Classical formulation of the spectroscopy of nonadiabatic excited-state dynamics

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A general classical formulation of the spectroscopy of nonadiabatically coupled electronic states is developed within the theoretical framework of the classical electron analog model due to Meyer and Miller. Adopting the Heisenberg representation for the calculation of the electric polarization, several approaches are presented to establish a quantum-classical correspondence. It is shown that a consistent classical formulation is obtained by replacing the quantum-mechanical commutator, which appear in quantum-mechanical perturbation theory, by the corresponding classical Poisson brackets which come from classical perturbation theory. The more usual practice of replacing the Heisenberg dipole operators directly by the corresponding classical dipole functions is shown to be an approximation to classical perturbation theory. For a coupled electronic three-state system explicit expressions are derived for the nonlinear polarization. Furthermore the practical application to femtosecond pump-probe spectroscopy is discussed in some detail.

I. INTRODUCTION

Due to the exponential increase of numerical effort with the number of degrees of freedom in quantum computations, classical trajectory calculations are a popular approach to simulate the dynamics of polyatomic systems.\textsuperscript{1} In cases where both the system under consideration and the observable to be calculated have an obvious classical analog (say, the product momentum distribution after a scattering event), the application of classical mechanics to simulate molecular dynamics is a straightforward and well-established matter.

It is less obvious, though, how to employ a classical treatment to account for the quantum mechanical degrees of freedom corresponding to several coupled electronic states. This is necessary, however, in order to describe nonadiabatic interactions, such as intersections and avoided crossings of potential energy surfaces, and also to calculate optical spectra involving several electronic states. A number of approaches have been proposed for incorporating electronic degrees of freedom into a classical theory, such as a variety of the surface hopping model of Tully and Preston,\textsuperscript{2-6}"rigorous" semiclassical methods,\textsuperscript{7-9} and a variety of classical path models (i.e., classical nuclear motion coupled to time-dependent electronic motion).\textsuperscript{10-13} Most of the work, however, has been concerned with the calculation of nonadiabatic transition rates. Only a few studies have addressed the (semi)classical evaluation of spectra involving several electronic states,\textsuperscript{14-19} or even in the presence of nonadiabatic dynamics.\textsuperscript{20,21}

An appealing simple way that describes both electronic and heavy particle degrees of freedom on the same dynamical footing is the classical electron analog (CEA) model due to Meyer and Miller.\textsuperscript{12} The basic idea is to replace a set of electronic states by a set of classical action-angle variables, thus obtaining a classical Hamiltonian for the complete set of all heavy particles and electronic degrees of freedom, the dynamics of which is then determined by integrating the classical equations of motion. The model has been found to describe a variety of processes at least semi-quantitatively, including the evaluation of nonadiabatic collision cross sections,\textsuperscript{13,22} the calculation of non-Born-Oppenheimer dynamics of conical intersections,\textsuperscript{23,24} and photodissociation of nonadiabatic coupled states both in the gas phase\textsuperscript{20} and in solution.\textsuperscript{21}

The CEA approach provides a classical function for any quantum-mechanical operator, in particular for the electronic dipole operator, the expectation value of which is the electric polarization. The CEA model therefore allows for the classical evaluation of the polarization, from which all spectroscopic information can be calculated. As a first demonstration of this concept, the CEA model has recently been applied to calculate time- and frequency-resolved pump-probe spectra of a vibronically coupled multimode system.\textsuperscript{25}

In this paper we generalize this approach by developing a general classical formulation of the spectroscopy of nonadiabatically coupled electronic states. Specializing first to linear response, Sec. III discusses in some detail different approaches to evaluate the electronic dipole correlation function (DCF) classically, the Fourier transform of which yields the cw absorption spectrum. The standard prescription, below referred to as the "primitive classical DCF", is to use the expressions of quantum-mechanical time-dependent perturbation theory as a starting point for the classical theory. It is shown, however, that it is more consistent to proceed purely classically by treating the interaction with the radiation field by classical time-dependent perturbation theory. This is accomplished by replacing the quantum-mechanical commutator stemming...
from quantum-mechanical perturbation theory by the classical Poisson bracket. In this way one obtains without further manipulation a complex DCF (thereby giving absorption and emission), and it is shown that the primitive classical DCF results as a limiting case.

The concepts developed for the linear case generalize straightforwardly to the nonlinear response, which is considered in Sec. IV. In Sec. V we apply the theory to the case of femtosecond pump-probe spectroscopy (for recent theoretical reviews see Refs. 26–28), and discuss some issues concerning the practical evaluation of the CEA formalism.

II. THE CLASSICAL ELECTRON ANALOG (CEA) MODEL HAMILTONIAN

In a diabatic electronic representation, the Hamiltonian and the electric dipole operator for a molecular system with nonadiabatically coupled electronic states can be written as ( " " denotes a quantum-mechanical operator)

\[ H = \sum_{k=0}^{F-1} |\varphi_k\rangle \langle \varphi_k| + \sum_{k,k', \delta_k=0}^{F-1} |\varphi_k\rangle \hat{V}_{kk'} |\varphi_{k'}| , \] (2.1)

\[ \hat{\mu} = \sum_{k,k'=0}^{F-1} |\varphi_k\rangle \mu_{kk'} |\varphi_{k'}| . \] (2.2)

Here \( \hat{T} \) represents the kinetic energy operator, the \( \hat{V}_{kk'} \) are the diagonal diabatic potential matrix elements, and the \( \mu_{kk'} \) represent the nonadiabatic couplings by an intramolecular interaction and the coupling to the radiation field, respectively. We want to treat the presumably strong nonadiabatic couplings exactly, to all orders, whereas the field-matter interaction, serving solely as a probe to measure the molecular dynamics, is treated perturbatively.

