P)$  distributions, i.e. it reduces to  $\rho_Q(Q)$  when integrated over  $P$  and vice versa. Simple formulas are obtained for the harmonic oscillator eigenfunctions and for many coordinates one can resort to the normal mode treatment [144]. The general anharmonic case and the thermal distribution on the vibrational states can also be treated, although with a non negligible increase of the computational burden [145]. Wigner's  $\rho_W(\mathbf{Q}, \mathbf{P})$  is often used to sample IC's in trajectory calculations. Two important disadvantages must be considered. One is that  $\rho_W(Q, P)$  is not

guaranteed to be positive, and is indeed negative in certain  $Q, P$  regions for the excited states of an harmonic oscillator ( $v > 0$ ). In the spirit of Wigner’s theory one should use  $\rho_W(\mathbf{Q}, \mathbf{P})$  as a weight in averaging the results of trajectory calculations [146, 147], but the existence of trajectories that contribute with negative weights to a given observable (for instance a quantum yield or a cross section) worsens the convergence to a statistically stable result. As a consequence, more trajectories would be needed to obtain the same accuracy, which is a severe drawback when using a direct strategy. Another possibility is to modify the Wigner function to make it everywhere positive, by relaxing the constraint of consistency with the  $\rho_Q(\mathbf{Q})$  and  $\rho_P(\mathbf{P})$  distributions, as proposed by Husimi [148]. A practical way to sample the IC’s according to Husimi’s function  $\rho_H(\mathbf{Q}, \mathbf{P})$  in surface hopping simulations has been discussed by Kube *et al* [147]. As an alternative, one can abandon Wigner’s theory and use the product distribution  $\rho_{QP}(\mathbf{Q}, \mathbf{P}) = \rho_Q(\mathbf{Q})\rho_P(\mathbf{P})$ , which means the  $\mathbf{Q}$ ’s and  $\mathbf{P}$ ’s are sampled independently [149]. Notice that, for the harmonic oscillator ground state, which is the most commonly assumed initial state,  $\rho_W(\mathbf{Q}, \mathbf{P})$  coincides with  $\rho_{QP}(\mathbf{Q}, \mathbf{P})$ .

Another important problem concerns the vibrational energy and is shared by all the sampling procedures of the nuclear phase space based on the quantum distributions we have examined so far. Both the Wigner function  $\rho_W(\mathbf{Q}, \mathbf{P})$  and the product  $\rho_{QP}(\mathbf{Q}, \mathbf{P})$  yield an average classical energy  $\langle E^{(cl)} \rangle$  that equals the quantum mechanical eigenenergy  $E^{(QM)}$ . However, a broad distribution of  $E^{(cl)}$  energies is obtained: for instance, in the case of a single harmonic oscillator with frequency  $\omega$  and quantum number  $v = 0$ , the energy probability density is  $(2/\hbar\omega)\exp(-2E^{(cl)}/\hbar\omega)$ . As a consequence, each trajectory starts with a different  $E^{(cl)}$ , which may lead to unphysical results when the available energy is a crucial parameter, for instance when it determines the accessibility of a transition state or a CoIn. A solution to this problem is offered by a combination of the microcanonical “orthant” sampling [150] with the wanted distribution ( $\rho_W, \rho_H$  or  $\rho_{QP}$ ). Sun and Hase [144] apply the orthant algorithm to sample in a uniform way the normal mode coordinates  $\mathbf{Q}$  and momenta  $\mathbf{P}$  with the constraint  $E^{(cl)} = E^{(QM)}$ ; then, each generated point  $(\mathbf{Q}, \mathbf{P})$  is subjected to von Neumann’s rejection procedure, using the  $\rho_W(\mathbf{Q}, \mathbf{P})$  distribution. Because of the energy constraint, the sampled  $(\mathbf{Q}, \mathbf{P})$  points do not conform exactly to  $\rho_W$ , but they approximate it the more closely the larger is the number of internal coordinates (with six or more coordinates the approximation is quite good). With a variant of this procedure one can also sample the phase space in the neighborhood of a CoIn [151]. While a single vibrational state or a microcanonical distribution can be satisfactorily sampled by the Wigner+orthant combination, it is harder to conciliate the quantum



distribution of coordinates and momenta with a sharply determined energy level for a given normal mode. This may be a problem in simulating processes where IVR is the crucial step, as in vibrational predissociation [152] or when energy transfer to a specific mode is required to approach a CoIn. Further modifications of the sampling of IC's can be introduced to mitigate the ZPE leak problem, for instance by reducing the initial energy of high frequency modes that contribute most to this problem [153].

When the thermal distribution of the initial vibrational states must be taken into account, in principle a separate simulation could be run for each state. In such cases, however, QWD is advantageously replaced by density matrix based methods (see for instance Berkelbach *et al* [154]), that exceed the scope of this paper. Temperature effects are important in the presence of low frequency modes, that are almost ubiquitous in large molecules or supramolecular systems. As a consequence, the normal mode approximation usually applied to represent the initial wavepacket is often inadequate because of large anharmonicities. Moreover, the large displacements that are typical of low frequency modes are incompatible with the normal coordinate approximation and may lead to unrealistic geometries due to mode mixing. As a consequence, when sampling the QM distributions the slow modes require a special treatment (see for instance the case of methyl rotation in acetone [155]). On the other hand, the classical representation of nuclear dynamics most of the times is sufficiently realistic for slow modes. The trajectory IC's for a canonical distribution can be obtained by Monte Carlo sampling or by a ground state molecular dynamics with an adequate thermostat [156–158] (see our treatment of azobenzene photoisomerization in solution for an example [7]).

Even in the case of single state or microcanonical IC's, the energy issue is somewhat less problematic when the dynamics is triggered by the absorption of light with a broad spectrum, as with ultrashort pulses, because then a certain spread of initial energies is inherent to the physical process. Of course, the modeling of optical excitation in trajectory simulations cannot be as rigorous as in QWD, a major issue being quantum decoherence [37]. A pioneering attempt to introduce the field-molecule interaction in direct nonadiabatic trajectory calculations is the SERID method (Semiclassical Electron-Radiation-Ion Dynamics), proposed by Allen and coworkers [159–162]. SERID adopts a mean-field description of the nuclear motion and the vector potential coupling between molecule and radiation (the same choices are shared by Takatsuka and coworkers [163,164]). The dynamics starts in the ground state and a light pulse of arbitrary shape and strength populates the excited state(s). The total lack of decoherence of the mean-field ansatz constitutes a severe drawback of

SERID. In fact, the nuclear trajectory is driven by an average potential that depends on the state populations. This introduces an unphysical dependence of the excited state dynamics on the parameters of the radiation field. For instance, with a small excitation probability the molecule would remain trapped near the initial ground state minimum, whereas in QWD a wavepacket in an excited PES would move downhill however small the associated state population.

Recent work on nonadiabatic trajectories with field-molecule coupling has privileged surface hopping [165–167], most notably within two implementations called FISH [168–174] (Field Induced Surface Hopping) and SHARC [175–178] (Surface Hopping in the Adiabatic Representation including arbitrary Couplings). Even in the SH framework, quantum decoherence is a critical issue when mixing field-induced and nonadiabatic transitions. In fact, after a light pulse two or more electronic states can be populated, and give place to interference when the molecule experiences nonadiabatic couplings during the trajectory. However, in many situations the quantum wavepackets would be decoupled before entering the nonadiabatic region: for instance, in the excited state the molecule may undergo geometrical relaxation, while remaining almost stationary in the ground state. We showed that the ODC decoherence corrections improve very much the agreement with QWD results [37]. In surface hopping with explicit molecule-radiation interactions another problem arises, namely how to implement energy conservation. Since field-induced transitions do change the total energy, in SHARC the energy conservation is enforced after a hop only if the potential energy difference of the states involved lies outside the laser bandwidth [175]. A recipe of more general applicability consists in partitioning the transition probability into field and nonadiabatic contributions, and to warrant energy conservation only when the latter contribution prevails [37].

At low radiation intensities, as common in photochemistry experiments, taking into account explicitly the field-molecule interaction in the simulation of nonadiabatic dynamics is unpractical, given the small rate of field-induced transitions. In such cases perturbation theory applies and the field-induced transition probability is proportional to the squared transition dipole between the initial state 0 and the final one  $k$ ,  $\mu_{0k}^2$ . With a radiation pulse of carrier frequency  $\nu$ , the resonance condition  $|U_k - U_0| \simeq h\nu$  holds more or less precisely depending on the shape and length of the pulse. The above considerations suggest a practical recipe for the sampling of initial conditions, that dispenses with running a simulation with explicit consideration of the radiation. Here we schematically describe the procedure (see examples of applications for more

details [7, 16, 17, 30, 36, 179, 180]):

- (1) A transition energy window  $[\Delta E_{min}, \Delta E_{max}]$  is chosen according to the excitation process (narrower for almost monochromatic light, wider for broadband excitation), and a user-defined parameter (a squared transition dipole)  $\mu_{ref}^2$  is set.
- (2) A set of  $(\mathbf{Q}_i, \mathbf{P}_i)$  phase space points is sampled from the desired distribution  $\rho(\mathbf{Q}, \mathbf{P})$  for the initial PES  $U_0$ , and the steps 3 to 5 are repeated for each point.
- (3) The transition energies  $U_k(\mathbf{Q}_i) - U_0(\mathbf{Q}_i)$  of the electronic states considered in the simulation are computed, along with the corresponding transition dipoles  $\mu_{0,k}(\mathbf{Q}_i)$ .
- (4) The sum  $\mu_{tot}^2$  of the squared transition dipoles of the eligible states, i.e. those with transition energies in the interval  $[\Delta E_{min}, \Delta E_{max}]$ , is computed. The maximum number of trajectories to be launched from the  $(\mathbf{Q}_i, \mathbf{P}_i)$  IC's,  $N_{max}$ , is given by  $\mu_{tot}^2 / \mu_{ref}^2$ , approximated to the next integer (if there are no eligible states,  $N_{max} = 0$ ).
- (5) The interval  $[0, N_{max} \mu_{ref}^2]$  is partitioned in subintervals corresponding to the eligible excited states, each one of length  $\mu_{0,k}^2$ , plus a dummy subinterval. For  $N_{max}$  times, a pseudo-random number  $X$ , contained in the  $[0, N_{max} \mu_{ref}^2]$  range, is generated. If  $X$  falls in the subinterval belonging to the excited state  $k$ , a trajectory is launched with IC's  $(\mathbf{Q}_i, \mathbf{P}_i)$ , in the electronic state  $k$ . If  $X$  falls in the dummy subinterval, no trajectory is launched.

