Interplay of non-Markovian relaxation and ultrafast optical state preparation in molecular systems: The Laguerre polynomial method

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The interplay of femtosecond optical excitation and retarded vibrational relaxation in a molecular system is studied using the non-Markovian version of the Quantum Master Equation. To solve non-Markovian equations with an arbitrary memory kernel an expansion with respect to Laguerre polynomials is introduced and the applicability of the method is tested. The non-Markovian effects are identified and parameter regimes are indicated where these effects become predominant. For an early time region just after the optical excited state preparation it is demonstrated that the convolutionless quantum master equation with a time-dependent Redfield-tensor may give a reasonable approximation of the correct non-Markovian dynamics. © 2001 American Institute of Physics. [DOI: 10.1063/1.1334619]

I. INTRODUCTION

Dissipative quantum dynamics, the reduced density operator, the Quantum Master Equation (QME), etc. are concepts well-known since the fifties and early sixties and documented in a number of excellent textbooks.[1–4] In particular, these ideas have been used to describe relaxational phenomena in molecular systems and to achieve a quantum mechanical foundation of chemical reaction dynamics. Focusing on optical experiments, electronic transitions, and vibrational motion, the research work done up to the late eighties can be characterized by the following peculiarity. The time scale of preparing an excited molecular state (typically in the nanosecond and picosecond region) appeared to be much longer than the characteristic time nuclear degrees of freedom (DOF) needed to reach equilibrium (subpicosecond region). In the course of numerical simulations this particular aspect allowed for certain time coarse-graining removing unimportant ultrafast fluctuations from the description or, in other words, it was not necessary to account for non-Markovian, i.e., retardation effects in the intramolecular relaxation processes. (In this respect, the simulation of electronic and nuclear spin dynamics has to be considered as a field of its own.)

Meanwhile, optical pulses with a duration of less than 10 fs are available and one can detect coherent nuclear dynamics (dynamics unaffected by environmental fluctuations).[5–7] This experimental achievement initiated a renaissance of dissipative quantum dynamics, putting emphasis on the description of ultrafast nuclear dynamics in polyatomic systems and systems in the condensed phase.[5,6,8,9]

If methods of dissipative quantum dynamics should be applied, it is necessary that one can separate the whole set of nuclear DOF into a small subset of active DOF and a remaining large set of passive DOF (forming a thermal environment). In the next step one introduces the reduced statistical operator (reduced density operator, RDO)

$$\hat{\rho}(t) = \text{tr}_R\{\hat{W}(t)\}, \tag{1}$$

which comprises a description of all active DOF by reducing the whole statistical operator $\hat{W}(t)$ to the state-space of the active DOF. This reduction procedure is the source of retardation effects in the coupling between the active and the passive system.

Propagating the RDO on a time scale of some tens of femtoseconds, any time coarse-graining is forbidden and dissipative quantum dynamics asks for proper incorporation of retardation effects between the active system and the environment (reservoir). The need for such a more sophisticated description becomes obvious if one imagines an experiment where: (i) the nuclear oscillation period of the molecules lies in the range of 50 fs up to 100 fs; (ii) the molecule is dissolved in a solvent with a correlation time again of about 100 fs; and (iii) the molecule is excited by a laser pulse with duration of some 10 fs (similar to experiments done, for example, at iodine in a solvent[10] or in rare gas clusters[11]). Trying to simulate such an experiment, one must account for the interference of all three mentioned characteristic time scales. It is the main aim of the present paper to study such an interference of (a) vibrational dynamics, (b) retarded coupling to the environment, and (c) ultrafast laser-pulse excitation. Emphasis will be put on non-Markovian effects.

Different ways have been suggested to determine the RDO of an open molecular system. The equation-of-motion approach via the so-called QME is the most common way used in the past (see, e.g., Refs. 1–4). The path-integral representation of the density matrix has been studied in the last decade (for a review see, e.g., Ref. 12) and recently the application of the TDSCF (time-dependent self-consistent field) method could be worked out.[13] Comparing all of these methods, application of the equation-of-motion approach has the great advantage that one computes, in a direct way, thermal averaged quantities and, in contrast to the path-integral approach, one can describe systems with some hundreds of energy levels.

Concentrating on the treatment based on an equation-of-motion for the RDO, different attempts already exist to describe non-Markovian dynamics. To account for the time nonlocallity in a few simple level systems, the density matrix

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theory can be combined with the Laplace transformation method.[14–16] Additionally, this approach allows us to relate the effect of dissipation described in the time domain to the frequency domain. For example, non-Markovian dynamics can be related to the frequency dependence of the absorption line broadening (see also Refs. 17, 18). To treat non-Markovian dynamics in larger systems, one makes the assumption that the spectral density of the environmental modes can be well represented a (at least arbitrary large) number of Lorentzian-type functions. The resulting exponential form of the memory kernel offers the possibility to transfer the non-Markovian equation to a new set of Markovian equations defined for the density matrix, as well as some new auxiliary functions.[19,20] Replacement of the time nonlocality by adding some fictitious modes to an existing system was suggested in Ref. 21. The additional modes can be treated within a Markov approximation and must be chosen in such a manner that they reproduce the spectral density of the environment. Clearly, if one needs too many fictitious modes to approximate the spectral density, the approach becomes inefficient.

In the present work we present a method of treating non-Markovian equations-of-motion by introducing an expansion with respect to special polynomials.[22,23] Such an expansion will enable us to convert the respective integro-differential equations-of-motion into algebraic ones. From earlier work[24,25] it follows that the most suitable set of special functions is given by the orthonormal set of Laguerre polynomials defined as

$$L_n(x) = \frac{1}{n!} e^x \left(\frac{d}{dx} \right)^n (x^n e^{-x}). \tag{2}$$

Besides the other different properties explained below, Laguerre polynomials obey the following important equation

$$\int_0^x d\bar{x} L_n(x - \bar{x}) L_m(\bar{x}) = L_{n+m}(x) - L_{n+m+1}(x). \tag{3}$$

This represents the key relation to handle any type of time nonlocality. If all ingredients of the non-Markovian density matrix equation are expanded with respect to the Laguerre polynomials, the difficulty to treat the retardation effects has been overcome.

Before discussing the Laguerre polynomial expansion method in detail in Sec. IV and using it to study the interplay of optical excitation and vibrational relaxation in Sec. V, we comment on some general aspects of the QME. In Sec. II the basic RDO equations-of-motion at the presence of an external field pulse are given. The model is specified in Sec. III A. Some detailed derivations are placed in the Appendix.

II. EQUATION-OF-MOTION FOR THE REDUCED DENSITY OPERATOR

Before concentrating the discussion to the molecular system of interest we recall the general equation which governs the dynamics of an open molecular system. This equation is the well-known Nakajima–Zwanzig equation or an approximate variant of it[26,27] (see also Refs. 2–4, 9). Our

discussion will be based on the following separation of the complete Hamiltonian, which is standard in dissipative quantum dynamics

$$H = H_S(t) + H_{S-R} + H_R. \tag{4}$$

The first part describes the molecular system of interest (active system with Hamiltonian H_{mol}) together with its coupling to an external radiation field [with Hamiltonian $H_{\text{field}}(t)$]

$$H_S(t) = H_{\text{mol}} + H_{\text{field}}(t). \tag{5}$$

The molecular contributions will be specified later. For the coupling to the radiation field we have in mind a description within the electric dipole approximation

$$H_{\text{field}}(t) = -\mathbf{E}(t)\hat{\mu}. \tag{6}$$

Here $\mathbf{E}(t)$ is the electric field strength of a laser pulse (or a sequence of pulses) and $\hat{\mu}$ denotes the molecular dipole operator. The coupling of the active system to the reservoir is given by H_{S-R}, whereas the reservoir is described by H_R.

A. Reduced equation-of-motion

The dynamics of the active system is described by RDO $\hat{\rho}$ [cf. Eq. (1)]. The resulting exact equation-of-motion is known as the Nakajima–Zwanzig identity (if convolutionless versions of RDO equations are considered alternative types of exact equations are also known[28])

$$\frac{\partial}{\partial t} \hat{\rho}(t) = \hat{I}(t; \hat{W}(t_0)) - i\mathcal{L}_S(t)\hat{\rho}(t) - \hat{D}(t, t_0; \hat{\rho}). \tag{7}$$

Concrete expressions of all parts can be found in Appendix A. We only mention here that the first term on the right-hand side of Eq. (7) is responsible for the decay of correlations between the active system and the reservoir presented at the initial time t_0. The Liouvillian formed by H_S is denoted by $\mathcal{L}_S(t)[\equiv \mathcal{L}_{\text{mol}} + \mathcal{L}_{\text{field}}(t)]$, and dissipation is described by the term $-\hat{D}$. If necessary, one has to extend $\mathcal{L}_S(t)$ by the mean-field term of the system-reservoir coupling (see Appendix A). For the following, however, it is important that all terms on the right-hand side of Eq. (7) depend on the external field.

The dissipative part $\hat{D}(t, t_0; \hat{\rho})$ incorporates the convolution of the density operator $\hat{\rho}(t)$ and a memory kernel (memory superoperator)

$$\hat{D}(t, t_0; \hat{\rho}) = \int_0^{t-t_0} d\tau \mathcal{M}(t, t-\tau; \mathbf{E}) \hat{\rho}(t-\tau). \tag{8}$$

Since the external field enters the memory kernel, the time-dependence of $\mathcal{M}$ is twofold. But in the case where the external field is absent, we can write

$$\lim_{\mathbf{E} \to 0} \mathcal{M}(t, t-\tau; \mathbf{E}) = \mathcal{M}_0(\tau). \tag{9}$$

This memory kernel is supposed to die out with the characteristic time t_{mem}.

B. Initial conditions and laser-pulse excitation

As already pointed out above, Eq. (7) includes a term which describes the decay of correlations present between the active system and the reservoir at the initial time t_0. After starting the evolution these initial correlations tend to zero on a time scale comparable to t_{mem}, and $\hat{I}$ should be negligible for $t>t_0+t_{mem}$. Since the exact form of the density operator equation includes a retarded coupling to the reservoir, the occurrence of such initial correlations is unavoidable. They compensate the incomplete retarded system-reservoir coupling for initial times $t<t_0+t_{mem}$. In a description of dissipative quantum dynamics, where a time coarse-graining has been introduced which neglects a time-resolution comparable to t_{mem}, one can neglect initial correlations and can change to a Markov approximation as in Eq. (8).