The CEA model is based on the observation that for a finite dimensional quantum mechanical system a formally exact classical analog can be defined by representing the quantum-mechanical states \( \{|\varphi_k\rangle\} \) by \( F \) pairs of classical action-angle variables \( \{n_k, \theta_k\} \). Within this theoretical framework the classical function \( A \) corresponding to an arbitrary quantum-mechanical operator \( \hat{A} \) defined on an \( F \)-dimensional Hilbert space, is given by (\( \hat{A} = 1 \))

\[ A(n,q) = \sum_{k=0}^{F-1} n_k A_{kk} + \sum_{k,k', \delta_k=0}^{F-1} \sqrt{ \left( n_k + \frac{1}{2} \right) \left( n_{k'} + \frac{1}{2} \right) } e^{i(q_k-q_{k'})} A_{kk'}, \] (2.3)

where \( A_{kk'} \) are the diabatic electronic matrix elements of \( \hat{A} \). To obtain a dynamically consistent model within the framework of classical S-matrix theory, modifications have been employed in the off-diagonal terms. The most important application of (2.3) is \( \hat{A} = H_{eh} \) defining the CEA Hamiltonian function, which depends parametrically (through the matrix elements \( H_{kk'}(x) \)) on the nuclear coordinates \( x \). By adding the classical nuclear kinetic energy one obtains the complete classical vibronic Hamiltonian

\[ \hat{H}(p,x,n) = \frac{\hat{p}^2}{2\mu} + \sum_{k=0}^{F-1} n_k V_k(x) + \sum_{k,k', \delta_k=0}^{F-1} \sqrt{ \left( n_k + \frac{1}{2} \right) \left( n_{k'} + \frac{1}{2} \right) } e^{i(q_k-q_{k'})} V_{kk'}(x). \] (2.4)

The time evolution of both heavy-particle degrees of freedom \( \{p_i, x\} \) and electronic degrees of freedom \( \{n_k, q\} \) are then described consistently by Hamilton's equations

\[ \dot{p}_i(t) = -\frac{\partial H}{\partial x_i} \quad \dot{x}_i(t) = \frac{\partial H}{\partial p_i}, \quad (i=1,..,N_{mod}) \] (2.5a)

\[ \dot{n}_k(t) = -\frac{\partial H}{\partial q_k}, \quad \dot{q}_k(t) = \frac{\partial H}{\partial n_k}, \quad (k=0,..,F-1). \] (2.5b)

For further reference it is useful to specialize the general Hamiltonian above to a standard model problem, representing the lowest few electronic states of a molecular system. A typical case for a polyatomic molecule is that two excited states \( \{|\varphi_1\rangle \) and \( |\varphi_2\rangle \) \) are coupled by an intermolecular interaction \( \hat{V}_{12} \), whereas the coupling of the excited states to the well-separated electronic ground state \( |\varphi_0\rangle \) may be neglected. Employing furthermore the selection rule that only the \( |\varphi_2\rangle - |\varphi_0\rangle \) transition is dipole-allowed in absorption and emission, the quantum-mechanical system is defined as

\[ \hat{H} = \sum_{k=0}^{2} |\varphi_k\rangle \langle \varphi_k| + \{|\varphi_1\rangle \hat{V}_{12} |\varphi_2\rangle + h.c., \] (2.6)

\[ \hat{\mu} = |\varphi_2\rangle \mu_{20} |\varphi_0\rangle + |\varphi_0\rangle \mu_{02} |\varphi_2\rangle, \] (2.7)

describing the commonly encountered situation of a bright excited electronic state \( |\varphi_2\rangle \) coupled to a dark background state \( |\varphi_1\rangle \).

To simplify the CEA Hamiltonian corresponding to (2.6) we note that in general only \( F=1 \) electronic action-angle variables are independent, as the CEA model conserves the total electronic probability (i.e. \( \sum n_k = 1 \) ). Furthermore, since by assumption only the two excited electronic states are nonadiabatically coupled, the population of the electronic ground state \( n_0 = 1 \) and the sum of the excited-state electronic populations \( n_1 + n_2 \) is constant over the motion, depending only on initial conditions (e.g. for absorption \( n_0 = 1 \), for emission \( n_0 = 0 \)). Introducing the canonical transformation

\[ n = n_2, \quad q = q_2 - q_1, \quad n_0 = 1 - n_1 - n_2, \quad Q = q_0 - q_1, \] (2.8)

the CEA model Hamiltonian finally becomes


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The transition to classical mechanics is most clearly performed by representing the dipole operator in the Heisenberg picture

\[ \hat{\mu}(t) = e^{i\hat{h}t}\hat{\mu}e^{-i\hat{h}t}, \]

\[ = \hat{\mu}_2(t) + \hat{\mu}_20(t), \]

Note that, in contrast to Eq. (2.2), both \( \hat{\mu}(t) \) and \( \hat{\mu}_20(t) \) are operators in an electronic and vibrational product space. Employing first-order perturbation theory (cf. Sec. IV), the absorption spectrum can be written as

\[ I_A(\omega) = \int_0^\infty dt E(t) e^{-i\omega t} \langle \psi_0 | [\hat{\mu}(t), \hat{\mu}(0)] | \psi_0 \rangle | \psi \rangle, \]

(3.2)

where \( | \psi \rangle \) denotes the initial vibrational wavefunction of the electronic ground state and \( T_2 \) is the phenomenological total dephasing time of the optical transition. For a continuous electric field, \( E(t) = e^{i\omega t} + c.c. \), and within the standard rotating-wave approximation,\(^{32}\) we obtain the more familiar relation

\[ I_A(\omega) = 2 N e \int_0^\infty dt e^{i\omega t} e^{-i\omega T_2} C_{QM}(t), \]

(3.3)

stating that the rate of absorbed photons is directly given by the Fourier transform of the quantum-mechanical dipole correlation function

\[ C_{QM}(t) = \langle \psi | \langle \psi_0 | [\hat{\mu}(t), \hat{\mu}(0)] | \psi_0 \rangle | \psi \rangle, \]

(3.4a)

\[ = \langle \psi | \langle \psi_0 | \hat{\mu}_2(t) \hat{\mu}_2(t) | \psi_0 \rangle | \psi \rangle. \]

(3.4b)

To evaluate Eqs. (3.2) and (3.3) classically we first note that according to (2.9) the CEA dipole function is given by

\[ \mu(t) = \mu_20(t) + \mu_2(t), \]

(3.5)

At this point there are several possible options to establish a quantum-mechanical/classical correspondence:

(i) Classical evaluation of Eq. (3.4a) or Eq. (3.4b) by replacing the dipole operator \( \hat{\mu}(t) (\hat{\mu}_20(t)) \) by the corresponding CEA dipole function \( \mu(t) (\mu_2(t)) \), e.g.,

\[ \mu_2(t) \rightarrow \mu_2(t), \]

(3.6)

As this is the simplest way to evaluate the DCF (3.4) classically, we refer to it as the primitive classical DCF.