In this way, the probability density of launching a trajectory in state  $k$  with IC's  $(\mathbf{Q}, \mathbf{P})$  is given by the initial state density  $\rho(\mathbf{Q}, \mathbf{P})$ , multiplied by a factor proportional to  $\mu_{0,k}^2(\mathbf{Q})$ , but vanishes if  $U_k(\mathbf{Q}) - U_0(\mathbf{Q}) \notin [\Delta E_{min}, \Delta E_{max}]$ . The  $\mu_{ref}^2$  parameter regulates the average number of trajectories launched with the same IC's. The algorithm can be applied to single state, microcanonical or canonical initial densities  $\rho(\mathbf{Q}, \mathbf{P})$ , however obtained.

## 2.4 Coupling schemes and time propagation.

The sets of equations (1-3) for QWD and (13-15) for nonadiabatic trajectory methods are quite general, in the sense that we did not specify a particular choice of the electronic basis  $\varphi_k(\mathbf{q}; \mathbf{Q})$ . We shall examine first the electrostatic approximation, whereby the magnetic interactions are neglected. In this case, transitions only take place within a given spin-manifold, so for an even number of electrons only singlet electronic states are normally considered. In the adiabatic representation the  $\varphi_k(\mathbf{q}; \mathbf{Q})$  states are identified with the eigenstates

$\psi_k$  of the electrostatic Hamiltonian  $\hat{\mathcal{H}}_{el}$ , so that  $H_{kl}^{(el)} = U_k \delta_{kl}$ . The adiabatic states  $\psi_k$  are numbered according to their energy ordering, and normally a dynamical treatment takes into account the first few of them, say up to  $k = n_{st}$ . This is quite reasonable as far as the states with  $k > n_{st}$  are not energetically accessible at any molecular geometry for the considered molecular process. Of course  $n_{st}$  is kept as small as viable, to reduce the computational burden. This is important in dynamics calculations, especially in direct QWD methods where all  $n_{st}$  energy gradients must be computed and the number of coupling matrix elements increases as  $n_{st}^2$ . Moreover, the methodological requirements for determining larger numbers and various kinds of excited states are increasingly exacting, which translates into a faster than linear growth of the costs. Within a PES-fitting strategy, exceptions to the rule of considering the  $n_{st}$  lowest states are quite possible, for instance by projecting out of the electronic subspace one or more “intruder” states that are very weakly coupled to the others. In the fitting process, the PES’s can be modified so that the crossings with the intruder states are eliminated. When computing the electronic states on the fly it is more difficult to implement such adjustments. Exceptions to the real energy ordering are automatically enforced whenever the quantum chemistry method is not able to represent certain kinds of states, for instance Rydberg states because of basis set limitations.

All quantum chemistry methods are devised to determine adiabatic states, within specific approximation schemes. However, it is possible to define alternative representations of the electronic structure. The concept of diabatic electronic states [10, 181–192], already implicit in the work of Landau and Zener on electronic transitions at curve crossings, was initially developed to facilitate the treatment of nonadiabatic dynamics. When two electronic states of different nature are weakly coupled and their PES’s tend to cross, in avoided crossing regions the DNAC’s  $G_{kl}^{(r)}(\mathbf{Q})$  and  $T_{kl}^{(r)}(\mathbf{Q})$  are large and they diverge at a CoIn point [8–12, 183, 185, 186]. In principle, it is advisable to tackle the problem in a representation where the interstate couplings are as small as possible. In practice, before the development of efficient methods to compute the DNAC matrix elements in the 1980’s [10, 88, 193–205], one reason to use a diabatic basis was to get rid of the DNAC’s. A set of electronic states  $\eta_i(\mathbf{q}; \mathbf{Q})$  is called diabatic if the DNAC’s  $G_{ij}^{(r)}(\mathbf{Q}) = \langle \eta_i | \frac{\partial}{\partial Q_r} | \eta_j \rangle$  vanish. In general, this condition cannot be fulfilled for all the internal coordinates in a polyatomic [206]. As a consequence, several definitions of “quasi-diabatic” states have been proposed [10, 181–192], with the common objective of avoiding the divergence of the DNAC’s at CoIn points, and possibly to make them negligible at all relevant geometries. These conditions are practically equivalent to imposing that the  $\eta_i$ ’s do not undergo rapid changes as functions of the nuclear

coordinates  $\mathbf{Q}$ . A number of recipes have been devised to determine (quasi-)diabatic states: some require computing the DNAC's, but most dispense with this task and are based on the (almost) invariance of the  $\eta_i$  wavefunctions or related properties versus changes of the  $\mathbf{Q}$ 's [10, 181–192]. In many methods the conversion from the adiabatic to the diabatic basis (“diabatization”) is performed by a non-singular (often unitary) transformation, so that both basis sets span the same electronic subspace. It must be stressed that to define a quasi-diabatic basis in a complex system is seldom a trivial task, for instance when several reaction pathways are considered or intruder states are present in the starting adiabatic set [184]. The quasi-diabatic states one obtains not only depend on the chosen definition, but also on details of the diabatization procedure, such as the number of states themselves [191]. This means that the  $H_{ij}^{(el)}$  and  $\langle \eta_i | \frac{\partial}{\partial Q_r} | \eta_j \rangle$  matrix elements are affected by such choices, and so is the computed dynamics, especially if the dynamic couplings are altogether neglected.

The choice between the adiabatic or a (quasi-)diabatic representation has not the same implications in the QWD, mean-field or surface hopping approaches. In QWD, if no Hamiltonian terms are neglected, it is just a question of choosing a different basis of electronic times nuclear wavefunctions to span the relevant subspace. In principle, differences arise only as far as the truncation of the  $\Phi_I(\mathbf{Q}, t)$  basis does not allow to represent accurately the time-dependent  $\Psi(\mathbf{q}, \mathbf{Q}, t)$ , eq. (1). Within trajectory methods, the mean-field approach can also guarantee the invariance of the results with respect to choosing different electronic basis sets, provided they span the same subspace. Surface hopping, on the contrary, lacks this invariance property, first of all because the trajectories will depend on the PES's on which they run (the  $U_k$ 's in the adiabatic mode or the  $H_{ii}^{(el)}$ 's in the diabatic one); for a given energy, certain regions of the nuclear coordinate space will be classically accessible in one mode and not in the other. Except in crossing regions, the adiabatic PES's offer a more realistic description of the molecular energetics than the diabatic ones. A second source of discrepancy between the results obtained in the two modes is inherent to the hopping model, that works quite well when the transition probability is localized in narrow regions and therefore short time intervals, much less when it is small but not negligible for a long time [31]. In the adiabatic mode the localization condition is usually satisfied, because the DNAC's  $G_{kl}^{(r)}$  are large when the energy difference  $U_k - U_l$  is small and these two circumstances cooperate in increasing the transition probability. On the contrary, the couplings  $H_{ij}^{(el)}$  between diabatic states are not directly related to the  $H_{ii}^{(el)} - H_{jj}^{(el)}$  energy differences. Surface hopping dynamics is therefore preferably run in the adiabatic mode, except in limiting cases where the  $H_{ij}^{(el)}$  couplings are very small

for physical reasons, so that transitions can occur only close to degeneracy points ( $H_{ii}^{(el)} \simeq H_{jj}^{(el)}$ ). This condition is met, for instance, when charge or energy transfer take place between centers that are weakly coupled, because of distance or other reasons; then, the diabatic states are very naturally identified by the localization of charge or excitation [190,191,207], as implicit in Marcus' theory [208].

Nowadays the diabatic state concept is mainly invoked to investigate cases of (almost) intersecting PES's, that are important in the charge or energy transfer processes just mentioned, as well as in ultrafast photoreactions and excited state decays. Models of CoIn's can be built to interpret experimental data or to explore the role of the relevant parameters [10–12,117,118,188,207,209]. In such models the adiabatic PES's are identified as eigenvalues of an effective Hamiltonian, built on a (quasi-)diabatic basis. This is the only way to understand the physical features of the PES crossings [8–12] and to reproduce them by simple functions of the nuclear coordinates. Therefore, models of the same kind are needed to fit the ab initio data (energies and DNAC's) in the proximity of PES crossings [10,38,133,140,184,188–190], in order to run PES-fitting simulations. A favorable case for PES-fitting is met with clusters of rare gases or other systems where atom-atom pairwise interactions represent sufficiently well the electronic states and their PES's; then, the diatomics-in-molecules [210] (DIM) representation provides a set of approximately diabatic states and a good tool to fit ab initio or experimental data (see Heitz et al for an application [211]). In general, in a well conceived diabatic basis the  $H_{ij}^{(el)}$  matrix elements are smooth functions of the nuclear coordinates and therefore can be easily interpolated or fitted.