Obviously, in the contrary case of a time resolution much below t_{mem}, initial correlations, together with retardation effects of the system-reservoir coupling (non-Markovian effects), must be accounted for. If retardation is considered but initial correlations are neglected, the time-dependence of the density operator (its matrix elements) displays artificial oscillations for an initial time interval extending from t_0 to t_0+t_{mem} (or somewhat larger times). This has recently been demonstrated for the dissipative dynamics of a single molecular DOF moving in a double-well potential.[20]

The situation changes if one considers (as will be the case here) the action of field pulses driving the system out of equilibrium. Now it is not necessary to deal with initial correlations. According to their decay with the characteristic time t_{mem}, one can arrange the presence of the field-pulses for times where the influence of initial correlations already vanished. For numerical simulations this means that one should allow evolution of the system freely without the action of the external field for a larger time interval when compared to t_{mem}. Therefore, if the field-pulse acts, a correct description of non-Markovian molecular dynamics has already been achieved.

The field influence on the system dynamics can be considered to establish new initial conditions for $\hat{\rho}$ (this is best seen for a pulse short compared to t_{mem}, as well as any other characteristic time of the active system). But this takes place without contributions in the density matrix equations being similar to the initial correlation terms $\hat{I}[t;\hat{W}(t_0)]$. Therefore, one can expect that the interplay of non-Markovian dynamics and short pulse excitations are similar to the time evolution of $\hat{\rho}$ observed for times just after starting the evolution with retardation accounted for but without the consideration of initial correlations. The following considerations are devoted to clarifying this statement.

We suppose that the external field begins to deviate from zero (arrival time of the pulse in the probe) at time t_{field}, where $t_{field}\gg t_0$. Thus for any $t_0\ll t<t_{field}$, the field-free version of Eq. (7) would be valid, and should describe the equilibrium situation between the active system and the reservoir. We will denote the respective equilibrium version of the reduced density operator by $\hat{\rho}_{eq}$. If the exact expression for the memory kernel is taken we expect $\hat{\rho}_{eq}=\text{tr}_R\{\hat{W}_{eq}\}$, where $\hat{W}_{eq}$

is the canonical equilibrium statistical operator of the active system plus reservoir, proportional to $\exp-(H_{mol}+H_{S-R}+H_R)/k_BT$. If the field-free memory kernel $\mathcal{M}_0$ is used in the second Born approximation we get (see, e.g., Ref. 9)

$$\hat{\rho}_{eq}=\exp(-H_{mol}/k_BT)/\text{tr}_S\{\exp(-H_{mol}/k_BT)\}, \quad (10)$$

i.e., the canonical statistical operator of the active system. Although the concrete computations presented in the following sections have been done in the framework of the second Born approximation, it is not necessary for the reasoning below to use this approximation.

Since equilibrium should be established for $t_0\ll t<t_{field}$ we get from Eq. (7) (note the replacement of $t-t_0$, which is much larger than zero, by ∞)

$$0=-i\mathcal{L}_{mol}\hat{\rho}_{eq}-\int_0^{\infty}d\tau\mathcal{M}_0(\tau)\hat{\rho}_{eq}. \quad (11)$$

For $t>t_{field}$, thus for times when the field already acts, the whole Eq. (7) [with $\hat{I}(t;\hat{W}(t_0))=0$] applies. To solve this equation for times $t>t_{field}$ we introduce a formal decomposition of the RDO according to

$$\hat{\rho}(t)=\Delta\hat{\rho}(t)+\hat{\rho}_{eq}, \quad (12)$$

where $\Delta\hat{\rho}(t)$ vanishes for times less than t_{field}. Inserting Eq. (12) into Eq. (7) we obtain for $t>t_{field}$

$$\frac{\partial}{\partial t}\Delta\hat{\rho}(t)=-i\mathcal{L}_S(t)\Delta\hat{\rho}(t)$$
$$-\int_0^{t-t_{field}}d\tau\mathcal{M}(t,t-\tau;\mathbf{E})\Delta\hat{\rho}(t-\tau)$$
$$-i\mathcal{L}_{field}(t)\hat{\rho}_{eq}-i\mathcal{L}_{mol}\hat{\rho}_{eq}$$
$$-\int_0^{t-t_0}d\tau\mathcal{M}(t,t-\tau;\mathbf{E})\hat{\rho}_{eq}. \quad (13)$$

Here, the parts depending on $\hat{\rho}_{eq}$ (the three last terms on the right-hand side) act as inhomogeneities. Indeed, one can interpret these inhomogeneities as terms replacing $\hat{I}$ in Eq. (7).

If one neglects the less important effect of the field influence on the memory kernel (and notes $t-t_0\gg0$), the last term in Eq. (13) is compensated by the foregoing one [compare to Eq. (11)] and $i\mathcal{L}_{field}(t)\hat{\rho}_{eq}$ remains as the inhomogeneity. But, in difference to $\hat{I}$, this inhomogeneity substantially deviates from zero for the whole time the external field is present.

C. Markov approximation

To have the QME in the Markov approximation as a reference case at hand we shortly remind to its derivation. If one wants to apply this approximation it is necessary that on the time scale the memory kernel does not decay with any substantial change of the RDO appears. This is best proven in the interaction representation [compare Eq. (A1)] where the reversible part of the dynamics has been removed from $\hat{\rho}(t)$. If the Markov approximation is justified one introduces

$$\hat{\rho}(t-\tau)\approx\mathcal{U}_S^+(t,t-\tau)\hat{\rho}(t), \quad (14)$$

where the time-evolution superoperator has been defined in Eq. (A2). Inserting this approximation into Eq. (8) we can write

$$\hat{D}(t,t_0;\hat{\rho}) \approx \mathcal{R}(t,t_0;\mathbf{E})\hat{\rho}(t)$$

$$\equiv \int_0^{t-t_0} d\tau \mathcal{M}(t,t-\tau;\mathbf{E})\mathcal{U}_S^+(t,t-\tau)\hat{\rho}(t). \qquad (15)$$

The definition of the dissipative superoperator $\mathcal{R}$ is obvious. It realizes time local, and also the time-dependent dissipation which, additionally, is influenced by the presence of the external-field pulse. In the case where $t-t_0 \gg t_{\mathrm{mem}}$ we can replace the upper limit of the τ-integral by ∞. If the external field dependence is neglected, the dissipative superoperator $\mathcal{R}_0$ (its matrix elements) becomes identical with the so-called Redfield tensor entering the *standard Markovian QME*

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i\mathcal{L}_S(t)\hat{\rho}(t) - \mathcal{R}_0\hat{\rho}(t). \qquad (16)$$

Next we combine the separation, Eq. (12), with the Markov approximation, Eq. (15), and obtain

$$\frac{\partial}{\partial t}\Delta\hat{\rho}(t)$$

$$= -i\mathcal{L}_S(t)\Delta\hat{\rho}(t) - i\mathcal{L}_E(t)\hat{\rho}_{\mathrm{eq}} + \mathcal{R}(t,t_{\mathrm{field}};\mathbf{E}=0)\Delta\hat{\rho}(t). \qquad (17)$$

Since the limit $\mathbf{E}\to 0$ has been taken with respect to the dissipative part, all terms proportional to $\hat{\rho}_{\mathrm{eq}}$ disappear, except $-i\mathcal{L}_E(t)\hat{\rho}_{\mathrm{eq}}$. Furthermore, we note that the dissipative superoperator $\mathcal{R}$ remains time-dependent. It will be demonstrated below that the use of $\mathcal{R}(t,t_{\mathrm{field}};\mathbf{E}=0)$ for times $t-t_{\mathrm{field}}$ in the range of t_{mem} will give a proper reproduction of the correct solution of the non-Markovian Eq. (13).

To distinguish the standard Markovian QME from Eq. (17), the latter will be named the Markovian QME with *time-dependent Redfield-tensor*. A detailed comparison is given below for all three versions of the QME, i.e., of the standard Markovian QME, the non-Markovian QME, and of the Markovian QME with time-dependent Redfield-tensor.

III. THE MOLECULAR MODEL AND RELATED DENSITY MATRIX EQUATIONS

A. The model

To test the conclusions obtained in the previous section and to illustrate the polynomial method of solving the non-Markovian QME, we chose a sufficiently simple model of a molecular system. Following previous work,[29,30] it seems appropriate to take the minimal model applicable for the description of ultrafast optical data obtained for a dissolved dye molecule. This minimal model will serve as a references system and will be used to study the interplay of the external-field excitation of the molecule and the non-Markovian relaxation of the vibrational DOF in the populated excited electronic state.

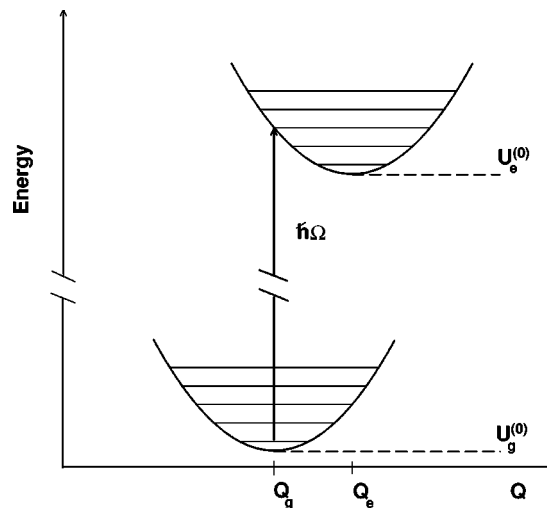Therefore, the respective quantum mechanical model should consist of at least two electronic levels modulated by

FIG. 1. Scheme of the minimal molecular system used for the numerical calculations.

a single effective vibrational coordinate Q. Accordingly, the complete molecular Hamiltonian H_{mol} follows as (compare to Fig. 1):

$$H_{\mathrm{mol}} = \sum_{a=e,g} H_a(Q)|\varphi_a\rangle\langle\varphi_a|. \qquad (18)$$

$H_a(Q)$ are the vibrational Hamiltonian corresponding to the ground ($a=g$) and excited electronic state ($a=e$) with harmonic oscillator potential energy surfaces (PES)

$$U_a(Q) = U_a^{(0)} + \frac{\hbar\omega_{\mathrm{vib}}}{4}(Q-Q_a)^2. \qquad (19)$$

According to Ref. 29 we take $\hbar\omega_{\mathrm{vib}} = 190$ meV. The difference $U_e^{(0)} - U_g^{(0)}$ is set equal to 2 eV and for the dimensionless displacement between the ground- and excited-state PES we use $Q_e - Q_g = \sqrt{10}$. Such a value corresponds to a Frank–Condon transition to the second excited vibrational level of the excited electronic state.

