Modeling of decoherence and dissipation in nonadiabatic photoreactions by an effective-scaling nonsecular Redfield algorithm

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Abstract

Nonadiabatic photoisomerization dynamics in a condensed-phase environment is studied within the framework of Redfield theory. Considering several measures of decoherence and dissipation, the relaxation behavior of various models of nonadiabatic cis–trans photoisomerization is investigated. Several levels of relaxation theory are compared: The full Redfield theory (including all terms of the relaxation tensor), the secular approximation to it (including only the resonant terms) and the popular Bloch model (which also neglects terms that are resonant by accident). Although these approximations are shown to work well for the single-mode model, they are found to lead to significant deviations for various two-mode models. The latter behavior is expected to be generic for multidimensional systems, which typically exhibit numerous near-degeneracies of the level spacings. To correctly describe the relaxation dynamics, while still retaining the advantageous $N^2$ scaling of the Bloch model, a “nonsecular” algorithm is proposed that systematically includes the most important nonsecular terms. The algorithm correctly reproduces the results of the full Redfield theory, while the numerical effort is reduced by typically an order of magnitude for the examples considered.

1. Introduction

In recent years, there has been considerable interest in photoinduced ultrafast reactions in a condensed-phase environment. Experimentally, the reactions can be investigated by femtosecond nonlinear spectroscopy techniques and include, for instance, electron-transfer processes on surfaces and biological systems [1], proton-transfer reactions in biomolecules [2,3], or photoisomerizations like the isomerization of the retinal molecule in rhodopsin upon irradiation [4]. The theoretical description of photochemical reactions in terms of direct ab initio or semiempirical molecular-dynamics simulations has become possible just recently, see [5] for a recent review. Employing a level of theory that is appropriate for excited electronic states, however, the calculations are quite tedious and still restricted to short times. Alternatively, a suitable model of the photoinduced dynamics may be employed in order to gain an understanding of the essential physics involved.

One widely used method to describe an ultrafast photoreaction in a condensed phase environment is the so-called Redfield theory, which was originally developed in the context of nuclear magnetic resonance [6]. This theory is based on the partitioning of the overall system into a relevant part (the “system”) and the remaining degrees of freedom (the “bath”). The system comprises the electronic states involved in the reaction and those molecular modes that are most important for the photoreaction, while the remaining intramolecular and solvent degrees of freedom constitute the bath. The interaction between system and bath is treated perturbatively up to second order and the bath degrees of freedom are traced out within the Markov approximation for the
relaxation operators. The resulting equation of motion for the reduced density matrix of the system scales as $N^3$ ($N$ being the dimension of the reduced density matrix of the system) and represents a computationally straightforward method for the quantum description of dissipative reaction dynamics. It has been successfully applied to a variety of systems describing ultrafast energy- and electron-transfer reactions [7–14], to conical-intersection models [15], and to photoisomerization models [16,17].

For large molecular systems with several vibrational modes, however, the $N^3$-scaling for the propagation of the Redfield equation is despite the nowadays available computer power still time-consuming. An elegant way to circumvent the $N^3$-scaling are stochastic wavefunction methods, which replace a density-matrix calculation by an statistical average over wave-packet propagations [18–22]. Alternatively, one may invoke further approximations to Redfield theory such as the secular approximation for the relaxation operators [23,28] or the diabatic damping approximation [20,24]. In the secular approximation, only the secular elements of the relaxation tensor are considered. This leads to a decoupling between the diagonal ("populations") and the off-diagonal ("coherences") elements of the density matrix (Bloch model). The resulting equation of motion is computationally very attractive since only the populations need to be propagated numerically and it thus scales as $N^2$. The neglect of the nonsecular terms, however, may lead to severe artifacts such as the suppression of coherent transients [11,15,25–27].

In the present work, we develop an algorithm that in addition to the secular terms systematically includes the most important nonsecular terms of the relaxation tensor. The scaling of this algorithm is $f \cdot N^2$ with $f \ll N$. The performance of this so-called nonsecular algorithm is demonstrated for a previously proposed model of nonadiabatic cis–trans photoisomerization, which is coupled to a harmonic bath [16,17]. Furthermore, we study the effects of the secular approximation and the systematic consideration of nonsecular terms on the decoherence behavior of a molecular system. To this end, we introduce several measures of decoherence and discuss the decoherence time. It is shown that this time crucially depends on the type of crossing between the electronic states of the system.