In direct dynamics the PES and DNAC fitting problem is bypassed, so the diabaticization is seldom applied. An exception is the vMCG method (see section 2.1), that makes use of a very simple conversion from the adiabatic to a quasi-diabatic representation devised by Köppel and coworkers [10,185,186]. Köppel's procedure is noticeable in that it only makes use of energy data (no wavefunction properties), namely the current point adiabatic energies and their derivatives, plus their geometrical relationship with the crossing seam. Of course this implies a certain preliminary knowledge of the PES's, and the practical application to direct dynamics may be non trivial with complicated PES crossing topologies [212]. On the other hand, one should consider that some preparatory work is almost unavoidable in all direct dynamics methods, as discussed in the next section. An improved diabaticization strategy that addresses such problems has been recently proposed in the vMCG context [213].

When the spin-orbit coupling (SOC) is introduced, radiationless transitions

between states with different spin (InterSystem Crossing, ISC) become possible [214]. The most usual way these phenomena are presented and simulated is by reference to “pure” spin electronic states, i.e. eigenstates of both  $S_z$  and  $S^2$ . In this case the SOC is an electronic coupling term, that contributes to the  $H_{ij}^{(el)}$  matrix elements of eqs. (3) and (15). The electronic basis in principle may be adiabatic or diabatic in the meaning seen above, i.e. with reference to the electrostatic Hamiltonian, but in both cases we shall call it “spin-diabatic” because of the invariance of the spin properties of the states versus geometry changes, and because of the role played by the SOC. A spin-diabatic representation may be simply constructed by choosing a set of eigenstates of the electrostatic Hamiltonian for each spin-manifold. This approach is very practical, because one can make use of the usual SOC-free computational techniques, and introduce the SOC’s only to run the dynamics. An alternative is to use an electronic basis made of eigenstates of the complete Hamiltonian, including the spin-orbit contribution. Such states are “spin-coupled” (i.e. mixtures of states with different  $S_z$  and  $S^2$ ), and will be called “spin-adiabatic”. With small SOC’s the corresponding PES give place to weakly avoided crossings, while with the large SOC’s normally encountered in heavy atoms systems, the spin-adiabatic PES’s differ substantially from the spin-diabatic ones. The “spin-adiabatic” states are coupled by derivative matrix elements of the  $\langle \psi_k | \frac{\partial}{\partial Q_r} | \psi_l \rangle$  type, that depend on the mixing of states belonging to the same as well as to different spin-manifolds [34].

The results of a well converged QWD calculation with SOC’s in principle do not depend on the adiabatic/diabatic choice, as in the SOC-free case. Within the PES-fitting approach it is more convenient to represent by analytic functions the spin-diabatic PES’s and the SOC’s, rather than the spin-adiabatic quantities, because their dependence on the nuclear coordinates is more regular. In direct QWD calculations as well the spin-diabatic basis is preferable, because the gradients and Hessians of the SOC-free PES’s are commonly available in electronic structure programs, contrary to those of the spin-coupled ones. In nonadiabatic trajectory calculations, however, the spin-diabatic approach presents two drawbacks. One is a lack of rotational invariance, due to the fact that the spin-diabatic basis is defined with reference to a fixed spin quantization axis [34]. This artifact is often eliminated by reducing each spin-multiplet to one (rotationally invariant) state that interacts through SOC with the other multiplets. However, the reduction can be rigorously performed only in simple cases (for instance, one triplet and one singlet state) [34]. Another problem arises when the SOC’s are large (heavy atoms), because then the spin-diabatic PES’s do not represent accurately the energetics of the molecule. For instance, in photodissociations generating atomic fragments both mean-field

and surface hopping methods do not treat properly the spin-orbit split multiplets, and may even predict dissociation in energetically non-accessible states. Both issues, rotational invariance and state energies, are correctly dealt with in the spin-adiabatic representation. In the PES-fitting strategy, once the SOC-free PES's and the SOC's have been represented by analytic functions, one can build the full Hamiltonian matrix and obtain its eigenvalues (the spin-adiabatic PES's), their gradients and the SOC-induced derivative couplings. As already noted, most quantum chemistry packages do not compute the derivatives of SOC matrix elements, with rare exceptions [33], so a fully direct spin-adiabatic approach is seldom feasible.

The choice of the basis, adiabatic or (quasi-)diabatic, also affects the numerical problem of integrating the TDSE, either in the full quantum version, eq. (3), or in the purely electronic one, eq. (13). We shall not examine the plethora of algorithms that have been devised to propagate the wavefunction by fixed or variable time steps  $\Delta t$  [215]. In the trajectory based methods we have two integrators, one for Newton's equations and one for the electronic TDSE. It is a common experience that the latter problem is often more exacting than the former [216–220]. Whatever the algorithm, the faster and the more unpredictable is the variation of the Hamiltonian matrix elements (PES's and couplings), the smaller must be  $\Delta t$  to guarantee an accurate integration. Particularly troublesome for trajectory methods are the sharp peaks in the DNAC's that occur in the proximity of conical intersections, and most frequently when two states of different nature (spin symmetry or localization of charge/excitation) are weakly coupled. In such cases  $\Delta t$  must be sufficiently shorter than the time width of the peak of the coupling  $\langle \psi_k | d/dt | \psi_l \rangle$  that appears in eq. (15), otherwise the peak itself may be completely ignored or its height severely underestimated [51,201,218,219]. A smaller time step of course means a heavier computational burden, especially when running on the fly dynamics, because the number of steps is inversely proportional to  $\Delta t$ . In large molecules with many electronic states involved in nonadiabatic processes [218] such weakly avoided crossing situations are quite likely to occur. In these cases a (quasi-)diabatic representation might be preferable because it would allow to integrate the TDSE with a sufficient accuracy for a smaller computational effort. Unfortunately it is not easy to perform a general diabatization for many states in complex molecules, especially within the direct dynamics approach.

A partial solution of the TDSE integration problem in difficult cases is to use two different time steps: the trajectory is propagated by one larger step, which is then divided into several smaller steps by interpolating the molecular geometry, and the TDSE is solved with the finer grid [218,220]. This procedure



is computationally convenient only provided the calculation of DNAC’s is fast as compared with those needed for the trajectory integration, i.e. the PES gradient and, for some algorithms, also its Hessian. In fact, the DNAC’s must be computed at each small time step, to resolve even the narrowest peaks. A different strategy consists in performing a “local” diabaticization [27, 219], which is specific for each trajectory and does not aim to eliminate all DNAC’s, but only the time-derivative coupling terms  $\langle \psi_k | d/dt | \psi_l \rangle = \dot{\mathbf{Q}}^t \mathbf{G}_{kl}$ . To this purpose it is sufficient to compute the overlap of the adiabatic states at the initial and final points of the time step,  $\langle \psi_k(t) | \psi_l(t + \Delta t) \rangle$ . The overlaps provide information about the overall change of the wavefunctions across the time step, so a state switch is never overlooked [51]. The propagation algorithm based on the local diabaticization [27] proved to be much more stable than the DNAC based ones when increasing the time step, in tests on charge and excitation transfer dynamics [219].

### 3 The electronic structure problem.

Both in the PES-fitting and in the direct approaches the choice of the quantum chemistry method for solving the electronic structure problem is crucial. Accuracy versus computational burden is the most obvious requirement, and it concerns the PES’s of ground and excited states, as well as their wavefunctions, on which all couplings depend (DNAC’s, SOC’s and field-molecule interactions). As we shall see, the consistency between PES and wavefunctions is also an important issue. These and other requirements will be discussed in this section with reference to the most used quantum chemistry methods.

The fitting or interpolation of the PES’s and couplings in principle requires electronic structure calculations at an  $N_C$ -dimensional mesh of geometries, where  $N_C$  is the number of internal coordinates (possibly reduced with respect to the real system, to run model simulations). The computational burden therefore increases exponentially with  $N_C$ . Using approximate potentials, such as harmonic stretching or bending terms for bonds not involved in reactive processes, may reduce the number of electronic structure calculations. The simplification is most effective if minima, transition states and possibly also Minimum Energy Pathways (MEP) can be located, which requires the determination of gradients and Hessians. In the presence of PES crossings, effective Hamiltonians in the diabatic representation must be set up, as discussed in section 2.4. Simplified quadratic models have been proposed also for conical intersections [207] and can be used to fit quantum chemistry data,

usually after locating the minimum of the PES crossing seam with ad hoc algorithms [221–224].

As already discussed in section 2, with direct approaches the number of electronic structure calculations depends primarily on the simulation time  $T_S$  and, for trajectory methods, is also proportional to the number of trajectories. In principle, no preliminary characterization of the PES’s is needed, but the time propagation requires the knowledge of the PES gradients and possibly also of the Hessians, depending on the integrator. Moreover, one needs the inter-state couplings, i.e. DNAC’s, SOC’s, time-derivative matrix elements  $\langle \psi_k | d/dt | \psi_l \rangle = \dot{\mathbf{Q}}^t \mathbf{G}_{kl}$  or wavefunction overlaps  $\langle \psi_k(t) | \psi_l(t + \Delta t) \rangle$ . These requirements restrict the choice of viable quantum chemistry methods, in somewhat different ways for the PES-fitting and the direct approaches.

### 3.1 Ab initio methods.

Configuration mixing frequently characterizes excited states, particularly in the case of PES crossings, and also in the intermediate phases of many reactive processes, either thermal or photochemical. Configuration Interaction (CI) based methods are therefore the standard choice. Most often the molecular orbitals (MO) are determined by a Multi Configurational SCF (MCSCF) calculation, and more specifically by the Complete Active Space variant of MCSCF, i.e. CASSCF [12, 225, 226]. Running a separate “state specific” calculation for each electronic state (SS-MCSCF or SS-CASSCF) is often not possible because of convergence problems for the higher states, and would also complicate the determination of transition matrix elements (couplings and other properties) due to the non orthogonality of MO’s and states. For this reason, “state average” calculations (SA-MCSCF or SA-CASSCF) are usually run, whereby the average of the energies of all states of interest is variationally minimized. The optimization of an MCSCF wavefunction is a non-linear problem with many solutions, i.e. local minima of the energy in the space of the MO coefficients [227–229]. It is not easy to guarantee convergence to the global minimum, or to continuously connected minima for different molecular geometries, especially when the CAS space is replaced by reduced subspaces such as RAS or ORMAS [229] to decrease the computational burden. As a consequence, the PES’s as well as all other electronic matrix elements may show discontinuities as functions of the nuclear coordinates. When using state averaging, a further source for sudden changes in the MCSCF solution upon geometry variation is the possibility of root switchings that modify the subset of states to be optimized [66, 230]. As far as such discontinuities are small enough

and connect two physically acceptable solutions, they can be smoothed out in PES-fitting procedures. The problem is more serious when running direct dynamics, because it leads to numerical integration errors. Correction algorithms can be applied in combination with standard trajectory integrators [231].

