A semiclassical self-consistent-field approach to dissipative dynamics. II. Internal conversion processes

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A semiclassical time-dependent self-consistent-field (TDSCF) formulation is developed for the description of internal conversion (IC) processes in polyatomic molecules. The total density operator is approximated by a semiclassical ansatz, which couples the electronic degrees of freedom to the nuclear degrees of freedom in a self-consistent manner, whereby the vibrational density operator is described in terms of Gaussian wave packets. The resulting TDSCF formulation represents a generalization of familiar classical-path theories, and is particularly useful to make contact to quantum-mechanical formulations. To avoid problems associated with spurious phase factors, we assume rapid randomization of the nuclear phases and a single vibrational density operator for all electronic states. Classically, the latter approximation corresponds to a single trajectory propagating along a "mean path" instead of several state-specific trajectories, which may become a critical assumption for the description of IC processes. The validity and the limitations of the mean-path approximation are discussed in detail, including both theoretical as well as numerical studies. It is shown that for constant diabatic coupling elements $V_{kk'}$ the mean-path approximation should be appropriate in many cases, whereas in the case of coordinate-dependent coupling $V_{kk'}(\mathbf{x})$ the approximation is found to lead to an underestimation of the overall relaxation rate. As a remedy for this inadequacy of the mean-path approximation, we employ dynamical corrections to the off-diagonal elements of the electronic density operator, as has been suggested by Meyer and Miller [J. Chem. Phys. **70**, 3214 (1979)]. We present detailed numerical studies, adopting (i) a two-state three-mode model of the S_1-S_2 conical intersection in pyrazine, and (ii) a three-state five-mode and a five-state sixteen-mode model of the $\tilde{C} \to \tilde{B} \to \tilde{X}$ IC process in the benzene cation. The comparison with exact basis-set calculations for the two smaller model systems and the possible predictions for larger systems demonstrate the capability of the semiclassical model for the description of ultrafast IC processes. © *1995 American Institute of Physics.*

I. INTRODUCTION

Novel experimental evidence as provided by femtosecond spectroscopy has prompted considerable interest in the theoretical investigation of photoinduced relaxation dynamics such as ultrafast internal conversion and electron and proton transfer processes.[1] There has been significant progress in the development of quantum-mechanical techniques in order to describe these dissipative phenomena, including path-integral methods,[2–5] time-dependent self-consistent-field (TDSCF) schemes,[6–12] and the reduced density-matrix approach.[13–18] Most of the quantum-mechanical methods, however, are in practice restricted to the description of model systems consisting of a one-dimensional "system" coordinate which is coupled to a harmonic "bath." Being interested in the study of more realistic models for dissipative dynamics (including, e.g., multidimensional reaction coordinates and realistic solvent potentials), classical and semiclassical approaches such as surface-hopping[19–24] and classical-path techniques[8,25–32] are therefore still the methods of choice.

The surface-hopping approach is the most popular quantum-classical scheme to describe molecular dynamics on coupled electronic potential-energy surfaces (PESs). The idea is to propagate classical trajectories on a single adiabatic PES until, according to some "hopping criterion," the trajectory "hops" to another adiabatic surface. This way it is en-sured that the system always propagates on a *single* PES, which is an important requirement for the description of reactive scattering processes. Owing to the hopping processes, however, the coherence of the wave function is destroyed after a relatively short time, which may represent a serious shortcoming for the description of bound-state relaxation dynamics involving several transitions between electronic PESs. Classical-path methods, on the other hand, propagate the classical degrees of freedom self-consistently in an *averaged* potential, the value of which is determined by the instantaneous populations of the different quantum states. This way the coherence of the wave function is conserved, but one has to deal with problems arising from the concept that the trajectory propagates on a "mean path," which may lead to unphysical results in applications to reactive scattering, where the system is asymptotically in a single electronic state.[33]

The present work has been motivated by the finding that the simple classical-path concept describes surprisingly accurately the ultrafast electronic and vibrational relaxation dynamics of bound-state systems. In particular it has been shown to reproduce almost quantitatively complex structures of time-dependent observables such as electronic population probabilities and mean positions and momenta of vibrational modes. Examples include electron-transfer dynamics of the dissipative two-level system (often referred to as spin-boson

model),[34] ultrafast electronic decay processes triggered by conically intersecting PESs,[35–37] and simple photoisomerization processes.[38]

In a preceding paper,[34] henceforth referred to as paper I, we have proposed a semiclassical TDSCF ansatz which couples the electronic degrees of freedom to the nuclear degrees of freedom in a self-consistent manner. The resulting TDSCF formulation represents a generalization of existing classical-path theories,[8,25–32] and is particularly useful to make contact to quantum-mechanical formulations, thus exploring the validity of the semiclassical ansatz. The method has been applied to the spin-boson model with an Ohmic bath, which is one of the best-studied model problems of dissipative quantum dynamics.[39,40] Employing the semiclassical TDSCF ansatz, we have derived the approximations leading to the classical-path equations of motion, thus revealing the criteria for the validity and applicability of this concept. It has been shown that the assumption of complete randomization of nuclear phases represents the central approximation of the approach. This condition is fulfilled, for example, if the electronic relaxation dynamics is strong enough to ensure that the nuclear phases get randomized rapidly enough to be unimportant for the overall time evolution of the system. In particular, the randomization assumption makes it possible to perform the trace over the nuclear variables through quasiclassical sampling of the nuclear initial conditions, which has been found to be the main reason for the success of the semiclassical approach in the description of dissipative dynamics.

In this work we want to extend the formulation developed in paper I to the description of internal conversion (IC) processes in polyatomic molecules. Unlike the idealized properties of the spin-boson Hamiltonian, the PESs pertaining to the individual electronic states of a more realistic molecular model system may differ substantially. Therefore the assumption of a mean path, i.e., the propagation of a single trajectory in an averaged potential instead of several state-specific trajectories, may become critical. As has been shown in paper I, however, the assumption of a mean path is essential in order to perform the classical sampling of the bath degrees of freedom. A major point of the present paper is therefore to elucidate the limitations and the effects of the mean-path approximation for the description of IC processes.

To this end we adopt a semiclassical TDSCF formulation that describes the vibrational wave function of the system in terms of Gaussian wave packets,[6,8,10,41,42] and compare the equations of motion for a "multiconfiguration ansatz" (i.e., with individual vibrational wave functions for each electronic state) to the corresponding equations of motion resulting from a "single configuration ansatz" (i.e., with a single vibrational wave function for all electronic states). The analysis elucidates the nature of the mean-path approximation, and therefore allows to define criteria for its validity. It is shown that the TDSCF formulation can be improved, when dynamical corrections ("Langer-like modifications") are employed to the electronic equations of motion as has been suggested by Meyer and Miller.[28] The effects of these corrections are discussed in some detail, and are shown to depend on the form of the nonadiabatic coupling, i.e.,

whether the coupling is a constant or depends on a nuclear coordinate.

The theoretical considerations are accompanied by detailed numerical studies which are compared to exact quantum-mechanical basis-set propagations. As model systems we consider (i) a two-state three-mode model of the $S_1 - S_2$ conical intersection in pyrazine,[43] which has been adopted by several authors as a standard example of electronic relaxation,[36,44–46] and (ii) a three-state five-mode and a five-state sixteen-mode model of the $\tilde{C} \rightarrow \tilde{B} \rightarrow \tilde{X}$ IC process in the benzene cation.[37,47–49] We introduce time-dependent observables that characterize the electronic and vibrational relaxation dynamics of molecular systems, including, in particular, electronic state-specific observables, which represent a stringent test of the mean-path approximation. We give conditions to determine the value of the dynamical corrections, and discuss criteria which indicate the reliability of the method. The comparison with reference quantum calculations for smaller systems (with up to five vibrational modes) and the possible predictions for larger systems clearly demonstrate that the semiclassical model is a powerful method for the description of ultrafast IC processes.

II. THEORETICAL FORMULATION

A. Model system

In a diabatic electronic representation,[50] the Hamiltonian for a molecular system comprising N_{el} coupled electronic states can be written as

$$H = \sum_{k=1}^{N_{el}} |\varphi_k\rangle h_k \langle\varphi_k| + \sum_{k \neq k' = 1}^{N_{el}} |\varphi_k\rangle V_{kk'} \langle\varphi_{k'}|, \quad (2.1a)$$

where $h_k = T + V_k$ denotes the vibrational Hamiltonian of the diabatic electronic basis state $|\varphi_k\rangle$ and $V_{kk'}$ represents the diabatic coupling between the electronic states $|\varphi_k\rangle$ and $|\varphi_{k'}\rangle$. Most of the theoretical analysis in this section is independent of a specific form of the diabatic potential elements V_k, $V_{kk'}$. For later reference and in order to introduce some notation, however, it is convenient to specify a simple model for the Hamiltonian (2.1). As is common practice in vibronic coupling theory,[51,52] we thus approximate the diabatic potential matrix elements V_k and the diabatic couplings $V_{kk'}$ by a Taylor expansion in (dimensionless) normal coordinates x_j, yielding in lowest order

$$h_k = E_k + h_0 + \sum_{j=1}^{N_{mod}} \kappa_j^{(k)} x_j, \quad (2.1b)$$

$$h_0 = \sum_{j=1}^{N_{mod}} \tfrac{1}{2} \omega_j (p_j^2 + x_j^2). \quad (2.1c)$$

Here h_0 represents the harmonic oscillator Hamiltonian comprising N_{mod} nuclear degrees of freedom, ω_j, x_j, and p_j denoting the vibrational frequency, the position, and the momentum of the jth oscillator. E_k is the vertical transition energy of the diabatic state $|\varphi_k\rangle$, and $\kappa_j^{(k)}$ denotes the gradient of the excitation energy with respect to the totally symmetric coordinates x_j.

In molecular physics, two cases of the diabatic coupling $V_{kk'}$ are of particular interest: (i) the coupling is constant

$$V_{kk'} = g_{kk'}, \tag{2.2a}$$

leading to an *avoided crossing*[53] of the adiabatic PESs, and (ii) the coupling is linear in one (or several) coordinates x_c (the so-called coupling modes)

$$V_{kk'} = \lambda_{kk'} x_c, \tag{2.2b}$$

leading to a *conical intersection*[53] of the adiabatic PESs. For $N_{el}=2$, the first case is often referred to as "spin-boson problem," as the Hamiltonian (2.1) with (2.2a) is equivalent to the Hamiltonian of the dissipative two-level system.[39] The latter case, which we will refer to as "vibronic-coupling problem," represents the standard case of IC through a photochemical funnel.[54] Interestingly, it has been found that the different topology of the PESs in the two cases leads to qualitatively different electronic and vibrational relaxation dynamics.[55] Furthermore it should be stressed that the vibronic coupling $V_{kk'}$ converts an otherwise separable harmonic system into a nonseparable multidimensional problem.