The coupling to the radiation field has been already introduced in Eq. (6). It is characterized by off-diagonal dipole operator matrix elements

$$\langle\varphi_e|\hat{\mu}|\varphi_g\rangle = \mathbf{d}_{eg}. \qquad (20)$$

The electric field is used in the form

$$\mathbf{E}(t) = \mathbf{n}\mathcal{E}(t)e^{i\Omega t} + \mathrm{c.c.} \qquad (21)$$

with $\mathcal{E}(t)$ and Ω denoting the pulse envelope and frequency, respectively, and $\mathbf{n}$ defines the field polarization. The pulse amplitude, as well as the transition dipole moment, will be specified later.

The system-bath interaction is considered in a form diagonal with respect to the electronic quantum numbers

$$H_{S-R} = \sum_a \hat{\mathcal{K}}_a \Phi_a(Z). \qquad (22)$$

The operator $\hat{\mathcal{K}}_a = K_a(Q)|\varphi_a\rangle\langle\varphi_a|$ acts in the active system state-space with $K_a(Q)$ exclusively defined in the vibrational state-space. The quantity $\Phi(Z)$ operates in the space of res-

ervoir states. Z denotes the set of reservoir coordinates described by the reservoir harmonic oscillator Hamiltonian H_R. Its detailed properties will be specified by introducing the related spectral density.

B. Density operator equation

For the following we will deal with the case of a sufficient weak field intensity. It should be of such a low value that the following two approximations are allowed. First, we provide that it is sufficient to consider the excited-state population linear with respect to the intensity. This will enable us to reduce the description of the complete excited-state dynamics to the computation of the electronic diagonal matrix element of the reduced density operator. Some details on the respective derivation can be found in Appendix B. Using the separation, Eq. (12), we have exclusively determined $\Delta\hat{\rho}_{ee}$. Which field-intensity region can be used has already been discussed in Ref. 29.

As a second consequence of the considered weak-field case we neglect the field-dependence of the memory kernel (cf. the discussion in Ref. 30). It results in the following density operator equation

$$\frac{\partial}{\partial t}\hat{\sigma}(t) = \frac{i}{\hbar}[H_e, \hat{\sigma}(t)]$$
$$- \hat{D}_{ee}(t - t_{\text{field}}; \hat{\sigma}) + \hat{F}_{ee}(t, t_{\text{field}}; \mathbf{E}). \quad (23)$$

This equation directly follows from Eq. (B15). Note the identification

$$\hat{\sigma} = \Delta\hat{\rho}_{ee}. \quad (24)$$

The dissipative part, $\hat{D}_{ee}$, is obtained from Eq. (B5), and the external-field-dependent source term $\hat{F}_{ee}$ is given in Eq. (B16). In our calculation we use the following form of the quantity $J(\omega)$:

$$J_{ee}(\omega) = \Theta(\omega)J_0 j(\omega), \quad (25)$$

where $j(\omega)$ has been normalized to 1 in the frequency interval between 0 and ∞ and $\Theta(\omega)$ denotes the unit-step function. Further we use the following *ansatz*[30,31]

$$j(\omega) = \frac{\omega}{\omega_c^2} e^{-\omega/\omega_c}. \quad (26)$$

Here we introduced a cutoff frequency ω_c, which corresponds to the characteristic memory time τ_{mem} on which the correlations of the reservoir DOF decay. The inverse of ω_c will be denoted as t_c and called the correlation time.

C. Energy representation

For the numerical determination of the density matrix we must change from the operator expression $\hat{\sigma}$ to a concrete representation. In the present case it is most appropriate to take the harmonic oscillator, such as eigenstates of the vibrational Hamiltonian H_a, which will be denoted by $|\chi_{aM}\rangle$. Then, the density matrix, which will be calculated in the following, reads

$$\sigma_{MN}(t) = \langle\chi_{eM}|\hat{\sigma}(t)|\chi_{eN}\rangle. \quad (27)$$

From Eq. (23) we directly obtain the following density matrix equation:

$$\frac{\partial}{\partial t}\sigma_{MN}(t) = -i\omega_{MN}\sigma_{MN}(t)$$
$$- \sum_{K,L}\int_0^t d\tau \mathcal{M}_{MN,KL}(\tau)\sigma_{KL}(t-\tau) + F_{MN}(t). \quad (28)$$

Note the special choice $t_{\text{field}} = 0$, and the abbreviation $\omega_{MN} = (E_{eM} - E_{eN})/\hbar$, where the E_{eM} are the *eigenvalues* of H_e. The tetradic matrix $\mathcal{M}_{MN,KL}(\tau)$ following from the memory kernel superoperator reads in detail

$$\mathcal{M}_{MN,KL}(\tau) = \delta_{M,K}\sum_A M_{LA,AN}(-\tau)e^{i\omega_{AM}\tau}$$
$$+ \delta_{N,L}\sum_A M_{MA,AK}(\tau)e^{i\omega_{NA}\tau}$$
$$- M_{LN,MK}(-\tau)e^{i\omega_{NK}\tau}$$
$$- M_{LN,MK}(\tau)e^{i\omega_{LM}\tau}, \quad (29)$$

with

$$M_{MN,KL}(\tau) = C_{ee}(\tau)\langle\chi_{eM}|K_e|\chi_{eN}\rangle\langle\chi_{eK}|K_e|\chi_{eK}\rangle. \quad (30)$$

The energy representation of the inhomogeneity is obtained as

$$F_{MN} = \frac{|\mathbf{d}_{eg}|^2}{\hbar^2}\sum_L \langle\chi_{eM}|\chi_{gL}\rangle\langle\chi_{gL}|\chi_{eN}\rangle f(E_{gL})$$
$$\times \mathcal{E}(t)\int_0^t d\bar{t}\mathcal{E}(\bar{t})e^{-i(\omega_{ML} - \Delta\omega)(t-\bar{t})} + \text{h.c.} \quad (31)$$

Here, $f(E_{gL})$ denotes the thermal distribution versus the electronic ground-state vibrational levels. The field-pulse envelope $\mathcal{E}$ was introduced in Eq. (21). For the concrete computations we take the following form

$$\mathcal{E}(t) = \frac{A}{\tau_p}\sqrt{\frac{2}{\pi}}e^{-2(t-\tau_f)^2/\tau_p^2}. \quad (32)$$

The time τ_f where the pulse reaches its maximum must be chosen large compared to τ_p to get $\mathcal{E}(t=0)\approx 0$. We set $\tau_f = 50$ fs. The field amplitude A [cf. Eq. (32)] together with the transition dipole moment is not explicitly specified. Instead we choose $A\times\mathbf{nd}_{eg}$ in such a manner to achieve an excited-state population sufficiently smaller than 1. For our computation this choice guarantees $\sigma_{NN}(t\to\infty)\lesssim 10^{-3}$. Besides the envelope we introduced in Eq. (31), the quantity $\Delta\omega$ gives the detuning between the energetic distance of both PES and the photon energy, i.e.,

$$\Delta\omega = \Omega - (U_e^{(0)} - U_g^{(0)})/\hbar. \quad (33)$$

If we take the standard Markovian QME, Eq. (17), the dissipative part of Eq. (28), reads $\sum_{KL}\mathcal{R}_{MN,KL}\sigma_{KL}$, where the complex Redfield-tensor reads

$$\mathcal{R}_{MN,KL} = \delta_{M,K} \sum_A \hat{M}^*_{NA,AL}(-\omega_{AL})$$

$$+ \delta_{N,L} \sum_A \hat{M}_{MA,AK}(\omega_{KA})$$

$$- \hat{M}^*_{KM,NL}(-\omega_{NL}) - \hat{M}_{LN,MK}(\omega_{KM}). \qquad (34)$$

Here, $\hat{M}_{MN,KL}(\omega)$ denotes the half-sided Fourier transform of the function introduced in Eq. (30) [note $\hat{M}_{MN,KL}(\omega) = \hat{M}^*_{KL,NM}(-\omega)$]. The usual Redfield-tensor is obtained as the real part of the above given expression.[1,9] Finally, the time-dependent Redfield-tensor $\mathcal{R}_{MN,KL}(t,t_{\text{field}};\mathbf{E}=0)$ introduced in Eq. (17) follows from Eq. (34) in replacing $\hat{M}_{MN,KL}(\omega)$ by

$$\bar{M}_{KM,NL}(\omega,t) = \int_0^{t-t_{\text{field}}} d\tau e^{i\omega\tau} M_{KM,NL}(\tau). \qquad (35)$$

The last two versions of the QME are local in time, so the solution can be found by a standard Runge–Kutta-type method.[32]

IV. LAGUERRE POLYNOMIAL EXPANSION

A. Conversion of the density matrix equation to the algebraic form

To obtain the solution of the non-Markovian density matrix equation (28), we expand all parts with respect to the Laguerre polynomials, Eq. (2). Therefore, we note their orthogonality with respect to the scalar product

$$(f,g) = \int_0^\infty dx e^{-x} f(x) g(x). \qquad (36)$$

In carrying out the expansion, time argument t has to be replaced by the dimensionless variable x

$$x = t/t_{\text{char}}, \qquad (37)$$

where the time constant t_{char} roughly fixes the characteristic time interval in which the function to be expanded by Laguerre polynomials can be properly described. Since we will consider the correlation functions decaying on a time scale of some 10 fs we set $t_{\text{char}} = 10$ fs. [Indeed, such a value is large enough to avoid any suppression of $C_{ee}(t)$ by an exponential prefactor.]