MCSCF or CASSCF do not yield accurate results for excitation energies and in general for states or geometries that differ as to the dynamic correlation [12, 225, 226]. This drawback is normally more serious for small configuration subspaces, but the convergence towards a full CI result may be slow and computationally costly. Valid alternatives are the multi-reference CI (MR-CI) treatments using CASSCF zeroth-order wavefunctions, that can be either variational (MR-CI) [12, 225] or based on perturbation theory (CASPT2 [232], NEV-PT [233]). In all variational methods the PES's are simply related to the wavefunctions by  $U_k(\mathbf{Q}) = \langle \psi_k | \hat{\mathcal{H}}_{el} | \psi_k \rangle$ , which guarantees their mutual consistency. This means, for instance, that the DNAC's diverge or take large values at conical intersections or weakly avoided PES crossings, and in section 2.4 we have already stressed the importance of this coincidence for the nonadiabatic dynamics. With exact eigenfunctions, this is guaranteed by the Hellmann-Feynman formula

$$G_{kl}^{(r)}(\mathbf{Q}) = \left\langle \psi_k \left| \frac{\partial \hat{\mathcal{H}}_{el}}{\partial Q_r} \right| \psi_l \right\rangle (U_l - U_k)^{-1} \quad (23)$$

For CI or MCSCF wavefunctions the contribution to  $G_{kl}^{(r)}(\mathbf{Q})$  due to the CI coefficient derivatives takes an analogous form:

$$G_{kl}^{(r,CI)}(\mathbf{Q}) = (\mathbf{C}_k^{(CI)})^t \frac{\partial \mathbf{H}^{(CI)}}{\partial Q_r} \mathbf{C}_l^{(CI)} (U_l - U_k)^{-1} \quad (24)$$

where  $\mathbf{C}_k^{(CI)}$  is an eigenvector of the CI matrix  $\mathbf{H}^{(CI)}$ . Such consistency may be lost when applying theoretically or empirically based corrections to the PES's, without adapting the wavefunctions accordingly. This is why in nonadiabatic dynamics single state perturbative CI methods cannot be applied, but rather one needs multi-state treatments based on effective Hamiltonian perturbation theory [232–234], possibly coupled with diabaticization procedures [181].

Large scale post-CASSCF methods are seldom applied in direct dynamics, because of their computational cost and because not all quantum chemistry packages support the calculation of PES gradients and DNAC's [203, 204] at these levels of theory (see however some examples of simulations on small systems [235–237]). They are instead routinely used to compute data for use in PES-fitting procedures. The MCSCF based methods are rivaled by Valence

Bond (VB) approaches [238], that span essentially the same applicability range and can also be complemented by perturbation corrections [239]. The ab initio VB methods are not frequently used in dynamics, although the VB wavefunctions lend themselves to a more direct analysis of the electronic structure and are a good starting point for the determination of diabatic states. Altogether, direct simulations with high quality ab initio methods are still rather limited as to propagation times and size of the molecular systems that can be treated (see Table 1). Also the number of trajectories in surface hopping calculations is usually kept in the order of some tens, which corresponds to a rather poor sampling of initial conditions.

### 3.2 Density Functional Theory.

A valid alternative to ab initio methods in computing excited state properties is provided by time-dependent Density Functional Theory (TD-DFT) [240]. In the usually applied linear response version, TD-DFT can be assimilated to single excitation CI (CIS), but yields much better excitation energies. In many cases, the accuracy of results obtained by combining ground state DFT and TD-DFT is at the level of the best ab initio methods, with a much smaller computational effort, especially for large systems. However, the method fails in some typical situations that are particularly important in excited state dynamics. A well known artifact is the underestimation of the energy of charge transfer states, that can be partially corrected by modifying the long range behavior of the exchange potential [241] and/or by switching to second order response TD-DFT [242]. Also very effective in this respect is the application of many body Green's function theory to compute excited states [243]. A more fundamental problem is the single determinant character of standard DFT, that may be inadequate at geometries where the first TD-DFT state is lower in energy than the DFT ground state, or close to it [223]. Moreover, TD-DFT fails in reproducing the double cone shape of the PES's at a CoIn between ground and excited states. In several cases one (instead of two) degeneracy lifting coordinate is found [223, 244, 245]. This fact is connected with the limitations to single determinant density for the Kohn-Sham ground state and linear response for the TD-DFT treatment (HF+CIS produces the same crossing seam topology, because of Brillouin's theorem). Such a drawback may seriously affect the prediction of  $S_1 \rightarrow S_0$  decay rates, while the transitions between excited states should be correctly dealt with. An interesting comparison of ab initio, TD-DFT and semiempirical direct dynamics was provided by Barbatti *et al* [246], who simulated the decay of the  $S_1$  state of 9H-adenine with several methods.

The determination of DNAC’s in TD-DFT is less direct than in wavefunction based methods [88, 195, 197–200]. A wavefunction ansatz is applied, whereby the ground state is represented by the Kohn-Sham determinant and the excited states in the form of a CIS, using either the Kohn-Sham virtual orbitals or one linear response orbital for each of the occupied ones. The latter choice allows to apply density functional perturbation theory to compute the DNAC’s analytically. An alternative is to use finite differences in the time variable to compute the  $\langle \psi_k | d/dt | \psi_l \rangle$  couplings [247]. Recently an approach that avoids the explicit construction of wavefunctions has been proposed [202]. The calculation of second derivative matrix elements has also been implemented [205]. De Carvalho *et al* have derived Breit-Pauli SOC matrix elements within the TD-DFT formalism [248]. TD-DFT has found numerous applications in direct dynamics simulations, of which we quote just a few [170, 247, 249–251].

The single determinant limitation is somewhat relieved by the Restricted Open Kohn-Sham (ROKS) approach, whereby the energy corresponding to a singlet configuration  $\Phi_1$  with two unpaired electrons can be minimized [252]. While  $\Phi_1$  and the Kohn-Sham closed shell determinant  $\Phi_0$  are generally non-orthogonal, two orthogonal eigenstates can be obtained by diagonalizing an effective Hamiltonian in the  $\{\Phi_0, \Phi_1\}$  basis [194]. A rather arbitrary ansatz about the off-diagonal element is needed in order to build the 2x2 Hamiltonian matrix. This approach guarantees the correct topology of  $S_0/S_1$  CoIn’s, and both energy gradients and DNAC’s can be computed analytically. In the present formulation it is limited to the first two singlet states, but has been used in several simulations involving fairly large systems [253–257].

Fully multi-reference DFT approaches have also been proposed. For instance, Grimme’s DFT/MRCI method exploits information from a DFT calculation to build an effective CI matrix with a set of empirical rules and parameters [258]. For this method (as for TD-DFT), SOC matrix elements are available [214], but no analytical energy gradients nor DNAC’s have been implemented. A more recent proposal is to use information from constrained DFT (C-DFT) calculations to set up the effective CI matrix (C-DFT-CI) [244, 245]. In C-DFT, the molecule is partitioned into fragments, and the density is optimized by imposing constraints on the total charge and spin of each fragment. By using different localization criteria, C-DFT can directly produce a set of quasi-adiabatic states, that are approximately identified with the respective Kohn-Sham determinants  $\Phi_I$ . The adiabatic states are obtained by diagonalization of the the effective CI Hamiltonian in the  $\Phi_I$  basis (notice that the computational route goes from diabatic to adiabatic states, so is just opposite to the usual one, discussed in section 2.4). The multireference DFT methods here discussed

are based on approximations that must be computationally validated, but the PES's they yield are eigenvalues of an hermitian effective Hamiltonian, so they exhibit the correct crossing topology [244, 245]. The analytic gradients of the C-DFT-CI energies have been implemented [245], so this method is suitable for direct dynamics. Its main limitation is probably the need to identify a priori an adequate diabatic representation and the associated constraints, which is straightforward in many charge or energy transfer problems, but not always so for one-chromophore valence excitations.

### 3.3 Semiempirical methods.

Semiempirical methods are faster than both *ab initio* and DFT, so they are a popular choice for direct dynamics simulations. They rely on simplifications of the electronic Hamiltonian, among which the removal of the core electrons and a set of drastic approximations as to how to compute the one- and two-electron integrals. Given this starting point, no refinement of the semiempirical technology can guarantee accuracy without a validation against *ab initio* or experimental data. Standard semiempirical methods [259] were devised to treat ground state molecules near their equilibrium geometries, so they cannot be used as such in nonadiabatic dynamics. Semiempirical treatments of excited states have been usually limited to single excitation CI (CIS), as in the case of ZINDO/S [260]. While ZINDO/S yields reasonable excitation energies near ground state minima, it shares the drawbacks already discussed for *ab initio* CIS or linear response TD-DFT as to the description of photochemical pathways: namely, it cannot correct for the monoconfigurational description of the ground state and it cannot represent correctly the crossing seams involving the ground state.