The time evolution of the wave function $|\Psi(t)\rangle$ under the model Hamiltonian (2.1) is described by the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle. \tag{2.3}$$

We assume that at the time $t=0$ the system is exclusively in the upper electronic state (e.g., $|\varphi_2\rangle$) and in the ground state of the vibrational Hamiltonian h_0. This initial condition corresponds to a photoexcitation of the electron from an initial electronic state (e.g., $|\varphi_0\rangle$) to the upper ($|\varphi_2\rangle$) state.

B. TDSCF ansatz and equations of motion

As motivated in the Introduction, we wish to compare the equations of motion for a semiclassical TDSCF ansatz with individual vibrational wave functions for each electronic state [henceforth referred to as multiconfiguration (MC) ansatz] to the equations of motion resulting from a TDSCF ansatz with a single vibrational wave function [henceforth referred to as single-configuration (SC) ansatz]. In both cases, the derivation of the equations of motion has been performed by several workers,[8,10,41,42] and is therefore only sketched briefly. For the sake of notational convenience, we will in the following refer to a single nuclear coordinate x (instead of $\sum_j x_j$). Furthermore we want to specialize on a coupled electronic two-state system; problems associated with the general case of $N_{el}>2$ are considered in Sec. III C.

The MC ansatz for the wave function $|\Psi(t)\rangle$ can be written as[8,10]

$$|\Psi(t)\rangle = \sum_{k=1,2} \chi_k(t) |\varphi_k\rangle |\Phi_k(t)\rangle, \tag{2.4}$$

where the $\chi_k(t)$ are complex numbers, describing the dynamics of the electronic degrees of freedom, and $|\Phi_k(t)\rangle$ denotes the vibrational wave function, accounting for the dynamics of the nuclear degrees of freedom in the diabatic

electronic state $|\varphi_k\rangle$. To make the ansatz unambiguous, we impose that the vibrational wave functions $|\Phi_k(t)\rangle$ are normalized, i.e.,

$$\langle \Phi_k(t) | \Phi_k(t) \rangle = 1, \tag{2.5a}$$

and that

$$\langle \Phi_k(t) | \dot{\Phi}_k(t) \rangle = 0. \tag{2.5b}$$

Inserting the MC ansatz (2.4) into the time-dependent Schrödinger equation (2.3), we obtain

$$i \dot{\chi}_k = \langle \Phi_k | h_k | \Phi_k \rangle \chi_k + \langle \Phi_k | V_{kk'} | \Phi_{k'} \rangle \chi_{k'}, \tag{2.6}$$

$$i |\dot{\Phi}_k\rangle = (h_k - i\dot{\chi}_k/\chi_{k'}) |\Phi_k\rangle + \chi_{k'}/\chi_k V_{kk'} |\Phi_{k'}\rangle, \tag{2.7}$$

where $k=1,2$ and $k \neq k'$. The vibrational wave functions $|\Phi_k(t)\rangle$ are assumed to be Gaussian wave packets[56]

$$\begin{aligned}\Phi_k(x,t) = \pi^{-1/4} \exp\{ &-\tfrac{1}{2}[x-x_k(t)]^2 \\ &+ ip_k(t)[x-x_k(t)] + i\gamma_k(t)\},\end{aligned} \tag{2.8}$$

which are completely described by the trajectory $x_k(t)$, the corresponding momentum $p_k(t)$, and the action integral $\gamma_k(t)$. Employing the Dirac–Frenkel–McLachlan time-dependent variational principle[57]

$$\langle \delta\Psi | i\partial/\partial t - H | \Psi \rangle = 0, \tag{2.9}$$

it is straightforward to show that the equations of motion for the trajectory $x_k(t)$ and the momentum $p_k(t)$ are given by[8,10]

$$\dot{x}_k = \omega p_k + 2\Im m \, \chi_{k'}/\chi_k \langle \Phi_k | (x-x_k) V_{kk'} | \Phi_{k'} \rangle, \tag{2.10}$$

$$\dot{p}_k = -\frac{\partial V_k(x_k)}{\partial x_k} - 2\Re e \, \chi_{k'}/\chi_k \langle \Phi_k | (x-x_k) V_{kk'} | \Phi_{k'} \rangle. \tag{2.11}$$

Analogously, the SC ansatz for the wave function $|\Psi(t)\rangle$ is written as[8,10]

$$|\Psi(t)\rangle = \sum_{k=1,2} e^{i\eta_k} \chi_k(t) |\varphi_k\rangle |\Phi(t)\rangle. \tag{2.12}$$

Contrary to the MC ansatz (2.4), the vibrational dynamics is described by a single vibrational wave function $|\Phi(t)\rangle$, which, in analogy to (2.8), depends on the trajectory $x(t)$ and momentum $p(t)$. For convenience, we have furthermore introduced a phase function η_k,[9,10] which is not of further interest for the evaluation of the observables introduced above. Insertion of the SC ansatz into the time-dependent Schrödinger equation (2.3) yields the equations of motion for the electronic and vibrational wave function

$$i \dot{\chi}_k = \langle \Phi | h_k | \Phi \rangle \chi_k + \langle \Phi | V_{kk'} | \Phi \rangle \chi_{k'}, \tag{2.13}$$

$$i |\dot{\Phi}\rangle = (n_1 h_1 + n_2 h_2 + 2\Re e \, \chi_1^* \chi_2 V_{12}) |\Phi\rangle. \tag{2.14}$$

It is seen that within the TDSCF approximation the electronic equations of motion reduce to a coupled two-level system with explicitly time-dependent coefficients. The nuclear dynamics is described by the single vibrational wave function $|\Phi(t)\rangle$ propagating in an averaged potential, weighted by the electronic population probabilities

$$n_k(t) = |\chi_k(t)|^2. \tag{2.15}$$

Employing again the variational principle (2.9), the nuclear equations of motion pertaining to the SC ansatz are derived as

$$\dot{x} = \omega p, \tag{2.16}$$

$$\dot{p} = -\langle \Psi(t)|\frac{\partial H}{\partial x}|\Psi(t)\rangle,$$

$$= -\sum_{k=1,2} n_k \frac{\partial V_k(x)}{\partial x} - 2\Re e\; \chi_k^* \chi_{k'} \frac{\partial V_{kk'}(x)}{\partial x}. \tag{2.17}$$

Equations (2.16) and (2.17) are recognized as the well known equations of motion of a classical-path formulation.[8,25–32] Contrary to the MC ansatz leading to a formulation with state-specific trajectories $x_k(t)$, the SC ansatz results in a formulation with a mean trajectory $x(t)$ driven by the "Ehrenfest force" $m\dot{p}(t)$.

C. Mean-path approximation

In this section we want to discuss the mean path approximation, that is, the underlying assumption leading from the MC ansatz (2.4) to the SC ansatz (2.12). Intuitively, it is clear that in the limit

$$\Delta x \equiv x_2(t) - x_1(t) \to 0, \tag{2.18a}$$

$$\Delta p \equiv p_2(t) - p_1(t) \to 0, \tag{2.18b}$$

the MC ansatz becomes equivalent to the SC ansatz. Let us try to assess the validity of condition (2.18). Due to the initial preparation of the system, Eq. (2.18) is exact at the time $t=0$, and should therefore be a good approximation for short times, too. In a dissipative system the *mean values* of the momenta fluctuate around zero for long times.[44] Condition (2.18b) is therefore also valid for long times and should approximately hold for intermediate times as long as the vibrational relaxation is fast enough. The validity of Eq. (2.18b) for longer times is not easy to foresee as it depends on how different the geometries of the two electronic states $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are. If the overall coupling of the system is distributed over many weakly coupled vibrational modes (and therefore the geometry change in each individual mode is small), the approximation should be justified. If the overall coupling of the system is contained in a few strongly coupled vibrational modes, however, the approximation may break down for longer times.

To consider the nuclear equations of motion, it is useful to recall the relation between the mean path variables $x(t)$ and $p(t)$ and the state-specific variables $x_k(t)$ and $p_k(t)$

$$x = n_1 x_1 + n_2 x_2, \tag{2.19a}$$

$$p = n_1 p_1 + n_2 p_2, \tag{2.19b}$$

where the time dependency of the variables has been dropped for notational convenience. Taking the time derivative of (2.19) and inserting the MC equations of motions for $x_k(t)$ (2.11) and $p_k(t)$ (2.11), we obtain the MC equations of motion for the mean position $x(t)$ and the mean momentum $p(t)$

$$\dot{x} = \omega p, \tag{2.20}$$

$$\dot{p} = -\sum_{k=1,2} n_k \frac{\partial V_k(x_k)}{\partial x_k}, \quad V_{12} = g, \tag{2.21}$$

$$= -\sum_{k=1,2} n_k \frac{\partial V_k(x_k)}{\partial x_k} - 2\Re e\; \lambda \chi_1^* \chi_2 \langle \Phi_1 | \Phi_2 \rangle$$

$$+ (p_2 - p_1)[\dot{n}_2 - \Re e\; \lambda \chi_1^* \chi_2 \langle \Phi_1 | \Phi_2 \rangle (p_2 - p_1)],$$

$$V_{12} = \lambda x. \tag{2.22}$$

It is interesting to note that for constant diabatic coupling ($V_{12} = g$) the MC equations of motion for $x(t)$ and $p(t)$ are identical to the SC equations. In the case of coordinate-dependent coupling ($V_{12} = \lambda x$), the equation for the mean position $x(t)$ is still identical, whereas the equation for the mean momentum $p(t)$ differs considerably from (2.17). In this case we obtain a correction term to the SC equation that vanishes for small Δp, and the off-diagonal term is augmented by the vibrational overlap integral

$$\langle \Phi_2 | \Phi_1 \rangle = \exp\{-\tfrac{1}{4}(x_2 - x_1)^2 - \tfrac{1}{4}(p_2 - p_1)^2$$
$$+ i/2(p_2 + p_1)(x_1 - x_2) + i(\gamma_2 - \gamma_1)\}. \tag{2.23}$$

It is seen that the SC ansatz neglects the nuclear phase difference acquired by the trajectories. Furthermore the strength of the diabatic coupling is somewhat overestimated. In the limit (2.18), the MC equations, of course, reduce to the SC equations.