(ii) Classical evaluation of Eq. (3.2) by replacing the quantum-mechanical commutator by the classical Poisson bracket

\[ [\hat{\mu}(t), \hat{\mu}(0)] \rightarrow i\hbar \{\mu(t), \mu(0)\}, \]

(3.7)

which is shown below to be equivalent to replacing the quantum-mechanical perturbation theory, leading to (3.2), by classical perturbation theory.
The primitive CEA dipole correlation function

In order to obtain the (primitive) classical analog to the quantum-mechanical DCF (3.4) we employ the correspondence (3.6) and simulate the projection on the initial state \( \langle \psi_0 | \psi \rangle \) by sampling over initial conditions, i.e.,

\[
C_{QM}(t) \rightarrow C_{CEA}(t) = \langle \mu_{Q2}(t) \mu_{20}(0) \rangle. \tag{3.8}
\]

Inserting (3.6) into (3.8), and denoting the averaging over the initial positions \( x_i(0) \), momenta \( p_i(0) \), and electronic phases \( q_k(0) \) explicitly by integrals, gives

\[
C_{CEA}(t) = \int dx(0) \int dp(0) \rho(x(0),p(0)) \times \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\varphi}{2\pi} |\mu_{Q2}|^2 \times (n_0 + \frac{1}{2}) \left( n(0) + \frac{1}{2} \right) \left( n(t) + \frac{1}{2} \right) \exp \left( i \varphi(0) - Q(0) - q(t) + Q(t) \right). \tag{3.9}
\]

The phase term in the exponential function can be evaluated by formal integration of the equations of motion (2.10d),(2.10f), yielding

\[
y(0) - Q(0) - q(t) + Q(t) = - \int_0^t dt' \left( V_2 - V_0 + V_{12} \sqrt{\frac{3-n_0-n}{\frac{3}{2}+n} \cos q(t)} \right). \tag{3.10}
\]

Rewriting the averaging as a sum over, say, \( N_{traj} \) trajectories, and normalizing to \( C_{CEA}(0) = 1 \), one finally obtains

\[
C_{CEA}(t) = \frac{1}{N_{traj}} \sum_{r=1}^{N_{traj}} d_r(t) d_r^*(0), \tag{3.11}
\]

\[
d_r(t) = \mu_{Q2} \sqrt{n(t) + \frac{1}{2}} \exp \left( -i \int_0^t dt' \right) \times \left( V_2 - V_0 + V_{12} \sqrt{\frac{3-n_0-n}{\frac{3}{2}+n} \cos q(t)} \right). \tag{3.12}
\]

for the primitive CEA DCF.

In connection with (3.3), Eqs. (3.11) and (3.12) given a simple and physically clear picture of the linear response of a vibronically coupled system. The arguments of the exponential functions in (3.3) and (3.12) display the resonance condition of the electronic transition, where the time integration accounts for the fact that the potentials depend on time through the trajectory \( x(t) \). In the uncoupled case (i.e., \( V_{12} = 0 \)), the excited state population \( n(t) = \) const, and the spectrum is solely determined by the vertical electronic energy difference \( V_2 - V_0 \), stating the classical Franck-Condon principle. The nonadiabatic coupling \( V_{12} \) introduces an additional term into the resonance condition, reflecting the change of the adiabatic potential energy surfaces due to the vibronic coupling. Furthermore, the factor \( \sqrt{n(t) + \frac{1}{2}} \) accounts for the fact that for \( V_{12} \neq 0 \) only a part of the electronic excited-state population is in the optically accessible bright state.

Finally, it is interesting to note that the correspondence

\[
\hat{\mu}(t) \rightarrow \mu(n(t),q(t)) = \mu \left( \sqrt{n_0 + \frac{1}{2}} \right) \left( n + \frac{1}{2} \right) \cos (q_2 - q_0), \tag{3.13}
\]

instead of (3.8) does not result in the same classical DCF, although quantum-mechanically Eqs. (3.4a) and (3.4b) are clearly equivalent. If Eq. (3.13) is used to evaluate the DCF, the exponential function in (3.12) is replaced by a cosine function and the DCF is therefore real, which in turn results in a symmetric absorption spectrum [i.e. \( I_4(\omega) = I_4(-\omega) \)]. This flaw can be remedied, however, by noting that

\[
\hat{\mu}(t) \rightarrow \mu(n(t),q(t)) = \mu \left( \sqrt{n_0 + \frac{1}{2}} \right) \left( n + \frac{1}{2} \right) \cos (q_2 - q_0). \tag{3.14}
\]

Equation (3.16) provides a general prescription for obtaining an approximation to the imaginary part of the quantum mechanical DCF from a classical trajectory calculation. Since the imaginary part is directly proportional to \( \pi \), it vanishes in the completely classical limit. It has been shown for the case of a classical description of infrared spectroscopy that the correspondences (3.14) and (3.16) yield the correct quantum-mechanical expressions for a harmonic system. Evaluating (3.14) and (3.16) for an uncoupled system (see the Appendix) results again (up to a constant) in the primitive DCF (3.12), thus justifying ansatz (3.6). For a coupled system, however, the evaluation of the Poisson bracket (3.16) yields additional terms that, entering only the imaginary part of the DCF, make this approach somehow unsymmetric. As discussed below, one obtains a more consistent formulation by employing the commutator/poisson bracket correspondence at an earlier stage.

C. Classical perturbation theory

So far we have been concerned with the classical evaluation of the electronic DCF (3.4), which is an expression resulting from quantum-mechanical time-dependent perturbation theory. Proceeding more consistently classically, however, here we consider classical time-dependent perturbation theory, i.e. solving Hamilton’s Eqs. (2.10) iteratively with respect to the classical interaction Hamiltonian.
\[ H_{\text{int}} = -\mu \cdot E(t), \]
\[ = -2\mu E(t) (n_0 + \frac{1}{2}) (q_0 - q_0), \]

(3.17)

where, henceforth, the vector notation will for simplicity be dropped. This can be done either explicitly, or equivalently by replacing the quantum-mechanical commutator \( [\hat{\mu}(t), \hat{\mu}(0)] \) in Eq. (3.2) by the classical Poisson bracket \( \{\mu(t), \mu(0)\} \), which in general can be written as

\[ \{\mu(t), \mu(0)\} = \sum_{k=0}^{N_{\text{mod}}} \left( \frac{\partial \mu(t)}{\partial x_k(0)} \frac{\partial \mu(0)}{\partial \mu(0)} + \frac{\partial \mu(t)}{\partial \mu(0)} \frac{\partial \mu(0)}{\partial x_k(0)} \right), \]

(3.18)

where

\[ \frac{\partial \mu(t)}{\partial f(0)} = \sum_{k=0}^{N_{\text{mod}}} \left( \frac{\partial \mu(t)}{\partial x_k(0)} \frac{\partial q_k(0)}{\partial f(0)} + \frac{\partial \mu(t)}{\partial q_k(0)} \frac{\partial x_k(0)}{\partial f(0)} \right), \]

(3.19)

and \( f \) denotes an arbitrary canonical variable \( (p_k x_k, q_k) \).