Carrying out the expansions for the density matrix we get

$$\sigma_{MN}(t_{\text{char}}x) = \sum_{n=0}^\infty \sigma_{MN}^{(n)} L_n(x). \qquad (38)$$

If we set $t=0$ this expansion reduces to [note $L_n(x=0)=1$]

$$\sigma_{MN}(t=0) = \sum_{n=0}^\infty \sigma_{MN}^{(n)}. \qquad (39)$$

Using the scalar product Eq. (36) the expansion coefficients of the density matrix introduced in Eq. (38) are obtained as

$$\sigma_{MN}^{(n)} = \int_0^\infty dx e^{-x} L_n(x) \sigma_{MN}(t_{\text{char}}x). \qquad (40)$$

The algebraic equations determining the expansion coefficients are obtained from the expansion of the original equation-of-motion (28). To do this we use relation (3) and[25,33]

$$\frac{\partial}{\partial x} L_n(x) = -\sum_{m=0}^{n-1} L_m(x). \qquad (41)$$

It results in the recurrence relation for the density matrix expansion coefficients $\sigma_{MN}^{(n)}$:

$$\sum_{KL} ((it_{\text{char}}\omega_{MN}+1)\delta_{MK}\delta_{NL} + t_{\text{char}}^2 \mathcal{M}_{MN,KL}^{(0)})\sigma_{KL}^{(n)}$$

$$= \sigma_{MN}(t=0) - \sum_{m=0}^{(n-1)} \left(\sigma_{MN}^{(m)} + t_{\text{char}}^2 \sum_{KL} \{ \mathcal{M}_{MN,KL}^{(n-m)} \right.$$

$$\left. - \mathcal{M}_{MN,KL}^{(n-m-1)} \} \sigma_{KL}^{(m)} \right) + t_{\text{char}} F_{MN}^{(n)}. \qquad (42)$$

If the coefficients $\mathcal{M}_{MN,KL}^{(n)}$, as well as $F_{MN}^{(n)}$, are known, the density matrix may be deduced.

B. Determination of memory kernel expansion coefficients

Computing the memory kernel expansion coefficients $\mathcal{M}_{MN,KL}^{(n)}$ in similarity to Eq. (40), a detailed inspection of relation (29) demonstrates that we must handle contributions of the type

$$\tilde{C}^{(n)} = \int_0^\infty dx \, L_n(x) e^{i\Delta\tilde{\omega}x} e^{-x} C_{ee}(\pm t_{\text{char}}x). \qquad (43)$$

Here, $\Delta\tilde{\omega} = t_{\text{char}}\Delta\omega$, where $\Delta\omega$ denotes one of the various transition frequencies.

To calculate the above given type of integrals we proceed as follows. First we note that $C_{ee}(t)$ follows from an inverse Fourier transformation according to Eq. (B11). In the general case this Fourier transformation must be carried out numerically, and, consequently, the values of the function $C_{ee}(t)$ are given for a set of points $t_0,t_1,\ldots,t_N$ on the time axes (corresponding to $x_0,x_1,\ldots,x_N$). Such a set may be interpolated by so-called cubic splines,[32] which result in a function, analytical by parts, and continuous up to the second derivative. Then, between any two points x_j, x_{j+1} of the set, the function $C_{ee}(xt_{\text{char}})$ is represented by a cubic polynomial, and the integral Eq. (43) turns to a sum of the integrals

$$\tilde{C}_{\text{spl}}^{(n,j)} = \int_{x_j}^{x_{j+1}} dx \, L_n(x) e^{i\Delta\tilde{\omega}x} e^{-x} C_{\text{spl}}^{(j)}(\pm xt_{\text{char}}), \qquad (44)$$

with $C_{\text{spl}}^{(j)}(t)$ being a spline interpolation of $C_{ee}(\pm t)$ in the interval $[t_j,t_{j+1}]$. For all of these integrals special recurrence formulas may be derived. Accordingly, the complete expansion coefficient, Eq. (43), may be computed in any

degree of accuracy, for any order of the polynomial expansion, and any value of $\Delta\omega$. Details on the derivation of the recursion formulas are given in Appendix C.

In the same manner we can calculate the expansion coefficients $F_{MN}^{(n)}$ of the field term in Eq. (28). Therefore, $F_{MN}(t_{\text{char}}x)$ is determined for the discrete set of time arguments $t_0, t_1, \ldots, t_N$, and the respective spline approximation is used to calculate $F_{MN}^{(j)}(t_{\text{char}}x)$ according to Eq. (44).

C. Applicability and accuracy of the polynomial method

It has been already highlighted in Ref. 25 and can be made obvious by an inspection of Eq. (42), i.e., that the accuracy of the memory kernel expansion determines the accuracy with which we can compute the density matrix elements. Having at hand a sufficiently good approximation of the memory kernel for the time interval $[t_1, t_2]$, one may expect that the density matrix expansion results in the same accuracy.

A convenient way to proof the convergence of the expansion is to compute the contribution given by the last few terms in the expansion while enlarging the number of expansion coefficients. However, in a case where function $f(t)$, to be expanded, is known, we can easily check the accuracy of the actual expansion $f_{\exp}(t;N) = f_{\exp}(t_{\text{char}}x;N) = \sum_{n=0}^{N} f^{(n)} L_n(x)$ of order N by introducing

$$\epsilon(t_1, t_2; N) = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} dt \, |f(t) - f_{\exp}(t;N)|. \quad (45)$$

The expression gives the absolute value of the difference between the original function and its Nth order expansion averaged with respect to the time interval $[t_1, t_2]$. Since we are mainly interested in noting how the Laguerre polynomial expansion may be improved by enlarging the expansion order, we will use the quantity $\epsilon(t_1, t_2; N)$ instead of an expression defining a relative deviation.

If function $f(t)$ is not known, one must compare different orders N of the expansion, say N and $N + \Delta N$ ($\Delta N > 0$). For this reason one may introduce as a measure of accuracy

$$\Delta\epsilon(t_1, t_2; N + \Delta N, N) = \frac{t_{\text{char}}}{t_2 - t_1} \int_{t_1/t_{\text{char}}}^{t_2/t_{\text{char}}} dx \left| \sum_{n=N+1}^{N+\Delta N} f^{(n)} L_n(x) \right|. \quad (46)$$

In Fig. 2 we demonstrate the accuracy of the polynomial expansions of the correlation function, the density matrix elements, and the field term.

The quantities $\epsilon(0, 300\,\text{fs}; N)$ and $\epsilon(0, 300\,\text{fs}; N + 100, N)$ [Eqs. (45) and (46), respectively] are presented in part (a) of Fig. 2 as a function of N for the correlation function $C_{ee}(t)$, Eq. (B11) ($1/\omega_c = t_c = 10\,\text{fs}$ and $100\,\text{fs}$). Both measures show a strong decay for N less than 10^3. Afterward a saturation appears if N is further increased. This behavior points out the fact that the accuracy of the expansion reaches its limit if it coincides with the accuracy of the spline approximation. Of course, this can be improved by shortening the step length of the spline approximation. Thanks to the smoother behavior of the $C_{ee}(t)$ with $t_c = 100\,\text{fs}$, as compared with $t_c = 10\,\text{fs}$,
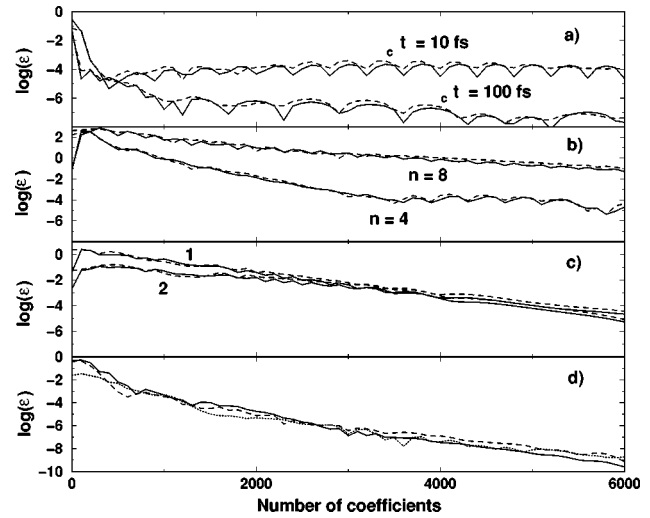

FIG. 2. Accuracy of the Laguerre polynomial expansions. The measure $\epsilon(t_a = 0, t_b = 300\,\text{fs}; N)$, Eq. (45) and $\Delta\epsilon(t_a = 0, t_b = 300\,\text{fs}; N + 100, N)$, Eq. (46) are drawn versus the expansion order N. (a) ϵ (solid line) and $\Delta\epsilon$ (dashed line) determined for the correlation function $C_{ee}(t)$ with different t_c. (b) The same as in (a) but for the function $C_{ee}(t)e^{in\omega_{\text{vib}}t}$, the single value $t_c = 10\,\text{fs}$, and different n. (c) The same as in (a) but for the time-dependent part $\mathcal{E}(t)\int_0^t d\bar{t}\,\mathcal{E}(\bar{t})\exp{-i(n\omega - \Delta\omega)(t - \bar{t})}$ of the field term, Eq. (31). Curve pair 1: $n = 0$; curve pair 2: $n = 8$. (d) $\Delta\epsilon$ ($t_a = 0$, $t_b = 300\,\text{fs}$; $N + 100, N$) versus N for the diagonal elements of the harmonic oscillator density matrix. Solid line: ρ_{00}, dashed line: ρ_{44}, dashed-dotted line: ρ_{88} (for all other parameters see Sec. III A).

the corresponding spline approximation with the same step length is more accurate. This also leads to higher accuracy in the polynomial expansion.