Let us next consider the electronic equations of motion (2.6) and (2.13). These equations describe a driven two-level system, that can be characterized by the two time-dependent observables

$$\Delta E(t) = \langle \Psi(t)\{|\varphi_2\rangle h_2 \langle \varphi_2| - |\varphi_1\rangle h_1 \langle \varphi_1|\}\Psi(t)\rangle, \tag{2.24}$$

$$V_c(t) = 2\Re e\langle \Psi(t)|\varphi_1\rangle V_{12}\langle \varphi_2|\Psi(t)\rangle, \tag{2.25}$$

where $\Delta E(t)$ represents the mean value of the diabatic electronic energy gap and $V_c(t)$ denotes the mean diabatic coupling. Inserting the MC and SC ansatz, respectively, and assuming $V_{12} = g + \lambda x$ we obtain

$$\Delta E(t) = n_2 E_2 - n_1 E_1 + \begin{cases} \tfrac{1}{2}\omega[n_2(p_2^2 + x_2^2) - n_1(p_1^2 + x_1^2)] + n_2 \kappa_2 x_2 - n_1 \kappa_1 x_1 & \text{(MC)}, \\ \tfrac{1}{2}\omega[(n_2 - n_1)(p^2 + x^2)] + (n_2 \kappa_2 - n_1 \kappa_1)x & \text{(SC)}, \end{cases} \tag{2.26}$$

$$V_c(t) = 2\Re e \chi_1^* \chi_2 \begin{cases} (g + \lambda/2(x_1 + x_2 + i(p_2 - p_1))\langle \Phi_1 | \Phi_2 \rangle & \text{(MC)}, \\ g + \lambda x & \text{(SC)}. \end{cases} \tag{2.27}$$

Note that for "symmetric" coordinate shifts ($\kappa_2 = -\kappa_1$) as assumed in the spin-boson model, the tuning of the electronic energy gap $\Delta E(t)$ owing to the linearly coupled modes is described correctly by the SC ansatz. Because the SC ansatz uses the averaged quantities $x(t)$ and $p(t)$ for the evaluation of the $\frac{1}{2}\omega[\ldots]$ term, however, it is expected to underestimate the magnitude of the electronic energy gap.

The accuracy of the SC approximation for the mean diabatic coupling $V_c(t)$ is seen to depend strongly on the form of the coupling V_{12}. In the case of constant coupling $V_{12} = g$, $V_c(t)$ misses the overlap integral $\langle \Phi_1 | \Phi_2 \rangle$, which mainly corresponds to the neglect of nuclear phases. In the case of coordinate dependent coupling $V_{12} = \lambda x$, the situation is more complicated. Besides the neglect of the overlap integral and a term that vanishes with Δp, the SC ansatz replaces $\lambda/2(x_1 + x_2)$ by $\lambda(n_1 x_1 + n_2 x_2)$, which represents a somewhat problematic approximation. This is because, due to the weight by the electronic populations n_k, the bilinear expression $\lambda(n_1 x_1 + n_2 x_2)$ amounts to a dynamically rather different coupling than $\lambda/2(x_1 + x_2)$. For this reason and because of the missing Δp term, one may expect that the SC ansatz underestimates the mean diabatic coupling.

To summarize, it has been shown that the mean-path approximation should be an appropriate assumption for the spin-boson problem (i.e., for $V_{12} = g$ and $\kappa_2 = -\kappa_1$), which is in accordance with the finding of paper I. In this case the equations of motion for the nuclear degrees of freedom are identical in the SC and MC formulations, and the tuning of the electronic energy gap $\Delta E(t)$ due to linearly coupled modes is described correctly by the SC ansatz. The neglect of nuclear phases in $V_c(t)$ and the differences in the $\frac{1}{2}\omega[\ldots]$ term in $\Delta E(t)$ should not be a critical approximation as long as $\Delta x, \Delta p$ do not become too large. In the case of coordinate dependent coupling $V_{12} = \lambda x$, however, the SC approximation of the mean diabatic coupling was found to become problematic.

D. Dynamical corrections

In order to improve the SC ansatz in the case of coordinate-dependent diabatic coupling, we introduce "dynamical corrections" into the SC equations of motion, as has been suggested by Meyer and Miller in the theoretical framework of the classical electron analog model.[28] The basic idea of the classical electron analog model is to replace the N_{el} complex electronic variables χ_k by $2N_{el}$ real classical action-angle variables

$$\chi_k(t) = \sqrt{n_k(t)} e^{-iq_k(t)}. \qquad (2.28)$$

Here the action variables n_k are identical to the electronic populations defined in (2.15), and the angle variables q_k represent the electronic phases. Introducing the classical Hamiltonian function

$$H(\mathbf{p},\mathbf{x},\mathbf{n},\mathbf{q}) = \sum_k n_k h_k(\mathbf{p},\mathbf{x}) + \sum_{k \neq k'} \sqrt{n_k n_{k'}}\, e^{i(q_k - q_{k'})} V_{kk'}(\mathbf{x}), \qquad (2.29)$$

the equations of motion for the electronic and nuclear degrees of freedom (2.13) and (2.16), (2.17) can be rewritten as[27,28]

$$\dot{n}_k(t) = -\frac{\partial H}{\partial q_k}, \quad \dot{q}_k(t) = \frac{\partial H}{\partial n_k}, \quad (k=1,\ldots,N_{el}), \quad (2.30)$$

$$\dot{p}_j(t) = -\frac{\partial H}{\partial x_j}, \quad \dot{x}_j(t) = \frac{\partial H}{\partial p_j}, \quad (j=1,\ldots,N_{mod}), \quad (2.31)$$

i.e., both electronic and nuclear degrees of freedom formally obey Hamilton's equations.

It should be noted that the classical electron analog model is not the only way to obtain canonical equations of motion for both electronic and nuclear degrees of freedom. Defining $\chi_k(t) = \alpha_k(t) + i\beta_k(t)$ and introducing a similar Hamiltonian function as (2.29), it has been shown by Strocchi that the time evolution of the "Cartesian electronic variables" α_k, β_k is also given by Hamilton's equations.[58]

The formulation of the equations of motion in terms of electronic action-angle variables, however, allows to introduce "Langer-like modifications" into the coupling matrix elements of the Hamiltonian function (2.29), i.e., one makes the replacement[28]

$$\sqrt{n_k n_{k'}}\, V_{kk'} \rightarrow \sqrt{(n_k + \gamma)(n_{k'} + \gamma)}\, V_{kk'}, \qquad (2.32)$$

where γ is a constant. To understand the effects of the correction term γ it is instructive to again consider an electronic two-state system. Introducing furthermore the canonical transformation[59]

$$\begin{aligned} n &= n_2, & q &= q_2 - q_1, \\ N &= n_1 + n_2 = 1, & Q &= q_1, \end{aligned} \qquad (2.33)$$

the electronic equations of motion read

$$\dot{n}(t) = 2\Im m\, \langle \Phi_2 | V_{21} | \Phi_1 \rangle \sqrt{(1+\gamma-n)(n+\gamma)}\, e^{iq}, \qquad (2.34)$$

$$\dot{q}(t) = \langle \Phi_2 | V_2 | \Phi_2 \rangle - \langle \Phi_1 | V_1 | \Phi_1 \rangle$$
$$+ \Re e\, \langle \Phi_2 | V_{21} | \Phi_1 \rangle \frac{1-2n}{\sqrt{(1+\gamma-n)(n+\gamma)}}\, e^{iq}. \qquad (2.35)$$

Equations (2.34) and (2.35) are for $\gamma = 0$ equivalent to the MC expression (2.6); the corresponding SC expression (2.13) is easily obtained by setting $|\Phi_k\rangle = |\Phi\rangle$. Note that the differential equation (2.35) has singularities at $n = -\gamma$ and $n = 1 + \gamma$, reflecting the fact that these values of n are branch points for the angle variable q. As has been discussed in detail by Herman and co-workers,[32,60] these singularities may result in abrupt phase changes of the semiclassical wave function, and need therefore be taken care of, if one intends to pursue a "rigorous" semiclassical description (i.e., according to classical S-matrix theory[61]). In the present work, however, we restrict ourselves to a more approximate treatment, i.e., we perform a quasiclassical average over initial conditions and neglect all interferences between individual trajectories [see Eq. (2.39) below]. In this case, possible discontinuities of the electronic phase q do not affect the evaluated quantities.

From (2.34) it is clear that $\dot{n} \to 0$ whenever n approaches $-\gamma$ and $1+\gamma$, i.e., the electronic action variable $n(t)$ is restricted to the interval $-\gamma < n < 1+\gamma$. Note, however, that $n(t)$ corresponds to a population *probability*, which should be restricted to $0 < n < 1$. The γ-modification therefore results in the curious fact that an electronic state can be "over-populated" (or "under-populated") by the value of γ. Generalizing to a model with N_{el} electronic states, a analogous analysis reveals that the action variables $n_k(t)$ $(k=1,...,N_{el})$ can take on values from $-\gamma$ to $1+\gamma(N_{el}-1)$. For $\gamma \neq 0$ the evaluation of physically meaningful observables thus requires a mapping of the continuous variable $n(t)$ onto discrete quantum numbers (e.g., through a histogram method, see Sec. III A), which ensures that the mean electronic population probability is restricted to $[0,1]$.

Let us consider the consequences of the γ corrections on the electronic dynamics. Firstly note that the mean diabatic coupling $V_c(t)$ is increased due to the correction. As a rough estimate of this effect one may consider the quantity

$$V_{\text{eff}} = 2/\pi \int_{-\gamma}^{1+\gamma} dn \sqrt{(1+\gamma-n)(n+\gamma)} = (1/4 + \gamma + \gamma^2),$$
(2.36)

the value of which, for example, is doubled for $\gamma \approx 0.21$. The second main consequence of the modifications is an increase of the magnitude of the diabatic electronic energy gap $\Delta E(t)$ defined in Eq. (2.24). Writing $\Delta E(t) = E_1 + n(E_1 + E_2) + (\kappa_2 - \kappa_1)x$, it is clear that an enlarged range of possible values of n also results in a enlarged range of $\Delta E(t)$. It has been shown above that in the case of coordinate-dependent coupling V_{12} the SC ansatz underestimates both the electronic energy gap $\Delta E(t)$ and the mean diabatic coupling $V_c(t)$. The γ modifications therefore may correct this inadequacy of the SC ansatz to a certain extent. In the case of constant coupling V_{12}, however, the modifications would lead to an overestimation of the mean diabatic coupling $V_c(t)$, and should therefore be omitted.