It is seen that in classical perturbation theory the first-order correction to the field-free trajectory is given by the first derivatives of the CEA dipole function with respect to the full set of initial conditions. While in general the evaluation of the Poisson bracket for a multidimensional system is a cumbersome numerical task, it is instructive to consider some important special cases and properties of (3.18), the derivations of which are given in the Appendix.

First note that in the linear response case (3.2), i.e. for \( t_1 = 0 \) and \( t_2 = t \), the first term of (3.18) vanishes

\[ \{\mu(t), \mu(0)\}_{\text{px}} = 0, \]

(3.20)

reflecting the fact that the heavy particle initial conditions \( p(0), x(0) \) are chosen independently of the electronic initial conditions \( n_k(0), q_k(0) \).

We have seen in the previous section that one obtains different results for the classical DCF depending on whether one replaces the dipole operator \( \hat{\mu}(t) \) or \( \hat{\mu}_0(t) \) by its corresponding CEA dipole function, although the quantum-mechanical expressions (3.4a) and (3.4b) are clearly equivalent. This ambiguity does not occur if one employs classical perturbation theory. It is easy to show that, analogous to quantum mechanics, one has

\[ E(t) \{\mu(t), \mu(0)\} = 2 \Im \langle \hat{\mu}^* \rangle \{\mu_0(t), \mu_20(0)\}, \]

(3.21)

where

\[ E(t) = \hat{\mu}(t) + \hat{\mu}^*(t), \]

(3.22)

and again the rotating-wave approximation has been employed.

Furthermore, one can rewrite the second term of (3.18) as

\[ \{\mu(t), \mu(0)\}_{\text{px}} = \mu(t) \mu(0) F \left( \frac{\partial \mu(t)}{\partial \mu(0)}, \frac{\partial \mu(t)}{\partial \mu(0)}, \frac{\partial \mu(t)}{\partial \mu(0)}, \frac{\partial \mu(t)}{\partial \mu(0)} \right), \]

(3.23)

where, as indicated, \( F \) is a function of the first derivatives of the electronic action-angle variables with respect to their initial values. In particular, in the absence of vibronic coupling, \( F \) reduces to a constant, i.e. in the uncoupled case classical and quantum-mechanical perturbation theory yield the same result.

To relate the classical perturbation theory approach to the primitive DCF (3.12) derived above, we combine (3.12) and (3.20)-(3.22) to give

\[ C_{\text{CEA}}(t) = \frac{1}{N_{\text{traj}}} \sum_{r=1}^{N_{\text{traj}}} d_r(t) d_r^*(0) F_r(t), \]

(3.24)

where the \( d_r(t) \) and \( F_r(t) \) denote the CEA dipole function (3.12) and the function \( F \) pertaining to a single trajectory, respectively. Equation (3.24) shows that the primitive DCF (3.11) actually represents an approximation to the DCF obtained by classical perturbation theory [namely for \( F_r(t) = \text{const.} \), which becomes exact in the uncoupled case. Finally it should be pointed out that by employing classical perturbation theory one obtains a complex DCF, without the need of an ansatz (3.6) or a separate calculation of the imaginary part (3.16).

IV. GENERALIZATION TO NONLINEAR RESPONSE

So far we have restricted the discussion to the classical calculation of the cw absorption spectrum. In order to generalize these ideas to the nonlinear response, one needs to express the nonlinear polarization in terms of the CEA dipole function (3.5). To this end we first briefly review the quantum-mechanical expressions for the nonlinear polarization which are obtained through time-dependent density-matrix perturbation theory \( \text{with respect to the field-matter interaction (except for the case of the dipole operator \( \hat{\mu} \), we henceforth drop the " ^ " on operators) } \]

\[ H_{\text{int}}(t) = -\mu E(t). \]

(4.1)

It is convenient in carrying out time-dependent perturbation theory to change to the interaction picture, where the operator \( A'(t) \) in the interaction representation is related to the operator \( A(t) \) in the Schrödinger representation by the transformation

\[ A'(t) = e^{i\mathcal{H}t} A e^{-i\mathcal{H}t}. \]

(4.2)

In particular one has

\[ H_{\text{int}}'(t) = -\hat{\mu}(t) E(t), \]

(4.3)

where \( \hat{\mu}(t) \) can equivalently be regarded as Heisenberg operator for the total Hamiltonian \( \mathcal{H}_{\text{tot}} = H(t) \) or as dipole operator in the interaction representation for the total Hamiltonian \( \mathcal{H}_{\text{tot}} = H + H_{\text{int}} \). The calculation of the nonlinear polarization is usually performed in the density-matrix formalism, which allows for the appropriate description of phase and population relaxation processes.\(^{31}\)
Density matrix perturbation theory for the nonadiabatically coupled system (2.6) has recently been described in detail, and is therefore only sketched briefly.

The Liouville-von-Neumann equation in the interaction representation for the density operator $\rho'(t)$ reads

$$\frac{d}{dt} \rho'(t) = \left[ H_{\text{int}}(t), \rho'(t) \right] - i \Gamma'(t),$$

(4.4)

where

$$\Gamma'(t) = \frac{1}{T_1} \sum_{k,k'=1}^{2} \left| \langle \varphi_k | \rho'_{kk'}(t) | \varphi_{k'} \rangle \right|^2$$

and

$$+ \frac{1}{T_2} \sum_{k=1}^{2} \left| \langle \varphi_0 | \rho_{0k}(t) | \varphi_k \rangle \right|^2$$

(4.5)

is the nonradiative damping operator, accounting for the lifetime broadening ($1/T_1$) of the diagonal electronic matrix elements $\rho'_{kk}(t) = \langle \varphi_k | \rho'(t) | \varphi_k \rangle$ and the dephasing of the off-diagonal matrix element $\rho'_{0k}(t)$ relevant to the optical transition $| \varphi_0 \rangle \rightarrow | \varphi_k \rangle$. The polarization is the expectation value of the dipole operator (2.7)

$$P(t) = \text{Tr} \{ \hat{\mu}(t) \rho'(t) \},$$

(4.6)

and is evaluated by solving Eq. (4.4) iteratively with the initial condition

$$\rho'(0) = | \varphi_0 \rangle \langle \psi | \langle \psi | \langle \varphi_0 \rangle.$$  

(4.7)

The expression for the linear polarization reads

$$P^{(1)}(t) = i \int_0^t dt_1 \rho'(0) e^{-(i\omega_1 - \omega_2)/T_1} \text{Tr} \{ \hat{\mu}(t) [ \hat{\mu}(t_1), \rho'(0) ] \},$$