As in the *ab initio* realm, a CI with higher order excitations or a VB approach are needed for nonadiabatic dynamics. The latter was proposed by Bernardi, Olivucci and Robb [261] with the acronym MM-VB (Molecular Mechanics with Valence Bond) as a tool for modeling MC-SCF results. A wavefunction composed of one or more VB structures represents the bonds that undergo major changes in the chemical process under investigation (reactive center), while other parts of the molecule are described by a force field. The semiempirical Hamiltonian depends on a set of parameters that must be determined by fitting *ab initio* results. The force field parameters can be taken from standard Molecular Mechanics models [262], with the exception of those pertaining to atoms at the boundary with the reaction center, that must be adapted to the specific molecular system. Overall, the parameterization of multi-state

MM-VB is rather demanding, but a certain degree of transferability among homologous molecules is observed [263,264]. The applications of MM-VB to nonadiabatic dynamics [69,70,265,266] are rightly presented as pertaining to the direct approach, since electronic wavefunctions are computed as eigenfunctions of a (simplified) Hamiltonian. However, MM-VB can also be seen as an elaborated and potentially very accurate fitting procedure for ab initio results.

The FOMO-CI approach set up by our group [26–29] is more in line with the traditional semiempirical methods based on the neglect of differential overlap (NDO) [259]. To cope with the needs of excited state dynamics, we introduced some modifications with respect to the standard NDO practice. One is that the MO’s  $\phi_i$  are computed by floating occupation SCF, a pseudo-closed shell SCF where the density matrix is defined in terms of fractional occupation numbers  $n_i$ :

$$\rho(\vec{r}) = \sum_i n_i \phi_i^2 \quad (25)$$

The occupation numbers depend on the orbital energies  $\varepsilon_i$  as

$$n_i = 2 \int_{-\infty}^{\varepsilon_f} g(\varepsilon - \varepsilon_i) d\varepsilon \quad (26)$$

where  $g(x)$  is a bell-shaped function (usually a gaussian) normalized to 1, and the Fermi energy  $\varepsilon_f$  is determined by the requirement that the  $n_i$  sum up to the number of electrons. This method correctly describes homolytic bond breaking at MO level, even in the case of several photofragmentation channels [179,267], a problem that may be hard to tackle with SA-CASSCF. Moreover, it ensures a balanced treatment of degenerate orbitals, which is important for instance in the case of atomic or diatomic photofragments or in transition metal complexes. The SCF calculation is followed by a CI, with a number of configurations and a MO active space as small as possible but such as to ensure a correct treatment of the static correlation. In practice, FOMO-CI can be seen as a cheap substitute of SA-CASSCF, quite suitable in a semiempirical context but applicable also to ab initio calculations [268–270]. With respect to SA-CASSCF, FOMO-CI has the advantage that the results do not depend on the subspace of states that are optimized, and therefore is not prone to the root switching problem [230] discussed in section 3.1.

A reparameterization of the semiempirical Hamiltonian is needed also in the case of FOMO-CI, because most of the parameter sets in use (MNDO, AM1, PMn and the like [259]) have been optimized for restricted HF wavefunctions to represent ground state properties. However, standard parameter sets provide good starting points and in most cases do not need to be fully reop-

timized. The reparameterization can take into account both ab initio and experimental values concerning energy differences, stationary geometries, vibrational frequencies and wavefunction related properties. The optimization of the parameter set  $\mathbf{P}$  is performed by minimizing the weighted sum  $S(\mathbf{P})$  of squared differences between the semiempirically computed values and the target ones. Simplex minimization combined with simulated annealing and genetic algorithms have been employed to this aim [35, 271], because of the lack of analytic derivatives of  $S$  with respect to the  $\mathbf{P}$ 's and in order to explore multiple minima of  $S$  to improve the final results.

We list here the main features of the FOMO-CI direct dynamics, as it is implemented in a development version of the MOPAC 2002 package [272]. Items already discussed in this or other sections are very briefly summarized:

- (1) Surface hopping dynamics with “energy-based” [31] or “overlap-based” [32, 36, 37] quantum decoherence corrections. Of course the FOMO-CI electronic structure method can be coupled with other approaches to non-adiabatic dynamics, for instance FMS [116, 273].
- (2) Reparameterized NDO Hamiltonians.
- (3) Floating occupation SCF MO's and CI state energies and wavefunctions [26, 27].
- (4) Possibility of using different parameter sets in the SCF and CI calculations. While the CI parameters affect more directly the PES's and wavefunctions, the SCF parameters can be used to control the composition of the MO active space, for instance to prevent it to change suddenly in response to geometry variations [35].
- (5) Mixed Quantum Mechanics/Molecular Mechanics (QM/MM) method with electrostatic embedding and possibly covalent bonding between the QM and MM subsystems (see section 3.4).
- (6) Analytic gradients for CI states through Coupled Perturbed Hartree-Fock extended to the FOMO case, with the Z-vector technique (see appendices in Ciminelli *et al* [30] and in Cusati *et al* [35]). With this implementation the computational cost is practically independent on the number of coordinates, which is particularly important in QM/MM simulations.
- (7) Efficient algorithm for computing CI wavefunction overlaps at nearby geometries or subsequent time steps in a trajectory  $\langle \psi_k(t) | \psi_l(t + \Delta t) \rangle$ , needed for the local diabatization solution of the TDSE [27] (see section 2.4).
- (8) Simultaneous treatment of dynamic and spin-orbit couplings [34], with analytic gradients of the spin-adiabatic PES's [33] (see section 2.4).
- (9) Explicit interaction with electromagnetic fields of arbitrary shape [37].
- (10) State-specific corrections to the PES's. For each spin-manifold, the same



additive correction can be applied to all states, in the form of a function of the internal coordinates  $\Delta U(\mathbf{Q})$ . Moreover, the energy of each state can be modified with respect to the preceding one by multiplying the  $U_k - U_{k-1}$  energy difference by a positive scaling factor  $F_k(\mathbf{Q})$ . These corrections leave unchanged the position of the crossing seams, which is a necessary condition to guarantee the consistency with the computed wavefunctions, i.e. with the DNAC's. However, the energy and the optimized geometry of a CoIn can be modified [35].

The FOMO-CI method has been applied to direct dynamics simulations of a variety of molecular systems and nonadiabatic processes: photofragmentation of small molecules [155,179,267], photoisomerization of isolated molecules [116, 180,274], solutes [7,36], adsorbates [275] and supramolecular systems [16,17,30], and chemiluminescent reactions [276].

A similar method has been put forward and applied to several problems in organic photochemistry by Thiel and coworkers [216,217,246,277–282]. We list here the main features that distinguish Thiel's approach from the FOMO-CI direct dynamics. In the first place, they make use of the OM2 semiempirical Hamiltonian, without ad hoc reparameterizations nor floating occupation SCF MO's. CI energies and wavefunctions are determined by the unitary group technique (GUGA). The DNAC's are computed by the Z-vector technique [283], and usually only the variation of the CI coefficients, eq. (24), is taken into account, while the MO contribution is neglected [216]. A finite differences approximation of the time-derivative couplings can also be used. Finally, the integration of the TDSE is performed with very small time steps, by interpolating the electronic energies and the DNAC's along each nuclear trajectory step. Most of the features that characterize either the FOMO-CI or the OM2 based direct dynamics are compatible with both approaches, so mixed variants could be easily implemented if required by specific problems.

### 3.4 Environmental effects.

In most photochemical and photophysical processes the electronic excitation, the nonadiabatic dynamics and the chemical changes are localized in one or few molecules. Chromophores and reactive centers must be described by quantum chemistry methods, so they will be indicated as the QM (sub)system. If a chemical environment is present, it may deeply affect the dynamics. By chemical environment we mean any medium that does interact with the QM subsystem without undergoing electronic excitation nor chemical change, such

as a solvent, a polymer or biological matrix, or an adsorbing surface.

The environmental effects can be classified as “static” or “dynamic” [15]. The former refer to modifications of the PES, as functions of the QM nuclear coordinates, due to the interactions with the medium. A quantitative description of the static effects may be based on a full optimization of the medium coordinates, which is however complicated and only partially representative of the physical reality because of the existence of multiple minima. A more comprehensive definition involves a thermal averaging over the medium coordinates, as for instance in the Averaged Solvent Electrostatic Potential (ASEP) method [284]. The simplest way to characterize the static effects of a medium is to treat it as a continuum with macroscopically defined response properties, such as the dielectric constant or the refraction index. This is the gist of the Polarizable Continuum Model (PCM), that allows to produce free energy potential surfaces and to separate the slow and fast response of the medium [285–289]. Of course, the excited state dynamics can be affected by any modification of the PES’s, among which particularly important are those due to electrostatic interactions with the medium in systems that undergo electron or proton transfer. Especially relevant for the nonadiabatic transitions are changes in the energy gaps between electronic states and in the accessibility of crossing seams [190, 207, 288].

The medium does not equilibrate instantaneously in response to fast geometry changes and electronic transitions of the QM part [286–288]. This fact, combined with the thermal fluctuations of the environment, results in instantaneous interactions that depart from the mean values corresponding to the statically modified PES’s as defined above. Such “dynamic” interactions affect both the nuclear and the nonadiabatic dynamics. Typically, reacting moieties that move fast in photodissociations or isomerizations are hindered by the surrounding environment (“caging”) and may even bounce back; fast charge rearrangements (electron or proton transfers) may be energetically destabilized because the medium does not relax dielectrically in comparably short times (“dielectric friction”). One ubiquitous consequence is the energy transfer from the excited chromophores to the medium or, to a lesser extent, the other way around. In this field, Langevin type models play a role similar to the continuum ones for static medium effects, and are very useful to understand and to predict semiquantitatively the condensed state photodynamics [209, 290, 291]. However, only an atomistic description of the chemical environment is able to describe accurately both static and dynamic effects without introducing empirical parameters.