The rest of this paper is as follows: In Section 2, we give a brief review of Redfield theory and introduce the photoisomerization model. Special attention is given to the secular approximation and, furthermore, the nonsecular algorithm is developed. The performance of the nonsecular algorithm is demonstrated in Section 3 and the effects of the nonsecular terms on the dissipation and decoherence behavior at potential-energy crossings is discussed. Section 4 summarizes and concludes.

2. Theory

2.1. Redfield theory

In Redfield theory, the overall system is divided into a system part and a heat bath. Thus we have the total Hamiltonian

$$H = H_S + H_B + H_{SB},$$

(1)

where the system Hamiltonian $H_S$ is meant to include the most important degrees of freedom of the system, the bath Hamiltonian $H_B$ comprises the remaining system modes and the environment, and the coupling between system and bath is described by $H_{SB}$. As is common practice, the bath is described within the harmonic approximation ($\hbar = 1$ throughout),

$$H_B = \sum_x \frac{\omega_x}{2} (x^2 + p_x^2),$$

(2)

where $x$ and $p$ represent the position and momentum operator pertaining to the $x$th vibrational mode, respectively. Furthermore, we assume for the general system–bath interaction

$$H_{SB} = \sum_a Q_a F_a,$$  

(3)

where the sum runs over the system degrees of freedom, the operator $Q_a$ depends only on the corresponding system mode, and

$$F_a = \sum_x g_{ax} x_a$$  

(4)

acts only on the bath modes. The coupling constants $g_{ax}$ are chosen according to an Ohmic spectral density

$$J_a(\omega) = \pi \sum_x g_{ax}^2 \delta(\omega - \omega_x) = \eta_a \omega e^{-\omega/\omega_c},$$  

(5)

where the overall strength of the system–bath coupling is given by the dimensionless parameters $\eta_a$, while the cutoff frequencies $\omega_c$ describe the timescale distribution of the bath.

To describe the dissipative dynamics of the system, we have employed the Redfield approach, that is, a second-order perturbation theory with respect to the system–bath interaction combined with a Markov approximation for the relaxation operators [23,28]. Adopting the system eigenstate representation, $H_S |l\rangle = E_l |l\rangle$, the Redfield equation is then given as

$$\frac{\partial}{\partial t} \sigma_{ij} = -i\omega_{ij} \sigma_{ij} + \sum_{k,l} R_{ijkl} \sigma_{kl},$$  

(6)

where $\sigma$ denotes the reduced density-matrix characterizing the relevant system, $\omega_{ij} = E_i - E_j$, and $R_{ijk\ell}$ represents the Redfield relaxation tensor, which describes the interaction of the quantum system with the bath. The Redfield tensor can be expressed as
R_{ijkl} = \Gamma_{ijkl}^{+} + \Gamma_{ijkl}^{-} - \delta_{ij} \sum_{m} \Gamma_{imnk}^{+} - \delta_{ik} \sum_{m} \Gamma_{imnj}^{-}, \quad (7)
and for the system–bath interaction (3) its elements can be written as
\begin{align}
\Gamma_{ijk}^{+} &= \sum_{a} (Q_{a})_{ij} (Q_{a})_{ik} \int_{0}^{\infty} dt \, e^{-i\omega_{a} t} \langle F_{a} F_{a}(t) \rangle_{B}, \quad (8)
\Gamma_{ijk}^{-} &= \sum_{a} (Q_{a})_{ij} (Q_{a})_{ik} \int_{0}^{\infty} dt \, e^{-i\omega_{a} t} \langle F_{a}(t) F_{a} \rangle_{B}, \quad (9)
\end{align}
where \((Q_{a})_{ik} = \langle \hat{Q}_{a} | k \rangle\), \(F_{a}(t) = e^{i\mu_{a} t} F_{a} e^{-i\mu_{a} t}\), and \(\langle \cdot \cdot \cdot \rangle_{B}\) denotes the thermal average over the bath.