So far we have not addressed the question about the value of γ. Because of $-\gamma < n < 1+\gamma$, γ should be positive, otherwise it would not be possible that the system is completely in a single electronic state as it requires that $n=0,1$. In accordance with the well known modifications due to Langer,[62] Meyer and Miller have suggested a value of $\gamma = \frac{1}{2}$.[28] In order to obtain the correct semiclassical eigenvalues of a one-dimensional system that is restricted to the semi-infinite interval $[0,\infty]$, Langer has shown that one needs to add a "correction term" $\hbar^2(8mr^2)^{-1}$ to the potential, which results in the replacement $n \to n+\frac{1}{2}$ in the expression for the WKB eigenvalues. In the same spirit, Adams and Miller have derived an expression for semiclassical eigenvalues for potential functions defined on a arbitrary finite interval.[63]

The situation is more involved in the case of the semiclassical TDSCF formulation, where the electronic equations of motion (2.34) and (2.35) describe a nonlinearly driven oscillator. Similarly to Langer's case, the corresponding position x_{el} and momentum p_{el} are restricted to a finite interval through the relation $-\gamma < n = x_{el}^2 + p_{el}^2 < 1+\gamma$. Note, however, that in the case of constant $h_k, V_{kk'}$ (i.e., no nuclear

motion), the electronic equations of motion are *exact* for $\gamma = 0$, i.e., they are equivalent to the time-dependent Schrödinger equation for a two-level system.[28] The need for dynamical corrections therefore does not arise from the finite interval the variables x_{el}, p_{el} are restricted to, but is rather a consequence of the self-consistent-field approximation of the interaction of electronic and nuclear degrees of freedom. Unfortunately, we have not succeeded in finding a relation which would allow to calculate γ for a given system. Extensive numerical studies on a variety of model systems (see below) suggest a value of $\gamma = \frac{1}{4}$ in the case of coordinate-dependent coupling V_{12}. Note that this value corresponds to an increase of V_{eff} by a factor of 2.5, compared to a factor of 4.0 for $\gamma = 0.5$. Furthermore, it is shown in Sec. III A that it is possible to define a consistency criterion [Eq. (3.17)], which determines an upper bound for γ. As pointed out above, in the case of constant coupling V_{12} the modifications lead to an overestimation of the mean diabatic coupling $V_c(t)$, and should therefore be omitted.

E. Quasiclassical sampling procedure

It has been shown by several authors that the semiclassical approximation of a wave function can be considerably improved if, instead of a single Gaussian wave-packet, an expansion into many Gaussians is employed, the expansion coefficients of which are determined by evaluating the semiclassical Greens function.[64–67] These "rigorous" semiclassical methods, however, are known to become quite cumbersome for treating problems with many degrees of freedom. In paper I we have therefore proposed a simpler and more practical approach, which combines a semiclassical SC TDSCF ansatz with a quasiclassical sampling scheme.[34] It has been shown that the combination of these two techniques requires (i) to employ the mean-path approximation, and (ii) to assume rapid randomization of nuclear phases.[34] The latter condition allows to perform the trace over nuclear variables in terms of an incoherent sampling of nuclear initial conditions, which has been found to represent a much better approximation to describe quantum dissipative dynamics than the propagation of single or double trajectories as required for the SC (2.12) or MC (2.4) ansatz, respectively. In what follows, we briefly summarize the semiclassical TDSCF approach introduced in paper I and generalized it to incorporate the dynamical corrections discussed above.

To derive the semiclassical TDSCF approximation of paper I, it is convenient to change from the wave-function description adopted above to the more general density-matrix description. The generalization of the SC ansatz (2.12) to an expansion into Gaussian wave-packets can then be written as[34]

$$\rho(t) = \int dx_0 \int dp_0 \int dx_0' \int dp_0' \, c_{x_0,p_0}(t) c_{x_0',p_0'}^*(t)$$
$$\times \sigma_{x_0,p_0,x_0',p_0'}(t) \, |\phi_{x_0,p_0}(t)\rangle \langle \phi_{x_0',p_0'}(t)|, \quad (2.37)$$

where

$$\sigma_{x_0,p_0,x_0',p_0'}(t) = \sum_{k,k'} \chi_{x_0,p_0}^{(k)}(t) \chi_{x_0',p_0'}^{(k')*}(t) |\varphi_k\rangle\langle\varphi_{k'}| \quad (2.38)$$

represents the electronic density operator depending on the nuclear initial conditions $x_0 = x(t=0)$, $p_0 = p(t=0)$. The functions $c_{x_0,p_0}(t) = \sqrt{w_{x_0,p_0}} A_{x_0,p_0}(t)$ are the semiclassical expansion coefficients, where w_{x_0,p_0} denotes the Wigner distribution,[68] describing the initial distribution of the nuclear variables x_0, p_0, and $A_{x_0,p_0}(t)$ represents the semiclassical weight function derived by Herman and Kluk.[65]

Assuming that the nuclear phases become randomized rapidly, we may neglect the nondiagonal contributions to (2.37), thus yielding

$$\rho(t) = \int dx_0 \int dp_0 \, w_{x_0,p_0} \sigma_{x_0,p_0}(t) \, |\phi_{x_0,p_0}(t)\rangle\langle\phi_{x_0,p_0}(t)|, \tag{2.39}$$

$$\sigma_{x_0,p_0}(t) = \sum_{k,k'} \chi_{x_0,p_0}^{(k)}(t) \chi_{x_0,p_0}^{(k')*}(t) |\varphi_k\rangle\langle\varphi_{k'}|. \tag{2.40}$$

Owing to the approximation (2.39), each individual contribution $\sigma_{x_0,p_0}(t)$ and $|\phi_{x_0,p_0}(t)\rangle\langle\phi_{x_0,p_0}(t)|$ evolves independently from all other contributions (i.e., with different x_0,p_0). The time evolution of the total density operator $\rho(t)$ is therefore described by the incoherent addition of many trajectories, each one obeying the SC equations of motion for the electronic (2.13) and nuclear (2.14) degrees of freedom, respectively. Furthermore, it is easy to show that $A_{x_0,p_0}(t) = 1$ for potentials which are at most quadratic in x. For the model system (2.1) under consideration, the individual trajectories in (2.39) are thus solely weighted by the Wigner distribution w_{x_0,p_0}.

To introduce the dynamical corrections described above, it is advantageous to change to electronic action-angle variables defined in (2.28). The structure of the modifications (2.32) then suggest to rewrite the electronic density operator (2.40) as

$$\sigma_{x_0,p_0}(t) = \sum_{k} n_k |\psi_k\rangle\langle\psi_k| + \sum_{k \neq k'} \sqrt{(n_k + \gamma)(n_{k'} + \gamma)}$$
$$\times \exp i(q_k - q_{k'}) |\psi_k\rangle\langle\psi_k|, \tag{2.41}$$

where for notational convenience the arguments t, x_0, p_0 have been suppressed on the right hand side of (2.41). The resulting TDSCF ansatz for the total density operator [Eqs. (2.39) and (2.41)] combined with the corresponding equations of motion for the nuclear and electronic degrees of freedom [Eqs. (2.16), (2.17) and (2.30)] represent the working equations of the semiclassical TDSCF approach, and will be used for the computational studies in Sec. III.

To illustrate the formal considerations above by a concrete example, let us consider the evaluation of time-dependent mean values. The time-dependent mean value of an observable A is given by

$$A(t) = \mathrm{Tr}\{A\rho(t)\},$$
$$= \mathrm{Tr}_e \, \mathrm{Tr}_v\{A\rho(t)\}, \tag{2.42}$$

where

$$\mathrm{Tr}_e\{...\} = \sum_k \langle\varphi_k|...|\varphi_k\rangle, \tag{2.43}$$

$$\mathrm{Tr}_v\{...\} = \int dx \, \langle x|...|x\rangle \tag{2.44}$$

denote the trace over the electronic and nuclear degrees of freedom, respectively. Thinking of the electronic and nuclear variables as "system" and "bath" degrees of freedom, respectively, we can define a reduced density operator $\sigma(t)$

$$\sigma(t) \equiv \mathrm{Tr}_v\{\rho(t)\},$$
$$= \int dx_0 \int dp_0 \, w_{x_0,p_0} \sigma_{x_0,p_0}(t), \tag{2.45}$$

which describes the dynamics of the electronic "system" that is interacting with the nuclear "bath." Equation (2.45) clearly states the correspondence between the trace over bath variables (Tr_v) and the integration over initial conditions.

III. COMPUTATIONAL RESULTS

In this section we undertake detailed numerical studies to (i) investigate the applicability and limitations of the mean-path approximation, (ii) discuss the effects of the dynamical corrections introduced above, and (iii) demonstrate the capability of the semiclassical TDSCF approach for the description of ultrafast IC processes. To this end, we introduce time-dependent observables that characterize the electronic and vibrational relaxation dynamics of molecular systems, and consider as representative examples the IC processes in pyrazine and the benzene cation.

A. Time-dependent observables

To characterize the IC dynamics of a molecular system, it is useful to define time-dependent electronic and vibrational observables which illuminate this relaxation process. In the discussion of radiationless processes (as well as of any reactive process) the main quantity of interest is given by the rate of the reaction. Employing time-dependent wave-packet propagations on coupled electronic PESs, one directly evaluates the time-dependent population probabilities $P_k(t)$ of the kth electronic state. In the case that $P_k(t)$ may be fitted in some sensible way to an exponential function, the rate of the IC process is then given by $\dot{P}_k/P_k$.

The population of an electronic state can be defined in the diabatic or the adiabatic representation. In the case of surface crossings, as considered here, these two populations are not the same.[45] Transitions between *diabatic* electronic states are important for the interpretation of spectroscopic data,[47,52,69,70] as in the vicinity of a conical intersection the electronic dipole transition operator is only smooth in the diabatic representation.[50] Regarding IC as a chemical reaction, however, one is rather interested in the population probabilities of the *adiabatic* electronic states.

The time-dependent population probability of the diabatic electronic state $|\varphi_k\rangle$ is defined as the expectation value of the diabatic projector P_k

$$P_k(t) = \mathrm{Tr}\{P_k\rho(t)\}, \tag{3.1}$$

$$P_k = |\varphi_k\rangle\langle\varphi_k|. \tag{3.2}$$

Within the TDSCF formulation (2.39), the diabatic population probabilities $P_k(t)$ can be written as

$$P_k(t) = \sum_r w_r n_k^{(r)}(t), \tag{3.3}$$

where the Monte-Carlo integration over the nuclear initial conditions $\mathbf{x}_0, \mathbf{p}_0$ [cf. Eq. (2.45)] has been expressed by a sum over the collective index $r = \{\mathbf{x}_0, \mathbf{p}_0\}$. Employing the γ modifications introduced above, however, the classical action variables $n_k^{(r)}(t)$ no longer directly correspond to the population *probability* of state $|\varphi_k\rangle$, as $n_k^{(r)}(t)$ can take on continuous values from $-\gamma$ to $1 + \gamma(N_{el} - 1)$. To make correspondence to discrete electronic states (i.e., $n_k = 0$ or 1), we invoke a histogram method[71] of assigning the system to the diabatic electronic state with the largest $n_k(t)$, i.e.

$$P_k(t) = \sum_r w_r \chi(n_k^{(r)}(t)), \tag{3.4}$$

$$\chi(n_k) = \begin{cases} 1 & \text{if } n_k > n_{k'} \\ 0 & \text{otherwise}. \end{cases} \tag{3.5}$$

If the electronic state under consideration is degenerate (e.g., in case of the $\tilde{X}$ state of the benzene cation), the *total* population of the $\tilde{X}$ electronic state is evaluated, i.e., the sum of the corresponding action variables is histogrammed $\{\chi[n_{\tilde{X}_\alpha}(t) + n_{\tilde{X}_\beta}(t)]\}$.