In most cases the “environment” is the larger portion of the system and cannot

be treated at the same level as the QM subsystem in the electronic structure calculations. Layered approaches are applied to reduce the computational effort while describing accurately the QM part, possibly further partitioning the environment into subsystems according to their relevance as to the processes of interest. The “outer layers” will be described by hierarchically less accurate methods, and continuum models may be used to account for long range electrostatic interactions [289, 292]. The simplest hybrid approach and the most frequently applied in nonadiabatic dynamics is the QM/MM one, where the whole environment is described by a Molecular Mechanics force field (MM subsystem). Recent reviews [293–295] and many specific applications [7, 28, 29, 35, 53, 250, 251] are available, and we refer to them for all technical details. The QM/MM Hamiltonian is partitioned into three terms:

$$\hat{\mathcal{H}}_{tot} = \hat{\mathcal{H}}_{QM}(\mathbf{q}_{QM}, \mathbf{Q}_{QM}) + \hat{\mathcal{H}}_{MM}(\mathbf{Q}_{MM}) + \hat{\mathcal{H}}_{QM/MM}(\mathbf{q}_{QM}, \mathbf{Q}_{QM}, \mathbf{Q}_{MM}) \quad (27)$$

Here the suffixes *QM* and *MM* are the acronyms of the two subsystems and label the nuclear and electronic coordinates  $\mathbf{Q}$  and  $\mathbf{q}$ , and the three Hamiltonian terms.  $\hat{\mathcal{H}}_{QM}$  is the electronic Hamiltonian for the isolated QM subsystem and  $\hat{\mathcal{H}}_{MM}$  is the force field function that describes the environment. Different QM/MM methods are essentially characterized by the definition and role of  $\hat{\mathcal{H}}_{QM/MM}$ , that contains the interactions between the two subsystems.

In some of the earliest simulations of nonadiabatic dynamics of polyatomics in condensed phase [133]  $\hat{\mathcal{H}}_{QM/MM}$  was defined as a mere function of the  $\mathbf{Q}_{QM}$  and  $\mathbf{Q}_{MM}$  coordinates, which amounts to describing also the QM-MM interactions by a force field. As a consequence, the adiabatic wavefunctions  $\psi_k$  are (approximate) eigenfunctions of  $\hat{\mathcal{H}}_{QM}$ , as in the isolated QM subsystem. This is acceptable only when the mutual polarization of the two subsystems can be neglected and it is not necessary to consider state-specific static effects of the medium, such as solvent spectral shifts.

In order to acknowledge the influence of the environment on the QM wavefunctions,  $\hat{\mathcal{H}}_{QM/MM}$  must contain the individual Coulomb potentials between the QM nuclei and electrons and the MM atomic charges, so it also depends on  $\mathbf{q}_{QM}$ . While the dispersion and repulsion terms remain mere functions of  $\mathbf{Q}_{QM}$  and  $\mathbf{Q}_{MM}$ , the electrostatic term is added to  $\hat{\mathcal{H}}_{QM}$  and contributes to the determination of the wavefunctions  $\psi_k$ . The static environmental effects are therefore accounted for in a state-specific way. In this case, the analytic representation of crossing PES’s would be inextricably complicated without resorting to the diabatic representation. In fact, each diabatic state, with its typical charge distribution and polarizability, can be “dressed” with specific QM-MM interactions; i.e., the  $\langle \eta_k | \hat{\mathcal{H}}_{QM} | \eta_l \rangle$  matrix elements can be modi-

fied by the addition of QM-MM terms smoothly dependent on the  $\mathbf{Q}_{QM}$  and  $\mathbf{Q}_{MM}$  coordinates [293, 296]. The application of direct approaches is simpler and does not require a diabaticization procedure. Among the semiempirical electronic structure methods (see section 3.3), MMVB is by construction of QM/MM type, but also FOMO-CI and OM2 have been coupled with force fields to run simulations of complex systems [7, 16, 17, 28, 29, 35, 280]. Covalent bonding across the QM to MM boundary is allowed for by defining special atom types [29, 297].

## 4 Simulation outcomes and typical applications.

The ultimate goal of simulations is predictiveness [86], which in the present context means to be able to compute quantum yields, energy disposal and transient spectra, to describe reaction and decay mechanisms, and to correlate structure and reactivity. However, the unavoidable approximations done in solving the electronic structure and the dynamic problems, and the computational restrictions as to propagation times and system size, limit the ability of simulations to provide reliable predictions. In most cases, the winning strategy is a combination of experiment, theory and calculation. To this aim, it is important to simulate the very observables that are measured: for instance, one should be able to predict the spectroscopic transient signals as functions of time, in addition to the excited state populations. In fact the latter are not observables, and are related to the measured transients, but not always in a simple way, especially when different processes (such as geometrical relaxation, IVR, nonadiabatic decay) compete on the same time scale. When the simulation, on the basis of a theoretical model, yields the relevant observables, it can be validated by comparison with the experimental data. Conversely, the simulations can provide a detailed interpretation of transient spectra and other instrumental outputs; in other words, they can tell us what molecular response property has been really measured.

Final process outcomes include product branching ratios i.e. quantum yields, energy disposal distributions and vector correlations (see Persico *et al* [152] for an example). Such data are easily extracted from wavepacket or trajectory simulation results, with computational recipes similar to those in use for ground state simulations [156, 298]. Adopting direct or PES-fitting approaches in this context does not make a difference, save that in the latter case one can run more trajectories or wavepacket propagations in order to achieve a

better statistics (see section 4.3), without proportionally increasing the computational cost. Therefore, we shall not elaborate further on this issue and we shall rather concentrate on transient spectroscopic data.

## 4.1 Transient spectroscopy.

In QWD and in mean-field methods all the time-dependent properties, including the probe spectroscopic signals, are computed using the wavefunctions univocally defined by eqs. (1) and (14), respectively. On the contrary, in TSH one can choose between two alternatives, namely the wavefunction of the current state or the solution of the TDSE, eq. (14), as in the mean-field case. The former option is the standard one [106,107], but a combination of the two wavefunctions has been shown to yield better results at least in charge transfer problems [111]. Note that the introduction of decoherence corrections reduces the difference between the results obtained with the two options.

Several spectroscopic techniques rely on electronic transitions, although also time-resolved infrared absorption is exploited to monitor vibrational energy redistribution after electronic excitation and charge or energy transfer. We shall briefly review fluorescence (that may be upconverted to achieve femtosecond resolution), resonant Raman scattering, differential absorption and photoelectron spectroscopy. The computational difficulties in simulating the signals associated with these techniques increase in the same order as in the above list. To compute fluorescence transient spectra, one needs the transition energies and moments (usually dipoles) between the state on which the wavepacket or trajectory swarm is running, and the lower lying ones. Since usually all of these states are accessible by nonadiabatic transitions, it is anyway necessary to compute them, and the simulation of the fluorescence transient does not increase the computational burden. Also the resonant Raman spectroscopy deals with electronic levels lying within the energy of the exciting photon, but requires a quantum treatment of the vibrational modes [46], whereas the ultrafast fluorescence transients are usually featureless and can be reasonably well simulated by trajectory methods.

The differential absorption spectroscopy is a pump-and-probe method involving transitions to higher lying states (as well as to lower ones, by stimulated emission), which are often more difficult to determine, as they require more refined levels of computational theory and extended basis sets. In a typical case, the *cis*  $\rightarrow$  *trans* photoisomerization dynamics of rhodopsin was monitored by recording transient absorption spectra, and the latter were quite well

reproduced by on the fly SH simulations with SA-CASSCF electronic structure calculations; to compute the spectra, the SA-CASSCF transition energies were rescaled to match CASPT2 data [299]. Further examples of transient absorption and emission spectra, computed by surface hopping simulations, are found in our previous work on azobenzene [7,180,300] and in recent simulations of the photoisomerizations of furylfulgides [281,282]. The case of azobenzene illustrates what differences can arise in the lifetimes extracted from time-dependent excited state populations, versus those associated with spectroscopic transients of the different types, either experimental or simulated. For instance, a typical behavior shared by azobenzene and by other chromophores with short lived excited states, is that the fluorescence decays faster than the population, especially at the short wavelength end of the emission spectrum, due to the wavepacket motion towards lower regions of the excited PES and to the third power dependence of the emission rate on the frequency [7].

The simulation of photoelectron spectroscopy is even more exacting. In order to predict the intensity of the photoelectron signal as a function of the photon and of the ejected electron energies, one needs to determine the energy differences between electronic states of the neutral molecule and of the cation, and the associated photoionization cross sections. Precious information about the nature of the starting electronic state can be obtained by measuring the angular distribution of the photoelectrons, but the simulation of such features requires an additional computational effort [170,301,302]. Examples of simplified approaches are illustrated by a trajectory SH simulation of ethylene photodynamics [303] and an AIMS study of acetone photodissociation [304].

In principle, the electronic properties needed for the spectral simulations discussed above (PES's, transition moments and so on) must be computed at all the geometries explored by the time-dependent wavepackets or classical trajectories. In PES-fitting methods this is a further complication, because additional electronic matrix elements, strongly dependent on the nature and accuracy of the electronic wavefunctions, must be represented as functions of the internal coordinates. The use of direct methods then appears to be the most straightforward choice. However, as far as the probing process can be considered a negligible perturbation [305], it may be convenient to decouple the nonadiabatic dynamics calculation and the simulation of the monitoring signal. This allows to perform the latter task with the most appropriate quantum chemistry techniques, for instance to compute spectra by *ab initio* methods even when the dynamics was based on semiempirical or fitted PES's, or to treat the photoionization by Dyson theory after running AIMS with CASSCF [304].