Since Redfield theory is based on a second-order perturbation description of the system–bath coupling and the Markov approximation is invoked for the Redfield tensor, its applicability is limited to certain physical parameter regimes. In order not to violate the perturbative treatment, it is sufficient to have \(\eta_{p} \ll 1\) for \(T = 0 \, \text{K}\) [29]. The Markov approximation, on the other hand, requires that the bath correlation time \(\tau_{c}\) is short compared to the relaxation time of the system, i.e., \(\tau_{c} \gg \tau_{R} = |\text{Re}(R_{ijkl})|\). It should be noted, however, that both criteria can only be considered as qualitative conditions. More quantitative criteria can be given for systems that can be solved analytically, such as the damped harmonic oscillator [30–32] and the dissipative two-level system [33], or for systems in which numerically exact results as comparison exist [29]. For the systems in the present work, neither an analytical solution nor numerically exact results are available, that is, we have to resort to the qualitative criteria mentioned above.

2.2. Secular approximation

The right-hand side of the Redfield equation (6) can be evaluated without explicit construction of the Redfield tensor (7) by using a matrix multiplication scheme [34], which reduces the scaling of the numerical time propagation from \(N^{3}\) to \(N^{2}\) (\(N\) being the dimension of the reduced density matrix). A further reduction of the scaling can be achieved by employing the secular approximation to Redfield theory, which only considers the resonant terms of the Redfield tensor \(R_{ijkl}\), that is, terms satisfying
\begin{equation}
\omega_{ij} - \omega_{kl} = 0. \quad (10)
\end{equation}
The neglect of the coupling between \(\sigma_{ij}\) and \(\sigma_{kl}\) for \(\omega_{ij} - \omega_{kl} \neq 0\) is a good approximation as long
\begin{equation}
|\omega_{ij} - \omega_{kl}| \gg |R_{ijkl}| \quad (11)
\end{equation}
holds for these nonsecular terms, what can be rationalized as follows: In the interaction picture, the Redfield equation (6) is given by [6]
\begin{equation}
\frac{\hat{\sigma}}{\hat{t}} \sigma_{ij} = \sum_{kl} e^{i(\omega_{ij} - \omega_{kl}) t} R_{ijkl} \sigma_{kl}, \quad (12)
\end{equation}
where \(\hat{\sigma}\) denotes the density matrix in the interaction picture and is connected to the density matrix in the Schrödinger picture via \(\sigma_{ij} = \sigma_{ij} e^{i\omega_{ij} t}\). Eq. (12) shows, that the effect of \(R_{ijkl}\) averages to zero over a period of time \(1/|\omega_{ij} - \omega_{kl}|\) as long relation (11) is fulfilled, i.e., as long the density matrix can be considered unperturbed by relaxation during this time. The same argument emphasizes also the importance of the secular terms for the equation of motion (12).

The condition \(\omega_{ij} - \omega_{kl} = 0\) for the secular terms is satisfied in any of the following cases: (i) \(i = j, \, k = l\) and \(i \neq k\), (ii) \(i = k, \, j = l\) and \(i \neq j\), and (iii) \(i = j = k = l\). Moreover, further secular terms satisfying Eq. (10) may exist in systems with degenerate or regularly spaced levels. If one assumes that secular terms only exist in the first three cases, which might apply for rather anharmonic systems, we obtain the so-called Bloch model [23,28].

The Bloch model affects a decoupling of the diagonal and off-diagonal elements of \(\sigma\), where the populations obey the Pauli master equation,
\begin{equation}
\frac{\hat{\sigma}}{\hat{t}} \sigma_{ij} = \sum_{k} R_{ikj} \sigma_{kj}(t), \quad (13)
\end{equation}
while the coherences show an exponential decay,
\begin{equation}
\sigma_{ij}(t) = \sigma_{ij}(0) e^{(-\omega_{ij} + R_{ij}) t}. \quad (14)
\end{equation}
Since only the populations need to be propagated numerically, the Bloch model scales as \(N^{2}\) and is therefore computationally attractive. If, however, secular terms in addition to cases (i) to (iii) exist, the Bloch model is not a valid approximation. The secular approximation (10) by itself, on the other hand, should not be applied if several nonsecular terms exist, for which the relation (11) does not hold. The neglect of these nonsecular terms overestimates the relaxation rate and suppresses coherent transients of the electronic populations as is demonstrated in Section 3.