(4.8a)

$$- i \int_0^t dt_1 \rho'(0) e^{-(i\omega_1 - \omega_2)/T_1} \times \langle \psi | \langle \varphi_0 | [ \hat{\mu}(t), \hat{\mu}(t_1) ] | \varphi_0 \rangle | \psi \rangle,$$

(4.8b)

from which the linear response result (3.2) is readily obtained. Disregarding the damping operator [i.e. $\Gamma(t) = 0$], for the moment, the third-order polarization is given by

$$P^{(3)}(t) = i^3 \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \rho'(0) \rho'(0) \rho'(0) \times \text{Tr} \{ \hat{\mu}(t) [ \hat{\mu}(t_3), [ \hat{\mu}(t_2), [ \hat{\mu}(t_1), \rho'(0) ] ] ] \},$$

(4.9a)

$$- i^3 \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \rho'(0) \rho'(0) \rho'(0) \times \langle \psi | \langle \varphi_0 | [ [ [ \hat{\mu}(t), \hat{\mu}(t_3) ], \hat{\mu}(t_2) ], \hat{\mu}(t_1) ] | \varphi_0 \rangle | \psi \rangle.$$  

(4.9b)

In (4.8b) and (4.9b) the commutators are arranged in the form obtained by a perturbation expansion of the Heisenberg dipole operator

$$\hat{\mu}_H(t) = \exp \{ i (H + H_{\text{int}}) t \} \hat{\mu} \exp \{ - i (H + H_{\text{int}}) t \},$$

(4.10a)

$$= \hat{\mu}(t) + \hat{\mu}^{(1)}(t) + \hat{\mu}^{(2)}(t) + \hat{\mu}^{(3)}(t) + \cdots ,$$

(4.10b)

$P(t) = \langle \psi | \langle \varphi_0 | \hat{\mu}_H(t) | \varphi_0 \rangle | \psi \rangle,$  

(4.11a)

$$= P^{(1)}(t) + P^{(2)}(t) + \cdots ,$$  

(4.11b)

where in (4.11b) the zero-and second-order term vanishes due to the initial condition (4.7). As discussed above, knowing the quantum-mechanical perturbation expansion for the Heisenberg dipole operator, we immediately obtain the corresponding expression in classical perturbation theory by the replacement

$$[[[\hat{\mu}(t), \hat{\mu}(t_3)], \hat{\mu}(t_2)], \hat{\mu}(t_1)]$$

$$\mapsto (i\hbar)^3 \{ \{ \mu(t), \mu(t_3) \}, \mu(t_2), \mu(t_1) \}. $$

(4.12)

In the more general case, including phenomenological relaxation effects, evaluation of the commutators and use of the rotating-wave approximation, gives the nonlinear polarization as follows

$$P^{(3)}(t) = \mathcal{P}^{(3)}(t) + \mathcal{P}^{(3)}(t) + \cdots ,$$

(4.13a)

$$= \mathcal{P}^{(1)}(t) + \mathcal{P}^{(2)}(t),$$

(4.13b)

$$\mathcal{P}^{(3)}(t) = i^3 \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \times e^{-(i\omega_1 + \omega_2 - \omega)/T_2} e^{-i\omega_2 - \omega}/T_1 \times (\mathcal{P}^{(3)}(t_3) + \mathcal{P}^{(3)}(t_3) + \cdots ,$$

(4.14)

$$+ \mathcal{P}^{(3)}(t_3) + \mathcal{P}^{(3)}(t_3) + \cdots ,$$

(4.15)

where

$$C_{\text{QM}}(t,t_3,t_2,t_1) = \langle \psi | \langle \varphi_0 | \rho_{02}(t) \rho_{20}(t_2) \rho_{20}(t_1) | \varphi_0 \rangle | \psi \rangle.$$  

(4.16)

As has been discussed by many authors, the third-order polarization consists of two physically distinct components. The first term $\mathcal{P}^{(3)}(t)$ is often referred to as fluorescence-like emission since it is directly proportional to the (second-order) excited-state excess population, while the second term $\mathcal{P}^{(3)}(t)$ is referred to as coherent Raman-like emission. The nonlinear response of the molecular system is described by the four-time DCF $C_{\text{QM}}(t,t_3,t_2,t_1)$ that is a direct generalization of the (one-time) DCF pertaining to the linear case.

From Eqs. (4.14), (4.15) it is straightforward to employ the primitive classical approach for the calculation of the nonlinear polarization. In direct analog to the linear case we replace the quantum-mechanical four-time DCF by the corresponding primitive CEA DCF

$$C_{\text{QM}}(t,t_3,t_2,t_1) = \langle \psi | \langle \varphi_0 | \rho_{02}(t) \rho_{20}(t_2) \rho_{20}(t_1) | \varphi_0 \rangle | \psi \rangle.$$  

(4.16)
\[ C_{\text{QM}}(t_3,t_2,t_1) \rightarrow C_{\text{CEA}}(t_3,t_2,t_1) \]

where the superscript denotes the initial value of \( n_0 \), i.e., "1" for absorption and "0" for emission.

\[ \frac{1}{N_{\text{traj}}} \sum_{r=1}^{N_{\text{traj}}} d_r(t) d_r^*(t_3) d_r(t_2) d_r^*(t_1), \quad (4.17) \]

Note that Eq. (4.17) is computationally very appealing since it requires only the evaluation of the CEA dipole functions \( d_r(t) \). Employing the primitive classical approach, the computational effort to calculate the nonlinear response is (apart from the multiple time integrations) equivalent to the linear case.

The evaluation of the classical perturbation approach (4.12) on the other hand, requires (according to the definition of the Poisson bracket (3.18)) in addition the calculation of the first three derivatives of the electronic action-angle variables with respect to the full set of initial conditions, which renders the practical implementation rather cumbersome. As for the linear case, therefore, it is clear that the primitive approach Eq. (4.17) should be regarded as an approximation to the full classical perturbation theory. Since in general \( \{ \mu(t), \mu(0) \} \neq 0 \) the primitive approach and classical perturbation theory are not equivalent even in the uncoupled case. Because of its simplicity, the primitive classical approach is nevertheless the basis of most of the existing classical spectroscopy models.\(^{17-19}\)

Finally a problem should be addressed that arises from the fact that in the CEA model the trajectories are propagated on an averaged potential. Quantum-mechanically the difference between the fluorescence- and Raman-like emission is established through the different time ordering of the absorption/emission processes, which in turn determines at what time the propagation takes place in which electronic state. For example, the first term of (4.14)

\[ \langle \psi \mid \langle \phi_0 | \hat{\mu}_{20}(t_1) \hat{\mu}_{20}(t_2) \mid \phi_0 \rangle | \psi \rangle \], \quad (4.18) \]

corresponds to the process that at the times \( t_1, t_2 \) a photon is absorbed from the electronic ground state \( | \phi_0 \rangle \) to the excited state \( | \phi_2 \rangle \), and at \( t_3, t \) a photon is emitted from \( | \phi_2 \rangle \) to \( | \phi_0 \rangle \). It has been shown for the linear response case that, depending on the initial electronic action variable \( n_0 \), the CEA dipole function \( d_r(t) \) (3.12) describes either absorption (\( n_0 = 1 \)) or emission (\( n_0 = 0 \)). Evaluating the CEA DCF corresponding to (4.18) for the overall condition \( n_0 = 1 \), would therefore not correctly account for the emission processes pertaining to the times \( t_3, t \). Moreover, the CEA correlation functions, pertaining to the Raman and fluorescence terms, would be identical in the case of overall electronic initial conditions.