According to Eq. (29), which determines the memory function, $\mathcal{M}(t)$ terms of the type $C_{ee}(t)\exp(in\omega_{\text{vib}}t)$ have to be studied. In part (b) of Fig. 2 we again present ϵ and $\Delta\epsilon$ but defined for those expressions incorporating oscillating contributions and for $n = 4, 8$ and $t_c = 10\,\text{fs}$. Now we are expanding highly oscillating functions what leads to the slower increase of the accuracy. However, in the case of $n = 4$, for example, we reach saturation at the same accuracy as in the case of $n = 0$ with some 4000 coefficients. As has to be expected, the accuracy of the term with $n = 8$ is lower. In the case of such a highly oscillating term, we can, however, expect that their contribution is small and a less accurate expansion seems to be sufficient.

Next, in part (c) of Fig. 2 we show a similar picture for the expansion of the laser pulse. The field term does not show any dramatic oscillations and the functions die out very fast far from the center of the pulse, so that the method explained in Sec. IV B and Appendix C enables us to evaluate actual infinite integrals determining the expansion coefficients of the laser pulse with a high accuracy using a small finite interval. Interestingly, in parts (a), (b), and (c), we could observe that both quantities ϵ and $\Delta\epsilon$ are approximately of the same order. This indicates that they can be used alternatively.

Finally, the accuracy of the density matrix expansion is estimated where the only measure to be used is given by $\Delta\epsilon$, Eq. (46). The accuracy of this expansion is determined by the respective accuracy of the expansions of the memory
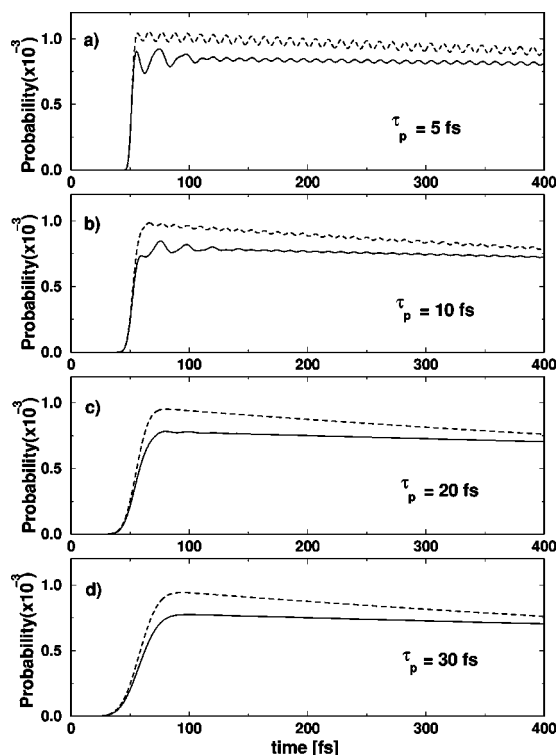
FIG. 3. Population of the second exited vibrational level in dependence on the pulse-length τ_p based on the solution of the non-Markovian (full line) and Markovian (dashed line) QME. $t_c = 30$ fs, $J(\omega_{\text{vib}}) = 1.9 \times 10^{-4}/\text{fs}$.

FIG. 4. Population of the second exited vibrational level in dependence on the pulse-length τ_p based on the solution of the non-Markovian (full line) and Markovian (dashed line) QME. $t_c = 20$ fs, $J(\omega_{\text{vib}}) = 1.9 \times 10^{-4}/\text{fs}$ (upper curves in graphs) and $J(\omega_{\text{vib}}) = 3.5 \times 10^{-4}/\text{fs}$.

kernel, the field term, and the expansion of the free dynamics of the system. Different contributions may be expanded with different accuracies. For the highly oscillating terms of the memory kernel, which do not substantially contribute to the dynamics, low accuracy seems to be sufficient. The expansion of the free dynamics part is naturally involved in the algebraic equation (42). Thus in part (d) of Fig. 2 we display $\Delta\epsilon(0,300\,\text{fs}; N+\Delta N, N)$ as a function of N for $\Delta N = 100$ and for the expansion of different matrix elements.

V. NUMERICAL RESULTS FOR THE MODEL SYSTEM

Of basic interest for the following would be the study of the ultrafast laser-pulse action and its interplay with the non-Markovian dynamics of the vibrational DOF, as well as the comparison of the non-Markovian dynamics with the dynamic behavior present in the limit of the Markov approximation. This latter comparison can be carried out in different ways.[34] Here, we will compare those types of non-Markovian dynamics which obey the same Markov limit as a common feature. Inspecting Eqs. (29) and (34) it becomes obvious that the requirement for the same Markov approximation is equivalent with the demand for the same Redfield-tensor. This can be translated to the requirement that the different types of correlation function $C_{ee}(t)$ used in the comparison should have the same values $C_{ee}(\omega)$ at certain frequencies. In the present case of a harmonic oscillator there remains only the single value $C_{ee}(\omega_{\text{vib}})$ of $C_{ee}(\omega)$ at which all correlation functions should coincide.

It is well-accepted fact that the positivity of the density matrix can be violated if the coupling strength to the reser-
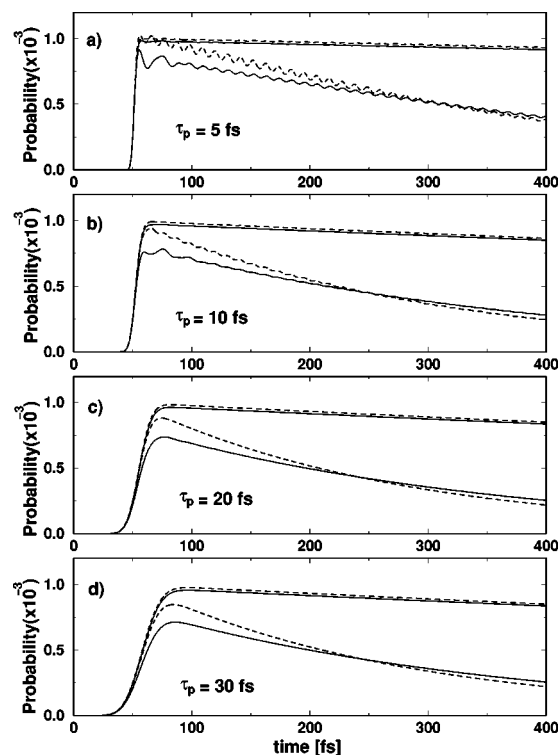
voir [J_0 in our case, see Eq. (25)] is enlarged beyond a critical value [see, e.g., Ref. 35]. This drawback has to be expected for the non-Markovian QME, too. But decreasing the decay time of $C_{ee}(t)$ one may reach the limit $C_{ee}(t) \sim \delta(t)$ resulting in the Lindblad form of dissipation.[9] Therefore, we have to expect that our simulations may show violation of the positivity of the density matrix but not if we shorten further and further the decay time of $C_{ee}(t)$.

Since in all cases we studied the duration of the laser pulse, which has been chosen to be considerably shorter than the typical decay time of the population of the vibrational levels, we neglect the dephasing contribution in the field source term [see Eqs. (B16) and (B17)].

We start the presentation of numerical calculations by displaying the population $\sigma_{22}(t) = P_2(t)$ of the second excited vibrational level (which is the level positioned in resonance to the applied light field). Figure 3 shows the time development of $P_2(t)$ in its dependence on the length of the laser pulse. In part (a) we can identify three kinds of the non-Markovian effects. First, one can immediately notice that P_2 reaches somewhat lower values in the non-Markovian case. This behavior reflects the fact that the dynamics is determined by the preceding states of the system. Further, we can observe that the fast oscillations of P_2 present in the Markov case become approximately twice as slow in the non-Markovian case. After a certain time interval this smaller oscillation frequency changes back to that of the Markov case, but with a smaller amplitude. Finally, an alternation of the decay rate of P_2 appears if one changes to the case of non-Markovian dynamics. (This latter effect can be
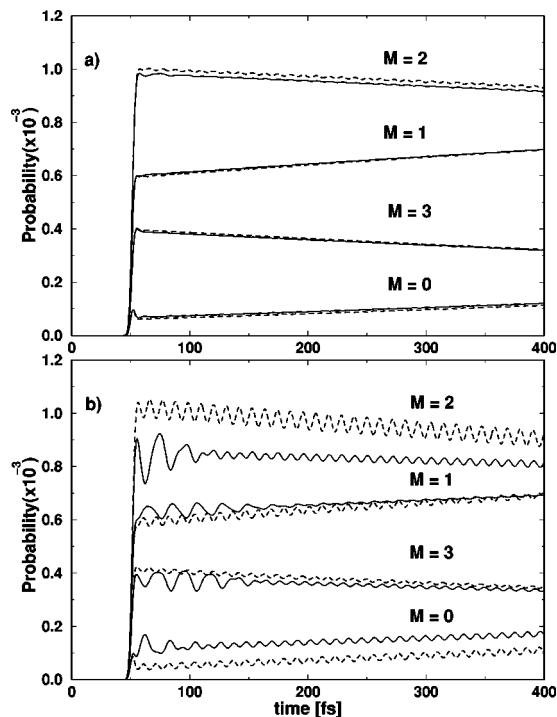
FIG. 5. Influence of the correlation time t_c on the dynamics of the occupation probabilities of the first four vibrational levels. Parameters: $J(\omega_{\mathrm{vib}})$ $= 1.9 \times 10^{-4}$, $\tau_p = 5$ fs, $t_c = 20$ fs and $t_c = 30$ fs in (a) and (b), respectively.

FIG. 6. Influence of the system bath coupling on the population dynamics of the first four vibrational levels ($\tau_p = 5$ fs, $t_c = 10$ fs). (a) $J(\omega_{\mathrm{vib}}) = 3.5$ $\times 10^{-4}/$fs. (b) $J(\omega_{\mathrm{vib}}) = 2.3 \times 10^{-3}/$fs.

seen more clearly in some other curves, presented below.) Comparing the results of Fig. 3 valid for different pulse lengths, one notices that the oscillating structures superimposed to P_2 disappear with pulses comparable or longer as the vibrational period $2\pi/\omega_{\mathrm{vib}}$.