2.3. Nonsecular algorithm

Our intention is to develop a nonsecular algorithm that improves upon the secular approximation and avoids at the same time the \(N^{3}\) scaling of Eq. (6). This “nonsecular algorithm” has to include in addition to the secular terms satisfying (10) the terms that do not fulfill relation (11) [35]. The crux here is to decide, which relaxation tensor elements \(R_{ijkl}\) for a given density matrix element \(\sigma_{ij}\) have to be considered. Starting from (11), the criterion
\begin{equation}
\frac{|R_{ijkl}|}{|\omega_{ij} - \omega_{kl}|} \geq \gamma \quad (15)
\end{equation}
can be derived, with improving results the smaller γ is chosen. For our model systems, γ = 0.003 turned out to be a good compromise between computational speed on the one hand and correctness on the other hand, yet the time saving was not as much as anticipated. Therefore, we switched to a condition, which focuses on the energy difference |ωij - ωkl| but neglects the value of |Rijkl|. That is, all Rijkl are taken into account, for which

\[ |ωij - ωkl| ≤ δ \]  

is fulfilled. It should be clear that \( δ = 0 \) is identical to the secular approximation (but not with the Bloch model) and that for \( δ \rightarrow ∞ \) the full Redfield equation (6) follows. For our models, \( δ = 0.01 \) eV turned out to be a good compromise between computational speed and correctness. If not indicated otherwise, this value will be used in the following.

In the implementation of this algorithm we save at time \( t = 0 \) for every pair of indices \( (i,j) \) the relevant indices \( k_{rel}, l_{rel} \), for which (16) is fulfilled. The Redfield equation in the nonsecular algorithm then reads

\[ \frac{d}{dt} \sigma_{ij} = -i\omega_{ij}\sigma_{ij} + \sum_{k,l \in \{k_{rel}, l_{rel}\}_{ij}} R_{ijkl}\sigma_{kl}. \]  

The multiplication scheme applied to evaluate Eq. (6) leading to a \( N^3 \) scaling can no longer be utilized within the present nonsecular algorithm, thus yielding a \( N^4 \) scaling in the limit of \( δ \rightarrow ∞ \). But as is shown in Section 3, one typically needs to include only relatively few nonsecular terms in order to get correct results. In fact, \( δ \) can be chosen as small that an overall scaling of \( f \cdot N^2 \) with \( f \ll N \) for the propagation of Eq. (17) is achieved.

The computational problem of the nonsecular algorithm is, that a large \( N \) requires a lot of computer main memory, because the indices \( k_{rel}, l_{rel} \) have to be saved for every pair of indices \( (i,j) \). Therefore, two further conditions for the choice of \( k_{rel}, l_{rel} \) have been tested. First, we consider only those \( R_{ijkl} \) for which

\[ |R_{ijkl}| ≥ δ \]  

is fulfilled. Numerical studies reveal, however, that \( δ \) has to be chosen relatively small in order to get the same results as for \( δ = 0 \) and thus the number of \( R_{ijkl} \) to be considered is not significantly decreased. Moreover, the relaxation tensor needs to be constructed explicitly to check on Eq. (18), which is not necessary in Eq. (17). Rather than checking on the value of \( R_{ijkl} \), it turns out to be much more effective to reduce the number of coherences taken into account by requiring that

\[ |σ_{kl}(t)| ≥ β. \]  

In numerical studies, \( β = 10^{-4} \) was determined to be a good parameter, which, on the one hand, significantly decreases the number of tensor elements \( R_{ijkl} \) taken into account and, on the other hand, does not change the numerical result compared to \( β = 0 \). Since the density matrix changes with time, now the actual choice of \( \{k_{rel}, l_{rel}\}_{ij} \) has to be rechecked after a certain time of propagation. For our systems, it is sufficient to readjust it every 100 fs. Since the criterion (19) significantly reduces the overall number of \( R_{ijkl} \) taken into account, i.e.,

\[ N_R = \sum_{ij} \sum_{k,l \in \{k_{rel}, l_{rel}\}_{ij}} R_{ijkl}, \]  

the computational time as well as the required main memory are also reduced. Another major advantage of this criterion is the progressive speed-up of the computational propagation, because the coherences \( σ_{ij} \) decay with time.