In a diabatic representation, the projector onto the kth adiabatic electronic state is defined by

$$P_k^{\text{ad}} = S(\mathbf{x}) P_k S^\dagger(\mathbf{x}), \tag{3.6}$$

where

$$S(\mathbf{x}) = \sum_{k,k'} |\varphi_k\rangle S_{kk'}(\mathbf{x})\langle\varphi_{k'}| \tag{3.7}$$

denotes the unitary transformation between the diabatic and adiabatic wave functions.[52,45] Quantum mechanically, the evaluation of the adiabatic population probabilities via Eq. (3.6) is a rather time-consuming task,[45] because it requires manipulations in the full electronic-vibrational product space. The semiclassical evaluation of the adiabatic projections (3.6), on the other hand, requires only manipulations of $N_{el} \times N_{el}$ matrices, as the transformation matrix $S(\mathbf{x})$ is readily obtained by diagonalizing the classical diabatic potential matrix. The population probability of the kth adiabatic state is given by

$$P_k^{\text{ad}}(t) = \text{Tr}\{P_k^{\text{ad}}\rho(t)\},$$

$$= \sum_r w_r \text{nad}_k^{(r)}(t), \tag{3.8}$$

where

$$\text{nad}_k(t) = \sum_i n_i p_{ii}^{(k)}$$

$$+ \sum_{i \neq j} \sqrt{(n_i + \gamma)(n_j + \gamma)} \, e^{i(q_i - q_j)} p_{ij}^{(k)}, \tag{3.9}$$

and $p_{ij}^{(k)}(\mathbf{x}) = \langle\varphi_i|P_k^{\text{ad}}|\varphi_j\rangle$ denote the electronic matrix elements of the adiabatic projector P_k^{ad}. If we allow for $\gamma > 0$,

we again need to map the electronic action variable $\text{nad}_k(t)$ onto discrete electronic states, i.e., Eq. (3.8) is augmented by the histogram function χ.

In the discussion of the mean-path approximation we have introduced the mean value of the diabatic electronic energy gap $\Delta E(t)$ (2.24) and the mean diabatic coupling $V_c(t)$ (2.25). A closely related quantity is given by the mean vibrational energy $H_k(t)$ contained in the diabatic state $|\varphi_k\rangle$, which is given by[72]

$$H_k(t) = \text{Tr}\{H_k\rho(t)\},$$

$$H_k = P_k(h_k - E_k + \epsilon_k), \tag{3.10}$$

where $\epsilon_k = \frac{1}{2}\sum_j \kappa_j^{(k)2}/\omega_j$ denotes the stabilization energy of the oscillator potential in the diabatic state $|\varphi_k\rangle$. Assuming $\epsilon_1 = \epsilon_2$, $E_1 = E_2$, the diabatic electronic energy gap (2.24) is given by $\Delta E(t) = H_2(t) - H_1(t)$. Similarly, the time-dependent energy content of the diabatic coupling is defined as

$$V_c(t) = \text{Tr}\{V_c\rho(t)\},$$

$$V_c = \sum_{k \neq k'} |\varphi_k\rangle V_{kk'}\langle\varphi_{k'}|. \tag{3.11}$$

According to Eq. (2.42), the semiclassical evaluation of $\Delta E(t)$ and $V_c(t)$ yields

$$H_k(t) = \sum_r w_r n_k^{(r)}\langle\phi_r|h_k - E_k + \epsilon_k|\phi_r\rangle, \tag{3.12}$$

$$V_c(t) = \sum_r w_r \sum_{k \neq k'} \sqrt{(n_k + \gamma)(n_{k'} + \gamma)} \, e^{i(q_k - q_{k'})}$$

$$\times \langle\phi_r|V_{kk'}|\phi_r\rangle. \tag{3.13}$$

The electronic populations $P_k(t)$ and $P_k^{(\text{ad})}(t)$ and the state-specific energies $H_k(t)$ and $V_c(t)$ are examples for electronic observables, i.e., the are obtained by averaging over all vibrational degrees of freedom. The simplest observables reflecting the vibrational dynamics of the system are the mean position and mean momentum of a specific vibrational mode x_j

$$x_j(t) = \text{Tr}\{x_j\rho(t)\} = \sum_r w_r x_j^{(r)}(t), \tag{3.14}$$

$$p_j(t) = \text{Tr}\{p_j\rho(t)\} = \sum_r w_r p_j^{(r)}(t). \tag{3.15}$$

The vibrational relaxation dynamics can also be analyzed in terms of the time-dependent energy content of a individual nuclear degrees of freedom[44,72]

$$E_j(t) = \text{Tr}\{E_j\rho(t)\},$$

$$= \sum_r w_r \sum_k n_k^{(r)} \frac{\omega_j}{2} \{p_j^{(r)2}(t) + (x_j^{(r)}(t) + \kappa_j^{(k)}/\omega_j)^2\}. \tag{3.16}$$

The energy content of coupling modes is obtained by replacing the $\kappa_j^{(k)}$ in (3.16) by $\lambda_{kk'}$,[73] where $\lambda_{kk'}$ is the vibronic coupling constant defined in (2.2b).

Note that the definitions of time-dependent energies are chosen such that the conservation of energy can be written as

$$E_{\mathrm{sum}}(t) \equiv \sum_k H_k(t) + V_c(t) = \sum_j E_j(t), \qquad (3.17\mathrm{a})$$

$$= \tilde{E} - \sum_k P_k(t)(E_k - \epsilon_k) \equiv E_{\mathrm{tot}}(t), \qquad (3.17\mathrm{b})$$

where $\tilde{E} = E_2 + \epsilon_{\mathrm{zp}}$ is the total energy of the system, consisting of the vertical excitation energy of the initially excited electronic state (say, $|\varphi_2\rangle$) and the vibrational zero-point energy ϵ_{zp}. $E_{\mathrm{sum}}(t)$ represents the time-dependent total vibrational energy acquired by the system. It can be expressed either as sum over the state-specific energies $H_k(t)$ and $V_c(t)$, or as sum over the mode-specific energies $E_j(t)$. Equation (3.17) describes the transformation of electronic energy $E_{\mathrm{tot}}(t)$, that has been put into the system via photoexcitation, into vibrational energy $E_{\mathrm{sum}}(t)$, i.e., the electronic relaxation in general results in an increase of vibrational energy. In an exact calculation as well as in a standard classical-path simulation, we therefore clearly have $E_{\mathrm{sum}}(t) = E_{\mathrm{tot}}(t)$.

Employing the γ modifications, however, Eq. (3.17) can no longer be taken for granted. It has been pointed out above that the diabatic population probability $P_k(t)$ should be evaluated using a histogram technique (3.4). It is not meaningful, however, to histogram the action variable $n_k(t)$ in Eq. (3.10) as well, because $H_k(t)$ represents the total vibrational energy of the diabatic state $|\varphi_k\rangle$, which is correctly given by Eq. (3.10). As a consequence, the total vibrational energy $E_{\mathrm{sum}}(t)$ may not longer be equal to $E_{\mathrm{tot}}(t)$. This is to say that, owing to the γ modifications, there is more vibrational energy $E_{\mathrm{sum}}(t)$ in the system as is provided through $E_{\mathrm{tot}}(t)$ by the electronic relaxation process! As $n_k(t)$ can take on continuous values from $-\gamma$ to $1 + \gamma(N_{\mathrm{el}} - 1)$, this is especially a problem for models including many electronic states, as we will find in the case of the benzene cation with $N_{\mathrm{el}} = 5$. To avoid this dynamical inconsistency, one has to choose γ small enough, that Eq. (3.17) is fulfilled, i.e., condition (3.17) determines an upper bound for the γ corrections.

B. The $S_1 - S_2$ conical intersection in pyrazine

As a first example we consider a simple two-state three-mode model of the $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$ states of pyrazine,[43] which has been adopted by several authors as a standard example of electronic relaxation.[36,44–46] Taking into account a single coupling mode (ν_{10_a}) and two totally symmetric modes (ν_1, ν_{6a}), Domcke and co-workers have identified a low-lying conical intersection of the two lowest excited singlet states of pyrazine, which has been shown to trigger IC and a dephasing of the vibrational motion on a femtosecond time scale.[43,44] A variety of theoretical investigations, including quantum wave-packet studies[44,45] and absorption and resonance Raman[74] as well as time-resolved pump-probe spectra[70] have been reported for this system. In the present work we adopt this model to study the applica-

bility and limitations of the mean-path approximation and to discuss the dynamical effects of γ modifications introduced above.

To ensure convergence, we have run 2500 trajectories in all simulations, although less than a hundred trajectories are sufficient to recognize the essential structures. The initial conditions for the nuclear variables $x_j(0), p_j(0)$ can either be sampled from the Wigner distribution,[68] or be obtained via classical action-angle variables, which was found to give almost identical results.[34] We have chosen the electronic initial conditions as $\chi_r^{(1)}(0) = 1$ and $\chi_2^{(2)}(0) = 0$, which corresponds to the electronic action-angle variables (2.33) $n(0) = 1$, q arbitrary. Interestingly, it did not make a difference whether we set $q = 0$ for each trajectory, or whether we performed a Monte-Carlo integration over the electronic angle variable q as suggested by Meyer and Miller.[28] In the case of $\gamma = 0$, one furthermore needs to assume $n(0) = 1 - \eta$, where η is a small number (say, 10^{-6}), to ensure that one does not start in a singularity of the differential equation (2.30). The quantum propagation of the wave function $|\Psi(t)\rangle$ has been performed by expanding $|\Psi(t)\rangle$ in a direct-product basis constructed from diabatic electronic states and harmonic-oscillator states, and solving the resulting system of coupled first-order differential equations using a Runge-Kutta-Merson scheme with adaptive step size.[44,70]

The comparison of the semiclassical simulations (full lines) and exact quantum calculations (dotted lines) is comprised in Fig. 1, which shows the diabatic electronic population probability $P_2(t)$ [panels (a)], the mean position $x(t)$ of the vibrational mode ν_{6a} [panels (b)], and the state-specific energies $H_k(t)$ and $V_c(t)$ [panels (c)]. Each semiclassically evaluated observable is plotted for three different values of the dynamical correction γ, namely for $\gamma = 0$ [panels (1)], $\gamma = \frac{1}{4}$ [panels (2)], and $\gamma = \frac{1}{2}$ [panels (3)].