A similar behavior as in Fig. 3 is shown in Fig. 4, but now with a correlation time shorter than the vibrational period $2\pi/\omega_{\mathrm{vib}}$. Using the same coupling strength as in Fig. 3 (upper curves), the situation changes considerably since we observe only a very small deviation between the case of non-Markovian and Markovian dynamics. On the other hand, while increasing the coupling strength J_0 we can again restore the situation from Fig. 3.

To further indicate the influence of the memory kernel decay time, e.g., the correlation time t_c on the dynamics, we display in Fig. 5 the population of the first four vibrational levels for the two different correlation times of 20 fs and 30 fs. Using the coupling strength of Fig. 3 we found in the case of $t_c = 10$ fs complete agreement between the Markovian and non-Markovian dynamics (not shown). This coincidence is somewhat weakened for $t_c = 20$ fs [Fig. 5(a)]. But for $t_c = 30$ fs the characteristics of the non-Markovian effects as described above arise (part b).

A situation where the correlation time t_c is shorter than the vibrational period $2\pi/\omega_{\mathrm{vib}}$ is considered in Fig. 6. Using the coupling strengths, J_0, already applied in Figs. 3 and 5, we again find complete agreement between the Markovian and non-Markovian type of dynamics. A small deviation between both cases can be observed in part (b) of Fig. 6. This part also shows that a further increase of J_0 may cause some small deviations between the Markov and non-Markov case.
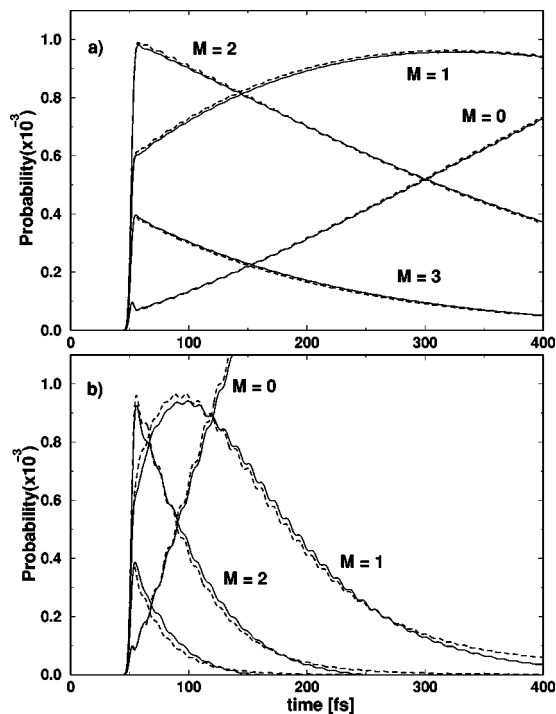
In particular, in the case of non-Markovian relaxation, the equilibrium value is reached slightly faster.

Let us summarize the phenomena which indicate a deviation of the non-Markovian type of relaxation from the Markov case. First, we observed a decrease of the light-pulse-induced vibrational levels population if non-Markovian relaxation is accounted for, and, second, the retardation effect somewhat slows down the relaxation. Finally, as a third hint on non-Markovian effects, we mention a reduction of the fast oscillations superimposed to the vibrational level populations. While the first two effects were found to be relatively unaffected by the pulse length, the oscillations are only present for pulse lengths sufficiently shorter than the oscillation period of the vibrational coordinate. Therefore, only the observation of these fast oscillations just after the pulse action can be considered a sufficiently clear hint on non-Markovian effects in the molecular dynamics.

At the end of this section we will compare the given correct description of non-Markovian dynamics with the approximate one introduced in Sec. II C via establishing the QME Eq. (17) with a time-dependent Redfield-tensor. Since the nonequilibrium part $\Delta\hat\rho$ of the complete RDO obeys a QME starting at time t_{field} and having the same inhomogeneity whether non-Markovian dynamics or Markovian dynamics (including a time-dependent Redfield-tensor) are considered, we expect that both approaches should give similar results. But a problematic issue of this comparison would be the choice of the time t_{field}. In Fig. 7 we present respective results for the case of an impulsive excitation (infinitely short laser pulse). In such a case t_{field} can be identified with the center of the pulse, and the agreement between both types of
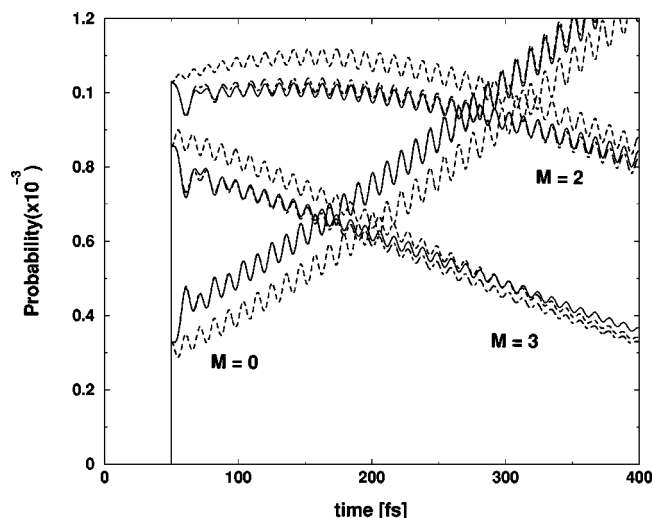
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FIG. 7. Population dynamics of some selected vibrational levels after impulsive excitation $[J(\omega_{vib}) = 3.5 \times 10^{-4}/fs$, $t_c = 20$ fs]. Full line: solution of the non-Markovian QME; dashed line: solution of the non-Markovian QME; dashed-dotted line; solution of Markovian QME with time-dependent Redfield-tensor.

dynamics is very good. Since the pulse is infinitely short the final population of the levels after the action of the pulse is the same for both, the Markovian as well as the non-Markovian case. However, details of the dynamics immediately after the pulse action differ in both cases.

For a situation with laser pulses of finite duration one may expect a similar result, as in the case of the impulsive excitation as long as the pulse length is shorter than the oscillation period of the vibrational coordinate. Indeed, choosing an optimal time t_{field} one is able to reproduce the results of the non-Markovian case quite well [see Fig. 8, curve (b)]. However, the agreement appears to be very sensitive to the
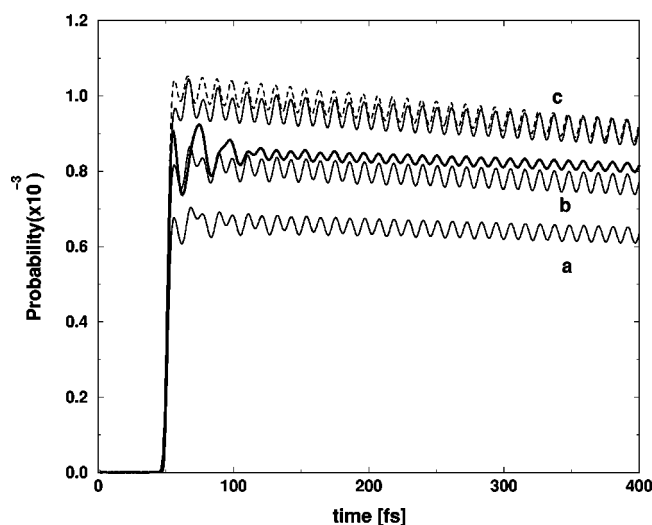

FIG. 8. Population dynamics of the second excited vibrational level $[J(\omega_{vib}) = 1.9 \times 10^{-4}/fs$, $t_c = 30$ fs, $\tau_p = 5$ fs, $\tau_f = 50$ fs]. Thick full line: solution of the non-Markovian QME; dashed line: solution of the Markovian QME; thin full lines; solution of Markovian QME with time-dependent Redfield-tensor. The initial time t_0 for the propagation with the time-dependent Redfield-tensor has been chosen in different ways. (a) $t_0 = \tau_f - 5$ fs; (b) $t_0 = \tau_f - 3.5$ fs; (c) $t_0 = \tau_f - 2.5$ fs.

choice of t_{field}. In particular, choosing t_{field} too close to the center of the pulse leads to an underestimation of the level populations created by the pulse [curve (a) in Fig. 8]. The opposite choice leads to a fast convergence to the corresponding standard Markov results as demonstrated by curve (c) of Fig. 8.

To conclude, we note that in the case of an instantaneous excitation, the approach using a time-dependent Redfield-tensor reproduces some of the non-Markovian effects quite well. In particular, one is able, within this approximation, to account for the initial dynamics leading to the difference in the occupation probability after the action of the pulse and also partly for the initial change of the fast oscillations superimposed to the populations. Finally, we underline that the given evaluation of the approach based on the time-dependent Redfield-tensor justifies earlier studies on the field-pulse alternation of dissipation.[30]

VI. CONCLUSIONS

To account for retarded (non-Markovian) couplings in the equation-of-motion which governs the time evolution of a reduced statistical operator, the Laguerre polynomial method has been introduced. This numerically exact approach offers the possibility to study the interplay of ultrafast laser-pulse state preparation and non-Markovian relaxation. Furthermore, non-Markovian relaxation may be compared with Markovian relaxation, which has been done for a broad set of different coupling strengths, pulse durations, and reservoir correlation times. Three different indications on non-Markovian relaxation could be identified, namely; (i) the difference in the vibrational level population after the pulse action; (ii) the change of the decay rate in the case of non-Markovian dynamics; and (iii) the decrease of the frequency which determines oscillations of the vibrational level populations.

The main advantage of the given approach is its flexibility with respect to the use of different types of reservoir correlation functions as well as spectral densities. There is no need to concentrate on a particular type of spectral density, as is necessary in the method used in Ref. 20. Furthermore, more distinct deviations of non-Markovian dynamics from the Markov case must be expected if the active system spectrum is not as regular as in the case of an harmonic oscillator and if more involved system-reservoir coupling functions are used. Respective studies are under work.