2.4. Model system

To study the effects of the systematic inclusion of nonsecular terms, we consider a previously proposed model of nonadiabatic cis–trans photoisomerization. We assume that the main aspects of the isomerizing system can be described by a model comprising two electronic states and the reaction coordinate φ. In addition, a vibrational mode \( q \) is included, that collectively accounts for all vibronically active modes. In the following, the model including only the reaction coordinate will be referred to as single-mode model and the latter one as two-mode model. In a diabatic electronic representation with the diabatic electronic ground state \( |ψ_{0}\rangle \) and the first excited state \( |ψ_{1}\rangle \), the system Hamiltonian is given as the sum of the kinetic energy \( T \) and the diabatic potential matrix \( \{V_{nm}\} \).

\[ H_S = \sum_{n,m=0,1} |ψ_m\rangle (Tδ_{nm} + V_{nm}) |ψ_n\rangle. \]  

Expressing the isomerization potentials in terms of cosine functions and employing the harmonic approximation for the vibrational mode \( q \), the matrix elements of the Hamiltonian are given as

\[ T = -\frac{1}{2} \frac{\partial^2}{\partial ϕ^2} - \frac{α}{2} ϕ^2, \]  

\[ V_{nm} = E_n + (-1)^n \frac{1}{2} \hat{V}_n (1 - \cos φ) + \frac{α}{2} q^2 + δ_{n0}q. \]  

For the single-mode model, all terms containing \( q \) in Eqs. (22) and (23) are neglected. Note that the torsional potentials are inverted, i.e., the upper diabatic potential for \( φ = 0 \) (cis configuration) becomes the lower one for \( φ = π \) (trans configuration). The electronic coupling \( V_{01} = V_{10} \) is different for the various models. In the single-mode model, the diabatic coupling is constant, \( V_{01} = λ_0 \), which leads to an avoided crossing of the corresponding adiabatic potential-energy curves. For the two-mode model, two different diabatic couplings are considered: The constant coupling \( V_{01} = λ_q \), as well as the coordinate dependent coupling \( V_{01} = λ_q. \) The mod-
The density operator is given by $\rho = \sum_{ij} \langle \psi_i | \rho | \psi_j \rangle | \psi_i \rangle \langle \psi_j |$, where $| \psi_i \rangle$ denotes the vibrational ground state of the system Hamiltonian (21). This initial condition corresponds to an impulsive excitation of the system in the $cis$ configuration by an ultrashort laser pulse at time $t = 0$.

The system–bath coupling is chosen to affect a high quantum yield of the $cis \rightarrow trans$ photoisomerization and the system operators $Q_a$ in Eq. (3) are hence of the form:

$$Q_\phi = | \psi_1 \rangle \langle \psi_1 | (1 - \cos \varphi),$$

$$Q_\theta = | \psi_1 \rangle \langle \psi_1 | \theta.$$  

Following Ref. [17], for the bath parameters $\eta_\varphi$ and $\omega_\varphi$, we assume in the case of the single-mode model $\eta_\varphi = 0.45$, $\omega_\varphi = 0.035$ eV and for both two-mode models $\eta_\varphi = 0.15$, $\omega_\varphi = 0.08$ eV, $\eta_\theta = 0.1$, $\omega_\theta = 0.19$ eV. The temperature of the bath was in all calculations set to zero. Several test calculations for a temperature $T = 300$ K showed that the results change only in details but not qualitatively.

3. Results and discussion

To discuss a nonadiabatic isomerization reaction, it is first helpful to introduce time-dependent observables that account for this process. A key quantity in the discussion of nonadiabatic $cis–trans$ photoisomerization dynamics is the population probability [36]

$$P_k(t) = \text{Tr}\{\sigma(t)\rho_k | \psi_k^{\text{ad}} \rangle \langle \psi_k^{\text{ad}} | \},$$

where

$$P_{\text{trans}} = \Theta(|\varphi| - \pi/2), \quad -\pi/2 \leq \varphi < 3\pi/2$$

denotes the projection operator onto the $trans$ configuration and $| \psi_k^{\text{ad}} \rangle \langle \psi_k^{\text{ad}} |$ represents the projection operator onto the $k$th adiabatic state, which can be calculated from the diabatic states $| \psi_k \rangle$ through a unitary transformation [37]. Similarly, we may define the population probability $P_{\text{cis}}(t)$ via the operator $P_{\text{cis}} = 1 - P_{\text{trans}}$.