To get an impression of the IC dynamics of the model, let us first look at the quantum results (dotted lines) of the electronic population probability $P_2(t)$ of the initially prepared S_2 state. The electronic population exhibits a slightly oscillatory initial decay on a time scale of about 50 fs, which is followed by pronounced quasiperiodical recurrences of the population. For times larger than 500 fs (not shown in Fig. 1), $P_2(t)$ fluctuates around its long-time limit of ≈ 0.33. It is interesting to note how the electronic decay exhibited by $P_2(t)$ is reflected in the vibrational relaxation of the system. Panels (b) shows the time evolution of the mean position $x(t)$ of the totally symmetric mode ν_{6a}, which, in the absence of vibronic coupling, would exhibit coherent harmonic oscillations. Owing to the electronic relaxation process, the vibrational motion is strongly damped and undergoes vibrational dephasing. Note that, analogously to the electronic relaxation, the vibrational dephasing process is completed within ≈ 500 fs.

The simulation results obtained by the semiclassical TDSCF model with different values for γ are seen to be in rather good agreement with the exact results for $P_2(t)$ and $x(t)$. The model nicely reproduces the initial decay, recurrences and long-time limits of these observables. Note, however, that the overall damping of $P_2(t)$ as well as of $x(t)$ is too weak for $\gamma = 0$ [panels (1), corresponding to a standard
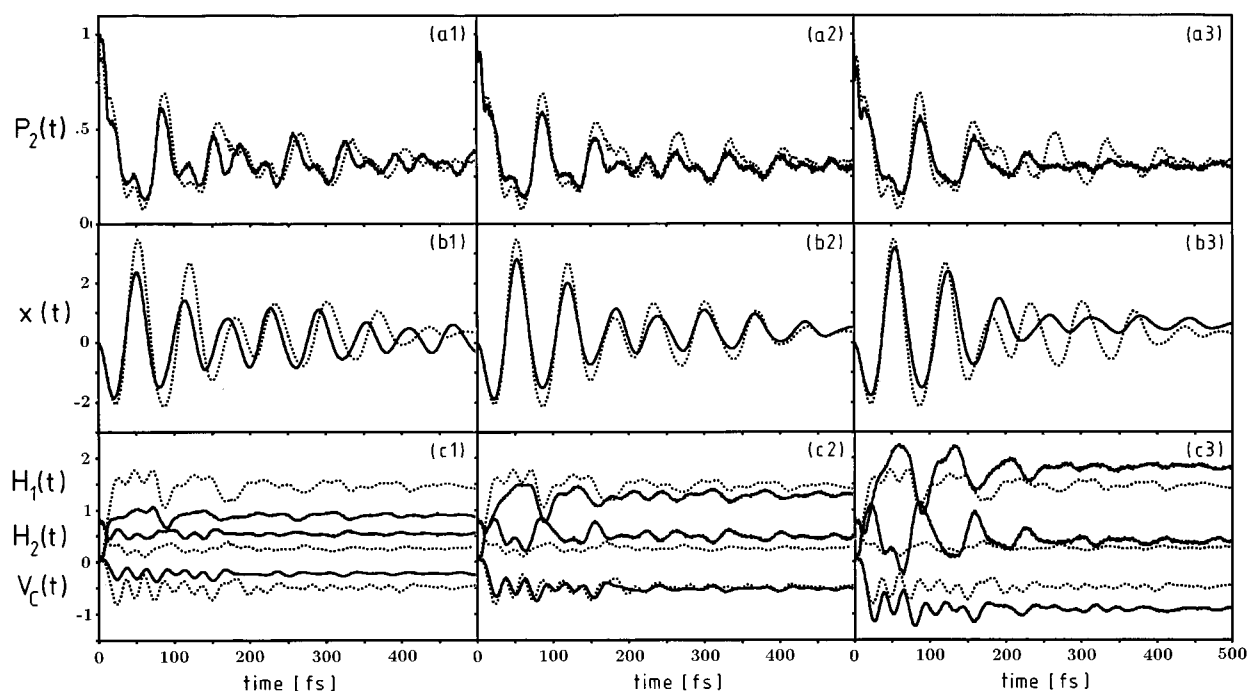
FIG. 1. Comparison of the results obtained by semiclassical simulations (full lines) and exact quantum calculations (dotted lines) for the two-state three-modes model of pyrazine. Panels (a) show the diabatic population probability $P_2(t)$, panels (b) the mean position $x(t)$ of the vibrational mode ν_{6a}, and panels (c) the state-specific energies $H_k(t)$ and $V_c(t)$. Each semiclassically evaluated observable is plotted for $\gamma=0$ [panels (1)], $\gamma=\frac{1}{4}$ [panels (2)], and $\gamma=\frac{1}{2}$ [panels (3)].

classical path model], and too strong for $\gamma=\frac{1}{2}$ [panels (3), corresponding to the classical electron analog model]. The value of $\gamma=\frac{1}{4}$ [panels (2)] appears to be the appropriate dynamical correction for this model system. In particular, for $\gamma=\frac{1}{4}$ the semiclassical results of both $P_2(t)$ and $x(t)$ are in phase with the quantum calculation, indicating that the overall coupling is correct.

To understand the effects of the dynamical corrections and to investigate the validity of the mean-path approximation, let us now consider the quantum results for the mean energies $H_k(t)$ and $V_c(t)$, which are shown in panels (c). Recall that initially the wave packet corresponding to the vibrational ground state in the S_0 has been impulsively excited into the S_2. Owing to this preparation of the system at the time $t=0$, there is initially no vibrational energy contained in the S_1 state [$H_1(0)=0$], while the vibrational energy contained in the S_2 state is given by the stabilization energy [$H_2(0)=\epsilon_2$]. The initial decay of $P_2(t)$, corresponding to an initial increase of the population in the S_1 state, is reflected by a rapid increase of the vibrational energy in the S_1 state to ≈ 1.5 eV. This is because the excess energy due to the initial S_2 excitation leads through the $S_2 \rightarrow S_1$ transition to highly excited vibrational levels in the S_1 state. The vibrational energy of the S_2 state, on the other hand, is seen to decrease slightly to ≈ 0.3 eV. Furthermore, the relaxation process is accompanied by the mean diabatic coupling $V_c(t)$ oscillating around its long-time value of ≈ -0.5 eV.

It is quite interesting to compare the quantum results for $H_k(t)$ and $V_c(t)$ to the corresponding semiclassical data obtained for different values of the dynamical correction γ. As

has been anticipated in the theoretical analysis of the mean-path approximation in Sec. II C, the standard classical path method (corresponding to $\gamma=0$) underestimates both the diabatic energy gap $\Delta E(t)$ and the mean coupling $V_c(t)$. Note that in the present model for pyrazine the classical path approximation predicts a long-time limit for the energy gap of $\Delta E(t) \approx 0.4$ eV, whereas the quantum value is ≈ 1.2 eV. The main flaw of the mean-path approximation thus is that the S_1 and the S_2 get about the same amount of vibrational energy of the system, which is in contrast to the quantum calculation, showing that the vibrational energy mainly goes into the S_1 state, i.e., the vibrational relaxation mainly takes place in the S_1 state. This inadequacy of the mean-path approximation cannot be completely remedied by the γ modifications, but, as has been shown in Sec. II C, increasing γ also increases the energy gap $\Delta E(t)$. More important for the relaxation process is the value of the overall nonadiabatic coupling $V_c(t)$, which is correctly reproduced for $\gamma=\frac{1}{4}$ [panel (c2)]. A value of $\gamma=\frac{1}{2}$ corresponding to the classical electron analog model [panel (c3)], is seen to exaggerate the diabatic coupling $V_c(t)$, which in turn causes a too fast relaxation of the electronic population probability $P_2(t)$ and the mean position $x(t)$, respectively.

To summarize, it has been shown that the semiclassical TDSCF model augmented with a dynamical correction of $\gamma=\frac{1}{4}$ reproduces the electronic and vibrational relaxation of the three-mode two-state model of pyrazine almost quantitatively. Similar studies on the relaxation dynamics of model systems for $C_2H_4^+$,[72] ozone,[75] and $C_6H_6^{+}$[49] have reconfirmed this finding.

C. The $\tilde{C} \to \tilde{B} \to \tilde{X}$ IC process in the benzene cation

Recently Köppel, Domcke, and Cederbaum have presented interesting quantum calculations of the ultrafast IC process in the benzene cation (Bz$^+$).[48,49] In his latest work,[49] Köppel has included five vibrational modes and explicitly accounted for the vibronic interactions between the $\tilde{X}\,^2E_{1g}$, $\tilde{B}\,^2E_{2g}$, and $\tilde{C}\,^2A_{2u}$ electronic states of Bz$^+$. Adopting this five-mode three-state model for Bz$^+$, he has performed time-dependent quantum wave-packet propagations and showed that the (initially excited) $\tilde{C}$ state decays irreversibly into the $\tilde{X}$ state within ≈ 250 fs.

In a preceding letter,[37] we have employed the classical electron analog model[28] to reproduce the quantum results of Ref. 49. In the present work, we discuss the $\tilde{C} \to \tilde{B} \to \tilde{X}$ IC process Bz$^+$ in some greater detail, addressing, in particular, the interplay between electronic and vibrational relaxation in this system. Furthermore it is shown that in the case of an electronic multistate model a large value for the dynamical correction γ (e.g., $\gamma = \frac{1}{2}$ as employed in the classical electron analog model) may lead to dynamical inconsistencies in the semiclassical simulation.