To account for both kinds of processes described by the quantum-mechanical DCF (4.18), we consequently have to apply the correct electronic initial condition to each single CEA dipole functions, i.e., the CEA DCF corresponding to (4.18) can be written as

\[ \frac{1}{N_{\text{traj}}} \sum_{r=1}^{N_{\text{traj}}} d_r^{(1)}(t) d_r^{(0)}(t_3) d_r^{(0)}(t_2) d_r^{(1)}(t_1), \quad (4.19) \]

\[ \langle \psi \mid \langle \phi_0 | \hat{\mu}_{20}(t_1) \hat{\mu}_{20}(t_2) \mid \phi_2 \rangle | \phi_0 \rangle | \psi \rangle \].

\[ \mathcal{D}^{(3)}(t) = i|\mu_{20}|^2 \int_0^\infty dt_1 e^{-i(t-t_1)/T_2} e^{-iT_1/T_2} \mathcal{D}^{(3)*}(t_3) \]

\[ \times \langle \psi \mid \langle \phi_2 | \mu_{20}(t) \mu_{20}(t_2) \mu_{20}(t_3) \mid \phi_2 \rangle | \psi \rangle \], \quad (5.1) \]

In the following we derive explicit classical expressions for PP spectra pertaining to the limit of impulsive excitation (5.1). Note that although Eq. (5.1) is similar to the linear polarization (4.8), its quantum-mechanical evaluation is much more involved.\(^{43}\)

In a typical PP experiment the pump pulse [electric field \( \mathcal{E}_1(t) \)] prepares at \( t = 0 \) a nonstationary state, which is interrogated at the time \( t = \Delta t \) by the probe pulse [electric field \( \mathcal{E}_2(t) \)]. The time- and frequency-resolved PP signal, defined as the differential transmission spectrum of the probe pulse (i.e. pump-on minus pump-off), is given by\(^{33,44}\)

\[ I(\omega, \Delta t) = 2 \omega \Im m \mathcal{E}_2(\omega) \mathcal{D}^{(3)*}(\omega), \quad (5.2) \]

where \( \omega \) is the frequency of the emission, \( \Delta t \) is the delay time, and \( \mathcal{E}_2(\omega) \) and \( \mathcal{D}^{(3)*}(\omega) \) denote the Fourier transforms of the probe field and the nonlinear polarization, respectively. Integration over all emission frequencies \( \omega \) yields the integral PP signal

\[ I(\Delta t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} I(\omega, \Delta t), \quad (5.3a) \]

\[ = 2\omega_I \Im m \int_{-\infty}^{\infty} dt \mathcal{E}_2(t) \mathcal{D}^{(3)*}(t), \quad (5.3b) \]

where \( \omega_I \) is the laser frequency of the probe pulse.

It is instructive first to consider the (completely) impulsive limit, i.e. the case that both the pump and the probe pulse are resonant and ultrashort compared to the dynam-
ics of the system. In this limiting case both PP signals (5.2) and (5.3) are independent of the properties of the laser fields and reflect only the dynamics of the molecular system. Evaluation of (5.1) and (5.3b) for an ultrashort probe pulse yields the impulsive integral signal:

\[ I_{\text{QM}}^{\delta}(\Delta t) = \omega_1 |\mu_{02}|^2 e^{-\Delta t/T_1} \times \langle \psi | \langle \varphi_2 | \hat{\beta}_{20}(\Delta t) \hat{\beta}_{02}(\Delta t) | \varphi_2 \rangle | \psi \rangle, \]  

\[ \equiv \text{const} \, P_2(t), \]  

\[ P_2(t) = e^{-t/T_1} \langle \Psi(t) | \varphi_2 \rangle \langle \varphi_2 | \Psi(t) \rangle. \]

\[ P_2(t) \] is the time-dependent total electronic population probability of the optically bright diabatic state \( |\varphi_2\rangle \). As discussed in detail elsewhere, the time-dependent electronic population probability directly monitors the electronic non-Born-Oppenheimer dynamics [in the uncoupled case \( P_2(t) = 1 \)] and is therefore a key quantity in the discussion of ultrafast relaxation dynamics on coupled potential energy surfaces. In the CEA model the electronic population dynamics is described by the classical action variable \( n(t) \) which, owing to the Langer-like modifications, can take on continuous values from \(-1/2\) to \(3/2\). Evaluating the impulsive integral PP signal classically by employing the primitive CEA dipole functions, one obtains:

\[ I_{\text{CEA}}^{\delta}(\Delta t) = \omega_1 |\mu_{02}|^2 e^{-\Delta t/T_1} \frac{1}{N_{\text{traj}}} \sum_{r=1}^{N_{\text{traj}}} (n_r(\Delta t) + 1), \]  

which would result in an electronic population probability \( P_2(t) \) ranging from 0 to 2. To correct for the Langer-like modifications and to make correspondence to discrete electronic states (\( n = 0 \) or 1) we invoke the standard histogram method of assigning the system to the electronic state to which \( n(t) \) is closest, i.e.

\[ P_2(t) = e^{-t/T_1} \frac{1}{N_{\text{traj}}} \sum_{r=1}^{N_{\text{traj}}} \chi(n_r(t)), \]  

\[ \chi(n) = \begin{cases} 1 & \text{if } n > \frac{1}{2} \\ 0 & \text{otherwise}. \end{cases} \]  

In using Eq. (5.7) to compute the classical electronic population probability, one needs to modify the definition of the CEA dipole function (3.12), to ensure that the PP signal in the impulsive limit is given correctly by Eq. (5.7). This can be accomplished by defining

\[ c_r(t) = \sqrt{2S} \chi(n_r(t)) d_r^{(0)}(t), \]

and replacing in (4.19) the CEA dipole functions \( d_r^{(0)}(t) \) by \( c_r(t) \). Note that the modification (5.9) applies only to CEA dipole function describing emission processes [i.e. \( n_0 = 0, n_1(t) + n_2(t) = 1 \)]. In the case of absorption [i.e. \( n_0 = 1, n_1(t) + n_2(t) = 0 \)] the electronic population remains in the electronic ground state, thus making the binning procedure (5.8) redundant.