3.1. Performance of the nonsecular algorithm

The gradual improvement of the nonsecular algorithm with increasing $z$ is demonstrated for the conical intersection model. The parameters of the models (AC, avoided crossing and CI, conical intersection) are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Single-mode model</th>
<th>Two-mode models</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I^{-1}$</td>
<td>$4.84 \times 10^{-4}$</td>
<td>$1.43 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>2.48</td>
<td>2.0</td>
</tr>
<tr>
<td>$\tilde{V}_0$</td>
<td>3.6</td>
<td>2.3</td>
</tr>
<tr>
<td>$\tilde{V}_1$</td>
<td>1.09</td>
<td>1.5</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>AC</td>
<td>CI</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.065</td>
<td>0.08</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.08</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The energy $E_0$ is always set to zero.

Fig. 1. The gradual improvement of the nonsecular algorithm due to increasing $z$ is shown for the two-mode conical-intersection model. The results for the populations $P^\text{sec}_k(t)$, $P^\text{non}_k(t)$ and the purity $\rho(t)$ are compared for the full Redfield tensor (black solid), the nonsecular algorithm with $z = 0.015$ eV (dotted), $z = 0.01$ eV (dashed), $z = 0.005$ eV (dotted-dashed), and the Bloch model (grey solid).
intersection model in Fig. 1. The population dynamics of $P_{1}^{\text{cis}}(t)$ and $P_{0}^{\text{trans}}(t)$ is shown for the first 500 fs in panels (a) and (b), respectively, and it is compared for the nonsecular algorithm with $\zeta = 0.005$ eV, $\zeta = 0.01$ eV, and $\zeta = 0.015$ eV, as well as for the Bloch model and the full-Redfield calculation. Starting at $P_{1}^{\text{cis}}(0) = 1$ due to initial condition (24), the excited-state cis population probability exhibits a rapid initial decay followed by several partial repopulations, until it approaches zero. The ground-state trans population, on the other hand, displays the build-up of photoproduct, which again reflects coherent wave-packet motion on coupled potential energy surfaces [17,38].

The results given in Fig. 1 show, that for times $t \gtrsim 100$ fs it is sufficient to take $\zeta = 0.01$ eV to describe the dynamics correctly (within the Redfield approach). The early dynamics ($t < 100$ fs), however, is less satisfactorily described by the nonsecular algorithm. The initial decay of $P_{1}^{\text{cis}}(t)$ and the initial rise of $P_{0}^{\text{trans}}(t)$ are even for $\zeta = 0.015$ eV still overestimated compared to the full-Redfield result. This is because at time $t = 0$ the system is in complete coherence. The coupling of the populations and the coherences as well as the coherence-coherence coupling are thus of great importance at early propagation times and their complete or partial neglect as in the Bloch model and the nonsecular algorithm with small $\zeta$, respectively, leads to a wrong description of the dynamics. The coherence-to-population transfer given by $R_{ijkl}$ with $k \neq l$ as well as the population-to-coherence transfer as represented by $R_{ijk}$ with $i \neq j$ affect a retarded initial population decay of $P_{1}^{\text{cis}}(t)$. The coherence-coherence couplings given by $R_{ijkl}$ with $i \neq j \neq k \neq l$, on the other hand, cause the system to stay in coherence for a certain time and in turn affects the population dynamics.

To study the decay of the coherence in some more detail, it is instructive to introduce the purity of a state [39],

$$\mathcal{P}(t) = \text{Tr}\{\sigma^{2}(t)\}, \quad (29)$$

which ranges from 1 for a pure state to 1/N for a completely mixed state. The entropy of a system shows the reverse behavior as $\mathcal{P}(t)$, which is easily to be seen from the linear entropy $S(t) = 1 - \mathcal{P}(t)$ [39]. Fig. 1(c), which shows the initial decay of $\mathcal{P}(t)$, confirms the finding that at early times the coherences need to be adequately considered in the master equation. As for the initial decay of $P_{1}^{\text{cis}}(t)$, the Bloch model and all the calculations based on the nonsecular algorithm lead to a too fast decay of $\mathcal{P}(t)$. Due to the high degree of coherence in the beginning, more tensor elements $R_{ijkl}$ would be necessary to describe the early dynamics correctly. Since for times later than 100 fs, $\zeta = 0.01$ eV yields satisfying results and we are particularly interested in the long-time dynamics of the system, we decided to choose $\zeta = 0.01$ eV in the remainder of this paper.