In the case of Bz$^+$, the model Hamiltonian (2.1) as given by Köppel amounts to an electronic five-state system labeled by $k = \tilde{X}_\alpha, \tilde{X}_\beta, \tilde{B}_\alpha, \tilde{B}_\beta, \tilde{C}$, i.e., the second excited electronic state ($\tilde{C}^2A_{2u}$) is represented by $|\varphi_{\tilde{C}}\rangle$, while $|\varphi_{\tilde{X}\alpha}\rangle, |\varphi_{\tilde{X}\beta}\rangle$ and $|\varphi_{\tilde{B}\alpha}\rangle$, $|\varphi_{\tilde{B}\beta}\rangle$ denote the degenerate electronic ground ($\tilde{X}\,^2E_{1g}$) and first excited ($\tilde{B}\,^2E_{2g}$) electronic state, respectively. Adopting matrix notation, the electronic potential matrix reads:[49]

$$\mathbf{V} = V_0 \mathbf{1} + \begin{pmatrix} E_X + \sum_{i=1}^{2} \kappa_i^{(X)} Q_i & \sum_{i=6}^{9} l_i^{(X)} \rho_i e^{-i\theta_i} & -\sum_{i=4}^{5} \kappa_i Q_i & 0 & 0 \\ \sum_{i=6}^{9} l_i^{(X)} \rho_i e^{i\theta_i} & E_X + \sum_{i=1}^{2} \kappa_i^{(X)} Q_i & 0 & \sum_{i=4}^{5} \kappa_i Q_i & 0 \\ -\sum_{i=4}^{5} \kappa_i Q_i & 0 & E_B + \sum_{i=1}^{2} \kappa_i^{(B)} Q_i & \sum_{i=6}^{9} l_i^{(B)} \rho_i e^{-i\theta_i} & \sum_{i=16}^{17} \lambda_i r_i e^{i\phi_i} \\ 0 & \sum_{i=4}^{5} \kappa_i Q_i & \sum_{i=6}^{9} l_i^{(B)} \rho_i e^{i\theta_i} & E_B + \sum_{i=1}^{2} \kappa_i^{(B)} Q_i & \sum_{i=16}^{17} \lambda_i r_i e^{-i\phi_i} \\ 0 & 0 & \sum_{i=16}^{17} \lambda_i r_i e^{-i\phi_i} & \sum_{i=16}^{17} \lambda_i r_i e^{i\phi_i} & E_C + \sum_{i=1}^{2} \kappa_i^{(C)} Q_i \end{pmatrix}. \tag{3.18}$$

The potential matrix (3.18) features three different kinds of vibronic interactions: the Jahn-Teller coupling owing to the degeneracy of the $\tilde{X}$ and $\tilde{B}$ states through the modes $\nu_6 - \nu_9$ (Wilson numbering), the coupling of the $\tilde{C}$ and $\tilde{B}$ states by the pseudo-Jahn–Teller active modes ν_{16} and ν_{17}, and the coupling of the $\tilde{B}$ and $\tilde{X}$ states by the modes ν_4 and ν_5. As has been discussed in detail elsewhere,[47–49,52] each of the vibronic interactions leads to a multidimensional conical intersection of the corresponding PESs.

To be able to perform quantum-mechanical wave-packet propagations, the Hamiltonian is simplified by neglecting the presumably weaker coupled modes $\nu_2, \nu_5, \nu_7, \nu_9$, and ν_{16}. Ignoring furthermore the degeneracy of the remaining vibrational modes ν_6, ν_8, ν_{17} and the $\tilde{X}$ and $\tilde{B}$ electronic states, the model system (3.18) reduces to the three-state five-mode Hamiltonian:[49]

$$\mathbf{H} = (T + V_0)\mathbf{1} + \begin{pmatrix} E_X + \kappa_1^{(X)} Q_1 - \sum_{i=6,8} l_i^{(X)} Q_i & \kappa_4 Q_4 & 0 \\ \kappa_4 Q_4 & E_B + \kappa_1^{(B)} Q_1 + \sum_{i=6,8} l_i^{(B)} Q_i & \lambda_{17} Q_{17} \\ 0 & \lambda_{17} Q_{17} & E_C + \kappa_1^{(C)} Q_1 \end{pmatrix}. \tag{3.19}$$

Using the model Hamiltonian (3.19), Köppel performed large-scale dynamical quantum calculations by solving numerically exactly the time-dependent Schrödinger equation. As an initial state it has been assumed that the system is in the vibrational ground state of neutral benzene shifted up vertically to the $\tilde{C}$ PES, corresponding to ionization from the electronic and vibrational ground state of neutral benzene. All parameters of the model Hamiltonians (3.18) and (3.19) are taken from Ref. 49. For a further discussion of the Hamiltonian (3.18) see Refs. 48 and 49.

Figure 2 compares the quantum (a) and semiclassical TDSCF (b) calculations of the diabatic population probabilities $P_k(t)$ for the five-mode three-state model [Eq. (3.19)] of Bz^+. The quantum calculation exhibits an oscillatory population decay of the initially excited $\tilde{C}$ electronic state, which is reflected in a rapid rise and similar beatings of the $\tilde{B}$ state population. After a somewhat delayed onset, the population of the $\tilde{X}$ electronic state exhibits a non-oscillatory rise and dominates over both the $\tilde{C}$ and $\tilde{B}$ electronic states after ≈ 120 fs. The TDSCF calculation, which has been evaluated for $\gamma = \frac{1}{4}$, is seen to reproduce the features of the quantum reference, e.g., transient beatings and long-time limits, fairly well. Except for the amplitude of the quantum beats and the classically somewhat to slow $\tilde{B} \rightarrow \tilde{X}$ decay, the agreement of quantum and semiclassical calculations is almost quantitative.

Let us now consider the electronic relaxation dynamics of the more realistic model system [Eq. (3.18)] for Bz^+, where the remaining vibrational modes $\nu_2, \nu_5, \nu_7, \nu_9$, and ν_{16} are included and the degeneracy of the (pseudo) Jahn-Teller modes and the $\tilde{X}$ and $\tilde{B}$ electronic states is explicitly taken into account. Figure 2c shows the diabatic population probabilities of the resulting sixteen-mode five-state model of Bz^+. The comparison of the five-mode three-state model (b) and the sixteen-mode five-state model (c) reveals that the inclusion of additional electronic and vibrational degrees of freedom results in (i) a large suppression of the coherent quantum beating and (ii) a faster and more complete IC process, i.e., within ≈ 300 fs the initially excited $\tilde{C}$ electronic state is almost completely decayed into the electronic ground state $\tilde{X}$ of the system.

It is interesting to compare the results of Fig. 2 with the corresponding data obtained with the classical electron analog model,[37] where the dynamical correction is $\gamma = \frac{1}{2}$. While the electronic population decay of the five-mode three-state model is for $\gamma = \frac{1}{2}$ only slightly faster than in Fig. 2(b), the classical electron analog simulation predicts for the sixteen-mode five-state model of Bz^+ an about two times larger rate for the $\tilde{B} \rightarrow \tilde{X}$ transition.[37] Although it is clear from Sec. II D that a larger dynamical correction results in stronger vibronic coupling and thus in a faster electronic relaxation, the effects of the γ modifications should certainly not dominate the dynamics of the system.

To check the consistency of the TDSCF calculation with dynamical corrections, we may compare the time-dependent energies $E_{\text{sum}}(t)$ (3.17a) and $E_{\text{tot}}(t)$ (3.17b). As has been shown in Sec. III A, in an exact calculation the total vibrational energy $E_{\text{sum}}(t)$ is equal to the loss of total electronic energy $E_{\text{tot}}(t)$, whereas simulations employing the γ modifications may lead to $E_{\text{sum}}(t) \neq E_{\text{tot}}(t)$. Figure 3 demonstrates this effect by showing the total vibrational energy $E_{\text{sum}}(t)$ (full lines) and the loss of total electronic energy $E_{\text{tot}}(t)$ (dotted lines) for $\gamma = \frac{1}{4}$ (a) and for $\gamma = \frac{1}{2}$ (b). While the mean energies obtained by the TDSCF model with $\gamma = \frac{1}{4}$ approximately fulfill the consistency criteria $E_{\text{sum}}(t) = E_{\text{tot}}(t)$, the two energies are seen to diverge considerably in the case of $\gamma = \frac{1}{2}$, leading to a spurious additional increase of the total
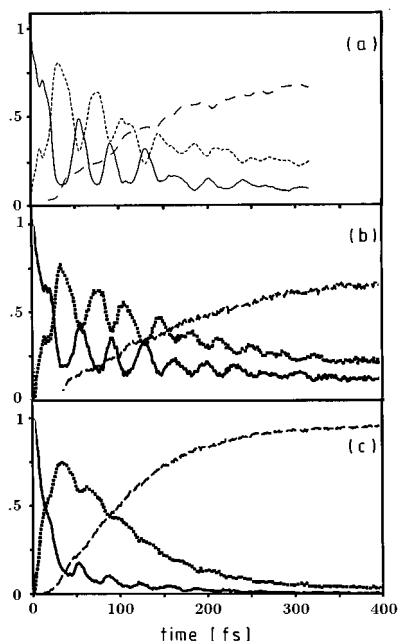
FIG. 2. Time-dependent population probabilities $P_k(t)$ of the $\tilde{C}$ (full line), $\tilde{B}$ (dotted line), and $\tilde{X}$ (dashed line) diabatic electronic states of the benzene cation. Panel (a) shows the quantum calculation [49], panel (b) the semiclassical calculation for the five-mode three-state model. The semiclassical calculation of the diabatic populations for the sixteen-mode five-state model of the benzene cation is shown in panel (c).
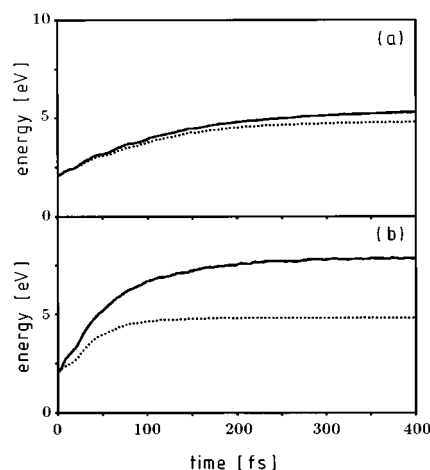
FIG. 3. Comparison of the total vibrational energy $E_{\text{sum}}(t)$ (full lines) and the loss of total electronic energy $E_{\text{tot}}(t)$ (dotted lines) for $\gamma = \frac{1}{4}$ (a) and for $\gamma = \frac{1}{2}$ (b). The energies have been evaluated semiclassically for the sixteen-mode five-state model of the benzene cation.
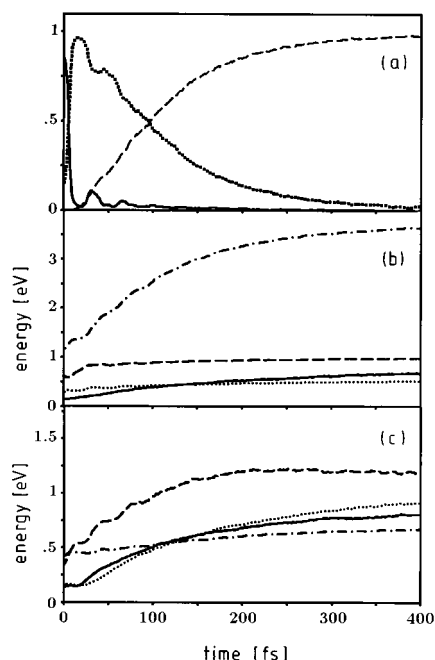
FIG. 4. *Adiabatic* population probabilities $P_k^{ad}(t)$ [panel (a)] and time-dependent energy content of various vibrational modes [panels (b) and (c)], obtained by a semiclassical calculation for the sixteen-mode five-state model of the benzene cation. Panel (b) shows the time-dependent energy content of the totally symmetric modes ν_1 and ν_2 (dashed line), the nontotally symmetric coupling modes ν_4 and ν_5 (full line), the pseudo-Jahn–Teller active modes ν_{16} and ν_{17} (dotted line), and the Jahn–Teller active modes $\nu_6 - \nu_9$ (dashed-dotted line). Panel (c) shows the time-dependent energy content of the Jahn–Teller active mode ν_6 (full line), ν_7 (dashed-dotted line), ν_8 (dashed line), and ν_9 (dotted line), respectively.