ACKNOWLEDGMENT

APPENDIX A: NAKAJIMA–ZWANZIG EQUATION WITH EXTERNAL FIELDS

According to the standard projection operator technique, one gets the reduced statistical operator $\hat{\rho}(t)$ from the complete time-dependent statistical operator $\hat{W}(t)$ by applying the projector (projection superoperator) $\mathcal{P} = \hat{R}_{eq} tr_R\{...\}$. Here, $\hat{R}_{eq}$ denotes the canonical statistical operator of the reservoir and the trace exclusively concerns the state-space

of reservoir states. If $\mathcal{P}$ and the orthogonal complement $\mathcal{Q}=1-\mathcal{P}$ are applied to the Liouville–von Neumann equation valid for $\hat{W}(t)$, one ends up with a strict equation for $\hat{\rho}(t)$ (see, for example, Ref. 9). This equation is known as the Nakajima–Zwanzig equation and has already been quoted in Eq. (7). In the following we list the concrete expressions for the initial correlation term $\hat{I}$ and the memory kernel $\mathcal{M}$. These expression somewhat deviate from the standard since the external field has been incorporated into the zero-order part, i.e., in $\mathcal{L}_S$.

Usually one derives the Nakajima–Zwanzig equation in the interaction representation for which the reduced density operator is given as

$$\hat{\rho}^{(I)}(t)=\mathcal{U}_S^+(t,t_0)\hat{\rho}(t). \tag{A1}$$

Since an external field has been incorporated the active system time-evolution superoperator $\mathcal{U}_S$ depends independently on t and t_0 and follows as a time-ordered exponential

$$\mathcal{U}_S(t,t_0)=T\exp\left(-\frac{i}{\hbar}\int_{t_0}^t d\bar{t}\mathcal{L}_S(\bar{t})\right). \tag{A2}$$

Changing back to the Schrödinger representation, the Nakajima–Zwanzig equation follows. We introduce the abbreviation

$$\langle\ldots\rangle_R=\mathrm{tr}_R\{\ldots\hat{R}_\mathrm{eq}\}, \tag{A3}$$

and obtain

$$\frac{\partial}{\partial t}\hat{\rho}(t)=\mathrm{tr}_R\{\mathcal{L}_{S-R}\mathcal{U}_{S+R}(t,t_0)\mathcal{S}(t,t_0)\mathcal{Q}\hat{W}(t_0)\}$$
$$-i(\mathcal{L}_S(t)+\langle\mathcal{L}_{S-R}\rangle_R)\hat{\rho}(t)$$
$$-\int_{t_0}^t d\bar{t}\langle\mathcal{L}_{S-R}^{(R)}(t)\mathcal{U}_S(t,t_0)\mathcal{S}(t,\bar{t})\mathcal{Q}\mathcal{U}_S(\bar{t},t_0)$$
$$\times\mathcal{L}_{S-R}^{(R)}(\bar{t})\rangle_R\times\hat{\rho}(\bar{t}). \tag{A4}$$

The first term on the right-hand side describes the influence of initial correlations, whereas the last term corresponds to the dissipative part $\hat{D}$ of the density operator equation. The time-evolution superoperator $\mathcal{U}_{S+R}$ is obtained from $\mathcal{U}_S$, Eq. (A2), if $\mathcal{L}_S$ is replaced by $\mathcal{L}_S+\mathcal{L}_R$, where $\mathcal{L}_R$ denotes the Liouvillian generated by the reservoir Hamiltonian H_R. The quantity $\mathcal{S}$ can be obtained from $\mathcal{U}_S$ by replacing $\mathcal{L}_S$ by $\mathcal{Q}\mathcal{U}_S(\bar{t},t_0)\mathcal{L}_{S-R}^{(R)}$. In this manner $\mathcal{S}$ incorporates the complete perturbation expansion with respect to the system-reservoir interaction.

As it can be seen from the second term on the right-hand side of Eq. (A4), the reversible part of the density operator equation has been extended by a mean-field-type term of the system-reservoir interaction. Finally the quantity $\mathcal{L}_{S-R}^{(R)}(t)$ introduced in the dissipative part of Eq. (A4) has to be understood as $\mathcal{L}_{S-R}$ translated into an interaction representation defined by $\mathcal{L}_R$ alone.

The second Born approximation of the memory kernel follows if one neglects, in the last term on the right-hand side of Eq. (A4), the superoperator $\mathcal{S}$, leading to

$$\mathcal{M}(t,\bar{t})=\langle\mathcal{L}_{S-R}^{(R)}(t)\mathcal{Q}\mathcal{L}_{S-R}^{(R)}(\bar{t})\}\rangle_R\mathcal{U}_S(t,\bar{t}). \tag{A5}$$

Using Eq. (22) the expression changes to (note the replacement of $t-\bar{t}$ by τ)

$$\int_0^{t-t_0}d\tau\mathcal{M}(t,t-\tau)\hat{\rho}(t-\tau)$$
$$=\sum_{a,b}\int_0^{t-t_0}d\tau(C_{ab}(\tau)[\hat{\mathcal{K}}_a,U_S(t,t-\tau)$$
$$\times\hat{\mathcal{K}}_b\hat{\rho}(t-\tau)U_S^\dagger(t,t-\tau)]-C_{ba}(-\tau)$$
$$\times[\hat{\mathcal{K}}_a,U_S(t,t-\tau)\hat{\rho}(t-\tau)\hat{\mathcal{K}}_bU_S^\dagger(t,t-\tau)]). \tag{A6}$$

APPENDIX B: THE DISSIPATIVE PART OF THE QME AND THE REDUCTION TO THE EXCITED-STATE PES

According to the presence of two different electronic levels, $\hat{\rho}(t)$ has to be expanded with respect to the electronic states yielding $\hat{\rho}_{ab}(t)$ which is just an operator in the vibrational state-space. For the separation of the density operator into an equilibrium part and a nonequilibrium deviation as introduced in Eq. (12) we get

$$\hat{\rho}_{ab}(t)=\delta_{a,b}\delta_{a,g}\hat{r}_\mathrm{eq}^{(g)}+\Delta\hat{\rho}_{ab}(t), \tag{B1}$$

with

$$\hat{r}_\mathrm{eq}^{(g)}=\frac{e^{-H_g/k_BT}}{\mathrm{tr}_\mathrm{vib}\{e^{-H_g/k_BT}\}}. \tag{B2}$$

The density operator $\Delta\hat{\rho}_{ab}(t)$ obeys the following equation [cf. Eq. (13) and note the neglect of the field-dependence of $\mathcal{M}$]

$$\frac{\partial}{\partial\tau}\Delta\hat{\rho}_{ab}(t)=\hat{I}_{ab}(t)-\frac{i}{\hbar}(H_a\Delta\hat{\rho}_{ab}(t)-\Delta\hat{\rho}_{ab}(t)H_b)$$
$$-\hat{D}_{ab}(t-t_\mathrm{field};\Delta\hat{\rho})$$
$$+\frac{i}{\hbar}\mathbf{E}(t)\sum_c(\mathbf{d}_{ac}\Delta\hat{\rho}_{cb}(t)-\mathbf{d}_{cb}\Delta\hat{\rho}_{ac}(t)). \tag{B3}$$

Here, the inhomogeneity is given as

$$\hat{I}_{ab}(t)=\frac{i}{\hbar}\mathbf{E}(t)(\delta_{ae}\delta_{g,b}\mathbf{d}_{eg}-\delta_{a,g}\delta_{e,b}\mathbf{d}_{ge})\hat{R}_\mathrm{eq}. \tag{B4}$$

The dissipative part reads

$$\hat{D}_{ab}(t-t_\mathrm{field};\Delta\hat{\rho})$$
$$=\int_0^{t-t_\mathrm{field}}d\tau(C_{aa}(\tau)K_aK_a(-\tau)\hat{\sigma}_{ab}(t-\tau,\tau)$$
$$+C_{bb}(-\tau)\hat{\sigma}_{ab}(t-\tau,\tau)K_b(-\tau)K_b-C_{ba}(\tau)$$
$$\times K_a(-\tau)\hat{\sigma}_{ab}(t-\tau,\tau)K_b-C_{ba}(-\tau)$$
$$\times K_a\hat{\sigma}_{ab}(t-\tau,\tau)K_b(-\tau)). \tag{B5}$$

To have a sufficient compact expression we introduced

$$K_a(-\tau) = U_a(\tau) K_a U_a^+(\tau) \tag{B6}$$

and

$$\hat{\sigma}_{ab}(t-\tau,\tau) = U_a(\tau) \Delta \hat{\rho}_{ab}(t-\tau) U_b^t(\tau), \tag{B7}$$

with the time-evolution operators denoted as

$$U_a(t) = e^{-iH_a t/\hbar}. \tag{B8}$$

The reservoir correlation functions read [cf. Eq. (A3)]

$$C_{ab}(t) = \frac{1}{\hbar^2} \langle U_R^+ \Phi_a U_R \Phi_b \rangle_R. \tag{B9}$$

To simulate the reservoir we provide that a normal mode analysis has been carried out. It results in an ensemble of independent harmonic oscillators which will be coupled linearly to the system DOF. Thus we suppose

$$\Phi_a(Z) = \hbar \sum_\xi k_\xi(a) Z_\xi, \tag{B10}$$

with k_ξ being a coupling constant of a corresponding harmonic oscillator with system DOF. For such a reservoir the correlation function takes the form (see, e.g., Ref. 9)

$$C_{ab}(t) = \int_{-\infty}^{+\infty} d\omega e^{-i\omega t}(1+n(\omega))(J_{ab}(\omega)-J_{ab}(-\omega)), \tag{B11}$$

with $n(\omega) = 1/(\exp(\hbar\omega/k_B T)-1)$ being the Bose–Einstein distribution and the quantities

$$J_{ab}(\omega) = \sum_\xi k_\xi(a) k_\xi(b) \delta(\omega - \omega_\xi) \tag{B12}$$

representing the spectral densities of normal modes.

In the case of an arbitrary strength of the applied field, all elements of $\Delta\hat{\rho}_{ab}(t)$ have to be considered. Here, we will concentrate on the case of weaker field strength realizing only marginal population transfer to the excited electronic levels. Then, one can reduce the whole description to the use of the quantity $\Delta\hat{\rho}_{ee}(t)$ describing vibrational dynamics on the excited-state PES initiated by the external-field pulse. It will enter the respective equation of motion in the second order corresponding to a linearization in the field intensity.