### 3.2. Dissipation at potential-energy crossings

It is interesting to study the performance of the nonsecular algorithm obtained for the various molecular models introduced above. To this end, Fig. 2 shows the results for the (a) single-mode, (b) avoided-crossing, and (c) conical-intersection models, again comparing the nonsecular algorithm ($\zeta = 0.01$ eV) with the Bloch model, the secular approximation, and the full-Redfield calculation. Shown is the dynamics of the population $P_{0}^{\text{trans}}(t)$ for the first three picoseconds. All three models are, apart from the initial dynamics, well described by the nonsecular algorithm, whereas the Bloch model and the secular approximation fail in the case of both two-mode models. For the single-mode model, on the other hand, the full-Redfield result is satisfactorily reproduced by both the secular approximation and the Bloch model. The findings for the single-mode model confirm that it is save to employ the Bloch model instead of the computationally more demanding secular approximation (i.e., nonsecular algorithm with $\zeta = 0$) whenever the system is rather anharmonic. Interestingly, also the crossing of the diabatic torsional curves does not lead to a failing of the Bloch model, which could be caused by (almost) degenerate eigenvalues. Due to the irregular level spacing in such anharmonic systems, the number of nonsecular terms that violate relation (11) is almost negligible and thus allows for the application of the Bloch

![Fig. 2. Comparison between the full Redfield tensor (solid), nonsecular algorithm with $\zeta = 0.01$ eV (dotted), secular approximation (dashed), and Bloch model (grey solid) for (a) the single-mode model, (b) the two-mode avoided-crossing model, and (c) the two-mode conical-intersection model.](image)
model instead of the nonsecular algorithm or full-Redfield calculation.

The inclusion of a harmonic mode in addition to the anharmonic reaction coordinate introduces regularities into the level spacing of the two-mode models. This does not only lead to a breakdown of the Bloch model, also the secular approximation by itself is no longer a valid approximation. The results for the two-mode models show that the secular approximation is not necessarily an improvement compared to the Bloch model. Only the consideration of the most important secular terms can predict the same dynamics as the full-Redfield calculation, while the computational speed is enhanced by an order of magnitude compared to the full-Redfield calculation. Using an AMD Opteron Processor 242 machine with 4 GByte main memory and a NAG Runge–Kutta–Merson integrator, representative numbers for the computational time needed for a 3 ps propagation of a two-mode model are: 6 days for the full-Redfield calculation, 12 hours for the nonsecular method, and 1 minute for the Bloch model.

It should be noted that the secular approximation may also affect the dynamics at long times. For example, the quantum yield of the cis → trans photoreaction [i.e., $P_{0}^{\text{com}}(t \to \infty)$] obtained for both two-mode models is approximately 5% lower for the Bloch model than for the nonsecular and full Redfield calculation (data not shown). The different relaxation behavior is caused by the system–bath coupling in Eqs. (25) and (26), which force the system to localize in a thermodynamically nonequilibrium state, that is, the energetically higher-lying trans configuration. If instead a system–bath coupling is chosen which affects the localization in the thermodynamic equilibrium state of the system (i.e., the cis ground state), all methods under consideration obtain the same long-time limit $P_{0}^{\text{com}}(t \to \infty) = 1$. These findings suggest that the relaxation behavior is susceptible to transient coherences, whenever the system is forced to localize in a nonequilibrium state. In such cases, the proper treatment of the nonsecular terms is important.

### 3.3. Decoherence at potential-energy crossings

In [17], it was found that a system involving a conical intersection (CI) (the “photochemical funnel”) isomerizes an order of magnitude faster than a system with an avoided crossing (AC), although the two models are – except for the topology of the crossing surface – identical. This high reaction speed of the photochemical funnel could be explained by a subtle interplay of the highly localized nonadiabatic coupling of the CI and the dissipative dynamics of the system. In the present work we wish to study the different timescales of decoherence caused by the two kinds of surface crossings.