## 4.2 Dynamics descriptors.

While we emphasize that the simulations should yield results as close as possible to the experimental reality, it is also useful to describe the complex nonadiabatic dynamics, graphically and numerically, by parameters that are not necessarily physical observables [86]. Such descriptors allow to compare results obtained with different computational methods and to discuss the reaction and decay mechanisms with heuristic arguments. The already mentioned populations of the electronic states (adiabatic or diabatic, spin-coupled or not) are an example of non-observable descriptors, at whatever level of theory they are computed. To characterize the time evolution of the electronic properties it is often more interesting to monitor the population of the diabatic states, rather than the adiabatic ones [111]. In principle, any approximation that implies abandoning a rigorous quantum formulation of the dynamics, such as treating classically the electromagnetic field or the nuclear motion, cannot yield true observables. So, for instance, it is interesting to point out at what molecular geometries the nonadiabatic transitions do occur, although the non-locality of quantum mechanics would forbid to formulate this very concept (see the discussion on optimal spawning by Yang *et al* [52]). In practice, the successful use in AIMS of localized basis sets and of the saddle-point approximation, eqs. (11-12), indicates that one can reasonably determine “where” the population transfer takes place at each time step. In FMS/AIMS or vMCG calculations, any quantification of descriptors involving single basis functions, or pairs of them, requires to perform a sort of Löwdin or Mulliken population analysis on the time dependent wavepacket [116,306]. In surface hopping it is straightforward to monitor the geometries where hops occur. In conclusion, we note that the interpretation of trajectory simulation results may be deceptively easy, but is usually justified as far as the computed observables are in good agreement with experiment or QWD.

## 4.3 Examples of applications.

In order to provide an overview of the capabilities of different methods, in Table 1 we list the main features of some selected simulations. For QM/MM calculations, the numbers of QM and MM atoms are entered separately. Whenever the dynamics is limited to a subset of all the nuclear coordinates, the number of active modes is given. We verify that trajectory methods can treat larger systems and longer simulation times than QWD. It is easier to scale up the number of atoms with direct methods, because PES fitting with many coor-

dinates is increasingly costly and complicated, unless the largest portion of the system can be treated with very simple force fields (e.g., rare gas clusters). On the other hand, the PES-fitting approach is more convenient for long simulation times.

More difficult is to assess the accuracy of the calculations. The quality of the PES’s and of the electronic wavefunctions is a prerequisite. When the relevant experimental or quantum chemistry data are available and reliable, PES-fitting can be very accurate. As noted in sections 3.1 and 3.2, the ab initio methods that are applied in direct simulations are often below the top level for practical reasons. However, the use of reparameterized semiempirical Hamiltonians and of state-specific corrections (see section 3.3) can yield accurate PES’s for rather large molecules.

As to the simulation approaches, MCTDH calculations, if well converged, are usually taken as benchmarks to validate all other methods. The accuracy of vMCG and AIMS/FMS simulations depends on a set of options and parameters that affect the convergence of the expansion. The latter is usually harder to achieve in all QWD methods, the longer is the propagation time, as discussed in section 2.1. Classical trajectory methods have some fundamental drawbacks, that can be only partially circumvented by an appropriate sampling of the initial conditions, plus quantum decoherence corrections and other ad hoc options (see section 2.2). The thoroughness of the IC sampling and the proper working of the SH stochastic algorithm require a large number of trajectories  $N_T$ , which is also listed in Table 1. In the same column we also report the number of QWD runs  $N_R$ , that may be more than one when a canonical or microcanonical distribution of IC’s is taken into account, or when the FMS/AIMS basis functions that span the initial wavepacket are propagated in a decoupled way (see section 2.1). The appropriate number of runs  $N_T$  or  $N_R$  very much depends on the kind of results sought for. For a binary choice, for instance the occurrence or not of a given reaction, one determines the probability (the quantum yield, in photochemistry) as the fraction  $\bar{\Phi}$  of trajectories undergoing that process. If  $\Phi$  is the theoretical probability and  $N_T$  the number of trajectories in one simulation, the statistical error (standard deviation) on  $\bar{\Phi}$  is

$$\Delta\bar{\Phi} = \sqrt{\frac{\Phi(1-\Phi)}{N_T}} \quad (28)$$

In SH simulations, both the sampling of the IC’s and the stochastic nonadiabatic trajectories do contribute to  $\Delta\bar{\Phi}$ ; the former is particularly important when the probability of the process is sharply dependent on the IC’s, for in-



stance because of total energy or initial conformation. In QWD simulations the time propagation is not stochastic, so the IC sampling alone determines  $\Delta\Phi$ . As an example, Toniolo *et al* [116] simulated the  $n \rightarrow \pi^*$  *trans*-azobenzene photodynamics by  $N_R = 20$  FMS runs; each run yielded a fractional photoisomerization probability, because it generated an average of about 17 basis functions (347 in total), traveling on the ground state PES either to the *cis* or to the *trans* isomer; we see therefore that the 20 FMS runs have the potentiality of representing a variety of final outcomes roughly equivalent to hundreds of trajectories. When the yield  $\Phi$  is small (rare events), the relative error is

$$\frac{\Delta\Phi}{\Phi} \simeq \frac{1}{\sqrt{N_T\Phi}} \quad (29)$$

An accurate determination of  $\Phi$  then requires a number of trajectories that increases in inverse proportion to  $\Phi$ . The determination of differential cross sections, transient spectra or energy disposal distributions obeys a similar rule, since it reduces to computing the probability of the occurrence of a given process within selected intervals of one or more measurable variables (energy, delay time, wavelength of adsorbed or emitted photons, etc); by requiring a good resolution, which amounts to reducing the widths of the intervals, what one monitors are inevitably rare events. As an example, the simulation of the very weak chemiluminescence emission generated by Al + H<sub>2</sub>O collisions required some 170000 trajectories.

In Table 1 we collected examples of many different simulated processes, all involving nonadiabatic transitions: they include photon adsorption and emission [7, 38, 46, 64, 276, 307], photoionization [170, 211], InterSystem Crossing [155, 308, 309], excitation energy transfer [310], exciton dissociation [311], ultrafast decay of nucleobases [312–315], hole or electron transfer [316–319], proton transfer [320, 321], anelastic and reactive scattering [276, 322], photoisomerization [116, 133, 179, 236, 237, 256, 320, 323, 324] and photodissociation [133, 155, 179, 325–330]. In practically all cases, excited state decay and geometrical relaxation are essential ingredients of the simulation. It must be clear that this is but a small sample of the recent production in this field: searching the topic “nonadiabatic dynamics” in the Web of Science database one finds about 2000 titles in the molecular physics and physical chemistry areas in the last 10 years.

## 5 Concluding remarks: mixing the direct and PES-fitting approaches and beyond.

In this paper we have reviewed state-of-the-art methods for the computational simulation of excited state dynamics, with focus on the methodological choice between two alternative strategies, here indicated as PES-fitting and direct, respectively. The former entails the preliminary determination and analytic representation of PES's and coupling matrix elements between electronic states, while in the latter such quantities are computed "on the fly" during the time propagation. The main advantage of the PES-fitting approach is that the computational burden of the simulation only consists in the integration of the dynamical equations, which makes it viable to simulate slow processes, to sample large sets of initial conditions, and to compare different methods and options for the dynamics. In particular, the knowledge of the PES's and couplings for all the relevant portions of the nuclear coordinate space allows to run quantum wavepacket dynamics with a minimum of numerical approximations. The direct approach dispenses with the preliminary work of computing and fitting the electronic structure data, which may be overly complicated in the frequent case of intersecting PES's, and extremely expensive for molecular systems with many internal coordinates. On the other hand, the cost of direct dynamics increases with the simulation time and with the number of simulation runs. The combined advantages and drawbacks of the two approaches shift the balance in favor of the direct one when simulating fast decay and/or reactive processes in complex molecular systems. The direct strategy is especially suited when a local knowledge of the electronic structure quantities is sufficiently adequate to predict the nonadiabatic dynamics, which is the ansatz underlying trajectory-based methods such as Surface Hopping.

The previous sections and in particular section 3 illustrate in detail the above considerations, but also show that the distinction between the PES-fitting and the direct approach is not so sharp. First of all, direct dynamics does not really dispense with a preliminary validation of the electronic structure approach. Even *ab initio* methods need a non trivial calibration (choice of basis set, orbital active space, etc) versus experimental data or computational results of higher accuracy, and more so the DFT based methods (choice of the exchange-correlation functional, representation of the excited states, etc). Semiempirical methods need reparameterization, which may be so extensive and targeted to a specific molecular system as to resemble an elaborated fitting procedure. In the second place, the PES's used in direct dynamics often contain additions and corrections in the form of simple functions of the nuclear coordinates. For

instance, the QM/MM methods are based on standard force fields to represent the MM subsystem, plus a variously parameterized term describing the interaction between the QM and MM subsystems. Another example are the state-specific corrections to the adiabatic PES's introduced by our group in the semiempirical context (see section 3.3), that can be also applied to ab initio PES's. The advantages of the PES-fitting and direct approaches can be combined by switching between the two during the integration of the dynamics, as shown by Thompson and Martínez in the framework of FMS [331]: the former is used in the regions of the PES's where the fitting is easier and more accurate, and the latter in the proximity of the PES crossings.

Running the dynamics by direct methods is a way to suitably sample the portions of the PES's relevant to the dynamic process of interest and to accumulate information about them, in order to switch to the PES-fitting approach in the "production" step. The GROW algorithm, originally proposed by Collins for adiabatic processes [332], combines the sampling along a swarm of trajectories with an efficient modified Shepard interpolation scheme, and allows to build an analytic PES as a function of the internuclear distances. Its extension to multi-state dynamics by nonadiabatic trajectories [333,334] or quantum wavepackets [335,336] relies on a quasi-diabatic representation of the electronic Hamiltonian. The diabatization can be "global", i.e. a general transformation valid for the whole internal coordinate space of interest [333–335], or "local", i.e. adapted to each PES crossing region [336]. A similar method, recently put forward by Zhu and Yarkony [337–339] represents the quasi-diabatic Hamiltonian matrix as a function of a redundant set of internal coordinates and focuses on the accurate representation of the crossing seams, by interpolating energy, gradient and DNAC data. The basic advantage of the GROW-like approaches is that the dynamics itself indicates which regions of the PES's must be represented by analytic functions, and the accuracy of the fitting is rigorously tested and improved as more data accumulate. After a sufficiently representative sampling, the interpolated PES's and couplings can be used to continue the simulation with a much smaller computational effort: for instance, one can run a larger number of trajectories to obtain a more reliable statistics, or switch to a more accurate method for the dynamics.