As it is well-known such a result is obtained if one determines $\Delta\hat{\rho}_{eg}$ linearly with respect to **E** and inserts the expression into the equation of motion for $\Delta\hat{\rho}_{ee}$. According to Eq. (B3) one obtains for the electronic off-diagonal density operator

$$\frac{\partial}{\partial t} \Delta\hat{\rho}_{eg}(t) = -\frac{i}{\hbar}(H_e \Delta\hat{\rho}_{eg}(t) - \Delta\hat{\rho}_{eg}(t) H_g)$$

$$-\hat{D}_{eg}(t-t_{\text{field}};\Delta\hat{\rho}_{eg}) + \frac{i}{\hbar} \mathbf{E}(t)\mathbf{d}_{eg}\hat{r}_{\text{eq}}^{(g)}. \tag{B13}$$

Solving this equation and inserting the result into the equation-of-motion for $\Delta\hat{\rho}_{ee}$ gives the desired closed description of the vibrational dynamics in the excited electronic state. To have an analytical expression we replace $\hat{D}_{eg}$ by a time-local expression $\hat{\Gamma}_e \Delta\hat{\rho}_{eg} + \Delta\hat{\rho}_{eg} \hat{\Gamma}_g$ and the respective

deviation $\Delta\hat{D}_{eg}$ from this expression. On the one hand, this procedure enables us to derive an analytical formula for the field-dependent source term in the equation-of-motion for $\Delta\hat{\rho}_{eg}$. And, on the other hand, we can improve the result step-by-step. The operators $\hat{\Gamma}_a$ realize dephasing and are given as

$$\hat{\Gamma}_a = \int_0^\infty d\tau C_{aa}(\tau) K_a K_a(-\tau). \tag{B14}$$

Instead of a contribution proportional to $\Delta\hat{\rho}_{eg}$, now the equation-of-motion for $\Delta\hat{\rho}_{ee}$ contains a source term and reads

$$\frac{\partial}{\partial t} \Delta\hat{\rho}_{ee}(t) = \frac{i}{\hbar}[H_e, \Delta\hat{\rho}_{ee}(t)]_- - \hat{D}_{ee}(t-t_{\text{field}};\Delta\hat{\rho}_{ee})$$

$$+\hat{F}_{ee}(t,t_{\text{field}};\mathbf{E}). \tag{B15}$$

For the source term one gets

$$\hat{F}_{ee}(t,t_{\text{field}};\mathbf{E}) = \frac{1}{\hbar^2} \int_{t_{\text{field}}}^t d\bar{t}(\mathbf{d}_{eg}\mathbf{E}(t))(\mathbf{d}_{ge}\mathbf{E}(\bar{t}))$$

$$\times \tilde{U}_e(t-\bar{t})\tilde{\rho}_{\text{eq}}^{(g)}\tilde{U}_g^+(t-\bar{t}) + \text{h.c.} \tag{B16}$$

The evolution operators $\tilde{U}_e(t)$ and $\tilde{U}_g(t)$ are defined according to

$$\tilde{U}_a(t) = \exp-\frac{i}{\hbar}(H_a - i\hbar\hat{\Gamma}_a), \tag{B17}$$

i.e., they are formed by a non-hermitian Hamiltonian including dephasing operators $\hat{\Gamma}_a$.

APPENDIX C: EVALUATION OF THE MEMORY EXPANSION COEFFICIENTS

In Sec. IV we claimed that, based on the spline approximation of the correlation function, the integrals Eq. (44) can be evaluated analytically. Here we give some details of this procedure. The function $C_{\text{spl}}^{(j)}(t)$ introduced in Eq. (44) is an interpolation of the correlation function by cubic splines, i.e.,

$$C_{\text{spl}}^{(j)}(xt_{\text{char}}) = \alpha(x)C_{ee}(x_j t_{\text{char}}) + \beta(x)C_{ee}(x_{j+1}t_{\text{char}})$$

$$+\gamma(x)C''(x_j t_{\text{char}}) + \delta(x)C''(x_{j+1}t_{\text{char}}). \tag{C1}$$

The four different expansion coefficients can all be expressed by the first one, which reads

$$\alpha(x) = \frac{x_{j+1}-x}{\Delta x} \equiv \frac{1}{\Delta x}(L_1(x) - L_1(x_{j+1})). \tag{C2}$$

Here, we introduced $\Delta x = x_{j+1} - x_j$. The remaining three coefficients are

$$\beta(x) = 1 - \alpha(x), \tag{C3}$$

$$\gamma(x) = \frac{(\Delta x)^2}{6}(\alpha^3(x) - \alpha(x)), \tag{C4}$$

and

$$\delta(x) = -\frac{(\Delta x)^2}{6}(\alpha^3(x) - 3\alpha^2(x) + 2\alpha(x)). \qquad \text{(C5)}$$

The second derivative C'' of $C_{ee}(xt_{char})$ at $x = x_j, x_{j+1}$ are computed using a standard interpolating algorithm.[34] The above given relations indicate that it is necessary to compute integrals of type Eq. (44) but with $C_{spl}^{(j)}(xt_{char})$ replaced by $\alpha(x)$ up to its third power. In carrying out these integrations it is useful to generate recurrence formulas. Therefore we define

$$a_n^{(m)} = \int_{x_j}^{x_{j+1}} dx (L_1(x))^m L_n(x) e^{i\Delta\tilde\omega x} e^{-x}. \qquad \text{(C6)}$$

In particular we have $a_0^{(1)} = a_1^{(0)}$, and

$$a_0^{(0)} = -\frac{1}{1-i\Delta\tilde\omega}[e^{-(1-i\Delta\tilde\omega)x}]_{x_j}^{x_{j+1}}, \qquad \text{(C7)}$$

where the abbreviation $[g(x)]_0^a = g(a) - g(b)$ has been introduced. These expression enables us to express the required integrals as

$$\int_{x_j}^{x_{j+1}} dx\,\alpha(x) L_n(x) e^{i\Delta\tilde\omega x} e^{-x} = \frac{1}{\Delta x}(a_n^{(1)} - a_n^{(0)}), \qquad \text{(C8)}$$

$$\int_{x_j}^{x_{j+1}} dx\,\alpha^2(x) L_n(x) e^{i\Delta\tilde\omega x} e^{-x}$$
$$= \frac{1}{\Delta x^2}(a_n^{(2)} - 2L_1(x_{j+1})a_n^{(1)} + (L_1(x_{j+1}))^2 a_n^{(0)}), \qquad \text{(C9)}$$

and

$$\int_{x_j}^{x_{j+1}} dx\,\alpha^3(x) L_n(x) e^{i\Delta\tilde\omega x} e^{-x}$$
$$= \frac{1}{\Delta x^3}(a_n^{(3)} - 3L_1(x_{j+1})a_n^{(2)} + 3(L_1(x_{j+1}))^2 a_n^{(1)}$$
$$- (L_1(x_{j+1}))^3 a_n^{(0)}). \qquad \text{(C10)}$$

Accordingly, the announced recursion formulas, which are essential for an efficient computation of a_n^m, read

$$a_n^{(0)} = \frac{1}{1-i\Delta\tilde\omega}\{[e^{i\Delta\tilde\omega x} e^{-x}(L_{n-1}(x) - L_n(x))]_{x_j}^{x_{j+1}}$$
$$- i\Delta\tilde\omega a_{n-1}^{(0)}\}, \qquad \text{(C11)}$$

and similarly for the other integrals

$$a_n^{(1)} = \frac{1}{1-i\Delta\tilde\omega}\{[L_1(x) e^{i\Delta\tilde\omega x} e^{-x}(L_{n-1}(x)$$
$$- L_n(x))]_{x_j}^{x_{j+1}} + a_{n-1}^{(0)} - a_n^{(0)} - i\Delta\tilde\omega a_{n-1}^{(1)}\}, \qquad \text{(C12)}$$

$$a_0^{(2)} = -\frac{1}{1-i\Delta\tilde\omega}\{[(L_1(x))^2 e^{i\Delta\tilde\omega x} e^{-x}]_{x_j}^{x_{j+1}} + 2a_1^{(0)}\}, \qquad \text{(C13)}$$

$$a_n^{(2)} = \frac{1}{1-i\Delta\tilde\omega}\{[(L_1(x))^2 e^{i\Delta\tilde\omega x} e^{-x}(L_{n-1}(x)$$
$$- L_n(x))]_{x_j}^{x_{j+1}} + 2a_{n-1}^{(1)} - 2a_n^{(1)} - i\Delta\tilde\omega a_{n-1}^{(2)}\}, \qquad \text{(C14)}$$

$$a_0^{(3)} = -\frac{1}{1-i\Delta\tilde\omega}\{[(L_1(x))^3 e^{i\Delta\tilde\omega x} e^{-x}]_{x_j}^{x_{j+1}} + 3a_0^{(2)}\}, \qquad \text{(C15)}$$

and

$$a_n^{(3)} = \frac{1}{1-i\Delta\tilde\omega}\{[(L_1(x))^3 e^{-i\Delta\tilde\omega x} e^{-x}(L_{n-1}(x)$$
$$- L_n(x))]_{x_j}^{x_{j+1}} + 3a_{n-1}^{(2)} - 3a_n^{(2)} - i\Delta\tilde\omega a_{n-1}^{(3)}\}. \qquad \text{(C16)}$$

At first glance the given formulas look too complex to be useful for integrating a function of a single variable. But, according to our efforts to reach a sufficient precision, they seem to provide the only way to get precise results even for Laguerre polynomials of the order 10^5 or higher. Moreover, these formulas, if accompanied by a routine to compute Laguerre polynomials via standard recurrence formulas,[34] can be put in a very compact computer code. Finally we note that the given spline interpolation scheme to integrate the product of a smooth and a highly oscillating function, such as polynomials of a high order and/or $\exp i\tilde\omega x$, may be used in many other cases.

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