The Redfield equation (6) and the master Eq. (17) for the nonsecular algorithm describe the decoherence as well as the dissipation of a system. The timescales of these processes are different, with decoherence dominating the dynamics at early times and dissipation as the major process at later times. The decoherence time $t_d$ may be defined as the time around which the decoherence dominated time evolution turns into dissipation dominated dynamics [39]. It can be estimated from the purity $P(t)$, which decreases rapidly until the time $t = t_d$, where also the modulus of the derivative of $P(t)$ decreases significantly [40]. For times $t > t_d$, the purity is only a slowly varying function and it changes on a timescale, which is characteristic for the dissipation of the energy of the system. The decoherence times $t_d$ for the AC and CI models can be deduced from the time evolution of $P(t)$, which is shown in Fig. 3(a) by dashed lines (obtained from nonsecular-algorithm calculations with $z = 0.01$ eV). Marked as vertical lines, the decoherence times $t_d \approx 1250$ fs for the AC model and $t_d \approx 250$ fs for the CI model differ by a factor of five. Due to the relatively large decoherence time in the case of the AC model, the change from decoherence to dissipation as dominating process is not as sharp as for the CI model. Here, the fast decoherence and the in turn efficient energy dissipation leads to an increase of $P(t)$ for $t > 500$ fs, which reflects the relaxation of the system to the electronic ground state. Note that the complete relaxation to the vibrational ground state would again yield a completely pure state. For the AC model, this relaxation has not yet progressed so far that $P(t)$ starts to increase.

![Fig. 3](image-url)
again. The comparison of \( \mathcal{P}(t) \) for the AC and CI models shows that the slower decoherence in the case of the AC causes an overall less efficient energy relaxation of the system, although the Redfield tensor elements \( R_{ijkl} \) mediating the dissipation are about the same for the AC and CI models.

Since the purity starts to increase with ongoing relaxation, we introduce another measure of coherence of the system given by

\[
C(t) = \mathcal{P}(t) - \sum_{i} \sigma_{ii}(t),
\]

which solely accounts for the coherences of the density matrix, yet has the drawback to be basis-set dependent. In Fig. 3(a), the dynamics of \( C(t) \) is shown as solid lines for both models. It is a decreasing function that at \( t \approx t_d \) approaches zero. To explore the time evolution of \( C(t \geq t_d) \), in panel (b) the decadic logarithm of \( C(t) \) is shown. For the CI model it is interesting to note, that after an initial decay of \( \log C(t) \) it passes through a minimum at \( t \approx 700 \) fs followed by a slight increase, until it starts to decrease again, yet much slower compared to the initial decay. The increase of \( \log C(t) \) between 750 fs and 1.5 ps is due to the fact that the dissipation leads to a transient coherent state in the electronic ground state, which in turn relaxes to its vibrational ground state and thereby destroying the coherences. For much later times, the same finding is made for the AC model (data not shown).

To demonstrate the positive side effect of the decoherence within the nonsecular algorithm, in Fig. 3(c) the decadic logarithm of \( N_R \) as defined in Eq. (20) is shown for the two-mode models. In both cases, \( \log N_R \) is apart from a slight initial rise a decreasing function. The comparison with panel (b) reveals, that the different slopes of the curves \( \log C(t) \) implies a similar difference in the slopes of the curves \( \log N_R \). For the CI model, \( \log N_R \) decreases over three orders of magnitude, whereas for the AC model the decrease is only about one order of magnitude. The decrease of \( N_R \) with time leads to a significant speed-up during a nonsecular-algorithm computation.

4. Conclusions

Employing various models of nonadiabatic \( \text{cis-} \text{trans} \) photoisomerization, we have studied the effects of nonsecular terms of the Redfield tensor on the relaxation dynamics of the system. It has been shown that the popular Bloch model as well as the secular approximation work well in the case of the single-mode model, but fail for the two-mode models under consideration. The latter behavior is expected to be generic for multidimensional systems which typically exhibit numerous near-degeneracies of the level spacings. To correctly describe the relaxation dynamics while still retaining the advantageous \( N^2 \) scaling of the Bloch model, we have developed a nonsecular algorithm that systematically includes the most important nonsecular terms. Various cut-off criteria were considered which exploit the properties of the stationary relaxation tensor as well as the time-dependent decoherence of the system. The resulting algorithm is in good agreement with the results of full Redfield theory, while the numerical effort is reduced by typically an order of magnitude.

Application of the nonsecular algorithm to the two-mode models has revealed a different decoherence behavior at the two kinds of surface crossing. To study the decay of decoherence, various measures of coherence have been introduced and a decoherence time has been defined. It has been found that the decoherence time of the avoided-crossing model is about a factor of five larger than for the conical-intersection model, which in turn leads to a less efficient energy relaxation of the avoided crossing system. The nonsecular algorithm is designed to make use of the decoherence and provides a progressive speed-up during computation. As multidimensional systems typically exhibit quite short decoherence times, this property of the nonsecular algorithm opens the way to treat large molecular systems beyond the secular approximation.

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References