Evaluating (5.2) for an ultrashort probe pulse, we obtain the quantum-mechanical differential transmission spectrum in the impulsive limit:

\[ I_{\text{QM}}^{\delta}(\omega, \Delta t) = 2\omega \delta m \mathcal{B}_2^{\delta}(\omega) \mathcal{P}_2^{\delta}(\omega, \Delta t), \]  

\[ = \gamma \omega |\mu_{02}|^2 e^{-\Delta t/T_1} \Re \int_0^\infty d\omega \omega e^{i\omega t} \times \langle \psi | \langle \varphi_2 | \hat{\beta}_{20}(\Delta t) \hat{\beta}_{02}(\Delta t + t) | \varphi_2 \rangle | \psi \rangle. \]  

As discussed in detail elsewhere\(^4\), the evaluation and interpretation of the impulsive time- and frequency-resolved PP signal is considerably more involved than in the case of the impulsive integral PP signal, since it reflects both electronic population dynamics as well as effects from coherent vibrational motion and from electronic dephasing of the optical transition.

The impulsive PP spectra (5.10) can be easily generalized to include effects caused by probe pulses with finite pulse duration. Expressed in terms of the impulsive polarization (5.10a) the differential transmission spectrum for finite probe pulses can be written as

\[ I(\omega, \Delta t) = 2\omega \Re m \mathcal{B}_2(\omega) \int_0^\infty dt \mathcal{P}_2(t) \mathcal{B}_2^{\delta}(\omega, t). \]  

Equation (5.11) clearly demonstrates the effects of finite duration of the probe pulse on the impulsive differential transmission spectrum. Due to the integration in (5.11) the time resolution of the signal is determined by the probe duration, while the spectral width of the probe pulse defines the “frequency window” of the observed PP spectrum. Furthermore it is clear that complete information on the observable molecular dynamics is already provided by the impulsive spectrum (5.10), which therefore is the quantity that we wish to evaluate classically.

Expressed in terms of the (histogrammed) CEA dipole functions, the classical impulsive differential transmission spectrum is given by

\[ I_{\text{CEA}}^{\delta}(\omega, \Delta t) = 2\omega |\mu_{02}|^2 e^{-\Delta t/T_1} \frac{1}{N_{\text{traj}}} \sum_{r=1}^{N_{\text{traj}}} \Re e c_r^\dagger(\Delta t) \times \int_0^\infty dt e^{i\omega t} e^{-t/T_2} c_r(\Delta t | t). \]

Note that the time- and frequency-resolved PP spectrum (5.12) represents rather specific information on the molecular dynamics which in turn makes the classical evaluation relatively complicated. Classical models, however, are known to work best for the calculation of highly averaged quantities. Although the differential spectrum is the more general quantity to calculate, it might be therefore advantageous for classical calculations to evaluate the simpler integral PP signal (5.3), which by definition is integrated over all emission frequencies. In contrast to its impulsive limit, the integral PP signal with finite probe pulse duration is frequency-resolved with respect to the carrier frequency of the probe pulse. Although of different physical
Having in mind to apply the classical model to large scale molecular dynamics simulations, the primitive approach is computationally very appealing, whereas the numerical evaluation of (multiple) Poisson brackets becomes quite cumbersome in many dimensions.

The primitive classical approach, however, may be expected to work reasonably well only for the calculation of averaged spectroscopic quantities. To this end we have discussed in some detail the application of the primitive classical model to femtosecond PP spectroscopy. Considering the limiting case of impulsive excitation, we have derived a rather compact expression for the integral stimulated emission PP spectrum. For a vibronically coupled three-state system with four vibrational degrees of freedom, it has been shown recently that the classical PP spectrum is in reasonable agreement with the exact quantum mechanical calculations.

It is well known that the photochemistry of complex systems is dominated in many cases by nonadiabatic processes such as internal conversion, electron transfer, and intersystem crossing, which often occur in combination with isomerization and dissociation of the molecular system. In particular, recent femtosecond experiments with a time resolution up to 10 fs have been shown to yield novel information on the complex ultrafast excited-state dynamics of these systems, which cannot be understood by simple rate-constant models or through the analysis of the generally diffuse absorption and emissions bands. Important examples are the intriguing quantum beats that have been observed in the PP spectra of various complex systems such as stilbene, triphenylmethane dyes, rhodopsin, and even bacterial reaction centers.

A microscopic theoretical description of these systems is only feasible within a classical treatment that is simple enough for a large scale molecular dynamics simulation. We are hopeful that the CEA model, which has been shown to provide a well-defined formulation of the spectroscopy of nonadiabatically coupled states, will be sufficiently accurate to contribute to the understanding of the still rather unexplored photochemistry of complex systems, which is exhibited in modern femtosecond experiments.

VI. CONCLUSIONS

Based on the theoretical framework of the CEA model, a classical formulation of the spectroscopy of nonadiabatically coupled electronic state has been outlined. Employing classical time-dependent perturbation theory with respect to the radiation field, it has been shown that the (nonlinear) electric polarization can be calculated in a consistent classical manner. Formally this is accomplished by replacing the commutators, occurring in quantum-mechanical perturbation theory, by classical Poisson brackets. It has been shown that in the resulting classical formalism to the treatment of nonadiabatic dynamics.

In the limiting case that we disregard all these higher-order dependencies on the initial conditions stemming from the evaluation of the Poisson brackets, we obtain the primitive classical approach, which is usually derived by performing quantum-mechanical perturbation theory and simply replacing the quantum-mechanical dipole operators by the corresponding classical dipole functions. This simple and popular approach, that has been considered by several authors has been extended within the CEA formalism to the treatment of nonadiabatic dynamics. Having in mind to apply the classical model to large scale molecular dynamics simulations, the primitive approach is computationally very appealing, whereas the numerical evaluation of (multiple) Poisson brackets becomes quite cumbersome in many dimensions.

The primitive classical approach, however, may be expected to work reasonably well only for the calculation of averaged spectroscopic quantities. To this end we have discussed in some detail the application of the primitive classical model to femtosecond PP spectroscopy. Considering the limiting case of impulsive excitation, we have derived a rather compact expression for the integral stimulated emission PP spectrum. For a vibronically coupled three-state system with four vibrational degrees of freedom, it has been shown recently that the classical PP spectrum is in reasonable agreement with the exact quantum mechanical calculations.