The approaches recalled or outlined in the last two paragraphs show that hybridizing the PES-fitting and direct strategies can extend the range of applicability of simulations and improve their accuracy. More drastic improvements are required to meet the challenge of multiscale phenomena. A host of important and complex photochemically initiated processes are of multiscale nature, both in the size of the system (many chromophores, strongly interacting

chemical environments) and in time: such are the workings of photosynthetic complexes, of visual pigments, of dye sensitized solar cells and of many photoresponsive materials. Several subprocesses exhibit overlapping time scales [15] and therefore must be simulated within the same general approach: the geometrical relaxation of excited molecules and the nonadiabatic decay can go from the femtosecond to the nanosecond time scale, vibrational energy transfer within a molecule and to the environment normally takes tens of picoseconds, while spin changing, electron transfer and excitation energy transfer can be much slower; finally, collective rearrangements, molecular diffusion and thermal reaction kinetics normally require times that are many orders of magnitude longer, but when these processes involve hot ground states their time scales may still overlap those of excited state dynamics. Encompassing several of these processes in the same simulation often requires methodological advances beyond the scope of this paper.

Several attempts have concentrated on switching in time from full fledged, atomistic, direct dynamics to standard Molecular Dynamics using force fields or even more simplified representations of the molecular reality. When the system has reverted to the ground state at not too distorted geometries, standard force fields are usually adequate, allowing to switch from a QM or QM/MM nonadiabatic trajectory to a fully MM adiabatic one; ad hoc procedures have been developed to deal with minor mismatches between the two PES's [340]. When many chromophores can be excited, simultaneously or sequentially, one may switch on the QM multistate description of single molecules for the appropriate time intervals, while the bulk of the system for most of the time is treated by atomistic or even coarse grained Molecular Dynamics: such is the procedure proposed by Doltsinis and coworkers to simulate the behavior of mesogenic azo-chromophores [257]. The information obtained from single chromophore photodynamics can be used to model more complex phenomena. For instance, from such information one can derive force fields that describe the switching from the excited to the ground state and allow to treat many chromophores at once to simulate the behavior of photoresponsive materials [341]. Using molecular rotation data provided by direct nonadiabatic dynamics and a stochastic model, our group simulated photo-orientation phenomena in viscous media that occur in time scales ranging from tens of picoseconds to orders of magnitude longer [19, 20]. Singlet fission rates in amorphous 5,12-diphenyl tetracene were computed by Mou *et al* by relatively short SH trajectories (200 fs) and found to depend on the conformation of chromophore pairs; such information was then used to model the phenomenon on a much longer time scale (1 ns) by kinetic Monte Carlo simulations [342].

A more ambitious goal is to parameterize the nonadiabatic transition rates as functions of a set of nuclear phase space variables, in order to reduce the cost of excited state dynamics simulations to that of standard ground state Molecular Dynamics. This is the gist of a simulation performed by Zannoni and coworkers for the azobenzene photoisomerization in different solvents, where the  $S_1 \rightarrow S_0$  Internal Conversion (IC) rate is assumed to be a simple function of the energy gap, which depends in turn on the nuclear geometry [343]. A similar treatment, with a more accurate reactive force field for the ground and first excited state, has been tried by Li and Hartke [344]. Extensive tests, taking into account the nuclear kinetic energies and other variables in addition to the energy gap, show the transferability of azobenzene IC rates from gas to condensed phase, even in viscous solvents that slow down considerably the photoisomerization [345].

While a single protocol of general applicability to multi-scale problems is not yet available, the above examples show that new tools and strategies for tackling particular classes of systems and processes are being devised by several groups.

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Table 1: A representative selection of nonadiabatic dynamics simulations performed with different methods.

system, process <sup>a</sup> , reference	dynam. method <sup>b</sup>	elec. struct. method <sup>c</sup>	QM/MM atoms <sup>d</sup>	n. of coords. <sup>e</sup>	duration $T_P$ (ps)	$N_T$ or $N_R$
pyrazine absorption spectrum [38]	MCTDH	PES-fit	10	24	0.18	1
C <sub>6</sub> H <sub>5</sub> -C≡CH <sup>+</sup> abs. spectrum [307]	MCTDH	PES-fit	14	36	0.30	1
ammonia photodissociation [325]	MCTDH	PES-fit	4	6	8	1
CH <sub>3</sub> I@resorc[4]arene photodyn. [326]	MCTDH	PES-fit	5/60	189	0.35	1
fullerene-oligothiophene CT [316]	G-MCTDH	PES-fit	90	60	0.25	1
formaldehyde photodissociation [327]	vMCG	CASSCF	4		~0.3	
pyrazine absorption spectrum [64]	MCE	PES-fit	10		0.20	50
pyrrole photodynamics [66]	MCE	CASSCF	10		0.15	24
azobenzene photoisomerization [116]	FMS	semiemp.	24		1.5	30
butadiene photoisomerization [323]	AIMS	CASSCF	10		0.20	20
GFP photodynamics in water [53]	AIMS	CASSCF	22/900		0.80	20
ethylene resonance Raman spectr. [46]	AIMS	MR-CI	6		0.05	3
ethylene photoisomerization [237]	AIMS	CASPT2	6		0.20	37
azomethane photodissociation [133]	TSH	PES-fit	10		500	500
azomethane photoisom. in water [133]	TSH	PES-fit	10/360		10	100
CaAr <sub>55</sub> photoelectron spectrum [211]	TSH	PES-fit	56		10	7500
ICl <sup>-</sup> photodiss. in CO <sub>2</sub> clusters [328]	TSH	PES-fit	2/42		50	50
F <sub>2</sub> photodissociation in solid Ar [329]	TSH	PES-fit	2/255		1.5	49
ICN photodissoc. at interface <sup>f</sup> [330]	TSH	PES-fit	3/2565		10	6000
ClOOCl on ice photodissociation [179]	TSH	semiemp.	4/648	204	0.15	365
azobenzene photoisom. in solution [7]	TSH	semiemp.	24/4750		15	~1200
PPV <sup>g</sup> oligomers exciton dissociation [311]	TSH	semiemp.	202		1.5	35
phenylene ethynylene dendrim. ET [310]	TSH	semiemp.	48		0.04	200
adenine decay in DNA strands [315]	TSH	semiemp.	14/12515	~5700	1.5	146
salicylideneaniline photoisomerization [320]	TSH	semiemp.	26		1	209
thymine relaxation [312]	TSH	semiemp.	15		1.6	327
Al+H <sub>2</sub> O chemiluminescence [276]	TSH	semiemp.	4		~1	169200
acetone ISC and photodissociation [155]	TSH	semiemp.	10		50	1042
thioguanine ISC [308]	TSH	semiemp.	16		10	377
Pb <sub>16</sub> Se <sub>16</sub> @ TiO <sub>2</sub> CT [317]	TSH	DFT	176/312		0.25	>100
water @ GaN CT [318]	TSH	DFT	60		1	4000
Ru(bpy) <sub>3</sub> photodyn. in water [250]	TSH	DFT	61/9896		0.05	2
indole photodynamics in water [251]	TSH	DFT	25/~3300		0.30	100
azobenzene photoisom. in bulk [256]	TSH	DFT	24/8208		2	40
quaterthiophene @ ZnO CT [319]	TSH	DFT	552		0.08	50
uracil photodynamics [313]	TSH	CASSCF	12		2.5	90
stacked aminopyrimidine decay [314]	TSH	CASSCF	12/38		3	45
CH <sub>2</sub> (CH) <sub>6</sub> NH <sub>2</sub> <sup>+</sup> photoisom. [324]	TSH	CASSCF	18		0.2	600
azaindole+(H <sub>2</sub> O) <sub>1-5</sub> proton transfer [321]	TSH	ADC(2)	18-30		0.3	400
CH <sub>2</sub> (CH) <sub>4</sub> NH <sub>2</sub> <sup>+</sup> photoisom. in hexane [236]	TSH	MR-CIS	17/3000		0.5	400
SO <sub>2</sub> ISC [309]	TSH	MR-CIS	3		0.7	111
Ag <sub>3</sub> time resolved photoel. spectrum [170]	FISH	DFT	3		2.0	48
scattering of NO from Au(111) [322]	IESH	PES-fit	2/528		10	~3500

- <sup>a</sup> ET = excitation energy transfer; CT = (electron) charge transfer; ISC = Inter-System Crossing.
- <sup>b</sup> Dynamical methods: MCTDH = Multi-Configurational Time-Dependent Hartree; MCE = Multi-Configurational Ehrenfest; G-MCTDH, vMCG = variational Multiconfiguration Gaussian wavepacket; FMS = Full Multiple Spawning; AIMS = ab initio Multiple Spawning; TSH = Trajectory Surface Hopping; FISH = Field Induced Surface Hopping; IESH = Independent Electron Surface Hopping.
- <sup>c</sup> Electronic structure methods: PES-fit = fitted or model PES and couplings; other acronyms, direct dynamics.
- <sup>d</sup> Number of atoms in the QM and MM subsystems; in PES-B methods, the QM atoms are identified as those belonging to the subsystem for which a multistate Hamiltonian has been fitted.
- <sup>e</sup> Number of active coordinates (only when smaller than three times the number of atoms).
- <sup>f</sup> Water/chloroform boundary.
- <sup>g</sup> Poly-p-phenylenevinylene oligomers.