vibrational energy $E_{\mathrm{sum}}(t)$ by almost 3 eV. Discarding the dynamical corrections completely, on the other hand, is not a satisfying solution either, because for $\gamma = 0$ the TDSCF calculation considerably underestimates the subsequent $\tilde{B} \rightarrow \tilde{X}$ rate. Compared to the two-state case discussed above, the validity of the mean-path approximation and the choice of the dynamical corrections are more critical for multistate systems, and require careful checks of the simulations.

Let us finally employ the semiclassical model to investigate the $\tilde{C} \rightarrow \tilde{B} \rightarrow \tilde{X}$ IC process of the sixteen-mode five-state model of Bz$^+$ in more detail. As has been pointed out above, in the semiclassical formulation it is quite easy to calculate observables pertaining to the *adiabatic* representation, while the actual propagation is performed in the *diabatic* representation. As an example, Fig. 4(a) shows the *adiabatic* population probabilities $P_k^{\mathrm{ad}}(t)$ defined in Eq. (3.8). It is seen that the adiabatic excited-state populations $P_2^{\mathrm{ad}}(t)$, $P_1^{\mathrm{ad}}(t)$ decay on the same time scale as the corresponding diabatic populations shown in Fig. 2(c), although the initial decay of $P_2^{\mathrm{ad}}(t)$ is even faster than in the diabatic case; within only ≈ 15 fs, the population of the $\tilde{C}$ state has decayed to 95% into the lower-lying $\tilde{B}$ state. Furthermore the coherent transients exhibited by the diabatic populations are almost completely suppressed in the adiabatic representation.

To study the microscopic origin of this ultrafast electronic relaxation, we particularly want to address the ques-

tion of intramolecular energy redistribution, i.e., how the initial photoexcitation energy of almost 5 eV is distributed among the vibrational modes of the molecule. To this end, Figs. 4(b) and 4(c) show the time-dependent energy content of some of the vibrational modes included in the model. As mentioned above, the model contains four different kinds of vibrational modes, the total vibrational energies of which are plotted in Fig. 4(b): The totally symmetric modes ν_1 and ν_2 (dashed line), the nontotally symmetric coupling modes ν_4 and ν_5 (full line), the pseudo-Jahn–Teller active modes ν_{16} and ν_{17} (dotted line), and the Jahn–Teller active modes $\nu_6 - \nu_9$ (dashed-dotted line). Figure 4(b) reveals that most of the electronic excitation energy is assumed by the degenerate Jahn–Teller modes $\nu_6 - \nu_9$, whereas the other vibrational degrees of freedom participate only scarcely in the intramolecular energy redistribution of the molecule. As a further illustration, Fig. 4(c) shows how the vibrational energy is divided up among the Jahn–Teller modes $\nu_6 - \nu_9$: the most important mode is ν_8 (dashed line, it also holds the largest vibronic coupling constants, see Ref. 49), while the remaining modes ν_6 (full line), ν_7 (dashed-dotted line), and ν_9 (dotted line) accept about the same vibrational energy. Note, however, that the low-frequency mode ν_6 with frequency $\omega_6 = 0.075$ eV is considerably higher vibrationally excited than the high-frequency mode ν_7 with frequency $\omega_7 = 0.393$ eV.

Figure 4 nicely elucidates the complex interplay of ultrafast electronic and vibrational relaxation in a polyatomic molecule. Furthermore it represents an interesting example of the highly efficient intramolecular energy redistribution of multimode Jahn–Teller systems. As has been discussed in detail in Ref. 52 for the example of a two-mode Jahn–Teller model of BF$_3^+$, the mode-mode interaction results in a particularly strong distortion of the adiabatic PESs, which in turn gives rise to the ultrafast IC process observed in these systems.

IV. SUMMARY AND CONCLUSIONS

We have outlined a semiclassical TDSCF approach for the description of ultrafast IC processes of polyatomic molecules. The formulation represents a generalization of familiar classical-path methods and can be considered as a combination of three well known techniques:

(i)   A TDSCF ansatz for the total density operator (2.37) which couples the electronic degrees of freedom to the nuclear degrees of freedom in a self-consistent manner, and describes the vibrational density operator in terms of Gaussian wave packets.

(ii) Approximation of the *semiclassical* expansion coefficients of the density operator (2.37) through *quasiclassical* sampling of the nuclear initial conditions (2.39). This approximation requires to employ a single vibrational density operator for all electronic states (i.e., the mean-path approximation), and to assume rapid randomization of the nuclear phases.

(iii) In the case of coordinate-dependent diabatic coupling $V_{kk'}(\mathbf{x})$, dynamical corrections are employed to the off-diagonal elements of the electronic density opera-

tor, which correct for the inadequacy of the mean-path approximation in these cases.

By virtue of point (i), both electronic and nuclear degrees of freedom are represented by a density operator, which allows to employ standard density-matrix rules, e.g., for the evaluation of time-dependent mean values and correlation functions. Furthermore it is straightforward within the TDSCF formalism to make contact to well-known approximations of dissipative quantum dynamics[34] such as the so-called noninteracting-blip approximation of Leggett and co-workers.[39] Also note that in the calculation of electronic correlation functions, the ansatz (2.39) takes into consideration the nuclear phases of the individual wave packets. Contrary to standard classical-path methods, the semiclassical TDSCF formulation therefore allows to roughly account for pure electronic dephasing effects.[76]

Point (ii) ensures that the method is practical and is truly applicable for complex systems including many degrees of freedom. We therefore do not attempt to evaluate the semiclassical Greens function, thus avoiding complex valued trajectories and complicated equations of motion which have to be evaluated iteratively or have to satisfy "double-ended" boundary conditions. The approximation (2.39) to the "rigorous" semiclassical expansion (2.37) relies on the assumption of randomization of nuclear phases, which makes it possible to perform the trace over the nuclear variables through quasiclassical sampling of the nuclear initial conditions [cf. Eq. (2.45)].

We have discussed in some detail the validity of the mean-path approximation which is the second assumption implied in the ansatz (2.39). Comparing the equations of motion pertaining to a multiconfiguration (MC) ansatz (2.4) to the corresponding equations of a single-configuration (SC) ansatz (2.12), we have shown that for constant diabatic coupling elements $V_{kk'}$, the mean-path approximation should be appropriate in many cases, which is in accordance with the findings of paper I. In this case the equations of motion for the nuclear degrees of freedom are identical in the SC and MC formulations, and the tuning of the electronic energy gap $\Delta E(t)$ due to linearly coupled modes is described correctly by the SC ansatz. In the case of coordinate-dependent diabatic coupling $V_{kk'}(\mathbf{x})$, however, it has been found that the mean-path approximation becomes problematic, which in general results in a underestimation of the vibronic coupling and thus of the overall relaxation rate. As a remedy for this inadequacy of the mean-path approximation, we have employed dynamical corrections to the off-diagonal elements of the electronic density operator, as has been suggested by Meyer and Miller.[28] The effects, merits as well as pitfalls, of these modifications have been investigated in detail. In particular, we have given a consistency criterion (3.17), which allows to determine an upper limit for the dynamical corrections, and have suggested a value of $\gamma = \frac{1}{4}$. (In accordance with the well known modifications due to Langer,[62] Meyer and Miller have used a value of $\gamma = \frac{1}{2}$.)

Employing (i) a two-state three-mode model of the $S_1 - S_2$ conical intersection in pyrazine,[43] and (ii) a three-state five-mode and a five-state sixteen-mode model of the

$\tilde{C} \to \tilde{B} \to \tilde{X}$ IC process in the benzene cation,[49] we have undertaken detailed computational studies to demonstrate the capacity of the semiclassical TDSCF approach for the description of ultrafast IC processes. The comparison to exact quantum-mechanical basis-set calculations reveals that the simple semiclassical method reproduces almost quantitatively electronic population probabilities and mean values for the energy content and the position of individual vibrational modes. It should be noted that the complex electronic and vibrational relaxation dynamics occuring on intersecting PESs is not reproduced by other approximative propagation techniques. Simple quantum-mechanical TDSCF methods, for example, neglect the correlations between the separated nuclear degrees of freedom, and therefore are able to account only for the very short-time dynamics of the system.[10,46] Even for in principle exact methods, such as path-integral[5] and multiconfiguration TDSCF[12] propagations, the calculation of electronic population probabilities turns out to be a demanding task because of these mode-mode correlations. The semiclassical TDSCF model explicitly accounts for these correlations through the coupled equations of motion, Eqs. (2.16) and (2.17). It therefore represents a suitable method for the modeling of ultrafast electronic relaxation processes in polyatomic molecules, where typically several (3-10) strongly coupled vibrational modes are involved in the IC process.[52,54]

On the other hand it is clear that the semiclassical TDSCF propagation is no "black-box" method, which can be applied blindly to any problem. Particularly in cases when several energetically well separated coupled electronic states are involved, careful checks of the simulations are advisable, including, e.g., sensitivity tests with respect to the choice of the dynamical corrections, initial conditions, and excitation energies. Another stringent test for the underlying approximation of the semiclassical model is the description of reactive processes. First results for simple *cis-trans* isomerization models have shown that the semiclassical approach seems to be capable to model the relaxation dynamics of this elementary chemical reaction.[38] The extension of the approach towards nonadiabatic photoisomerization processes is in progress and will be the subject of a further publication.

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