It is well known that the photochemistry of complex systems is dominated in many cases by nonadiabatic processes such as internal conversion, electron transfer, and intersystem crossing, which often occur in combination with isomerization and dissociation of the molecular system. In particular, recent femtosecond experiments with a time resolution up to 10 fs have been shown to yield novel information on the complex ultrafast excited-state dynamics of these systems, which cannot be understood by simple rate-constant models or through the analysis of the generally diffuse absorption and emissions bands. Important examples are the intriguing quantum beats that have been observed in the PP spectra of various complex systems such as stilbene, triphenylmethane dyes, rhodopsin, and even bacterial reaction centers.

A microscopic theoretical description of these systems is only feasible within a classical treatment that is simple enough for a large scale molecular dynamics simulation. We are hopeful that the CEA model, which has been shown to provide a well-defined formulation of the spectroscopy of nonadiabatically coupled states, will be sufficiently accurate to contribute to the understanding of the still rather unexplored photochemistry of complex systems, which is exhibited in modern femtosecond experiments.

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APPENDIX

We wish to prove some properties of the Poisson bracket of two CEA dipole functions

$$\{\mu(t_2), \mu(t_1)\} = \sum_{k=0}^{F-1} \left( \frac{\partial \mu(t_2)}{\partial \tilde{g}_k(0)} \frac{\partial \mu(t_1)}{\partial \tilde{g}_k(0)} - \frac{\partial \mu(t_2)}{\partial \tilde{n}_k(0)} \frac{\partial \mu(t_1)}{\partial \tilde{n}_k(0)} \right) + \sum_{l=1}^{N_{\text{mod}}} \left( \frac{\partial \mu(t_2)}{\partial \tilde{x}_l(0)} \frac{\partial \mu(t_1)}{\partial \tilde{p}_l(0)} - \frac{\partial \mu(t_2)}{\partial \tilde{p}_l(0)} \frac{\partial \mu(t_1)}{\partial \tilde{x}_l(0)} \right) + [\mu(t_2), \mu(t_1)]_\hbar + [\mu(t_2), \mu(t_1)]_\text{ps},$$

(A1)
where
\[
\frac{\partial \varphi(t)}{\partial f(0)} = \sum_{k=0}^{F-1} \left( \frac{\partial \varphi_k(t)}{\partial f(0)} + \frac{\partial \varphi_k(t)}{\partial \varphi_k(t)} \right),
\]
(A2)
and \(f\) denotes an arbitrary canonical variable \((p_k, x_k, q_k)\).

Using the CEA dipole function of the model specified above
\[
\mu(t) = \left( n_0 + \frac{1}{2} \right) \left( n_0 + \frac{1}{2} \right) \left( \mu_{02}(t) + \mu_{20}(t) \right),
\]
(A3)
only terms with \(k = 0, 2\) contribute in (A1) and (A2). It is furthermore convenient to write
\[
\{ \mu(t_2), \mu(t_1) \} \sim \{ \mu_{02}(t_2), \mu_{02}(t_1) \} + \{ \mu_{20}(t_2), \mu_{02}(t_1) \}
\]
(A4)
and refer in the following to the Poisson brackets of the CEA dipole function elements \(\mu_{02}(t)\) and \(\mu_{20}(t)\).

To prove Eq. (3.23), we note that in general
\[
\frac{\partial \mu_{02}(t)}{\partial n_k} = \frac{1}{2n_k + 1} \mu_{03}(t), \quad \frac{\partial \mu_{20}(t)}{\partial q_k} = \frac{1}{2n_k + 1} \mu_{03}(t) \quad (k = 0, 2),
\]
(A5)
yielding for the partial derivatives in Eq. (A2)
\[
\frac{\partial \mu_{02}(t)}{\partial f(0)} = \mu_{02}(t) \sum_{k=0, 2} \left( \frac{1}{2n_k + 1} \frac{\partial q_k(t)}{\partial f(0)} + \frac{1}{2n_k + 1} \frac{\partial n_k(t)}{\partial f(0)} \right)
\]
(A6)
Inserting \(\mu_{02}(t)\) in \(\mu_{02}(t)\), the Poisson brackets may be written in terms of an overall factor \(\mu(t_2)\mu(t_1)\) times a function \(F\), which contains the first derivatives of the electronic action-angle variables \(n_k, q_k\) with respect to the full set of initial conditions \(f(0) = \{ n_k(0), q_k(0), p_k(0), x_k(0) \}\)
\[
\{ \mu(t_2), \mu(t_1) \} = \mu(t_2) \mu(t_1) F \left( \frac{\partial n_k(t)}{\partial f(0)}, \frac{\partial q_k(t)}{\partial f(0)} \right).
\]
(A7)
Since at \(t = 0\) the initial electronic action-angle variables \(n_k(0), q_k(0)\) are chosen independently from the initial momenta \(p_k(0)\) and positions \(x_k(0)\) of the heavy particles degrees of freedom, we have
\[
\frac{\partial q_k(0)}{\partial f(0)} = 0, \quad \frac{\partial n_k(0)}{\partial f(0)} = 0 \quad (f = x_k p_k),
\]
(A8)
therefore proving Eq. (3.20)
\[
\{ \mu(t), \mu(0) \} \rho_k = 0.
\]
(A9)
In the uncoupled case \((V_{12} = 0)\) the electronic populations are constants of the motion
\[
\frac{\partial n_k(t)}{\partial n_k(0)} = \delta_{k,k'},
\]
(A10)
and one obtains for the electronic phases [cf. (2.10)]
\[
\frac{\partial q_k(t)}{\partial q_k(0)} = \delta_{k,k'},
\]
(A11)
showing that in this limiting case the function \(F\) in (3.23) reduces to a constant.

In order to prove Eq. (3.21) we have to calculate the mean value of the Poisson bracket \(\{ \mu(t), \mu(0) \}\). According to (3.9) the last two terms in (A4) vanish, since they contain the overall phase factor \(\exp[i q_k(0) + q_0(0)]\), which makes the integral over \(q_0\) to zero. Multiplying (6.4) with \(E(t) = \mathcal{E}^*(t) + \mathcal{E}^*(t)\) and taking in account only the resonant terms (i.e. employing the rotating-wave approximation), directly yields (3.21).
Quantum-mechanically, the evaluation of (4.8) requires only a single row of the eigenvector matrix, whereas the evaluation of (5.1) requires the full eigenvector matrix.

References:

45 Quantum-mechanically, the evaluation of (4.8) requires only a single row of the eigenvector matrix, whereas the evaluation of (5.1) requires the full eigenvector matrix.